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A STUDY OF BISIMINES OF TETRA-
METHYL-1,3-CYCLOBUTANEDIONE

BY

EDWARD ALBERT SCHMIDT

A thesis submitted
in partial fulfillment of the requirements for the
degree Doctor of Philosophy, Major in Chemistry of the
South Dakota
State University

1973

A STUDY OF BISIMINES OF TETRA-
METHYL-1,3-CYCLOBUTANEDIONE

This thesis is approved as a creditable and independent investigation by a candidate for the degree, Doctor of Philosophy, and is acceptable as meeting the thesis requirements for this degree, but without implying that the conclusions reached by the candidate are necessarily the conclusions of the major department.

A STUDY OF BISIMINES OF TETRA-
METHYL-1,3-CYCLOBUTANEDIONE

Abstract

EDWARD ALBERT SCHMIDT

Under the supervision of Dr. James J. Worman

Ten new aromatic and aliphatic bisimines of tetramethyl-1,3-cyclobutanedione, were prepared. These are: N,N'-di(o-methoxyphenyl)-2,2,4,4-tetramethyl-1,3-cyclobutanediimine (10), N,N'-di(o-ethoxyphenyl)-2,2,4,4-tetramethyl-1,3-cyclobutanediimine (11), N,N'-di(o-chlorophenyl)-2,2,4,4-tetramethyl-1,3-cyclobutanediimine (12), N,N'-dibenzyl-2,2,4,4-tetramethyl-1,3-cyclobutanediimine (13), N,N'-di(1-naphthyl)-2,2,4,4-tetramethyl-1,3-cyclobutanediimine (14), N,N'-di(2-6-dimethylanilino)-2,2,4,4-tetramethyl-1,3-cyclobutanediimine (16), N,N'-di(o-isopropylphenyl)-2,2,4,4-tetramethyl-1,3-cyclobutanediimine (17), N,N'-dicycloheptyl-2,2,4,4-tetramethyl-1,3-cyclobutanediimine (22), N,N'-dicyclooctyl-2,2,4,4-tetramethyl-1,3-cyclobutanediimine (24), and the mixed bisimine, N-phenyl-N'-cyclohexyl-2,2,4,4-tetramethyl-1,3-cyclobutanediimine (37). The various kinds of spectral data from mass, infrared, nuclear magnetic resonance, and ultraviolet spectroscopy are examined and their bearing on the structure of the bisimines is discussed: specifically, discussions of transannular participation and geometrical isomerization of the bisimine compounds are presented.

Steric considerations as well as the effect of the basicity of the primary amine on the extent of bisimine formation are shown. Eight

new open chain amides were prepared. These are: 4-methyl-3-N-phenylimino-2,2-dimethyl-N'-cyclohexylaminopentanoamide (38), N-cyclohexyl-2,2,4-trimethyl-3-oxovaleramide (20), N-cyclohexylidene-3-(2,2,4-trimethyl)-N'-cyclohexylvaleramide (21), N-cycloheptyl-2,2,4-trimethyl-3-oxovaleramide (23), N-cyclooctyl-2,2,4,4-tetramethyl-trimethyl-3-oxovaleramide (25), N-cyclopentyl-2,2,4,4-trimethyl-3-oxovaleramide (26), N-3-methylbutyl-2,2,4-trimethylbutyl-2,2,4-trimethyl-3-oxovaleramide (29), and N-adamantyl-2,2,4-trimethyl-3-oxovaleramide (32).

Attempts were made to react the bisimine compounds, N,N'-dicyclohexyl-2,2,4,4-tetramethyl-1,3-cyclobutanediimine (19), and N,N'-diphenyl-2,2,4,4-tetramethyl-1,3-cyclobutanediimine (9) with ionic nucleophiles, and these compounds were found to be essentially inert under the described experimental conditions. The addition of hydrogen chloride gas resulted in the formation of diphenyl-2,2,4,4-tetramethyl-1,3-cyclobutanediimmonium chloride (39), and dicyclohexyl-2,2,4,4-tetramethyl-1,3-cyclobutanediimmonium chloride (40). The aromatic bisimine 9 was catalytically reduced to the amine, 2,2,4,4-tetramethyl-N,N'-diphenyl-1,3-cyclobutanediamine (41), while the cyclohexyl bisimine 19 failed to react. The cyclohexylbisimine 19 did undergo a carbene reaction.

Photochemical studies of the cyclohexylbisimine 19 under an atmosphere of nitrogen, resulted in the formation of cyclohexylisocyanide (46), and dimethylketene-N-cyclohexylimine (44). Mass spectrometry was used extensively in the identification.

Biological growth of a mold, Penicillium frequentans, was observed in N-cyclohexyl-2-methylpropionamide (43), and in the dehydration product, dimethylketene-N-cyclohexylimine (44).

New monoimines produced were: 2,2,4,4-tetramethyl-3-cyclohexyliminocyclobutanone (35), and 2,2,4,4-tetramethyl-3-n-butyliminocyclobutanone (36).

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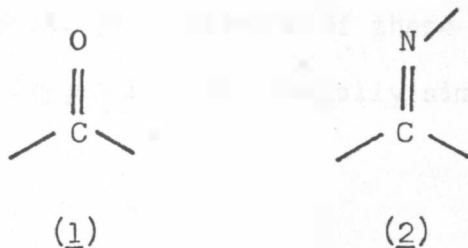
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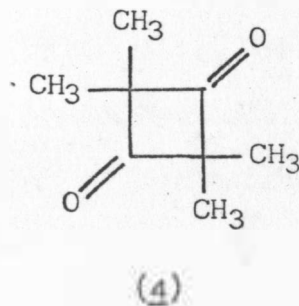
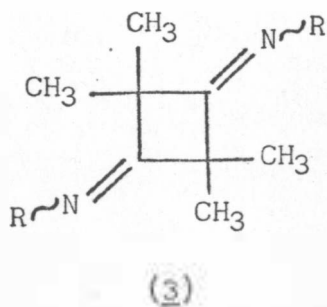


INTRODUCTION

The chemistry of compounds containing the carbonyl functional group 1 has been well studied.¹ On the other hand, less investigative work has been carried out on compounds containing the azomethine linkage 2. Previous work has centered around the preparation, physical properties, and reaction properties (thermal and photochemical) of the



simple monoimines. Because of the instability of the simple imines, a study, in this thesis, is directed mainly toward the more stable bisimines of a nonconjugated nature; namely, bisimines of tetramethyl-1,3-cyclobutanedione (3). These bisimines are structurally similar to tetramethyl-1,3-cyclobutanedione (4), a ketone about which much of the chemistry is known.²

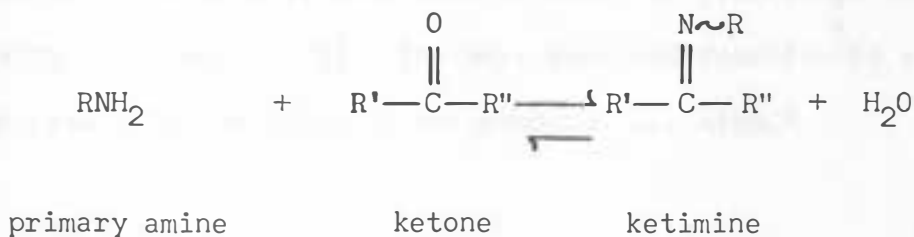
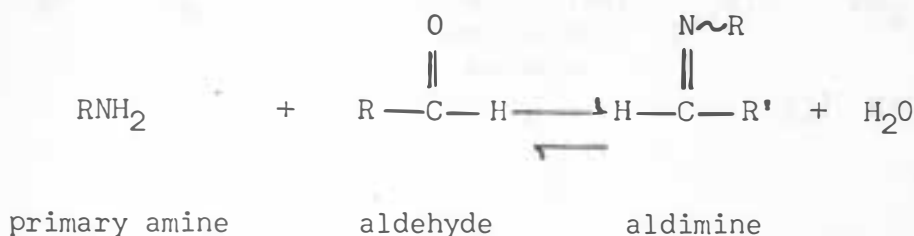


Bisimines of tetramethyl-1,3-cyclobutanedione, should be somewhat different in their physical and chemical properties than simple imines. The second imine group may interact with the first imine linkage, across the ring. This phenomenon is discussed on pages 8-10 and 110-118.

It was the purpose, therefore, of this work, to investigate the preparation, properties, and reactions of bisimines of 2,2,4,4-tetramethyl-1,3-cyclobutanedione, to determine the chemical effects of carbon π -bonded to nitrogen. Certain of these effects are compared to carbon π -bonded to oxygen in a structurally similar environment.

HISTORICAL

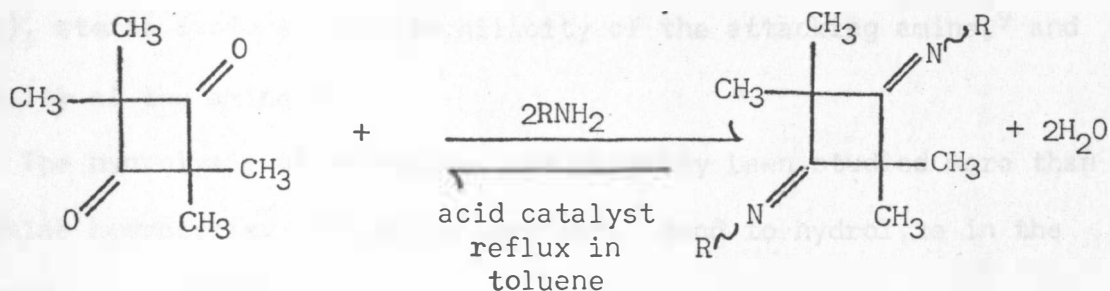
Imines have been prepared according to established procedures;³⁻⁵ the addition of primary amines to aldehydes forms aldimines, while the addition of primary amines to ketones results in the formation of ketimines as shown below:



The R groups represent aliphatic or aromatic groups. Imines have also been produced by other methods.^{6,7} Imines tend to undergo other reactions^{6,7} with a variety of reagents; water (hydrolysis), hydrogen (catalytically and chemically), primary amines, active hydrogen compounds, organometallic compounds, and other reagents. See reference 7 and pages 51-65 of this thesis for additional details and for other reactions. Imines are also characterized by imine-enamine tautomerization and syn-anti isomerization.⁶

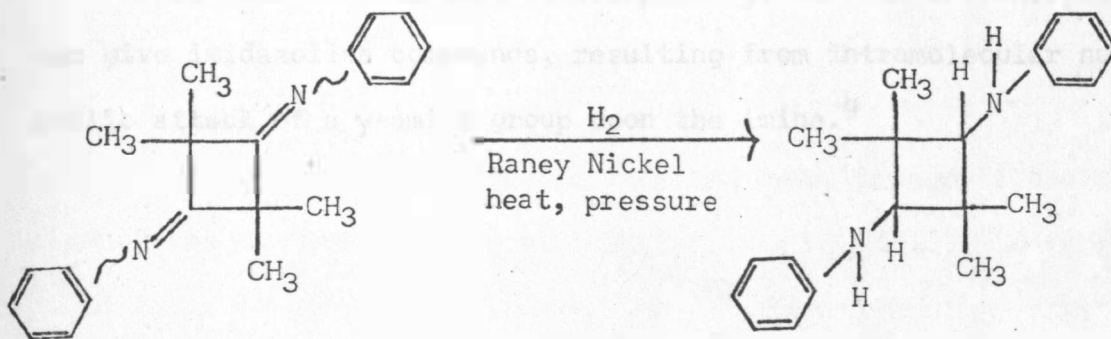
Preparation and Properties of Bisimines and Related Compounds

The preparation of bisimines of tetramethyl-1,3-cyclobutanedione, was first reported in 1961.⁸



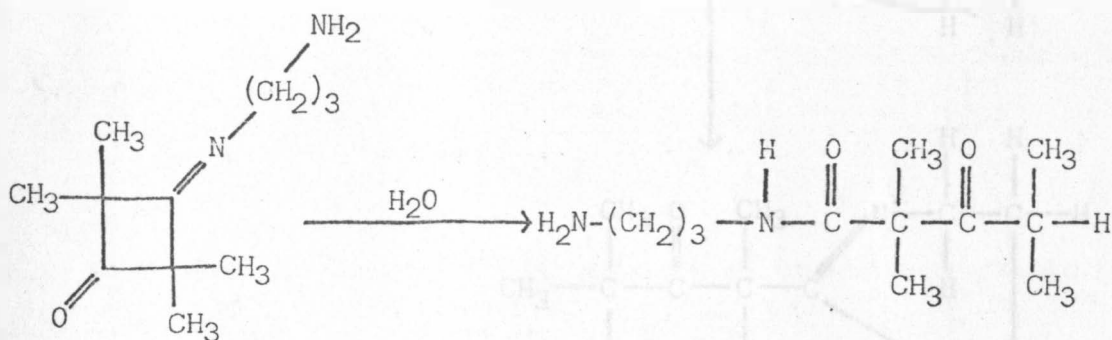
(3) R = phenyl or
cyclohexyl

Knowledge of bisimine chemistry was virtually nonexistent prior to this work, especially knowledge relating to properties and reaction chemistry of bisimines (3). The only reported reaction of a bisimine is the catalytic reduction of an aromatic bisimine.⁸

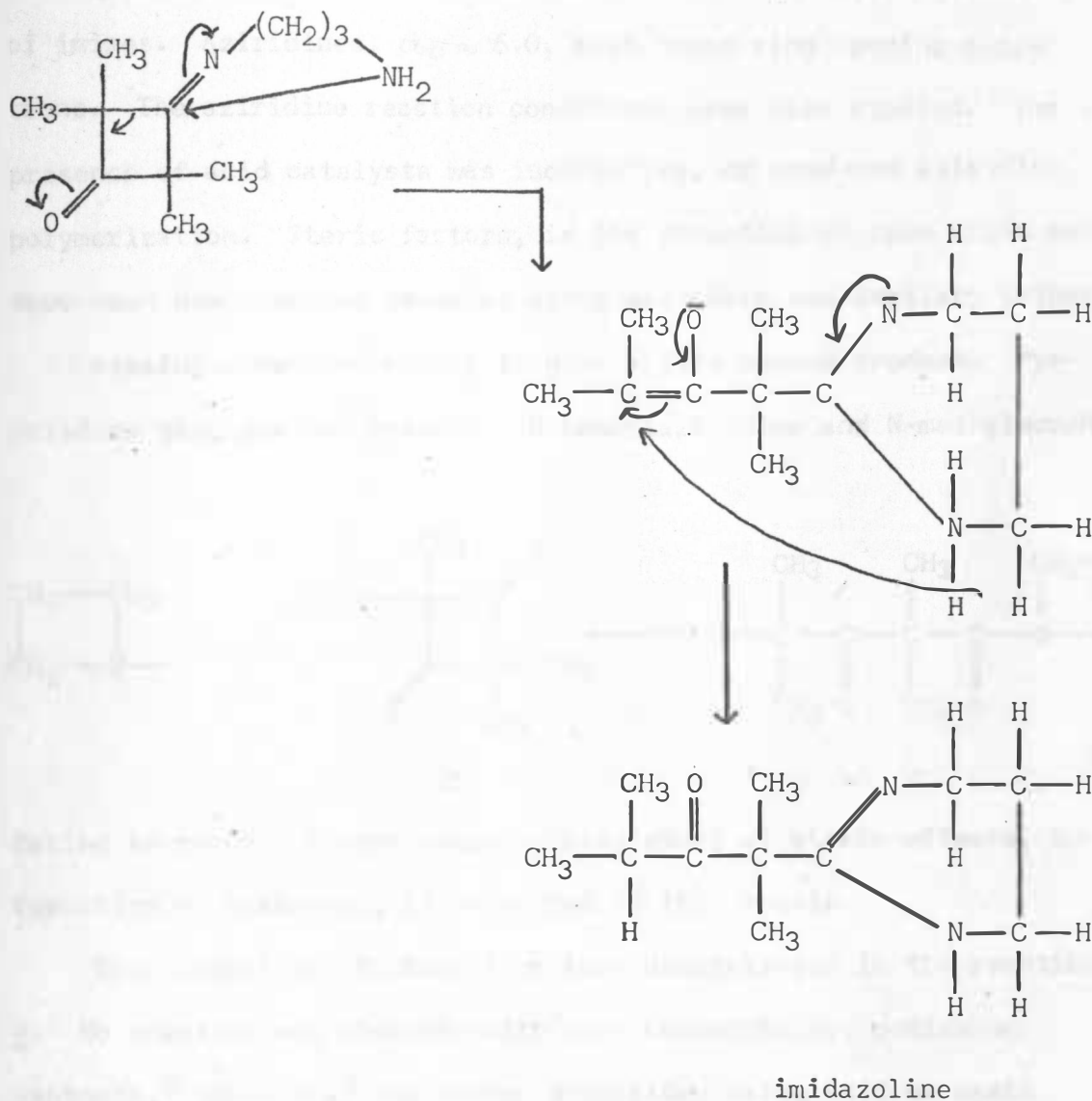


The reaction of tetramethyl-1,3-cyclobutanedione (4) with various amine nucleophiles has been demonstrated to be dependent on the reaction conditions⁹ (presence or absence of water and choice of solvent), steric factors,⁹ nucleophilicity of the attacking amine,⁹ and basicity of the amine.¹⁰

The hydrolysis of monoimines has probably been studied more than bisimine hydrolysis. Aliphatic monoimines tend to hydrolyze in the presence of water.⁹



Rapid removal of water, azeotropically, or with molecular sieves, can give imidazoline compounds, resulting from intramolecular nucleophilic attack of a γ -amino group upon the imine.⁹

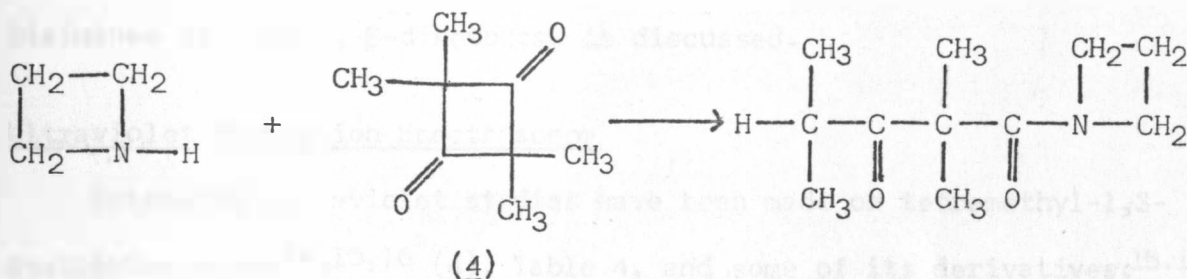


Bisimine hydrolysis and other reaction conditions relating to the preparations and reactions of bisimines is discussed in this thesis.

A basicity study has been described.¹⁰ Reactions of 4 with strongly basic amines, ethyl amine, $\text{pK}_b = 3.25$, result in ring opening reactions. Reactions of 4 with weakly basic amines,

aniline, $pK_b = 9.4$, result in condensation reactions; the formation of imines. Aziridines, $pK_b \approx 6.0$, also cause ring opening reactions. The aziridine reaction conditions were also studied. The presence of acid catalysts was ineffective, or produced aziridine polymerization. Steric factors, in the formation of open chain amides, have been demonstrated somewhat using secondary and tertiary amines.⁹

Azetidine reacted with 4 to give a ring opened product. Pyrrolidine gave similar results. N-benzylazetidine and N-methylmorpholine



failed to react. A more comprehensive study of steric effects, in the formation of bisimines, is presented in this thesis.

Nucleophilicity factors have been demonstrated in the reactions of 4. No reaction was observed with poor nucleophiles, potassium xanthate,⁹ thietane,⁹ and carbon disulfide, using acid or basic catalysts⁹ (except KOH which was reported to give diisopropyl ketone after hydrolysis).¹⁰ It might also be mentioned that sterically hindered aziridines also failed to react.¹⁰ These aziridines included N-phenylaziridine, N-butylaziridine, and the stronger base, N-cyclohexyl-3-azetidinol.

Geometrical Isomerization

Geometrical isomerization of aliphatic and aromatic monoazomethines, Figure 2, has been studied extensively by nmr.^{11,12,13} The configuration about the carbon-nitrogen double bond was established by the use of long range coupling constants and by variable temperature studies. More recently a report on the nmr conformational analysis of conjugated bisimines has appeared.⁸ The factors influencing isomerization about the azomethine grouping are still only vaguely understood. In this thesis the first example of geometrical isomerization of bisimines of cyclic, β -diketones, is discussed.

Ultraviolet Absorption Spectroscopy

Extensive ultraviolet studies have been made on tetramethyl-1,3-cyclobutanedione^{14,15,16} (4), Table 4, and some of its derivatives;^{15,16} in order to describe transannular participation between atoms containing no formal bonds.

An examination of transannular participation in the bisimines of 4 might show involvement of electrons through p atomic orbitals of nitrogen and carbon in the azomethine linkage. This can perhaps be represented by Figure 1.

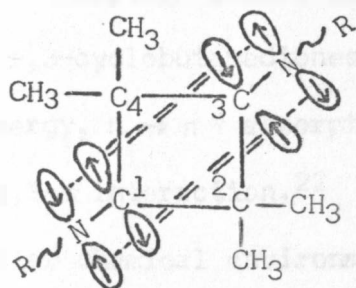
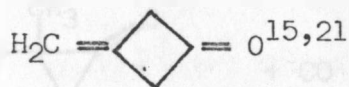
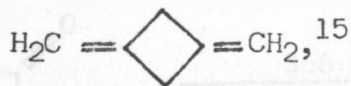


Figure 1. Transannular 1,3- π Interaction of Bisimines.

The dotted lines indicate interaction between p orbitals with resultant "partial" bond character. The amount of interaction is also believed to be influenced by the nature of the groups attached to carbon atoms 2 and 4.¹⁵

Studies involving cyclobutane rings have been of interest because of the possibility of transannular participation¹⁶⁻²⁰ (partial 1,3- π bonding or overlap across the ring). This interaction has been measured by noting the presence, magnitude, and splitting of transitions in the ultraviolet absorption spectra. No such interaction was observed in 1,3-dimethylenecyclobutane, and 3-methylenecyclobutanone.



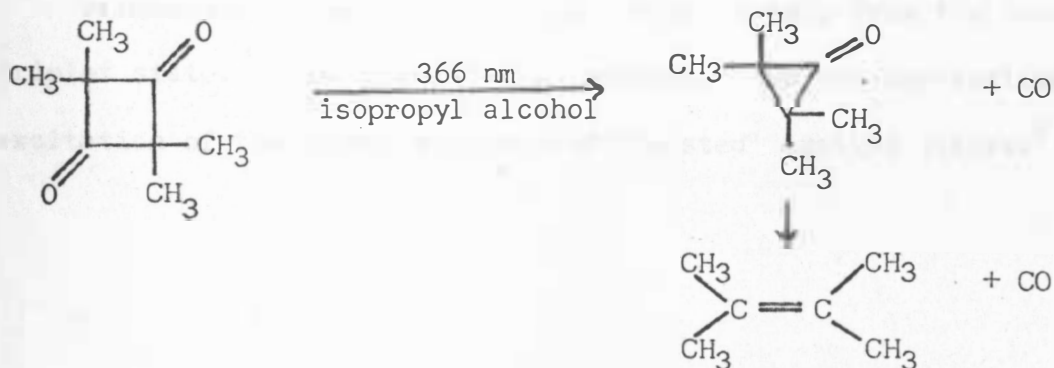
In addition, no splitting of the ultraviolet absorption spectra of tetramethyl-1,3-cyclobutanedithione (48) was observed.²²

There is believed to be a certain amount of transannular participation in tetrasubstituted 1,3-cyclobutanediones 4^{15,22}. The band separation of the lowest energy, $n \rightarrow \pi^*$ absorption band of 4, Figure 3, has been attributed to 1,3- π interaction.²² Compound 4, containing two carbonyl groups in similar chemical environments, would be expected to undergo only one $n \rightarrow \pi^*$ transition upon ultraviolet excitation if there were no 1,3- π interaction. The presence of two absorptions, Tables 6 and 7, is possibly caused by 1,3- π interaction across the cyclobutane ring.

Recent studies in photoelectron spectroscopy add a new dimension to the transannular participation concept.²² This is presented in detail in the Discussion of Results section.

Photochemistry

The photochemistry of carbon π bonded to oxygen in unconjugated ketones has been exhaustively studied.²⁴ The photolysis of tetramethyl-1,3-cyclobutanedione (4) leads to a Norrish Type 1 cleavage and forms tetramethylcyclopropanone; further reaction produces tetramethyl ethene.^{25,14}



The photochemistry of nitrogen π -bonded to carbon, the imines, has been studied to a limited extent.

Imines tend to be unreactive photochemically.⁷ Instead of reacting, imines tend to undergo radiationless decay of the excited state.²⁵ This deactivation of the excited state is believed to result from rotation about the π -bond in the excited state.^{7,27} Syn-anti(cis-trans) isomerization, Figure 2, is the major result of the deactivation.⁷

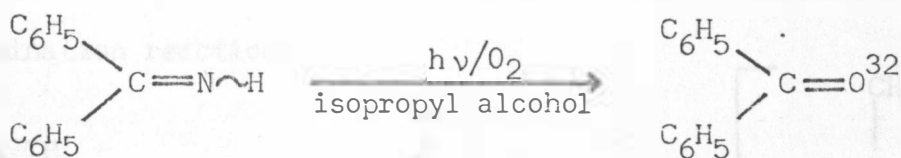
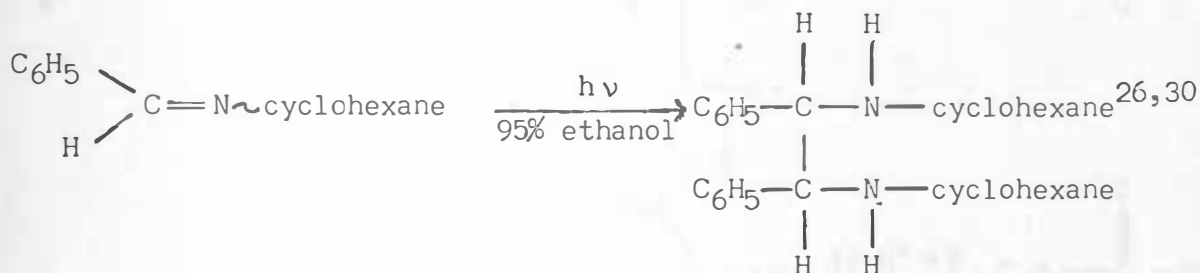


Figure 2. Imine Syn-anti Isomerization.

This isomerization has been studied since 1891.^{28,7} The rate of thermal isomerization is dependent on the temperature²⁹ and the nature of the attached substituents.⁷

Photochemical isomerization can occur rapidly from the excited triplet state. This isomerization probably involves non-vertical excitation of the imine acceptor and "twisted" excited states.⁷

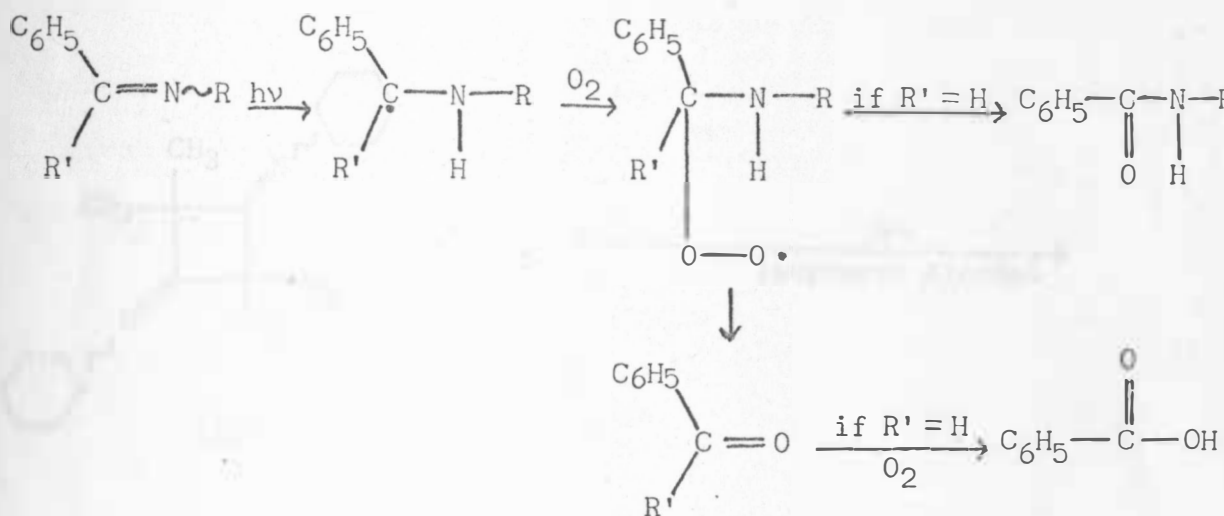
Imines will, however, undergo photochemical reduction,^{26,30,31} oxidation,³² hydrolysis,³³ and rearrangement reactions.³⁴



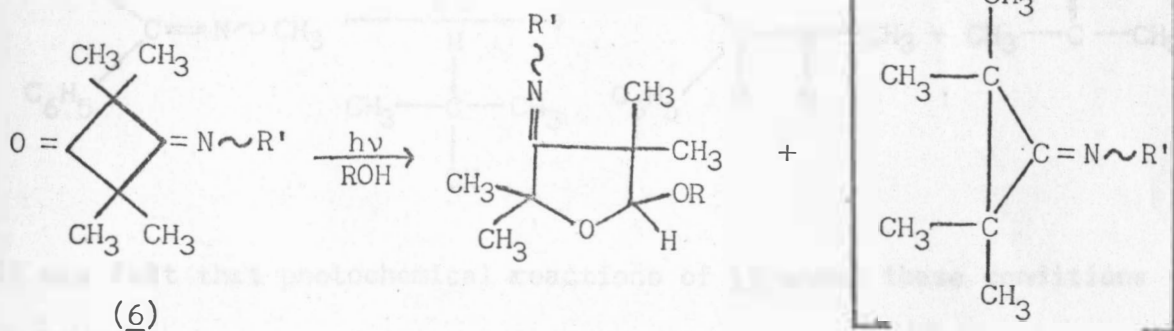
Imines, unlike carbonyl compounds, do not tend to undergo Norrish cleavages.³⁴

Ketyl radicals, not the excited states of the imines, are implicated as the active reducing agents. These ketyl radicals are derived from carbonyl compounds present as impurities in the reaction mixture, as added sensitizers, or as photogenerated species.³⁰

The photo-oxidation of imines is believed to proceed via a reaction path similar to that of the photo-reduction.³²



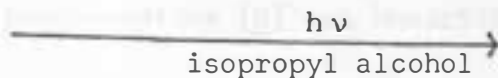
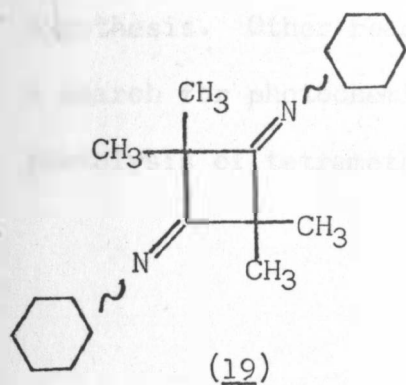
Cyclobutanonemonoimines, 6, tend to undergo insertion, addition, and elimination reactions.³⁵



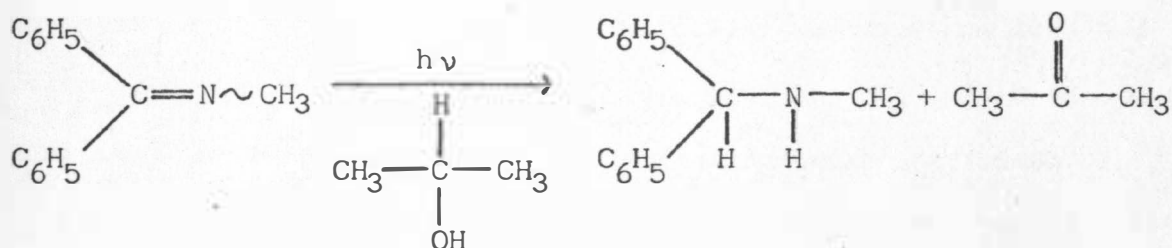
$\text{R}' = \text{CH}_3, n\text{-C}_4\text{H}_9, n\text{-C}_6\text{H}_{13},$

$\text{cyclo-C}_6\text{H}_{11}, \text{C}_6\text{H}_5$

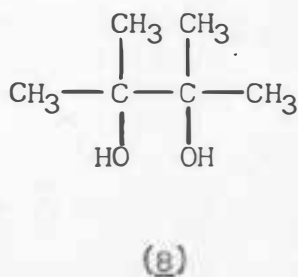
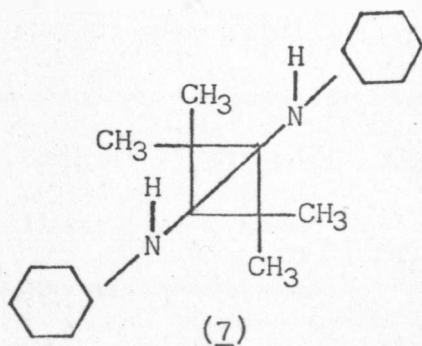
As the photochemistry of bisimines of tetramethyl-1,3-cyclobutanedione has not been investigated, photochemical studies of N,N'-dicyclohexyl-2,2,4,4-tetramethyl-1,3-cyclobutanediimine (19) were undertaken in this study.



Isopropyl alcohol will donate hydrogen atoms to imines during photochemical reactions.^{32,36}



It was felt that photochemical reactions of 19 under these conditions could lead to compounds of the type 7 and 8.



One of the purposes of this investigation was to test the above hypothesis. Other reactions were investigated as they became evident. A search for photochemical similarities to those occurring in the photolysis of tetramethyl-1,3-cyclobutanedione (4) was undertaken.

EXPERIMENTAL

The following experimental work was done at South Dakota State University located in Brookings, South Dakota, unless otherwise indicated.

All infrared spectra were obtained on Perkin-Elmer models 700 and 521 grating spectrophotometers except the following: infrared spectrum of dicyclohexyl-2,2,4,4-tetramethyl-1,3-cyclobutanediimmonium dichloride (40), taken on a Beckman IR-12 infrared spectrophotometer at the University of Wyoming located in Laramie, Wyoming; 2,2,4,4-tetramethyl-3-n-butyiminocyclobutanone (36), and 2,2,4,4-tetramethylcyclobutanedione (4), taken on a Beckman IR-5 spectrophotometer. Spectra were obtained neat or as potassium bromide wafers, using approximately 3.5 mg of sample in 97 mg of potassium bromide, unless otherwise indicated.

Nuclear magnetic resonance data were obtained on a Varian Model A60-A spectrometer at the normal operating temperature of 39°, with the following exceptions: Varian HA 100 nuclear magnetic resonance spectrum at 39° of N,N'-di(o-methoxyphenyl)-2,2,4,4-tetramethyl-1,3-cyclobutanediimine (10), obtained at the University of Wyoming; high temperature spectra of N,N'-dicyclohexyl-2,2,4,4-tetramethyl-1,3-cyclobutanediimine (19), 165°, and low temperature spectra of N,N'-di(o-chlorophenyl)-2,2,4,4-tetramethyl-1,3-cyclobutanediimine (12), 10°. Chemical shifts were reported as (δ) values relative to tetramethylsilane (tms), which was used as an external standard. The spectra were taken as neat samples or as CCl₄ solutions, unless otherwise indicated.

Electronic spectra were obtained in solution, using one centimeter silica cells, on a Beckman DK-2A ultraviolet recording spectrophotometer with the following exceptions: ultraviolet spectrum of dicyclohexyl-2,2,4,4-tetramethyl-1,3-cyclobutanediimmonium dichloride (40), obtained on a Beckman DB ultraviolet recording spectrophotometer at the University of Wyoming; and N,N'-dicycloheptyl-2,2,4,4-tetramethyl-1,4-cyclobutanediimine (22), obtained on a Beckman DB ultraviolet recording spectrophotometer. Spectral data including absorption maxima, molar absorptivity, and solvent used, are listed in Table 6, unless otherwise noted.

Mass spectral data were obtained on the following instruments: a Finnigan 3000 GC/MS mass spectrometer at South Dakota State University or at Augustana College, located in Sioux Falls, South Dakota, and on a Varian CH-5 mass spectrometer at the University of Wyoming. G.C. columns used consisted of 3 percent OV-1 on 60/80 mesh chromosorb W(HMDS), 5' x 1/8" i.d., operated at about 180°.

Elemental CH analyses were performed by a departmental technician at South Dakota State University.

Melting points were obtained using pyrex capillary tubes in a Thomas Hoover Capillary Melting Point apparatus and are in degrees Centigrade, uncorrected, as are boiling points.

Gas chromatography analyses were carried out on a Beckman GC-2A using a 30 percent SE 30 column on chromasorb P (20' x 3/5") 60-80 mesh packed with 30 g of Dow-Corning fluid, type 550 silicone, on 100 g of 42/60 C-2 firebrick.

Preparation of Aromatic Bisimines

Preparation of N,N'-Diphenyl-2,2,4,4-tetramethyl-1,3-cyclobutanediimine (9)

Into a 500 ml flask fitted with a Dean-Stark trap were placed 2,2,4,4-tetramethylcyclobutanedione (4), 50.00 g (0.388 mole); aniline, 72.32 g (0.777 mole); 4.17 g of p-toluenesulfonic acid monohydrate; 200 ml of toluene; and two boiling chips. Water was readily liberated upon refluxing; over 13 ml were collected in a few hours, which represented 93 percent yield for complete bisimine formation. The sample, which precipitated on cooling, was filtered with suction. The precipitate was recrystallized twice from ethanol. The filtrates solidified and were recrystallized from ethanol, aqueous ethanol, and hexane, giving 49.50 g of pure material, m.p. 141-142°. There was more impure solid remaining.

The structure of the bisimine compound was confirmed by uv (Table 6), ir, and nmr spectroscopy. The nmr spectrum in CDCl₃ gave δ 7.02(m, 10H, aromatic), δ 1.52(s, cis-CH₃), δ 1.26(s, trans-CH₃), and δ 1.01(s, cis-CH₃). The infrared spectrum showed bands at 3025, 2925, 1685, 1585, 1480, 1445, 1350, 1215, 1050, 840, 750, 710, and 685 cm⁻¹.

Anal. Cal'd for C₂₀H₂₂N₂: C, 83.72; H, 7.64.

Found: C, 83.07; H, 7.83.

Preparation of N,N'-Di(o-methoxyphenyl)-2,2,4,4-tetramethyl-1,3-cyclobutanediimine (10)

Into a 250 ml flask fitted with a Dean-Stark trap were placed 2,2,4,4-tetramethylcyclobutanedione (4), 15.00 g (0.116 mole); o-methoxyaniline, 28.70 g (0.233 mole); 0.1 g of p-toluenesulfonic acid monohydrate; 100 ml of toluene; and two boiling chips. The mixture was refluxed for 24 hours; 3.5 ml of water were collected, which represented 83.3 percent yield for complete bisimine formation. The resulting brown viscous liquid was evaporated under reduced pressure on a Rinco evaporator. The mixture crystallized on standing. Cold n-hexane was added, and the resulting mixture was filtered with suction, giving a brown residue which was recrystallized three times from n-hexane. White crystals were formed, m.p. 117.5-120°, decomposed. The viscous, dark-red filtrate was evaporated in the hood and recrystallized from n-hexane and identified by uv (Table 6), ir, and nmr spectroscopy. The nmr spectrum in CDCl_3 gave δ 6.92(m, 8H, aromatic), δ 3.79(s, 3H, cis-OCH₃), δ 3.78(s, 3H, trans-OCH₃), δ 1.55(s, cis-CH₃), δ 1.22(s, trans-CH₃), δ 0.89(s, cis-CH₃).

The infrared spectrum showed bands at 3055, 2995, 2960, 2915, 2855, 1670, 1570, 1485, 1440, 1430, 1355, 1300, 1270, 1235, 1170, 1100, 1050, 1015, 915, 740, and 700 cm^{-1} .

Anal. Cal'd for $\text{C}_{22}\text{H}_{26}\text{N}_2\text{O}_2$: C, 75.40; H, 7.48.

Found: C, 74.74; H, 7.48.

The compound was repeatedly recrystallized from aqueous ethanol and hexane, dried in a vacuum oven, sealed under nitrogen, and stored

in the dark at about 0°C. (Analyses' results tended to be low because of decomposition.) After being sealed for several months, the compound gradually became a black liquid mixture. The decomposition mixture consisted of the hydrolysis products, o-methoxyaniline and 2,2,4,4-tetramethylcyclobutanedione. The mass spectrum gave molecular ions at 123 and 140, respectively. The cleavage pattern of the latter compound was identical to an authentic sample of 4.

Preparation of N,N'-Di(o-ethoxyphenyl)-2,2,4,4-tetramethyl-1,3-cyclobutanediimine (11)

Into a 250 ml flask fitted with a Dean-Stark trap were placed 2,2,4,4-tetramethylcyclobutanedione (4), 15.00 g (0.117 mole); o-phenetidine (o-ethoxyaniline), 31.96 g (0.233 mole); 100 ml of toluene; 0.10 g p-toluenesulfonic acid monohydrate; and a boiling stick. The mixture turned dark red immediately upon heating.

About 3.5 ml of water were collected after refluxing for over nine hours, which represented 94.6 percent yield for complete bisimine formation. The toluene was evaporated under reduced pressure on a Rinco evaporator. The remaining dark, viscous liquid crystallized to give white crystals in the liquid; total weight, 47.24 g.

The contents of the flask were crushed, rinsed with n-heptane at room temperature, and the mixture filtered with suction, resulting in a brown filtrate and a brown residue. This residue was washed with n-heptane, giving 22.77 g of blue solid, which was recrystallized from n-heptane to give 5.99 g of pure white crystals, m.p. 127-130°. The

filtrates continued to solidify and were washed with n-hexane and recrystallized from n-hexane or aqueous ethanol giving the product in various stages of purity. The structure of the compound was shown to be the bisimine using uv (Table 6), ir, and nmr spectroscopy. The nmr spectrum gave δ 7.56(m, 8H, aromatic), δ 4.70(quartet, 4H, $-\text{OCH}_2$), δ 2.29(s, cis- CH_3), δ 2.09(t, 6H, CH_3 of OC_2H_5), δ 1.95(s, trans- CH_3), δ 1.66(s, cis- CH_3). The infrared spectrum included bands at 3025, 2980, 1685, 1575, 1435, 1105, 1030, 920, and 730 cm^{-1} .

Anal. Cal'd for $\text{C}_{24}\text{H}_{30}\text{N}_2\text{O}_2$: C, 76.58; H, 8.01.

Found: C, 74.35; H, 7.71.

Preparation of N,N'-Di(o-chlorophenyl)-2,2,4,4-tetramethyl-1,3-cyclobutanediimine (12)

Into a 250 ml flask fitted with a Dean-Stark trap were placed 2,2,4,4-tetramethylcyclobutanedione (4), 15.00 g (0.116 mole); o-chloroaniline, 20.73 g (0.233 mole); p-toluenesulfonic acid monohydrate, 0.12 g; 100 ml of toluene; and boiling chips. Small amounts of these reactants had previously been heated in a 25 ml Erlenmeyer flask and the liberation of water observed as it collected in a beaker containing toluene. This beaker was connected to the Erlenmeyer flask by means of a rubber stopper and glass tubing.

The mixture in the 250 ml flask was refluxed until the liberation of water ceased. After 46 hours, about 3.7 ml of water was collected which represented 80.09 percent yield for complete bisimine formation, Table 3.

The light yellow solution crystallized on standing to give white crystals in a brown solution. The mixture was filtered with suction, leaving a white residue which was recrystallized from n-hexane. The crystals were dried overnight in a vacuum oven at 46° , giving 14.94 g of white crystals. The compound was then taken up in a limited amount of hot n-hexane, 60 ml, and filtered with suction giving white crystals which appeared to melt all at once, m.p. $160-162^{\circ}$. The residue, on the other hand, appeared to melt more slowly from the bottom of the capillary tube to the top, m.p. $135-162^{\circ}$. The structure of the bisimine compound was confirmed by uv (Table 6), ir, and nmr spectroscopy. The nmr spectrum gave $\delta 7.07$ (m, 8H, aromatic), $\delta 1.33$ (broad s, 12H, $-\text{CH}_3$). The infrared spectrum showed bands at 3060, 2960, 2920, 1670, 1580, 1465, 1445, 1430, 1375, 1355, 1255, 1220, 1155, 1115, 1050, 1025, 930, 840, 750, 730, 670, and 540 cm^{-1} .

Anal. Cal'd for $\text{C}_{20}\text{H}_{20}\text{N}_2\text{Cl}_2$: C, 66.85; H, 5.61.

Found: C, 66.39; H, 5.89.

Preparation of N,N'-Dibenzyl-2,2,4,4-tetramethyl-1,3-cyclobutanediimine (13)

Into a 250 ml flask fitted with a Dean-Stark trap was placed 2,2,4,4 tetramethylcyclobutanedione (4), 15.00 g (0.116 mole); benzylamine, 24.97 g (0.233 mole); 0.08 g p-toluenesulfonic acid monohydrate; 100 ml of benzene; and boiling chips. About 2.4 ml of

water were collected after about 48 hours, which represented about 57 percent yield for complete bisimine formation.

The clear, yellow solution was evaporated under reduced pressure with a Rinco evaporator, resulting in a white solid. Hot n-hexane was added to the solid, and the small amount of salt was filtered by gravity. The filtrate slowly crystallized over a day; a small amount of cold n-hexane was added to make up for evaporation loss. The resulting white solid was filtered with suction.

The structure was confirmed by uv (Table 6), ir, and nmr spectroscopy. The nmr spectrum gave $\delta 7.21(s, 10H, \text{aromatic})$, $\delta 4.62(s, 4H, -CH_2-)$, $\delta 1.55(s, \text{cis-CH}_3)$, $\delta 1.43(s, \text{trans-CH}_3)$, and $\delta 1.35(s, \text{cis-CH}_3)$.

Recrystallizing the product from hot n-hexane resulted in the formation of crystals. A large amount of cold solvent was added on top of the crystals; upon filtration a day later, some decomposition may have occurred since 3.25 g of yellow crystals were obtained instead of white crystals.

Filtration of the yellow crystals resulted in a yellow filtrate. This filtrate was heated, diluted to about 50 ml, and allowed to stand. After a day there was observed some yellow precipitate, a yellow layer of n-hexane, and an orange oily layer. The orange, viscous layer was separated with a Pasteur pipette. The nmr spectrum of this layer showed that unidentified rearrangements had occurred, since

the cis-trans absorption signals were greatly distorted. Because of the decomposition, chemical analysis was not undertaken.

Preparation of N,N'-Di(1-naphthyl)-2,2,4,4-tetramethyl-1,3-cyclobutanediime (14)

Into a 500 ml flask fitted with a Dean-Stark trap were placed 2,2,4,4-tetramethyl-1,3-cyclobutanedione (4), 50.00 g (0.356 mole); 1-naphthylamine, freshly recrystallized from hexane and aqueous ethanol, 104.81 g (0.732 mole); p-toluenesulfonic acid monohydrate, 4.17 g; toluene, 232 ml; boiling chips; and boiling sticks. A large amount of 1-naphthylamine was used in the reaction since it readily decomposed on standing.

Refluxing was discontinued after eight hours. Twelve ml of water were collected in the Dean-Stark trap, which represented over 94 percent yield for complete bisimine formation, Table 3.

The mixture was cooled and filtered with suction, giving a small amount of white salt residue and a purple filtrate. The filtrate was cooled overnight to 0°, then filtered with suction to give purple-white crystals which were recrystallized from hot n-hexane and aqueous ethanol and filtered with suction, giving a water soluble salt.

The bisimine compound was obtained by evaporating the toluene solution and recrystallizing the solid from acetone. The bisimine was slightly soluble in hot acetone, and only 8.00 g of pure material were obtained, m.p. 188-191°. No more bisimine was purified because

of the difficulty in recrystallization procedures. Black tars were also observed to be present. The bisimine structure was confirmed by uv (Table 6), ir, and nmr spectroscopy. The infrared spectrum showed bands at 1670, 1180, 960, 795, and 775 cm^{-1} . The nmr spectrum obtained gave δ 8.05-6.67(m, 14H, aromatic), δ 2.00-1.72(broad s, cis-CH₃), δ 1.50-1.17(broad s, trans-CH₃), δ 0.92-0.07(broad s, cis-CH₃). Nmr integration of the broad methyl singlets showed the presence of approximately 75 percent of the trans isomer and 25 percent of the cis isomer, at approximately 39°.

Preparation of 2,2,4,4-Tetramethyl-3-(2,6-dimethylanilino)-cyclobutanone (15) and N,N'-Di(2,6-dimethylanilino)-2,2,4,4-tetramethyl-1,3-cyclobutanediimine (16)

Into a 500 ml flask fitted with a Dean-Stark trap were placed 2,2,4,4-tetramethylcyclobutanedione (4), 50.00 g (0.214 mole); 2,6-dimethylaniline, 52.36 g (0.431 mole); 0.50 g p-toluenesulfonic acid monohydrate; about 120 ml of toluene; two boiling chips; and two boiling sticks. Toluene, 45 ml, was added to the attached Dean-Stark trap and the mixture refluxed, with water being very slowly collected in the trap. After 13 days, about 4.5 ml of water were collected, which represented about 100 percent yield for complete monoimine formation.

The resulting mixture, containing a precipitate, was filtered with suction, giving a filtrate which was evaporated in an evaporating dish over a steam bath. An infrared spectrum of the resulting yellow liquid

confirmed the presence of the monoimine structure. Infrared bands observed were 1900, 1800, approximately 1700, 1595, 1380, 1255, 1205, 1160, 1095, 845, and 760 cm^{-1} .

The residue was washed with toluene, giving bisimine crystals, 8.36 g, m.p. $173-174^{\circ}$, and 3.52 g of less pure bisimine, m.p. $174-175^{\circ}$. The total amount of bisimine collected corresponded to about 15 percent yield for complete bisimine formation. An infrared spectrum in nujol included bands at 1680, 1585, 1350, 1250, 1210, 1155, 1085, 1050, 840, 760, and 730 cm^{-1} .

The remaining filtrate slowly solidified into 30.28 g of black solid, m.p. $55-70^{\circ}$. An infrared spectrum of the impure compound indicated the mixture to be largely monoimine.

Preparation of N,N'-Di(o-isopropylphenyl)-2,2,4,4-tetramethyl-1,3-cyclobutanediimine (17)

Into a 250 ml flask fitted with a Dean-Stark trap were placed 2,2,4,4-tetramethylcyclobutanedione (4), 20.00 g (0.143 mole); o-isopropylaniline, 38.95 g (0.287 mole); p-toluenesulfonic acid monohydrate catalyst, 0.33 g (0.0018 mole); 120 ml of toluene; two boiling chips; and two boiling sticks. After 28 hours of refluxing, 4-4.5 ml of water were collected, which represented 80-90 percent yield for complete bisimine formation. The solvent in the mixture was evaporated from an evaporating dish with no heat. A moist, red solid was obtained, 55.01 g of wet crystals.

The structure was confirmed by infrared spectroscopy. An infrared spectrum of a nujol mull included bands at 1675, 1600, 1485, 1365, 1290, 1235, 1170, 1090, 1060, and 770 cm^{-1} .

Water was added to the filtrate, forming a few grams of crystals, which were recrystallized from aqueous ethanol and n-hexane, giving 13.84 g of pure white solid. Chemical analysis was not needed for this study.

Preparation of 2,2,4,4-Tetramethyl-3-(2,6-diisopropyl)-anilinocyclobutanone (18)

Into a 500 ml flask fitted with a Dean-Stark trap were placed 2,2,4,4-tetramethylcyclobutanedione (4), 30.00 g (0.214 mole); 2,6-diisopropylaniline, 73.38 g (0.431 mole); p-toluenesulfonic acid monohydrate, 0.50 g; 165 ml of toluene; two boiling chips; and two boiling sticks. The mixture was refluxed. After five hours, 0.6-0.7 of water was collected, which represented 15-18 percent yield for complete monoimine formation. No more water was collected after 16 hours of additional heating.

The salt was filtered off with suction, and the filtrate was distilled to remove toluene, unreacted amine, and some unreacted ketone, $26-42^{\circ}$, at 1.5 mm.

The residue consisted of unreacted ketone suspended in a yellow liquid. The ketone was filtered with suction and the liquid distilled, $87-106^{\circ}$, at reduced pressure. An infrared spectrum confirmed the yellow liquid to be the monoimine. Various bands included 3470, 3400, 2975, 2900, 1800, 1755, 1700, 1620, 1465, 1390, 1370, 1274, 1055, and 750 cm^{-1} .

No additional purification of product was necessary for this study.

Preparation of Aliphatic Bisimines and

Aliphatic Open Chain Amides

Preparation of N,N'-Dicyclohexyl-2,2,4,4-tetramethyl-1,3-cyclobutanediimine (19)

Into a 250 ml flask fitted with a Dean-Stark trap were placed 2,2,4,4-tetramethylcyclobutanedione (4), 15.00 g (0.116 mole); cyclohexylamine, 23.11 g (0.233 mole); p-toluenesulfonic acid, 1.25 g; 100 ml of toluene; and a boiling chip. The mixture was refluxed and stirred. About 1.2 ml of water were collected after 26 hours.

The slightly yellow solution in the flask contained some white precipitate which was filtered with suction to give 1.28 g of cyclohexylamine-p-toluenesulfonamide, as confirmed by nmr, m.p. 181-183°. The nmr spectrum in CDCl_3 gave δ 8.07-7.10(m, 6H, aromatic and -NH-), δ 3.03(s, 1H), δ 2.38(s, 3H, -CH₃), δ 2.17-0.93(m, 10H, -cyclohexyl). The infrared spectrum of a nujol mull showed bands at 3040, 1530, 1175, 1115, 1030, 1005, 810, and 675 cm^{-1} .

The solvent was removed under high vacuum, 6.5-7.0 mm; fraction 1, 26-40°. Various other fractions were collected: fraction 2, 41-63, consisted of the open chain amide as the major product; fraction 3, 78-106°, 9.75 g of crude bisimine as major product; and fraction 4, 142-170°, 2.47 g of crude bisimine as the major product. All solids

were recrystallized separately from either acetonitrile or aqueous ethanol until sharp melting points of the bisimine portion were obtained. A yield of 35 percent of pure bisimine was obtained, 11.37 g, m.p. 150-151°. The bisimine structure was confirmed by uv (Table 6), ir, nmr, and mass spectroscopy. The nmr spectrum gave δ 3.50(m, 2H), δ 2.00-1.50(m, 20H, $-C_6H_{10}$), δ 1.47(s, cis-CH), δ 1.32(s, trans-CH₃), δ 1.20(s, cis-CH₃). The infrared spectrum of a KBr wafer showed bands at 2915, 2840, 1670, 1435, 1350, 1170, 1060, 1030, 950, and 890 cm^{-1} . A mass spectrum gave a molecular ion at 302.

Anal. Cal'd for $C_{20}H_{34}N_2$: C, 78.88; H, 11.26.

Found: C, 78.61; H, 11.14.

The remaining solids did not melt sharply after repeated recrystallizations from acetonitrile and aqueous ethanol. Broad melting point ranges were recorded between 52° and 132°. The infrared spectrum of a nujol mull showed bands at 3340, 1795, 1705, 1625, 1525, 1065, 1030, and 880 cm^{-1} . This spectrum indicated the presence of the open chain amide as the major product. A yield of 65 percent was obtained, 21.42 g.

The bisimine compound was again prepared. Into the 250 ml flask fitted with a Dean-Stark trap were placed

2,2,4,4-tetramethylcyclobutanedione (4), 75.00 g (0.582 mole); cyclohexylamine, 115.54 g (1.165 mole); p-toluenesulfonic acid monohydrate, over 6.25 g; 135 ml toluene; and five boiling chips. After refluxing for 23 hours, 9.2 ml of water were distilled from the solution. The yellow solution contained some white precipitate. The precipitate was filtered with suction, recrystallized from aqueous ethanol, and the bisimine structure confirmed by uv, nmr, and ir spectroscopy.

Preparation of N-Cyclohexyl-2,2,4-trimethyl-3-oxovaleramide (20)

The reaction for the preparation of the bisimine compound 19, was rerun several more times with modifications: into a 500 ml flask fitted with a Dean-Stark trap were placed 2,2,4,4-tetramethylcyclobutanedione (4), 50.00 g (0.387 mole); cyclohexylamine, 77.03 g (0.776 mole); 250 ml of benzene; and p-toluenesulfonic acid monohydrate catalyst present only in small amounts, 1 g or less. After 12 hours, only 1.1 ml of water were given off. The yellow solution contained a solid which was recrystallized from aqueous ethanol. The solid was determined to be the open chain compound 20 by nmr, ir, uv, and mass spectroscopy. A mass spectrum gave a molecular ion at 239. An infrared spectrum of a KBr pellet showed bands at 3320, 2960, 2920, 1702, 1630, 1625, 1525, and 1025 cm^{-1} . The nmr spectrum gave δ 5.98(d, 1H, -NH), δ 3.50-4.00 (broad s, 1H, $-\text{N}-\overset{\text{H}}{\underset{|}{\text{C}}}-$), δ 2.98(heptet, 1H, isopropyl H), δ 2.12-1.53 (m, 10H, cyclohexyl), δ 1.25(s, 6H, -CH₃), δ 0.95(d, 6H, -CH₃). The uv spectrum showed no absorption. No trace of the bisimine compound was observable. Chemical analysis was not undertaken. Differing amounts of the open chain amide were produced in minor amounts during each preparation of the bisimine.

preparation of N-Cyclohexylidene-3-(2,2,4-trimethyl)-N'-cyclohexylvaleramide (21)

Into a 1000 ml flask fitted with a Dean-Stark trap were placed 2,2,4,4-tetramethylcyclobutanedione (4), 225.00 g (1.748 mole); cyclohexylamine, 381.30 g (3.844 mole); p-toluenesulfonic acid monohydrate, 20 g; and 280 ml of toluene.

After refluxing the concentrated mixture for one day, about 23 ml of water were liberated. Water continued to be slowly azeotroped from the reaction mixture, and 5-10 additional ml were collected after 28 days. Water was still slowly being formed on termination of the reaction. Toluene was continually added during the reaction.

The mixture solidified instantly on cooling and was heated overnight on the steam bath in attempts to sublime any unreacted ketone. The mixture was then filtered with suction and the brown crystals recrystallized twice from aqueous ethanol, giving 73.25 g of wet, white crystals. The crystals appeared to be less soluble in hot ethanol than N,N-dicyclohexyl-2,2,4,4-tetramethyl-1,3-cyclobutanediimine (19). Water was continuously added to the filtrate until no more crystals were obtained, giving about 100 g of brown crystals differing in purity. Unusual bands in the uv spectrum, and an unusual melting point, 232-233°, indicated the compound was not the expected bisimine. The infrared spectrum of a KBr pellet included bands at 3320, 2910, 1620, 1435, 1305, 1265, 1240, 1080, and 890 cm⁻¹. The nmr spectrum obtained in trifluoroacetic acid gave δ 3.18(m, approx. 4H, -NH-, isopropyl H, and $\begin{array}{c} \text{H} \\ | \\ \text{N}-\text{C}- \\ | \end{array}$), δ 1.58-1.37(m, -cyclohexyl), δ 0.92(m, -CH₃). The ultraviolet

spectrum obtained in isopropyl alcohol gave λ_{\max} 270nm($\epsilon = 22.2$), λ_{\max} 225nm($\epsilon = 88.9$). The mass spectrum gave a molecular ion at 322.

Preparation of N,N'-Dicycloheptyl-2,2,4,4-tetramethyl-1,3-cyclobutanediimine (22)

Into a 500 ml flask fitted with a Dean-Stark trap were placed 2,2,4,4-tetramethylcyclobutanedione (4), 50.00 g (0.357 mole); cycloheptylamine, 83.60 g (0.738 mole); p-toluenesulfonic acid monohydrate, 4.17 g (0.025 mole); and 200 ml of toluene. The mixture was allowed to reflux for several days until it appeared no more water was being collected in the Dean-Stark trap. Between 6.2 ml and 7.2 ml of water were collected. The yellow solution was then allowed to stand for several days until crystallization ceased. The mixture was filtered with suction, giving white crystals and a yellow filtrate. The white crystals were recrystallized from aqueous ethanol giving 12.36 g of solid, m.p. 127-128°. The solid was dried in a vacuum oven and Abderhalen dryer over toluene and P₂O₅. The bisimine structure 22 was confirmed by uv (Table 6), nmr, and ir spectroscopy. The nmr spectrum gave δ 4.62(s, impurity), δ 3.50(m, 2H), δ 1.54(s, 24H, -cycloheptyl), δ 1.39(s, cis-CH₃), δ 1.23(s, trans-CH₃), δ 1.12(s, cis-CH₃). The infrared spectrum of a nujol mull gave bands at 1670, 1360, 1180, and 1065 cm⁻¹.

Anal. Cal'd for C₂₂H₃₈N₂: C, 79.94; H, 11.59.

Found: C, 78.44; H, 11.23.

Preparation of N-Cycloheptyl-2,2,4-trimethyl-3-oxovaleramide (23)

After filtering the crystals of 22, the remaining yellow filtrate was evaporated in an open flask for two days to enhance precipitation. The resulting dark brown solution containing dirty precipitate was filtered with suction. White crystals of starting ketone were obtained which were removed by sublimation at 110-134°, using water aspirator pressure.

The brown filtrate was evaporated with a Rinco evaporator and filtered. Evaporation of the filtrate resulted in a solid which was recrystallized from acetonitrile, then purified by sublimation for 45 minutes. After solidification, the mixture was recrystallized from aqueous ethanol and dried in a vacuum oven at 41°, giving the open chain amide 23 in differing degrees of purity; m.p. of purest fraction, 69-71°. The structure of the open chain amide was confirmed by ir, nmr, and mass spectrometry. The nmr spectrum gave δ 4.17(m, 2H), δ 3.33(heptet, 1H, isopropyl H), δ 2.20, and δ 1.88(broad m, 24H, -cycloheptyl), δ 1.60(s, 6H, -CH₃), δ 1.29(d, 6H, -CH₃). The infrared spectrum of a nujol mull gave bands at 3320, 1705, 1625, 1520, and 1025 cm⁻¹. A mass spectrum gave a molecular ion at 253.

Anal: Cal'd for C₁₅H₂₇O₂N: C, 71.10; H, 10.74.

Found: C, 71.63; H, 10.38.

Preparation of N,N'-Dicyclooctyl-2,2,4,4-tetramethyl-1,3-cyclobutanediimine (24)

Into a 250 ml flask fitted with a Dean-Stark trap were placed 2,2,4,4-tetramethylcyclobutanedione (4), 50.00 g (0.357 mole);

cyclooctylamine, 90.76 g (0.713 mole); p-toluenesulfonic acid monohydrate, slightly over 4.17 g (slightly over 0.022 mole); 150 ml of toluene; and two boiling chips. The pale-yellow mixture was stirred and refluxed for 24 hours. When liberation of water ceased, 5.0 ml were collected.

The mixture, after crystallizing upon cooling, was filtered with suction. Fifteen to 20 grams of collected crystals were recrystallized from aqueous ethanol and hexane with no heat, m.p. 99.5-102.5°. The bisimine structure was confirmed by uv (Table 6), ir, and mass spectrometry. The infrared spectrum of a nujol mull showed bands at 1670, 1365, 1180, and 1060 cm^{-1} . The nmr spectrum gave δ 3.50(m, 2H), δ 1.50(m, 28H, -cyclooctyl), δ 1.40(s, cis-CH₃), δ 1.25(s, trans-CH₃), δ 1.10(s, cis-CH₃). A mass spectrum gave a molecular ion at 338. No chemical analysis was undertaken.

Preparation of N-Cyclooctyl-2,2,4-trimethyl-3-oxovaleramide (25)

After filtering the crystals of 24, the remaining yellow filtrate was evaporated on a Rinco evaporator forming about 100 g of solid which was dissolved in cold ethanol and crystallized by the addition of two volumes of water. The mixture was filtered with suction giving crystals of 25, m.p. 74-85°. The filtrate was dissolved in warm hexane, filtered by gravity, and crystallized by cooling in ice. Suction filtration gave 60.36 g of pale yellow crystals and a yellow filtrate. These crystals were recrystallized from aqueous

ethanol (145 ml ethanol, 55 ml water) in an ice bath. White crystals were obtained, 43.46 g, m.p. 81-83°. The structure was confirmed by ir and mass spectrometry. The infrared spectrum of a nujol mull showed bands at 3295, 1695, 1520, and 1030 cm^{-1} . No chemical analyses were made. The mass spectrum gave a molecular ion at 267.

Preparation of N-Cyclopentyl-2,2,4-trimethyl-3-oxovaleramide (26)

Into a 250 ml flask fitted with a Dean-Stark trap were placed 2,2,4,4-tetramethylcyclobutanedione (4), 16.46 g (0.177 mole); cyclopentylamine, 20.00 g (0.235 mole); p-toluenesulfonic acid monohydrate, 1.37 g; and 89 ml of toluene. The mixture was refluxed for 24 hours and 2.6 ml of water were collected, which represented 61.5 percent yield for complete monoimine formation.

The resulting yellow solution contained no precipitate after standing at 0° for several days. The solution was evaporated in a crucible on the steam bath until about 30-40 ml of dark liquid remained, which crystallized to a dark brown, moist solid, 26.67 g, after standing at 0°.

The mixture was dissolved in warm n-hexane, filtered by gravity, and the filtrate crystallized upon cooling with ice. The mixture was filtered with suction, giving 8.46 g of brown crystals and a brown filtrate. These brown crystals were dissolved in 20 ml of ethanol and

filtered by gravity. Then 25 drops of water were added to the filtrate and the mixture was allowed to crystallize at 0°.

Needle-shaped white crystals were obtained, 5.28 g, m.p. 56-58°. The structure was confirmed to be the open chain amide (26) by nmr, ir, and mass spectroscopy. The nmr spectrum gave 5.97-5.64 δ (broad s, 1H, -NH), 2.92 δ (heptet, 1H, isopropyl H), 2.17-1.33 δ (m, 9H, -cyclopentyl), 1.66 δ (s, 6H, -CH₃), 0.87 δ (d, 6H, -CH₃). A mass spectrum gave a molecular ion at 225. The presence of NH stretching frequencies and the absence of imine stretching frequencies were noted in the infrared spectrum.

Addition of water to the filtrate resulted in more crystals of differing purity, m.p. 54.5-56°, m.p. 55-74°, and m.p. 73-81°, 8.46 g total. No bisimine compound was observed. Chemical analysis was not undertaken.

Preparation of n-Butylaminehydrochloride (27)

Into a 100 ml round bottom 19/22 ST flask, cooled by an ice bath, was placed n-butylamine, 14.63 g (0.20 mole). A 19/22 ST separatory funnel was fitted to the flask. Into the separatory funnel was placed 12 M HCl, 11.90 g. The HCl was added dropwise to the flask with cooling and shaking. This resulted in the evolution of a large amount of white gas. After the white smoke had disappeared, more HCl, 0.44 g, was added until the solution was neutral to litmus. The mixture did not crystallize even upon the addition of ether. Heating the mixture over a hot plate led to solidification and slight decomposition of

the salt. The salt was dissolved in hot chloroform, filtered hot, and carbon tetrachloride added, resulting in the formation of white crystals. The crystals were filtered with suction, giving 8.28 g of white, very wet appearing solid which was dried in a vacuum oven at low temperatures. An infrared spectrum of the solid as a nujol mull showed bands at 3600-2500, 2050, 1600, 1170, 1080, 1020, 920, 800, and 745 cm^{-1} .

Attempted preparation of N,N'-Di-n-butyl-2,2,4,4-tetramethyl-1,3-cyclobutanediimine (28)

Into a 250 ml flask fitted to a Dean-Stark trap were placed 2,2,4,4-tetramethylcyclobutanedione (4), 2.97 g (0.021 mole); n-butylamine hydrochloride (27), 6.97 g (0.064 mole, equivalent to 0.042 mole n-butylamine); 90 ml of nitrobenzene as solvent; and two boiling chips. The mixture was heated for about four hours, at which time two immiscible liquids distilled into the Dean-Stark trap. The contents of the reaction flask gradually darkened in color from light greenish-yellow to black. The contents of the trap contained a lower layer of about 1 ml consisting mainly of clear nitrobenzene and a two ml top layer. This top layer was slightly yellow and contained a few white crystals of starting ketone 4 and water.

The black liquid in the reaction vessel contained some white crystals, which were filtered with suction and washed with cold nitrobenzene. About 2.59 g of waxy, hygroscopic crystals were formed which were shown to be n-butylamine hydrochloride 27 by ir spectroscopy. An infrared spectrum was similar to an authentic sample of 27.

The black liquid was distilled under moderate vacuum, giving nitrobenzene and a brown liquid as distillates, 60-67°, at 2.4 mm. An infrared spectrum indicated the presence of nitrobenzene, 2,2,4,4-tetramethylcyclobutanedione (4), and the possibility of a small amount of open chain amide. The infrared spectrum showed bands at 3420, 3035, 2930, 2855, 2425, 1705, 1700, 1615, 1600, 1520, 1470, 1340, 1100, 1060, 1015, 925, 845, 785, 695, and 670 cm^{-1} .

An infrared spectrum of the black, viscous liquid remaining in the distillation flask indicated the presence of n-butylamine hydrochloride (27), with a small amount of nitrobenzene. The spectrum of a neat sample showed bands at 3600-2340, 2975, 2040, 1705, 1630, 1520, 1460, 1340, 1030, 840, and 700 cm^{-1} .

Preparation of N-3-Methylbutyl-2,2,4-trimethylbutyl-2,2,4-trimethyl-3-oxovaleramide (29)

Into a 250 ml flask fitted with a Dean-Stark trap were placed 2,2,4,4-tetramethylcyclobutanedione (4), 7.50 g (0.058 mole); 3-methylbutylamine, 10.16 g (0.116 mole); p-toluenesulfonic acid monohydrate, 0.06 g; 92 ml of toluene; and a boiling chip. The mixture was refluxed until water ceased to distill into the Dean-Stark trap. After one day, 0.8 ml of water was collected.

The mixture was evaporated on a Rinco evaporator to give an orange, viscous open chain amide 29. The infrared spectrum showed bands at 3340, 2940, 1705, 1630, 1520, 1460, 1375, 1360, 1275, 1075, 1030, and 990 cm^{-1} .

Attempted Preparation of 2,2,4,4-Tetramethyl-3-tert.
butyliminocyclobutanone (30)

Into a 250 ml flask fitted to a Dean-Stark trap were placed 2,2,4,4-tetramethylcyclobutanedione (4), 15.00 g (0.116 mole); 50 ml of warm benzene, tert.butylamine, 17.00 g (0.233 mole); and two small drops of concentrated sulfuric acid, which resulted in the formation of a small amount of white, water soluble amine sulfate. The precipitate was filtered with suction, which resulted in 0.04 g of material being obtained. The mixture was refluxed for 27.5 hours with no water being collected, indicating the lack of imine formation. The resulting clear liquid had a ketone and amine odor. A portion of the solution was evaporated on a Rinco evaporator, giving white crystals. An infrared spectrum of the crystals was identical to an authentic sample of 2,2,4,4-tetramethylcyclobutanedione (4).

The attempted preparation was rerun with modifications. Into a large test tube were placed 2,2,4,4-tetramethylcyclobutanedione (4), 7.50 g (0.058 mole); tert.butylamine, 8.50 g (0.116 mole); a large pinch of potassium carbonate catalyst; and 40 ml of benzene. The total volume of the solution was about 56.5 ml. The contents of the tube were frozen with liquid nitrogen, a vacuum was pulled on the tube using a water aspirator, and the tip of the tube was sealed. The tube was allowed to cool slowly and then placed in a sealed pipe in an oven at slightly over 100° for 6.5 hours. Upon cooling, the contents of the tube appeared to have slightly darkened in color.

A portion of the mixture was evaporated, and an infrared spectrum was taken of the remaining white solid. No evidence of a reaction was apparent.

The infrared spectrum of a nujol mull showed bands at 3375, 1745, 1655, 1515, 1265, 1220, 1030, 990, and 880 cm^{-1} . This residue was extracted with hot ethanol and filtered. An infrared spectrum taken of the residue was identical to an authentic sample of 2,2,4,4-tetramethylcyclobutanedione (4).

The reaction was attempted several more times using sealed tubes. These attempts were unsuccessful due to the tendency of sealed tubes to explode while being heated.

Attempted preparation of 2,2,4,4-Tetramethyl-3-isopropyliminocyclobutanone (31)

Into a 250 ml flask fitted to a Dean-Stark trap were placed 2,2,4,4-tetramethylcyclobutanedione (4), 15.00 g (0.116 mole); 150 ml of warm benzene; isopropylamine, 13.77 g (0.233 mole); and one small drop of concentrated sulfuric acid, which resulted in a very small amount of white precipitate. A couple of small crystals of p-toluenesulfonic acid were added, and the mixture was refluxed for about 13 hours. No water was liberated, so 30 ml of the mixture was set aside and four drops of concentrated sulfuric acid added to the remainder with continued refluxing for three more hours. No water was liberated, so several drops of water, one ml of concentrated sulfuric acid, and 0.50 g of p-toluenesulfonic acid were added along with two boiling chips. The solution turned cloudy upon

the addition of sulfuric acid but was still slightly basic to litmus. Refluxing was discontinued after two hours. The resulting solution contained a large amount of white precipitate, amine sulfate, which was filtered with suction. No indication of reaction was evident.

Preparation of N-Adamantyl-2,2,4-trimethyl-3-oxovaleramide (32)

Into a 250 ml flask fitted to a Dean-Stark trap were placed 2,2,4,4-tetramethylcyclobutanedione (4), 5.00 g (0.21 mole); adamantane amine, 11.14 g (0.074 mole); p-toluenesulfonic acid monohydrate, 0.46 g; 165 ml of toluene; two boiling chips; and a boiling stick. Water was liberated very slowly upon refluxing. After about two days, approximately 0.20-0.25 ml of water were collected, which represented 30-40 percent yield for complete formation of the open chain compound; 60-70 percent of the amine did not react.

The resulting yellow solution contained a white precipitate which was filtered with suction, giving 0.84 g of white crystals and a yellow filtrate. An infrared spectrum of the white solid after washing with toluene indicated the presence of salt. An infrared spectrum gave bands at 1610, 1180, 1020, 1000, and 800 cm^{-1} .

The filtrate was evaporated in an evaporating dish on a steam bath to give about 5.1 g of white solid. An infrared spectrum of the crude material as a nujol mull indicated the presence of unreacted amine and the open chain compound (32). An infrared spectrum gave bands at 3350, 2650, 1660, 1300, 1135, 1085, and 1030 cm^{-1} . The mixture was recrystallized from aqueous ethanol over a period of several days, giving

0.75 g of material, m.p. 99-150°. An infrared spectrum of a nujol mull showed the presence of impure open chain amide (32). An infrared spectrum gave bands at 3355, 1660, 1505, and 1035 cm^{-1} .

The mixture was recrystallized from n-hexane by dissolving it in cold n-hexane, filtering off the amine residue, and chilling. This gave 0.45 g of the open chain compound 32, m.p. 108-110°. An infrared spectrum was consistent with the structure.

Attempted preparation of N,N'-Di(tert.octyl)-2,2,4,4-tetramethyl-1,3-cyclobutanediimine (33)

Into a 1000 ml flask fitted to a Dean-Stark trap were placed 2,2,4,4-tetramethylcyclobutanedione (4), 56.07 g (0.40 mole); tert.octyl amine, 103.40 g (0.80 mole); p-toluenesulfonic acid monohydrate, 5.16 g; 300 ml of toluene, two boiling chips; and two boiling sticks. The mixture was stirred and brought to a reflux. After about one day, about 0.5 ml of water were collected, an amount which corresponded to the water content of the acid catalyst used. About 5.16 g of the acid catalyst were again added. After two days, no more water was being liberated, so the heating was discontinued. The total amount of water liberated was about 1 ml, an amount which corresponded to the amount of water in the acid catalyst used. Isolated products were identical to the starting materials.

Preparation of Monoimines and Mixed Bisimines

Preparation of 2,2,4,4-Tetramethyl-3-phenyliminocyclobutanone (34)

Into a 500 ml flask fitted to a Dean-Stark trap were added 2,2,4,4-tetramethylcyclobutanedione (4), 100.00 g (0.71 mole), and 100 ml of warm toluene, which dissolved most of the ketone. To this was added aniline, 66.30 g (0.71 mole); p-toluenesulfonic acid monohydrate, 1.65 g (0.0087 mole); 100 ml more toluene; and boiling chips. The mixture was refluxed for about five hours and then cooled, resulting in a white precipitate in a dark red solution. Over 12.5 ml of water were collected during this period.

The mixture was washed twice with 100 ml portions of saturated sodium bicarbonate solution, twice with 100 ml portions of distilled water, and dried one to two days over magnesium sulfate. It was then filtered, and the residue washed three times with toluene. The extract containing 86.5 ml of toluene was then distilled under high vacuum. Some ketone started subliming at 43° (0.2 mm). The toluene was distilled, $26-29^{\circ}$ (0.2 mm), followed by distillation of the rest of the material, $75-115^{\circ}$, (0.2 mm). This fraction was redistilled; the ketone started subliming about 38° . The first fraction was distilled at $61-98^{\circ}$ (1 mm), the second fraction at $98-110^{\circ}$ (1 mm), and the third fraction at $110-160^{\circ}$ (1 mm). An infrared spectrum of the first fraction showed the presence of starting material, monoimine 34, and open chain amide, the color darkening to red

upon standing for a couple of days. The second fraction contained about 50 ml total volume and was slightly green in color, with some solid material present. An infrared spectrum showed the presence of the monoimine 34 and starting ketone 4. The third fraction contained a few ml of viscous liquid and some white solid; an infrared spectrum indicated the presence of monoimine 34, bisimine 9, and less open chain amide and starting ketone 4 than the first fraction. The remaining residue consisted of monoimine 34, starting ketone 4, open chain amide, and bisimine 9.

Attempts were made to sublime the ketone material from the second fraction using water aspirator pressure, 94-113°. The mixture was cooled, filtered with suction and redistilled. The following fractions were obtained: fraction a, 84-89° at 0.36 mm, and fraction b, 65-135° at 0.25 mm. The material from fraction a was sublimed at 2 mm. The material then darkened in color and solidification occurred. Recrystallization of the 10.21 g of white crystals from aqueous ethanol gave pure bisimine 9, m.p. 137-140°. An infrared spectrum of these crystals was identical to the spectrum of N,N'-diphenyl-2,2,4,4-tetramethyl-1,3-cyclobutanediimine (9), previously prepared. Other impure crystals were present in lesser amounts.

The material from fraction b, about 50 ml, was pure monoimine 34, containing only a negligible trace of bisimine 9, as determined by ir, nmr, and uv spectroscopy (Table 6). An infrared spectrum gave bands at 3060 (weak), 2960, 2925, 2860, 1800, 1695, 1580, 1480, 1450, 1375, 1355,

1265, 1215, 1040, 835, 760, 735, and 690 cm^{-1} . The nmr spectrum gave approximately $\delta 7.2(\text{m}, 5\text{H}, \text{aromatic})$, approximately $\delta 1(\text{s}, 6\text{H}, -\text{CH}_3)$, and approximately $\delta 0.9(\text{s}, 6\text{H}, -\text{CH}_3)$.

The sample was sealed under nitrogen and wrapped in brown paper. After standing over a year, a darkening of the color was observed with the deposition of increasing amounts of white solid. A mass spectrum gave fragmentation ions at 140 and 93, corresponding to the starting materials, 2,2,4,4-tetramethylcyclobutanedione (4) and aniline, respectively. Chemical analysis of the monoimine 34 was not undertaken because of the tendency of this compound to undergo hydrolysis.

Preparation of 2,2,4,4-Tetramethyl-3-cyclohexyliminocyclobutanone (35)

Into a 1000 ml flask fitted with a Dean-Stark trap were placed 2,2,4,4-tetramethylcyclobutanedione (4), 100.00 g (0.712 mole); cyclohexylamine, 77.66 g (0.783 mole); p-toluenesulfonic acid monohydrate, 8.67 g (0.046 mole); 300 ml toluene; three boiling chips, and a boiling stick. The mixture was refluxed for about 28 hours, at which time the removal of water was complete when 5.2 ml of water were collected. The mixture was distilled twice, 81-113° at 1.3-1.5 mm, and then subjected to sublimation in order to remove excess starting ketone 4. The material was then recrystallized from aqueous ethanol and n-hexane twice giving the monoimine 35 in various stages of purity, m.p. 73-74°, about 37.59 g. The monoimine structure was confirmed by ir, uv (Table 6), and mass spectrometry.

An infrared spectrum of a nujol mull gave bands at 1800, 1690, 1265, 1190-1170, 1120, 1040, 960, and 885 cm^{-1} . A mass spectrum gave a molecular ion at 221. The nmr spectrum gave δ 3.50(m, 1H), δ 1.80-1.25(m, 10H, cyclohexyl), δ 1.15(s, 6H, CH_3 's), δ 1.03(s, 6H, CH_3 's).

Anal: Cal'd for $\text{C}_{14}\text{H}_{23}\text{N}$: C, 75.97; H, 10.47.

Found: C, 75.84; H, 10.22.

Also obtained by evaporation of the filtrates were about 65.82 g of a mixture consisting primarily of the open chain amide 20, with some monoimine 35 present. An infrared spectrum of a nujol mull showed bands at 3345, 1800, 1690, 1630, 1535, 1380, 1185, 1075, 1040, 960, and 890 cm^{-1} . About 11.88 g of salt were obtained, indicated by water solubility.

Preparation of 2,2,4,4-Tetramethyl-3-n-butyliminocyclobutanone (36)

Into a 100 ml flask fitted to a Dean-Stark trap were placed 2,2,4,4-tetramethylcyclobutanedione (4), 1.00 g (0.007 mole) in 10 ml of benzene; n-butylamine, 0.56 g (0.0072 mole); and one drop of concentrated sulfuric acid as catalyst, which resulted in the immediate formation of a greyish-white precipitate of amine sulfate. The mixture was stirred and heated slowly with a heating mantle in order to achieve gentle refluxing. After one hour, only a small amount of liquid had been distilled. The distillation was completed after about four more hours. The mixture in the flask had a slight amine odor and crystallized on standing. The benzene was removed with a Rinco evaporator.

The resulting mixture consisted of white crystals in a yellow, viscous liquid. This mixture was filtered with suction to give 0.21 g of wet crystals, which appeared to decompose on attempts to determine the melting point up to 253° . An infrared spectrum indicated the presence of the monoimine 36 and some open chain amide. The infrared spectrum showed bands at 3320, 2890, 1820-1750, 1540, 1460, 1375, 1085, 1040, 1015, and 1000 cm^{-1} . The viscous, yellow liquid crystallized in the suction flask to give 0.43 g of oily, white crystals which appeared to melt at $103-113^{\circ}$, wet (m.p. of starting ketone, $114-116^{\circ}$). It was concluded that the reaction did not go to completion.

The reaction was rerun on a larger scale. Into a 250 ml flask fitted to a Dean-Stark trap were placed 2,2,4,4-tetramethylcyclobutanedione (4), 10.00 g (0.071 mole); n-butylamine, 5.62 g (0.077 mole); 106 ml of warm benzene; and one drop of concentrated sulfuric acid.

The reaction was stopped after about 30 hours of refluxing and 0.7 ml of water were removed. The resulting light-greenish-yellow solution contained some waxy solid, so it was filtered with suction, and the residue was washed twice with small portions of ether, giving about 0.15 g of waxy solid. The filtrate was evaporated under reduced pressure on a Rinco evaporator to give about 17.24 g of viscous, yellow liquid. The infrared spectrum of this liquid indicated the presence of starting ketone 4, monoimine 36, open chain amide, and possible starting amide.

A 50 microliter sample of the viscous yellow liquid was injected into an Autoprep Gas Chromatograph Unit: oven temperature-205°; detector temperature-290°; injector temperature-120°. The column used was a 30 percent SE 30 3/5" x 20", flow rate-approximately 4 cc/sec. The following components with their relative abundance were obtained in this order: n-butylamine (impurity), starting ketone 4 (major), monoimine 36 (considerable), and open chain amide (slight).

The remaining viscous liquid was distilled under moderate vacuum, using water aspirator pressure, in order to isolate the monoimine. The distillate, 80-125°, at approximately 12 mm, weighed 7.25 g, and was shown by gc analysis to contain monoimine 36 as the major product and starting ketone 4 as the minor product. There remained about 3.59 g of orange, viscous liquid and starting ketone in the distillation flask. A large amount of ketone which precipitated out of the monoimine solution was then filtered with suction. This solution was then redistilled under high vacuum, and the fractions were analyzed by gc analysis as described above. The following fractions were collected: fraction 1, 2.83 g, 67-79° at 2.5-2.75 mm, contained considerable starting ketone 4, but monoimine 36 as the major product; fraction 2, 1.43 g, 67-89°, at 2.4-2.75 mm, contained monoimine 36 as the major product, and open chain amide, n-butylamine, and starting ketone 4 as minor products; and fraction 3, approximately 0.1 g, 90-113°, at 2.5-2.75 mm, consisted of open chain amide as major product and monoimine 36 as minor product. The structure of 36 was confirmed by ur (Table 6),

ir, and nmr spectroscopy. The nmr spectrum gave δ 3.38(m, 2H, $-\text{CH}_2\text{N}$), δ 1.61(m, 4H, $-\text{CH}_2-\text{CH}_2-$), δ 1.31(s, 6H, -ring CH_3), δ 1.21(s, 6H, ring CH_3), δ 1.04(m, 3H, $-\text{CH}_3$ of n-butyl). The infrared spectrum showed bands at 2960, 1800, 1695, 1455, 1270, and 1040 cm^{-1} .

Preparation of N-Phenyl-N'-Cyclohexyl-2,2,4,4-tetramethyl-1,3-cyclobutanediimine (37) and 4 Methyl-3-N-Phenylimino-2,2-dimethyl-N'-Cyclohexylaminopentanoamide (38)

Into a 250 ml flask fitted to a Dean-Stark trap were placed 2,2,4,4-tetramethyl-3-phenyliminocyclobutanone (34), 10.76 g (0.05 mole); cyclohexylamine, 5.22 g (0.053 mole); p-toluenesulfonic acid monohydrate, 0.55 g (0.003 mole); and 100 ml of toluene. The contents of the flask were shaken and the flask brought to a reflux. After reacting for 24-30 hours, 0.45 ml of water were collected in the Dean-Stark trap.

The mixture turned a different shade of yellow on cooling, followed by precipitation. The mixture was filtered to give about 0.75 g of white solid, m.p. 182-183°. The filtrate crystallized on standing to give 0.80 g of solid, m.p. 93-111.5°. No more precipitation occurred on attempts to evaporate the remaining liquid, so it was distilled under moderate vacuum: first cut, 77-101°; second cut, 102-115°. The remaining material in the distillation flask solidified in this flask, condenser, and distillation apparatus. An infrared spectrum of cut 1 indicated the material to be N-phenylmonoimine 34 and the open chain amide, 4-methyl-3-N-phenylimino-2,2-dimethyl-N'-cyclohexylaminopentanoamide (38). The white solid was recrystallized from aqueous ethanol,

0.76 g, m.p. 116-118.5°. The filtrate from this recrystallization solidified, giving 0.15 g which was recrystallized from n-hexane. Filtration of the mixture gave 0.10 g of residue, m.p. 117-118.5° and a filtrate which solidified, 0.05 g, m.p. 83-106°.

The liquids from cuts 1 and 2 were redistilled under a moderate vacuum, 105-116°, 4.60 g, corresponding to about 42.75 percent of unreacted material. An infrared spectrum showed the distillate consisted of the N-phenylmonoimine 34 as the major product and the imino open chain amide 38 as the minor product.

The white solid was recrystallized twice from aqueous ethanol, 0.53 g, m.p. 116-118.5°. An infrared spectrum of the white solid 37 gave bands at 2920, 2850, 1680, 1580, 1480, 1440, 1355, 1220, 1065, 1045, 760, and 695 cm^{-1} . The uv spectrum is given in Table 6. A mass spectrum gave a molecular ion at 296, and fragmentation ions at 151, 145, and other fragments.

Anal. Cal'd. for $\text{C}_{20}\text{H}_{28}\text{N}_2$: C, 81.03; H, 9.52.

Found: C, 80.67; H, 9.25.

Summary of product formation:

| <u>Compound</u> | <u>Estimated Percent Yield for Complete Compound Formation</u> |
|----------------------------------|--|
| Unreacted monoimine <u>36</u> | 50. |
| Salt | 3 |
| Bisimine <u>37</u> | 20 |
| Imino open chain amide <u>38</u> | 20 |

The brown solid residue remaining after the second distillation consisted mainly of the open chain amide 38 with some monoimine 35. The monoimine was distilled off under moderate vacuum, giving 0.70 g of 4-methyl-3-N-phenylimino-2,2-dimethyl-N'-cyclohexylaminopentanoamide (38), as determined by infrared spectroscopy. The infrared spectrum gave bands at 3300, 3050 (weak), 2910, 1660, 1585, 1525, 1440, 1215, 1065, 1045, 880, 760, and 690 cm^{-1} .

An unidentified compound, residue after the first distillation, was redistilled, 105-116°, at moderate vacuum. An infrared spectrum showed the presence of an unusual band at 2000 cm^{-1} . Other bands present were 3250-3300, 3050 (weak), 2960-2900, 1795, 1695-1620, 1540-1520, 1460-1435, 1375, 1365, 1040, 835, and 760 cm^{-1} .

Preparation of Immonium Salts

Preparation of Diphenyl-2,2,4,4-tetramethyl-1,3-cyclobutanediimmonium Dichloride (39)

Into a 500 ml flask were placed N,N'-diphenyl-2,2,4,4-tetramethyl-1,3-cyclobutanediimine (9), 4.54 g (0.015 mole); and 100 ml of ether. Solid sodium chloride, 5.94 g (0.10 mole), was placed in a 250 ml gas generating flask, and concentrated sulfuric acid, 9.80 g (0.10 mole), was added dropwise.³⁷ The resulting HCl gas was introduced into the ether solution. A white precipitate formed immediately in the ether solution. After about one hour, the large, white precipitate was filtered with suction giving 4.08 g of white flakes which dried

on crushing. The filtrate was evaporated over the steam bath, resulting in the same white solid. The crystals were combined and recrystallized by dissolving them in 45 ml of warm ethanol, filtering by gravity, adding about 35-40 ml of n-hexane, and storing them in a refrigerator, 10°. The resulting crystals precipitated after one day and were filtered with suction, giving light blue crystals, 2.20 g, m.p. 191.5-194.5°.

Gravimetric chloride determination³⁸ indicated the presence of two moles of chloride ion per mole of salt. The calculations are shown below:

$$\text{weight AgCl obtained} = 0.1574 \text{ g}$$

$$\begin{aligned} \text{moles AgCl obtained} &= 0.1574 \text{ g} / 143.337 \text{ g mole}^{-1} \\ &= 1.091 \times 10^{-3} \text{ moles} \end{aligned}$$

$$\text{moles Cl}^{-} \text{ originally present} = 1.091 \times 10^{-3} \text{ moles}$$

$$\text{weight of sample used} = 0.1696 \text{ g}$$

$$\begin{aligned} \text{moles of sample used} &= 0.1696 \text{ g} / 363.31 \text{ g mole}^{-1} \\ &= 4.67 \times 10^{-4} \text{ moles} \end{aligned}$$

$$\frac{\text{moles Cl}^{-} \text{ present}}{\text{moles sample used}} = \frac{1.09 \times 10^{-3}}{4.67 \times 10^{-4}} = 2.33 \approx 2$$

The sample was titrated to determine the equivalent weight. The sample was added to 50 ml water, the mixture boiled, and then titrated with dilute sodium hydroxide solution. The data and calculations are shown below:

Experimental Equivalent Weight

Normality of base = 0.100 N

Volume of base at pH 8 = 10.7 ml

$$\text{Equivalents of base} = \frac{(10.70 \text{ ml})(11)(0.100\text{N})}{(10^3 \text{ ml})}$$

$$= 0.00107 \text{ equivalents}$$

Weight of sample used = 0.18068 g

$$\text{Equivalent weight} = \frac{0.18068 \text{ g}}{0.00107 \text{ equivalents}} = \frac{168.86 \text{ g}}{\text{equivalent}}$$

Actual Equivalent Weight

$$\begin{aligned} \text{Equivalent weight} &= \frac{\text{formula weight}}{\text{equivalents of hydrogen ion}} \\ &= \frac{359}{2} = 179.5 \end{aligned}$$

Partial hydrolysis could account for the low analytical and experimental values. In addition, a blank was needed so 2,2,4,4-tetramethylcyclobutanedione (4) and aniline hydrochloride were also titrated. Titration of 2,2,4,4-tetramethylcyclobutanedione required a negligible amount of base. The aniline hydrochloride was recrystallized several times by dissolving the sample in warm ethanol, filtering by gravity, adding n-hexane to the filtrate, and filtering the precipitate with suction. Data and calculations for the titration of aniline hydrochloride are shown below:

Experimental Equivalent Weight

Normality of base = 0.1012 N

Volume of base at pH 8.1 = 14.04 ml

$$\text{Equivalents of base} = \frac{(14.04 \text{ ml})(0.1012 \text{ N})}{(10^3 \text{ ml})} = 0.001421 \text{ equivalents}$$

Weight of sample used = 0.18270 g

$$\text{Equivalent weight} = \frac{0.18270 \text{ g}}{0.001421 \text{ equivalents}} = 128.60 \text{ g equivalent}^{-1}$$

Actual Experimental Weight

$$\text{Equivalent weight} = \frac{\text{formula weight}}{\text{equivalents of hydrogen ion}}$$

$$= \frac{129.5}{1} = 129.5$$

An infrared spectrum of 39 as a nujol mull gave bands at 3300-2700, 2650, 2020, 1920, 1760, 1730, 1600, 1575, 1560, 1500, 1275, 1205, 1060, 745, and 690 cm^{-1} . The ultraviolet spectrum obtained in ethanol gave λ_{max} 344 nm($\epsilon = 13.5$), broad, and λ_{max} 294.5 nm($\epsilon = 48.2$) at a concentration of 6.54×10^{-3} M, and λ_{max} 233 nm($\epsilon = 447.6$) at a concentration of 2.61×10^{-4} M. Additional absorptions were believed to be present in the visible region. The nmr spectra also indicated hydrolysis was evident. The spectrum in trifluoroacetic acid gave δ 8.68-8.01(broad s, 2H, $\text{=}\overset{+}{\underset{\text{H}}{\text{N}}}\text{--}$), δ 6.83(s, 10H, $\text{-C}_6\text{H}_5$), δ 0.84(s, -CH_3).

The spectrum in CH_3OH was similar, also indicating hydrolysis. Elemental analyses were inconsistent because of incomplete combustion of salt-like compounds.

Preparation of Dicyclohexyl-2,2,4,4-tetramethyl-1,3-cyclobutanediiminium Dichloride (40)

Into a 500 ml reaction flask were placed N,N'-dicyclohexyl-2,2,4,4-tetramethyl-1,3-cyclobutanediimine (19), 8.71 g (0.029 mole), and 150 ml of ether. Solid sodium chloride, 11.89 g (0.20 mole), was placed in a 250 ml generating flask, and excess concentrated sulfuric acid, 25 ml, was added dropwise. The resulting HCl gas was introduced into the ether solution. The reaction was terminated after 15 minutes, yielding a large, white precipitate.

The precipitate was recrystallized from cold aqueous ethanol, filtered with suction, and the filtrate evaporated in an evaporating dish on a steam bath, m.p. 205-206.5°. The addition of 2M silver nitrate solution to an aqueous solution of 19 resulted in a white precipitate indicating the presence of chloride ion. Gravimetric chloride determination³⁸ indicated the presence of two moles of chloride ion per mole of salt. The calculations are shown below:

weight of AgCl obtained = 0.1743 g

moles AgCl obtained = $0.1745 \text{ g} / 143.337 \text{ g mole}^{-1}$

= 1.216×10^{-3} moles

moles Cl^- originally present = 1.216×10^{-3} mole

weight of sample used = 0.2084 g

moles of sample used = $0.2084 \text{ g} / 375.41 \text{ g mole}^{-1}$

$$= 0.5551 \times 10^{-3} \text{ mole}$$

$$\frac{\text{moles Cl}^- \text{ present}}{\text{moles sample used}} = \frac{1.216 \times 10^{-3}}{0.555 \times 10^{-3}} = 2.19 \approx 2$$

Chemical analysis was not undertaken because of the difficulty in obtaining accurate results with hydrochloride salts.³⁹

The uv spectrum showed the absence of absorption from 360 to 205 nm. In addition, hydrochloric acid was added to solutions of N,N'-dicyclohexyl-2,2,4,4-tetramethyl-1,3-cyclobutanediimine (19) in ethanol. Addition of only 2×10^{-3} ml of 50 percent HCl to a silica cell containing a 5.85×10^{-3} M solution of 19 in ethanol resulted in the disappearance of the imine $n \rightarrow \pi^*$ absorption bands and the formation of new bands: λ_{max} 265 nm (shoulder) ($\epsilon = 67.0$), λ_{max} 305 nm (broad), ($\epsilon = 5.6$). Addition of more HCl resulted in the disappearance of the shoulder, but still gave the low energy band, probably due to the hydrolysis product, 2,2,4,4-tetramethylcyclobutanedione.

Attempts to take the nmr spectrum using trifluoromaleic anhydride and tetramethylsilane were unsuccessful due to the extreme volatility of the mixture. The infrared spectrum of a nujol mull showed bands at 3230, 2910 (broad), 2730, 2680, 2620, 2575, 2520, 2055, 1965, 1680, 1605, 1550, 1230, 1175, 1125, 1070, and 1020 cm^{-1} .

Catalytic Reduction of Bisimines

Preparation and Purification of Raney Nickel Catalyst⁴⁰

Into a 2 l beaker was placed a solution of sodium hydroxide, 380 g, in 1.5 l distilled water. Ni-Al alloy, 306.77 g, was added over a period of several hours, keeping the temperature under 25°. Cooling was achieved by means of an ice bath and stirring by an efficient sparkless stirrer. The mixture was warmed to room temperature after the rate of hydrogen gas evolution markedly decreased. The mixture was then heated on the steam bath for several hours; no violent gas evolution was observed. After the catalyst settled, the supernatant was decanted; the solid slurry was transferred into a 2 l beaker and washed thoroughly three to four times with distilled water; and the mixture was allowed to stand in water for six days. Sodium hydroxide solution was added, 50 g in 500 ml distilled water, and the mixture decanted after thorough mixing. The mixture was rinsed, then thoroughly mixed and decanted five times with distilled water, so that the final solution was neutral to litmus paper. The mixture was washed, mixed, and decanted five to ten times more with distilled water, three times with ethanol, and three times with 95-100 percent ethanol and stored in brown bottles, completely immersed in dry ethanol. The yield was about 150 g of activated catalyst. Density of settled material was about 0.6 g/ml. Note: the activated catalyst is highly pyrophoric and must be completely immersed in the solvent at all times.

Preparation of 2,2,4,4-Tetramethyl-N,N'-diphenyl-1,3-cyclobutanediamine (41)

Procedure similar to that of Hasek, Elam, and Martin⁸ with modifications:

Into the rocking autoclave was placed 2,2,4,4-tetramethyl-N,N'-diphenyl-1,3-cyclobutanediimine (9), 10.00 g (0.035 mole), dissolved in 97 ml benzene. Activated Raney Nickel catalyst, 3.50 g, was added to this solution. The mixture was then hydrogenated; 90-108° at 1300-1550 pounds per square inch for about four hours. The mixture was cooled to room temperature and filtered with suction. This resulted in a gray solid of Raney Nickel and a filtrate, which was filtered by gravity several times through glass, wool-packed-funnels. This liquid was then evaporated in evaporating dishes on a steam bath to give a light yellow, clear, viscous liquid with an amine odor. The evaporation was watched carefully to avoid the possibility of fire being caused by any remaining activated catalyst present.

The weight of liquid product obtained was 8.95 g. The structure of the diamine was confirmed by ir spectroscopy.⁸ An infrared spectrum gave bands at 3435, 3045, 2950, 2870, 1605, 1505, 1320, 1260, 1125, and 750 cm^{-1} , identical to an authentic sample.⁸ A mass spectrum gave a molecular ion at 294. The crude liquid began to crystallize slowly after about one year.

Attempted Preparation of 2,2,4,4-Tetramethyl-N,N'-dicyclohexyl-1,3-cyclobutanediimine (42)

Into a rocking autoclave were placed 2,2,4,4-tetramethyl-N,N'-dicyclohexyl-1,3-cyclobutanediimine (19), 10.00 g (0.034 mole), dissolved in 97 ml benzene, and 3.50 g of activated Raney Nickel catalyst. The mixture was hydrogenated; 94-128° at 1450-1850 pounds per square inch for three hours. Filtration of the mixture, evaporation of the filtrate, and an infrared spectrum of the resulting solid as a nujol mull, showed the presence of starting bisimine. The spectrum showed major bands at 1675, 1275, 1245, 1180, 1070, 1045, 960, 890, 840, and 790 cm^{-1} .

The recovered Raney Nickel had not lost its activity as it remained highly pyrophoric.

Attempted Pyrolysis

Attempted Pyrolysis of N,N'-Dicyclohexyl-2,2,4,4-tetramethyl-1,3-cyclobutanediimine (19)

Into a 50 ml Erlenmeyer flask was placed N,N'-dicyclohexyl-2,2,4,4-tetramethyl-1,3-cyclobutanediimine (19), 0.10 g (0.031 mole). Glass tubing was inserted into the Erlenmeyer flask by means of a rubber stopper. Right angle bends were made in the glass tubing to allow the other end of the glass tubing to protrude into a beaker of water. The

Erlenmeyer flask was heated by means of a variac and oil bath of vegetable oil. The temperature was then raised slowly up to a maximum of 223° after three hours and 20 minutes. Only a few bubbles of gas were collected in the water, the bubbles consisting of air and water vapor. An infrared spectrum of the brown material remaining in the Erlenmeyer flask indicated the brown material to be largely unchanged starting material with possibly a small amount of open chain amide present. Very weak, new bands were present at 3500-3240, 1720, 1560, and 1595 cm^{-1} . The experiment could be repeated using larger quantities of 19 and heating at higher temperatures for a longer period of time.

Carbene Reaction

Reaction of N,N'-Dicyclohexyl-2,2,4,4-tetramethyl-1,3-cyclobutanediimine (19) with a Carbene

The reaction was carried out in a manner similar to that reported by Fieser and Fieser.⁴⁸ Into a 100 ml round bottom, one-necked flask were placed N,N'-dicyclohexyl-2,2,4,4-tetramethyl-1,3-cyclobutanediimine (19), 6.20 g (0.04 mole); sodium trichloroacetate, 7.54 g (0.081 mole); perchloroethylene, 32.45 g (0.352 mole); and diglyme, three to four ml. The sodium trichloroacetate had previously been prepared according to the method of Fieser and Fieser.⁴⁸ The flask was fitted to a water condenser and refluxed by means of a heating mantle attached to a variac.

The mixture turned orange after five minutes of refluxing, but refluxing was continued for an additional 25 minutes, heating was then discontinued for 15 minutes, then continued for an additional 35 minutes; total reaction time, 65 minutes.

The resulting dark brown solution containing white particles was filtered with suction to give a brown residue and a dark brown filtrate. The residue was washed twice with a few ml of perchloroethylene until the color turned nearly white, m.p. over 240° , indicating the presence of unreacted sodium trichloroacetate. An infrared spectrum of the filtrate, indicating the probable presence of open chain amide and diglyme, showed bands at 3500-3400 (broad), 2960, 1715 (weak), 1680 (broad), 1520, 1460, 1125, 1045, 920, and 790 cm^{-1} .

The filtrate was evaporated from an evaporating dish on a steam bath. The resulting brown crystals were filtered with suction, 0.12 g, m.p. $165-186^{\circ}$. Evaporation of the brown filtrate gave a brown, viscous liquid. An infrared spectrum showed bands at 3345, 2945, 2070 (weak), 1785, 1720-1620 (broad), 1530, 1460, 1385, 1190, 1040, 1005, 900, and 840 cm^{-1} .

An infrared spectrum of the brown crystals, as a nujol mull, showed bands at 3145, 2070, 1680 (weak), 1635, 1580, 1320, 1250, and 900 cm^{-1} .

Extraction of the viscous liquid with hot hexane gave 0.12 g of brown solid, m.p. $191-199^{\circ}$, and a brown, viscous liquid which solidified upon drying. The solid was extracted with ethanol and dried on the

steam bath. A mass spectrum at 320° gave peaks at 374, 239, 224, 196, 195, 169, 164, and other ions. The parent peak was not discernible.

The impure compounds were not identified due to difficulty in purification.

Ionic Reactions

Attempted Reaction between N,N'-Diphenyl-2,2,4,4-tetramethyl-1,3-cyclobutanediimine (9) and Sodium Amide

Into a one-necked 250 ml round bottom flask was placed about 135 ml liquid ammonia. To this was added, slowly and with stirring, crushed sodium amide, 2.00 g (0.051 mole), resulting in the deposition of a large amount of solid on the bottom of the flask. The bisimine 9, 1.70 g (0.0056 mole), was slowly added to the mixture with stirring. The mixture was stirred for about three to four hours until all the ammonia had evaporated. To the resulting solid was added cold hexane, and the mixture was shaken, then filtered with suction, giving a white solid and clear filtrate. The white solid was washed several times with hexane. The filtrate was evaporated in a hood to yield white, glossy crystals. An infrared spectrum of these unreacted crystals was superimposable with the infrared spectrum of N,N'-diphenyl-2,2,4,4-tetramethyl-1,3-cyclobutanediimine (9) taken previously.

Attempted Reaction between N,N'-Dicyclohexyl-2,2,4,4-tetramethyl-1,3-cyclobutanediimine (19) and Sodium Amide

Into a 250 ml Erlenmeyer flask was placed about 100 ml liquid ammonia. To this was added, slowly with stirring, crushed sodium

amide, 2.00 g (0.051 mole). The bisimine (19), 0.55 g (0.0018 mole), was added slowly with stirring. The mixture was stirred for two to three hours until the ammonia evaporated.

Cold hexane was added to the solid, and the mixture was filtered by gravity after shaking. The white residue of water soluble sodium amide was washed several times with cold hexane and stored. The filtrate was evaporated in a hood to yield a yellow, viscous liquid which slowly crystallized. An infrared spectrum of this white solid indicated it was essentially unreacted bisimine 19. There were very weak bands, characteristic of open chain amides, present at 3390, 1720, and 1565 cm^{-1} .

Attempted Reaction between N,N'-Diphenyl-2,2,4,4-tetramethyl-1,3-cyclobutanediimine (9) and Sodium Methoxide⁴¹

Into a dropping funnel was placed sodium methoxide, 0.28 g (0.052 mole), in 20 ml dry methyl alcohol. On top of the dropping funnel was attached a calcium chloride drying tube. The dropping funnel was attached to a 250 ml round bottom flask cooled by an ice bath; the contents were stirred by a magnetic stirrer.

The flask contained N,N'-diphenyl-2,2,4,4-tetramethyl-1,3-cyclobutanediimine (9), 1.50 g (0.0052 mole), in 20 ml dry methanol. The contents of the dropping funnel were added slowly with stirring to the round bottom flask. No change was observed upon the addition, but the mixture was stirred overnight.

About 100 more drops of sodium methoxide were added with stirring over a period of more than 15 minutes. No temperature elevation was noted. The mixture was heated with a heating mantle. The temperature appeared to fall in the neighborhood of $52-56^{\circ}$. Refluxing was then initiated at 65° and continued for 3.5 hours. White crystals appeared on cooling. The contents of the flask were filtered with suction, giving a small amount of white solid residue. An infrared spectrum of the solid was superimposable with the spectrum of the unreacted bisimine 9, taken previously.

The filtrate was evaporated under low heat and reduced pressure on a Rinco evaporator, resulting in a sticky, white solid. An infrared spectrum was very similar to the infrared spectrum of the unreacted bisimine 9, taken previously. The differences included a broad, weak band at 3400 cm^{-1} , a broadening of the bands at 1480 , 1445 , and 1435 cm^{-1} , and a new band at 855 cm^{-1} . The slight spectral differences were likely due to a trace of sodium methoxide present.

Attempted Reaction between N,N'-Diphenyl-2,2,4,4-tetramethyl-1,3-cyclobutanediimine (9) and Sodium Hydride⁴¹

Into a two-necked 250 ml round bottom flask was placed N,N'-diphenyl-2,2,4,4-tetramethyl-1,3-cyclobutanediimine (9), 0.85 g (0.0029 mole), in 95 ml of benzene. To this mixture was added about 1 g of a 50 percent oil, and 50 percent NaH mixture. One neck of the flask was then stoppered, and the other neck was attached to a CaCl_2 drying

tube. The flask was cooled with an ice bath and stirred by means of a magnetic stirrer. The temperature rose slowly during the addition of the NaH.

The contents of the flask were refluxed for over six hours. The resulting yellow solution contained a gray precipitate. This was filtered with suction and the gray residue washed several times with benzene, 0.55 g.

The filtrate was evaporated, and an infrared spectrum taken of the resultant white solid indicated the material to be unreacted bisimine 9.

Attempted Reaction between N,N'-Dicyclohexyl-2,2,4,4-tetramethyl-1,3-cyclobutanediimine (19) and Sodium Methoxide⁴¹

Attempted Reaction between N,N'-Dicyclohexyl-2,2,4,4-tetramethyl-1,3-cyclobutanediimine (19) and Sodium Hydride⁴¹

Photochemical Reactions of N,N'-Dicyclohexyl-2,2,4,4-tetramethyl-1,3-cyclobutanediimine (19)

One gram of N,N'-dicyclohexyl-2,2,4,4-tetramethyl-1,3-cyclobutanediimine (19) in 50 ml of isopropyl alcohol, was irradiated under varying conditions, Table 1. The solution was placed in a quartz test tube equipped with a needle valve to allow for gas escape during the course of a reaction. Two types of photochemical lamps were employed. One lamp was a complete spectrum Hanovia 450 watt medium pressure mercury lamp, and the second lamp was a modification of the Srinivasan-Rayonet-Griffin chamber reactor, wavelength 2537A° or 3500A°.

Table 1. Photochemical Reactions of N,N'-Dicyclohexyl-2,2,4,4-tetramethyl-1,3-cyclobutanediimine (

| Compound photolyzed | Grams (19) in 50 ml isopropyl alcohol | Excitation wavelength | Duration of photolysis | Reaction probability | Product description and comments | |
|---------------------|---------------------------------------|-----------------------|------------------------|----------------------|---|--|
| (19) | 1.00 | Complete spectrum | 48 hours | Reaction | Unidentified products. | No uv absorpti Ir band 1720 cm |
| (19) | 1.00 | 2537A° | 20 hours | No Reaction | Impure starting material (19). | |
| (19) | 1.00 | 2537A° | 118 hours | Reaction | Unidentified oil and solid. Unreacted (19). | Weak : band a 2150 cm ⁻¹ . |
| | | 2537A° | 218 hours | | Unidentified decomposition products. | |
| (19) | 1.00 | Complete spectrum | 18½ hours | No Reaction | Impure (19). | Weak r band a 1700 c |

Table 1. (Continued).

| Compound photolyzed | Grams <u>(19)</u> in 50 ml iropropyl alcohol | Excitation wavelength | Duration of photolysis | Reaction probability | Product description and comments |
|---------------------|--|-----------------------|-------------------------|----------------------|--|
| <u>(19)</u> | 0.60 | Complete spectrum | 12 $\frac{1}{2}$ hours | No Reaction | Impure <u>(19)</u> . |
| <u>(19)</u> | 0.60 | Complete spectrum | 12 hours and 35 minutes | Reaction | Unidentified compound and starting bisimine <u>(19)</u> . |
| <u>(19)</u> | 1.00 | Complete spectrum | 18 hours and 57 minutes | Reaction | Unidentified compound. Starting bisimine <u>(19)</u> and pinacol detected. |
| <u>(19)</u> | 1.00 | Complete spectrum | 204 hours | Reaction | Unidentified. Pinacol detected by ir. |
| <u>(19)</u> | 1.00 | Complete spectrum | 40 hours and 2 minutes | Reaction | Unidentified. Pinacol detected by ir. |

Table 1. (Continued).

| Compound photolyzed | Grams <u>(19)</u> in 50 ml isopropyl alcohol | Excitation wavelength | Duration of photolysis | Reaction probability | Product description and comments |
|---------------------|---|-----------------------|--------------------------|-------------------------|---|
| <u>(19)</u> | 1.00 g in 60 ml isopropyl alcohol | 3500A ° 2537A ° | 115 hours and 51 minutes | No Reaction Reaction | Unidentified. |
| <u>(19)</u> | 0.0016 mole benzophenone sensitizer added | 3500A ° | 3 hours | No Reaction | |
| <u>(19)</u> | 16.00 g <u>(19)</u> in 800 ml isopropyl alcohol | Complete spectrum | 213 hours | Reaction | Unidentified. Pinacol and acetone detected. |
| <u>(9)</u> | 1.00 g <u>(9)</u> | 2537A ° | 20 hours | No Reaction | Impure <u>(9)</u> . |
| <u>(9)</u> | 1.00 g <u>(9)</u> | 2537A ° | 118 hours | No Reaction | Impure <u>(9)</u> . |
| <u>(12)</u> | 1.00 g <u>(12)</u> | 2537A ° | 118 hours | No Reaction | Impure <u>(12)</u> . |

After irradiation, the resulting solutions were evaporated with suction on a Rinco evaporator, giving brown liquids and, occasionally, white solids. Product separation was attempted using recrystallization, suction filtration, vapor phase chromatography, and thin layer chromatography. Nmr, ir, uv, and mass spectrometry were utilized in product identification. Irradiation conditions and product description are summarized in Table 1.

In another experiment, Table 1, the bisimine 19, 16.00 g, was dissolved in 800 ml isopropyl alcohol and placed in the chamber using a Hanovia 450 watt medium pressure mercury lamp. The mixture was irradiated for nine days. The mixture was stirred for 166 hours, 20 minutes, and not stirred the last 46 hours and 40 minutes. The fragrant mixture was evaporated on a Rinco evaporator with little heat, resulting in a yellow-orange, slightly viscous liquid. About one-half of this mixture was subjected to distillation procedures. Mass spectral and infrared spectral data showed the presence of a large amount of pinacol. The infrared spectrum showed bands at 3400-3350 (very strong), 2975, 1650, 1540 (weak), 1465, 1375, 1160, 955, 885, and 835 cm^{-1} . The pinacol was distilled, 47-65° at approximately 1.5 mm. The infrared spectrum showed bands at 3400, 2980, 2925, 1460, 1360, 1150, 1100, 940, 875, and 820 cm^{-1} . The spectrum was identical to an infrared spectrum of pinacol. The mass spectrum gave a molecular ion at 118. The second fraction, containing isopropyl alcohol, and possibly some open chain amide, was distilled from 49.5-84°. An infrared

spectrum showed bands at 3410, 2980, 2920, 1750 (weak), 1660, 1565, 1460, 1365-1367, 1150, 1100, 1000 (weak), 940, 870, and 820 cm^{-1} . Nmr and ir spectra of the third fraction, 85-127° at approximately 105 mm, showed the possible presence of an unusual open chain amide. An infrared spectrum of the residue showed bands at 3320, 2980-2960, 1650, 1540-1530 (weak), 1460-1440, 1370-1360, 1140, and 940 cm^{-1} .

The third fraction was redistilled, 48.5-89.5° at 0.45-0.26 mm; the distillate came off quite slowly at times. The residue became more polymeric with increased distillation. Infrared and nmr spectra were somewhat inconclusive. Mass spectral data indicated a molecular ion at 233.

A portion of the original material (before distillation), showed the presence of seven components when introduced into a three percent OV-1 glass column of a gas chromatography unit of a Finnigan Quadropole Mass Spectrometer. The peaks were not identified.

An attempt was made to separate a portion of the original material before distillation, using column chromatography. The column consisted of silicic acid. Increasing the solvent polarity, n-hexane, 50 percent ethanol-hexane, ether, 50 percent ether-methanol, methanol, 50 percent methanol-50 percent water, and water, gave upon evaporation pinacol and unidentified liquids. Infrared stretching frequencies corresponding to ketone and open chain amide compounds were detected.

The presence of acetone was detected in other photolyses.⁴² N,N'-dicyclohexyl-2,2,4,4-tetramethylcyclobutanediimine (19) in

isopropyl alcohol (0.0662M) was irradiated at 2537A° for 96 hours and 144 hours. Oxygen gas was bubbled through the solution during the irradiation.⁴²

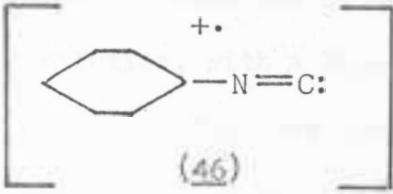
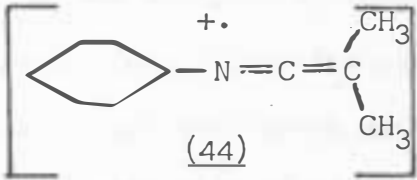
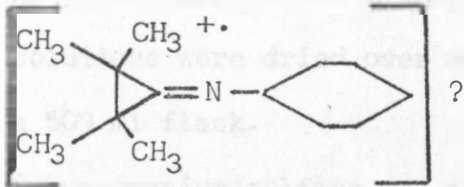
The cyclohexylbisimine 19 was irradiated under pure, dry nitrogen. Information regarding irradiation is given in Table 2. Ultraviolet spectra were taken of aliquots at time intervals other than those listed in Table 2: 9 minutes, 24 minutes, 54 minutes, 1 hour and 54 minutes, 3 hours and 57 minutes, and 8 hours and 57 minutes. A significant change appeared in the uv spectrum after 24 minutes, λ_{max} 246 nm. A mass spectrum of this aliquot, after standing for one day, showed no new significant molecular ions. The uv spectrum of the 54 minute aliquot had no absorption maxima. A mass spectrum of this aliquot after standing for one showed no new significant molecular ions, except possibly 109. Mass spectral patterns of proceeding aliquots showed the presence of many new compounds. The photolysis had gone too far to interpret accurately.

Additional samples of 19, of differing concentrations, were also photolyzed under pure, dry nitrogen, with no successful interpretation of results.

Preparation of N-Cyclohexyl-2-methylpropionamide (43)

Into a 500 ml round bottom, one-necked flask were placed isobutyronitrile, 20.36 g (0.44 mole); a solution of KOH, 42.00 g (0.75 mole), and NaOH, 18.00 g (0.45 mole) in 220 ml water; a few boiling chips; and a boiling stick. The flask was attached to a reflux condenser and heated by means of a heating mantle connected to a variac.

Table 2. Photolysis of N,N'-Dicyclohexyl-2,2,4,4-tetramethylcyclobutane diimine (19) Under a Dry Nitrogen Atmosphere.

| Total irradiation time | Mass of molecular ions present | Structure corresponding to molecular ions | Comments |
|--------------------------|---|---|---|
| 15 seconds 28 minutes | | | Observed only solvent and starting material, (19). |
| 41 minutes | 109 |  (46) | Mass spectrum and gas chromatography pattern identical to authentic sample of 46 (0.25 g 46 in 200 ml isopropyl alcohol). |
| 1 hour | 273 | | |
| 1½ hours | 109 109 386 151 | <p>(46) (46) Dimer of mass 193?</p>  (44) | Mass spectrum identical to authentic sample of 44 (about 0.2 g 44 in 175 ml isopropyl alcohol). |
| 2½ hours | 273 109 259 354 341 128 193 | | |
| | |  ? | |
| 4 hours, 44 minutes | 109, 353, 151, 155, 127, 263, 280, 265, 354, 341, 126, and others | | |

The mixture was brought to reflux. The solution turned deep yellow and ammonia gas was evolved. Refluxing was discontinued after about 30 hours as the evolution of ammonia gas ceased.

About 75 ml of water were added to the resultant orange solution, which was allowed to cool to about 40-50°.

A mixture of 50 ml concentrated sulfuric acid and 80 ml of water was added slowly in small portions through the condenser. A white precipitate formed in a white solution, with a brown aqueous layer on top. The mixture was very acidic (pH of two or less as measured with pH Hydrion paper). An additional solution of 10 ml concentrated sulfuric acid in 20 ml water was added, and the mixture was shaken.

The acid solution was then transferred to a 500 ml separatory funnel. The round bottom flask was rinsed with three 25 ml portions of benzene, and the rinsings were poured into the separatory funnel. The mixture was shaken vigorously and the bottom aqueous layer removed. The aqueous layer was extracted with 50 ml, 40 ml, and 30 ml portions of benzene, which were combined with the previous benzene extractions. The benzene extracts and the inside of the separatory funnel were washed with 30 and 25 ml portions of water, and the water was drawn off. The benzene solutions were dried over anhydrous magnesium sulfate overnight in a 500 ml flask.

The mixture of benzene and magnesium sulfate was filtered by gravity through glass wool. The magnesium sulfate was washed twice with 20 and 15 ml portions of benzene, and these benzene solutions were combined with the original.

The crude isobutyric acid in benzene was placed in a 500 ml round bottom one-necked flask. A reflux condenser containing a dropping funnel was attached to the flask. Into the dropping funnel was placed thionyl chloride, 59.50 g (0.50 mole). The thionyl chloride was added slowly and then the mixture was brought to a reflux by means of a heating mantle. The solution turned orange, and a trace of sharp, penetrating odor of SOCl_2 was still present after 25 hours, when refluxing was discontinued.

About 100 g of cyclohexylamine was dried for one day over anhydrous magnesium sulfate and filtered by gravity. Into a 1000 ml Erlenmeyer flask was placed anhydrous cyclohexylamine, 43.00 g (0.43 mole), dissolved in 40 ml benzene. The crude isobutyric acid chloride reagent was added slowly to the cyclohexylamine by means of a separatory funnel. White smoke was evolved and the mixture heated, but not excessively. The addition was complete after 15 minutes. More cyclohexylamine, 30.00 g (0.30 mole), in 65 ml benzene was added. The reaction was assumed to be complete, even though white smoke was still being evolved.

The mixture was heated on a steam bath for about 15 minutes to ensure a complete reaction. The mixture was cooled and filtered with suction. The white crystals of crude N-cyclohexylchlorosulfuramide were washed several times with benzene. The brown filtrate was filtered, giving more white crystals. These crystals, after washing with benzene, were combined with the other white crystals.

The white crystals were dissolved in hot ethanol and filtered; crystals appeared after filtration. These long, white, needle-shaped crystals, in a yellow liquid, were allowed to stand in the refrigerator for several days to ensure maximum precipitation.

The mixture was filtered with suction, giving 38.29 g of white, needle-shaped crystals, which were washed with hexane, m.p. 208-209°. As the crystals were water soluble, they were assumed to be the salt, N-cyclohexylchlorosulfuramide. An infrared spectrum of a nujol mull, showed bands at 3700 (weak), 2780 (weak), 2740 (weak), 2685 (weak), 2630 (weak), 2585 (weak), 2530 (weak), 2070 (weak), 1615 (weak), 1500, 1125 (weak), and 1025 (weak) cm^{-1} .

Hexanes were added to the yellow filtrate, giving 15.23 g of crystals of water soluble N-cyclohexylchlorosulfuramide. Evaporation of the filtrate gave 9.61 g of brown crystals, m.p. 199-203°; N-cyclohexylchlorosulfuramide, with some brown impurity.

The brown filtrate was evaporated in evaporating dishes over a steam bath. A brown, viscous solid with a goat-like odor was obtained, 48.80 g.

The brown solid was dissolved in hot ethanol, filtered hot, water added, and the mixture was allowed to stand overnight. The two liquid layers solidified and were filtered with suction. The addition of water to the filtrate resulted in the formation of more brown crystals which were filtered with suction. The crystals were dissolved in hot

n-hexane and crystallized at ice bath temperatures. The purest crystals were recrystallized from n-hexane, 3.03 g, m.p. 115-116°. A uv spectrum showed only end absorption. An infrared spectrum of the crude N-cyclohexyl-2-methylpropionamide (43), as a nujol mull gave bands at 3300, 3080, 1635, 1550, 1310, 1265, 1250, 1240, 1180, 1105, 980, 900, and 705 cm^{-1} . The remaining crystals of 43 were recrystallized from aqueous ethanol, then n-hexane.

Preparation of Dimethylketene-N-cyclohexylimine (44)

About 500 g of alumina were activated by heating in a muffle furnace for many hours at 360°C.⁴⁵ About 1050 ml of triethylamine was distilled twice. In the first distillation, the amine was distilled from a mixture of P_2O_5 and activated alumina, 88-93°. In the second distillation, the amine in P_2O_5 was distilled onto P_2O_5 , 89-95°. The distilling apparatus had been flamed and flushed with pure, dry nitrogen before each distillation.

The nitrogen had oxygen impurities, which were removed by bubbling it through a mixture of 16.8 g pyrogallol in about 130 ml of a 50 percent mixture (by volume) of KOH and H_2O . The nitrogen gas was then dried by passing it through a drying tube consisting of glass wool, drierite (magnesium sulfate), calcium chloride, and diphosphorus pentoxide.

A 2000 ml three-necked flask was flamed out and flushed with pure, dry nitrogen. Triethylamine, 300 ml, was added, and the mixture stirred with slight warming.

Into a 2000 ml round bottom three-necked flask was placed N-cyclohexyl-2-methylpropionamide (43), 20.00 g (0.118 mole). Previous to the addition, the flask was flamed out and flushed with pure, dry nitrogen. Triethylamine, 300 ml, was added, and the mixture was stirred with slight warming. Some of the amide appeared to settle at the bottom. Diphosphorus pentoxide, 75.0 g (0.54 mole), was added, along with 300 ml triethylamine. The mixture was shaken, warmed, and stirred. Alumina, 150 g (0.15 mole), along with 400 ml more amine, was added, and the system was flushed with pure, dry nitrogen.

The center neck of the flask was attached to two reflux condensers; one neck was equipped with a delivery tube to allow pure, dry nitrogen to be bubbled through the solution. The other neck was stoppered, but should have been equipped with a mechanical stirrer.⁴⁴

The solution in the flask was brought to a reflux by means of a heating mantle attached to a variac. Pure, dry nitrogen was bubbled continuously through the solution at first, then occasionally. After refluxing for seven and one-half hours, attempts were made to stir the viscous solid on the bottom of the flask. Refluxing was started again and continued for another seven and one-fourth hours. Total refluxing time, 14 and three-fourths hours.

A 50 ml aliquot was removed from the solution. An infrared spectrum of the aliquot showed the probable presence of dimethylketene-N-cyclohexylimine (44), as an absorption was noted at 2030 cm^{-1} .⁴⁶ The solvent was evaporated several times on a salt plate to obtain a larger concentration of keteneimine 44. An infrared spectrum showed a stronger band at 2030 cm^{-1} . The spectrum also showed bands at 3275, 2920, 2850, 1635, 1540, 1445, and 1370 cm^{-1} . Exposure of the sample to air resulted in evaporation of the keteneimine 44, the disappearance of the band at 2030 cm^{-1} , as well as the formation of a distinct keteneimine odor; the infrared spectrum resembled the spectrum of the starting N-cyclohexyl-2-methylpropionamide (43) taken previously. A mass spectrum of the aliquot showed the keteneimine 44 to be present in large quantities. The following molecular ions were observed: 101, 151, and 169; correspond to triethylamine, dimethylketene-N-cyclohexylimine (44), and N-cyclohexyl-2-methylpropionamide (43), respectively. A three percent OV-1 glass column was used at 115° , injector 88° , flow rate 10 cc/per minute, pressure = 10^{-6} torr, and $0.3\text{ }\mu\text{l}$ injection.

The contents of the 2 l flask were decanted into a 1 l flask. The triethylamine was distilled into a 1000 ml flask attached to the distilling column by means of a vacuum adapter. The adapter was attached by means of tygon tubing to a large coldfinger in a Dewar flask filled with liquid nitrogen. The distillation apparatus was

flushed with pure, dry nitrogen, flamed out, and flushed again with pure, dry nitrogen. The amine was distilled, 54-28° at 0.7 mm. No infrared band at 2030 cm^{-1} was observed in the spectrum of the distillate. A yellow liquid remained in the distillation flask as residue. The contents of the 2 l flask were rinsed three times with 75 ml portions of triethylamine and the amine was again distilled as previously described, 25-28° at 0.8-0.9 mm. After one-half hour, the contents of the distilling flask suddenly cooled and a white precipitate formed. The flasks were flushed with pure, dry nitrogen and stored in a refrigerator.

The keteneimine 44 was distilled, 53-100° at about 4 mm. About 0.5 g was obtained, which corresponded to about 2.18 percent yield. The structure was confirmed by ir, uv, nmr, and mass spectrometry. The infrared spectrum showed bands at 3400 (weak, amide impurity), 2950, 2880 (weak), 2050, 1670 (weak, amide impurity), 1455, 1380, 1300 (weak), 1260, 1100, 895, and 800 cm^{-1} . Although keteneimines are air-sensitive,⁴⁴ the rate of evaporation of 44 on a salt plate was observed to be much greater than the rate of reaction with air. The nmr spectrum gave δ 3.17-2.67(broad s, 1H), approximately δ 2.00-0.83(m, 17H, $-\text{CH}_3$'s and cyclohexyl ring). The uv spectrum in ethanol gave λ_{max} 287.5 nm (ϵ = 145.8). The mass spectrum gave 169 (amide impurity) and a molecular ion at 151.

Preparation of N-Cyclohexylformamide (45)

The procedure was adapted from L. F. Fieser, et al.⁴⁷ Into a 250 ml flask, fitted with a Dean-Stark trap, were placed cyclohexylamine, 24.75 g (0.25 mole), and 200 ml toluene. To this were added formic acid, 23.01 g (0.50 mole), and two boiling chips. An additional 35 ml toluene were placed in the Dean-Stark trap. The mixture was refluxed for four and one-fourth hours. Then more cyclohexylamine, 12.40 g (0.1250 mole), was added and refluxing was continued. Apparently there was considerable water present in the formic acid, and possibly cyclohexylamine, since over 14 ml water were collected in the Dean-Stark trap, 7.25 ml over the calculated yield.

The toluene and excess cyclohexylamine were distilled; then the N-cyclohexylformamide (45) was distilled as three fractions, at eight mm or less: the first fraction, 71.5-112°; the second fraction, 117-144°; and the third fraction, 147-153°. About 36.67 g of the formamide 46 were obtained, which corresponded to approximately 57 percent calculated yield. An infrared spectrum of the purer first two fractions showed bands at 3280, 3055, 2950, 2870, 1660, 1540, 1460, 1390, 1260 (weak), 1080 (weak), 1160 (weak), and 900 (weak) cm^{-1} . An infrared spectrum of the distilled formamide was similar to the spectrum taken before distillation.

Preparation of Cyclohexylisocyanide (46)

The procedure was adapted from that given by J. Casanova, et al.⁴⁹

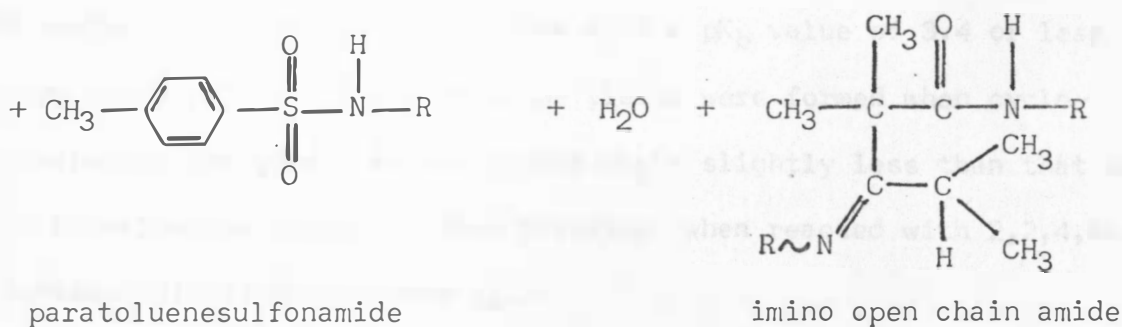
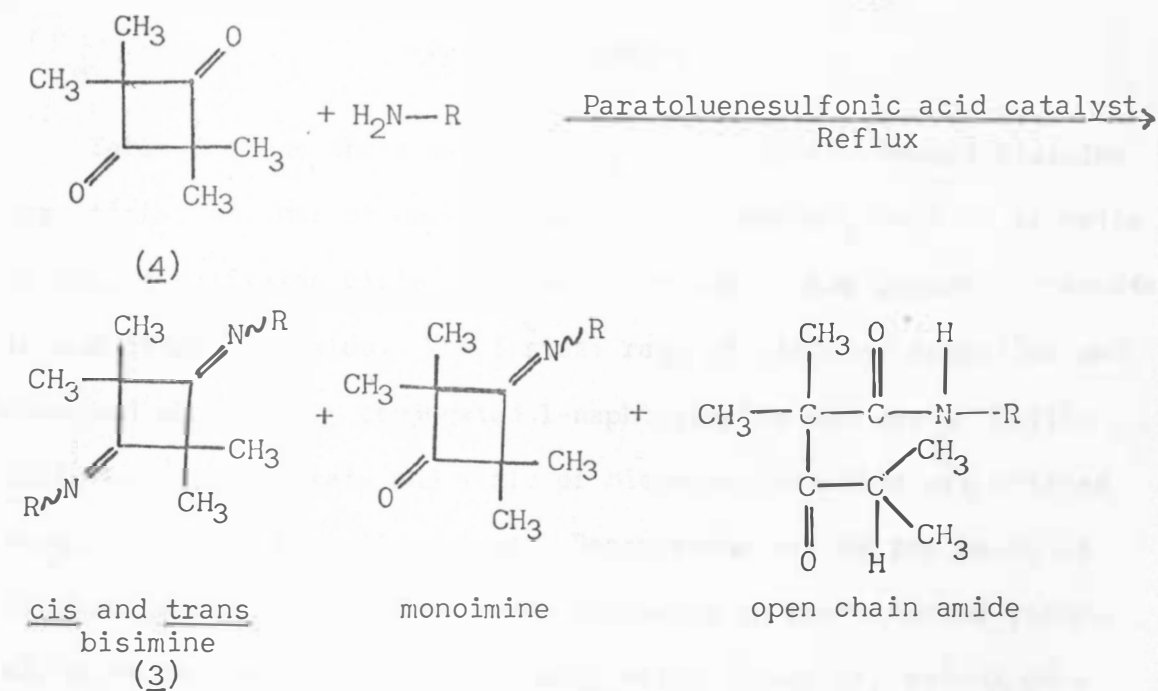
Into a 250 ml round bottom one-necked flask was placed N-cyclohexylformamide (45), 10.56 g (0.063 mole), which was then frozen by immersing the flask in liquid nitrogen. A mixture of p-toluene-sulphonyl chloride, 26.00 g (0.136 mole), and quinoline, 46.0 g (0.357 mole), was added to the flask and the contents immediately frozen to avoid the formation of large amounts of the isocyanide 46 which has an unpleasant odor.

The mixture was then warmed slowly and 46 was distilled as it formed into flasks immersed in liquid nitrogen. Several grams were obtained, 90-94° at about 1.5 mm. The structure was confirmed by ir, nmr, uv, and mass spectrometry. The uv spectrum showed the absence of absorption even up to a concentration of 0.0479 M. The mass spectrum gave 129 (quinoline impurity) and a molecular ion at 109. The infrared spectrum showed bands at 3355 (broad), 2995, 2900, 2150 (weak), 1465, 1380, 1340 (weak), 1310 (weak), 1160, 1135, 955, and 820 cm^{-1} .

DISCUSSION OF RESULTS

General Synthetic Scheme for Experimental Work

The bisimines (3) were prepared by reacting 2,2,4,4-tetramethylcyclobutanedione (4) with primary amines.



Product distribution is dependent upon a number of factors. One such factor is the basicity of the amine: weakly basic amines such as aromatic amines, favor the formation of monoimines and bisimines, Table 3. The formation of open chain amides and imino open chain amides is increased when more basic amines, such as aliphatic amines, are used.

Basicity Studies

Table 3 shows there may be a limiting basicity toward bisimine formation. The use of weakly basic primary amines, such as aromatic amines, facilitates bisimine formation rapidly, and generally results in quantitative yields. The fastest rate of bisimine formation was observed when highly conjugated 1-naphthylamine was used. Little difference in the rate and yield of bisimine formation was noticed among the other aromatic amines. Benzylamine may be the amine of highest basicity value that forms bisimines in quantitative yields. No amine used with a higher basicity value (lower pK_b value) gave quantitative yields of bisimines. The limiting factor toward bisimine formation may be an amine with a pK_b value of 3.4 or less (cyclohexylamine). Small bisimine yields were formed when cyclohexylamine was used. Amines having pK_b 's slightly less than that of cyclohexylamine failed to form bisimines when reacted with 2,2,4,4-tetramethylcyclobutanedione (4).

The generally accepted mechanism for imine formation involves attack of the nucleophilic primary amine at the carbonyl carbon with

Table 3. Bisicity Relationships.

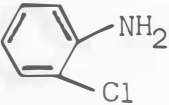
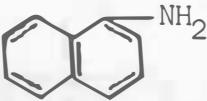
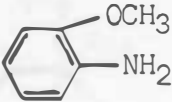
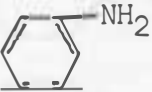
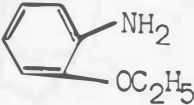
| Amine used | pK_b at 25° ⁵¹ | Approximate yield of bisimine percent | Approximate yield of open chain amide percent | Approximate yield of monoimine percent |
|---|-----------------------------|--|--|---|
|  | 11.4 | quantitative | 0 | 0 |
|  | 10.1 | quantitative | 0 | 0 |
|  | 9.5 | quantitative | 0 | 0 |
|  | 9.4 | quantitative | 0 | 0 |
|  | 8.8 | quantitative | 0 | 0 |

Table 3. Continued.

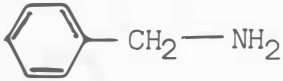
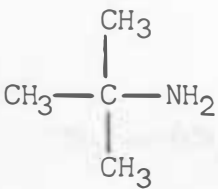

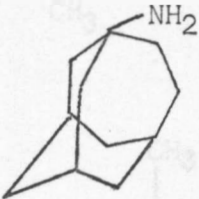
| Amine used | pK_b at 25° ⁵¹ | Approximate yield of bisimine percent | Approximate yield of open chain amide percent | Approximate yield of monoimine percent |
|---|-----------------------------|--|--|---|
|  | 4.6 | quantitative | 0 | 0 |
| (a)  | 3.5 | | | |
|  | unreported | 5 | 95 | negligible |
|  | unreported "quite basic" | 0 | 30-40 | negligible |

Table 3. Continued.

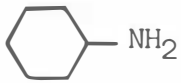
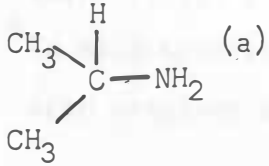
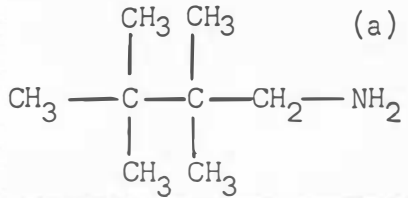
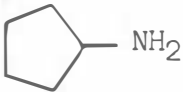
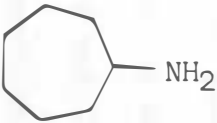
| Amine used | pK_b at 25° ⁵¹ | Approximate yield of bisimine percent | Approximate yield of open chain amide percent | Approximate yield of monoimine percent |
|---|-----------------------------|--|--|---|
|  | 3.4 | 20 | 50 | negligible |
| $CH_3 - (CH_2)_3 - NH_2$ (c) | 3.3 | 0 | 85 | 10 |
| $CH_3 - (CH_2)_3 - NH_2$ (b) | 3.3 | 0 | 20 | 65 |
|  (a) | 3.3 | | | |
|  (a) | 3.3 | | | |

Table 3. Continued.

| Amine used | pK_b at 25° ⁵¹ | Approximate yield of bisimine percent | Approximate yield of open chain amide percent | Approximate yield of monoisomer percent |
|---|-----------------------------|--|--|--|
|  | unreported | 0 | over 60 | negligible |
|  | unreported | 15 | over 40 | negligible |

^a Amine failed to react^b No acid catalyst used^c Acid catalyst used

subsequent loss of water, page 102. This would imply that the more basic amines would react faster.

It is also known that the cyclobutane ring of 2,2,4,4-tetramethylcyclobutanedione opens with strong base.^{10,9} As the pK_b gets smaller, open chain amide formation should predominate over bisimine formation, and this is observed.

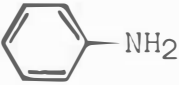
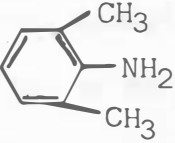
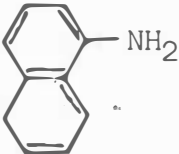
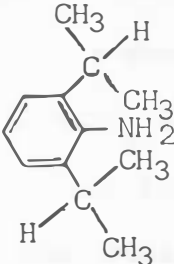
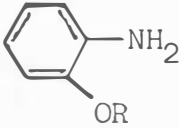
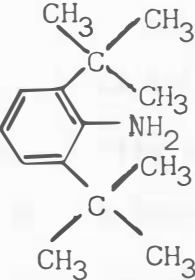
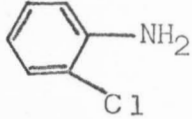

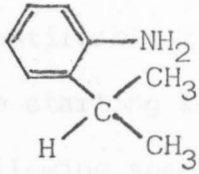
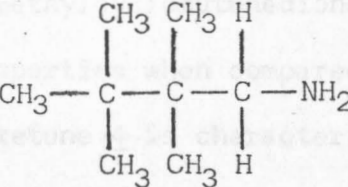
One additional factor to consider in bisimine formation, would be the steric effects of the attacking amine.

Steric Studies

The presence of one ortho substituent on primary aromatic amines does not appear to influence bisimine formation to any extent, Table 4, unless the substituent is rather large. Use of o-isopropylaniline resulted in a quantitative yield of bisimine formation 17, but the formation occurred at a slower rate than when aniline, o-chloroaniline, o-methoxyaniline, and o-ethoxyaniline were used.

An even more significant effect was observed when primary aromatic amines containing two ortho substituents were used. When 2,6-dimethylaniline was the amine used, the monoimine compound 15 was formed in almost quantitative amounts. Only 15 percent of the yield corresponding to complete bisimine formation 16 was observed. When 2,6-diisopropylaniline was the amine used, only about 15-18 percent yield for complete monoimine formation 18 was obtained. No bisimine compound was formed.

Table 4. Steric Relationships.

| Amine used | Amount of bisimine formed | Amine used | Amount of bisimine formed |
|--|---|---|--|
|  | quantitative |  | Small yield of bisimine formed extremely slowly; almost quantitative for monoimine formation |
|  | quantitative but fastest rate of formation |  | Significant monoimine formation |
|  | quantitative R = CH ₃ , C ₂ H ₅ |  | Reaction not attempted |
|  | quantitative |  | 0 |
|  | slow but quantitative |  | 0 |

It is suggested that the presence of one ortho substituent, larger than the isopropyl group, in primary aromatic amines, is one of the limiting factors toward quantitative bisimine formation. It is also suggested that there is a limiting factor toward complete monoimine formation. This limiting factor in primary aromatic amines apparently lies between two methyl groups ortho to the amino group (2,6-dimethylaniline), and two isopropyl groups ortho to the amino group (2,6-diisopropylaniline). The isopropyl groups of the formed monoimine 18 may repel the methyl groups of the cyclobutane ring sufficiently to prevent further attack by the amine; hence, no bisimine product was formed. Another striking steric effect was noted when aliphatic, carbocyclic, primary amines were used.

Attempts to prepare bisimines using other bulky amines were unsuccessful. The use of tertiaryoctylamine resulted in no reaction. Adamantaneamine formed about 30-40 percent of the open chain compound 32; the rest did not react. Basicity arguments other than steric arguments may be more appropriate in the case of adamantaneamine.

Bisimine Identification Studies

The bisimines of 2,2,4,4-tetramethylcyclobutanedione, were readily identifiable from their spectral properties when compared to those of the starting ketone. The starting ketone 4 is characterized by the following spectral data: the infrared spectrum shows carbonyl stretching frequencies of 1750 and 1715 cm^{-1} (doublet). The nuclear magnetic

resonance spectrum exhibits a single sharp resonance at 1.29δ . The ultraviolet spectrum shows absorptions at $\lambda_{\max} \approx 350$ and 390 nm, in cyclohexane.

Bisimines were characterized by the following spectral data (see Appendix, Table of Spectra). The ir spectra showed imine stretching frequencies at 1690 cm^{-1} . The nmr spectra showed proton resonances at three distinct field positions, Table 5 (approximately 0.8 to 1.4δ). The uv absorption spectra, Table 6, showed two $n \rightarrow \pi^*$ transitions at approximately $\lambda_{\max} = 260$ and 275 nm in cyclohexane for cyclic, aliphatic bisimines. Other tools used in identification included the mass spectrometer and carbon, hydrogen analysis.

Table 5. Methyl Resonances of Bisimines of 2,2,4,4-Tetramethylcyclobutanedione⁵²

| Compound | δ , ppm * | <u>trans</u> | <u>cis</u> |
|-----------|------------------|----------------------------------|------------|
| <u>9</u> | | 1.26 | 1.01, 1.52 |
| <u>19</u> | | 1.32 | 1.20, 1.47 |
| <u>10</u> | | 1.22 | 0.89, 1.55 |
| <u>12</u> | | 1.33 δ (broad singlet) | |

* δ values are reported in CCl_4 at a probe temperature of 35° using tetramethylsilane as the internal standard.

Table 6. Ultraviolet Absorption Spectral Data.

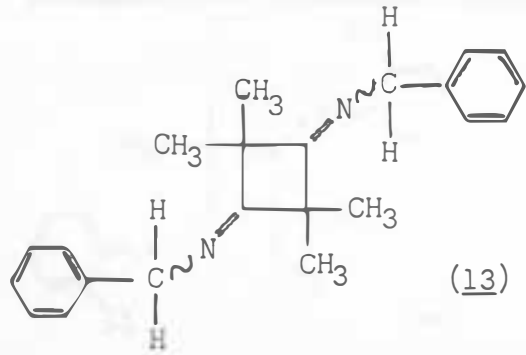
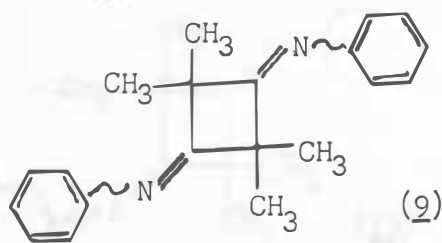
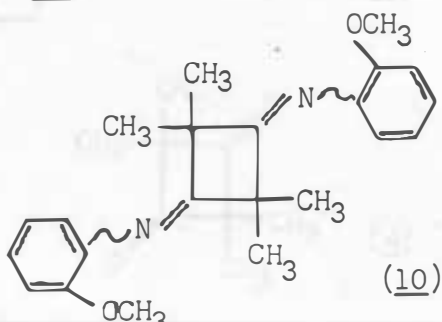
| Compound | Molar Absorptivity (ϵ) (liters mole ⁻¹ cm ⁻¹) | λ_{max} in cyclohexane (nm) | λ_{max} in 95% Etha (nm) |
|--|--|--|---|
|  (13) | 855 220 | 259 282 | 258 280 |
|  (9) | 2,857 3,729 | 275 296 | 274 289 |
|  (10) | 5,273 1,222 | 279 315 | 277 313 |

Table 6. (Continued).

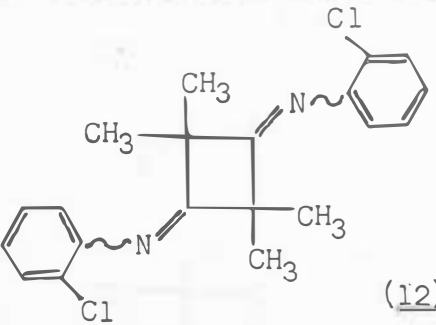
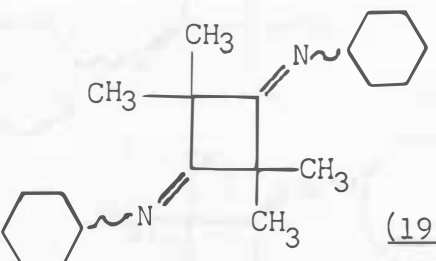
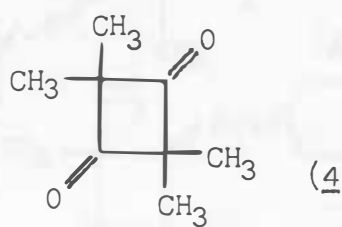
| Compound | Molar Absorptivity (ϵ) (liters mole ⁻¹ cm ⁻¹) | λ_{\max} in cyclohexane (nm) | 95% Eth (nm) |
|--|--|--|--------------------------|
|  (12) | 3,564 1,550 | 278 313 | 276 312 |
|  (19) | 157 146 | 263 273 | 249 265 |
|  (4) | 25 20 57 40 | 350 348 309 308 | 343 344 306 304 |

Table 6. (Continued).

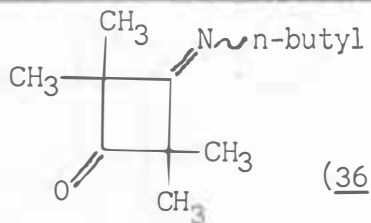
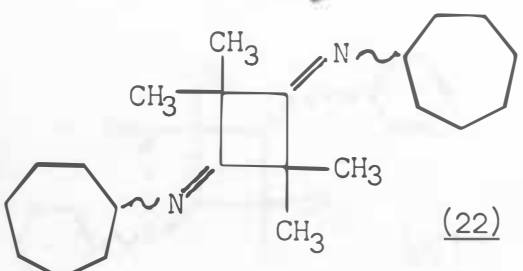
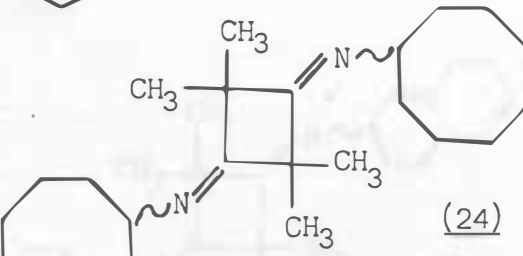
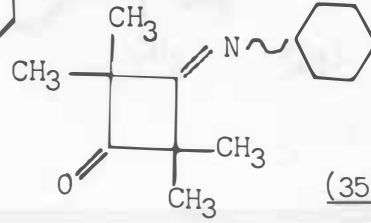
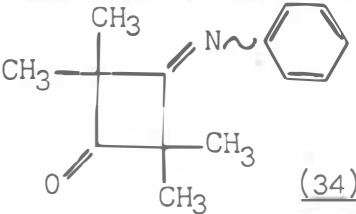
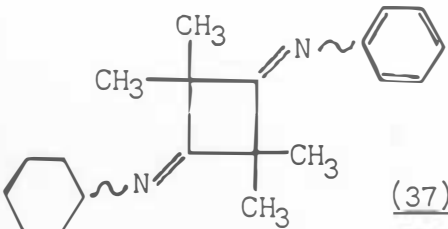
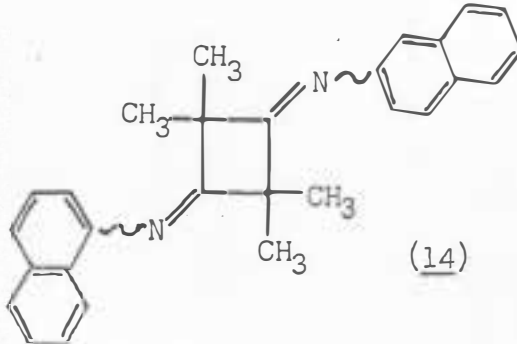
| Compound | Molar Absorptivity (ϵ) (liters mole ⁻¹ cm ⁻¹) | λ_{\max} in cyclohexane (nm) | λ_{\max} 95% Eth (nm) |
|---|--|--|-------------------------------------|
|  (36) | 133 53 49 | | 258 316 318 |
|  (22) | 142 144 | 260 274 | 247 262 |
|  (24) | 128 134 | 260 272 | 248 264 |
|  (35) | 112 24 27 20 | 268 208 322 336 | 259 805 318 333 |

Table 6. (Continued).

| Compound | Molar Absorptivity (ϵ) (liters mole ⁻¹ cm ⁻¹) | λ_{\max} in cyclohexane (nm) | λ_{\max} in 95% Etha (nm) |
|---|--|--|---|
|  (34) | 1,463 1,600 476 359 | 273 302 326 341 | 274 294 328 339 |
|  (37) | 1,367 968 | 272 302 | 268 295 |
|  (14) | 8,930 7,190 5,870 | 298 316 322 | 292 323 |

Open chain amides were characterized by the following spectral data: the ir spectra showed amide stretching and bending frequencies at about 3320, 1705, 1625, and 1520 cm^{-1} . The nmr spectra showed about $\delta 6.0$ (d, 1H, -NH), about $\delta 3.0$ (heptet, 1H, isopropyl H), about $\delta 1.25$ (s, 6H, $-\text{CH}_3$'s adjacent to carbonyl groups), and about $\delta 0.95$ (d, 6H, $-\text{CH}_3$'s on isopropyl groups). The uv spectra showed the absence of absorption. Mass spectra gave the molecular weights and appropriate fragmentation patterns. Chemical analyses were consistent with the structures.

The monoimines were characterized by the following spectral data: ir spectra showed imine stretching frequencies at 1800 cm^{-1} . The nmr spectra showed proton resonances at two distinct field positions, about $\delta 0.9$ to 1.15, due to different shielding of methyl groups on the cyclobutane ring. The uv spectra of 35 showed several absorption maxima due to $n \rightarrow \pi^*$ transitions, Table 6. The mass spectrum of 35 was consistent with the structure.

For the spectral data of other compounds, see experimental section.

NMR Studies

Bisimine geometrical isomers were prepared as shown:

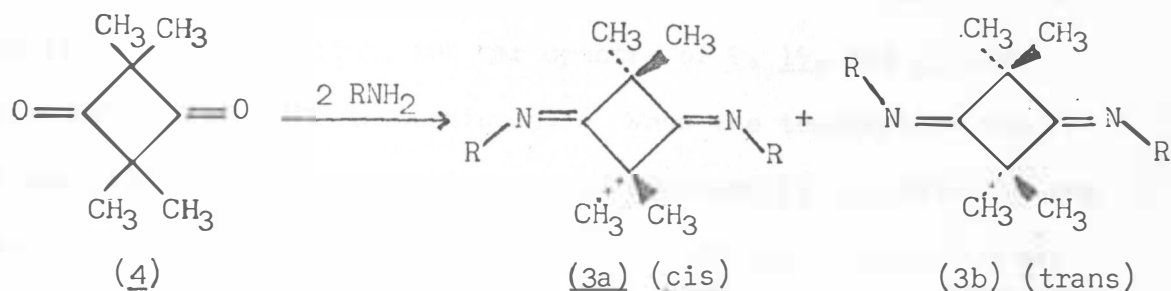


Figure 3. Bisimine Geometrical Isomers.

- 9, R = phenyl
19, R = cyclohexyl
10, R = o-methoxyphenyl
12, R = o-chlorophenyl

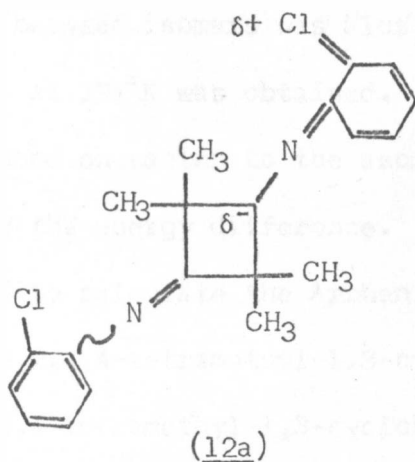
All spectral properties and elemental analysis of 9, 19, 10, and 12 were consistent with the structures.

At the probe temperature of 35° in CCl₄ the protons of the methyl groups of 2,2,4,4-tetramethylcyclobutanedione (4) exhibit a single, sharp resonance at 1.29δ. Under the same conditions, the methyl groups of the bisimine derivatives show proton resonance at three distinct field positions, Table 5.

The observed resonances are attributed to mixtures of *cis* 3a and *trans* 3b isomers. There are two nonequivalent methyls for 3a, and the combined high and low field singlets are attributed to this isomer.

The proton resonance of the equivalent methyl groups of the trans isomer 3a is assigned to the intermediate field singlet, which is the most intense. The high and low field singlets of the cis isomer are of equal area and represent 33 percent of the product mixture. To verify the isomerization, the nmr spectra of 9, 19, and 10 were observed at different temperatures.⁵² When the temperature was raised, the three separate singlets of compound 19 coalesced to one broad singlet at a temperature of 165°. A similar phenomenon was observed for compound 9. In the latter case, however, the coalescence temperature was 105°. This lower coalescence temperature in 9 may be due to resonance effects imparting more single bond character to the azomethine linkage. On cooling the samples to room temperature, the proton resonance of the methyl groups gradually returned to the original spectrum taken at 35° and possessed the same cis to trans ratio. That isomerization was being observed and that it was not simply restricted rotation about the R group attached to the nitrogen is demonstrated. Compound 12 at 35° shows a broad singlet for the proton resonance of the methyl groups, whereas three distinct singlets are observed at 10°. If simple rotation barriers were being observed, one would expect 19 to require a lower coalescence temperature than 12, and this is not observed. On the other hand, if cis-trans isomerization is being observed, 12 would be expected to have a lower coalescence temperature than 9 or 19, due to contribution of the resonance structure 12a which imparts less double bond character

to the azomethine linkage. Similar resonance structures are less predominant in 9 and absent in 19.



It is impossible on the 60 MHz instrument to detect two separate $-OCH_3$ resonances for the cis and trans isomers of 10. The 100 MHz spectrum shows two distinct singlets with a separation of 2Hz. The more intense low field singlet represents the o-methyl resonance of the trans isomer.

The free energy difference between isomers was calculated by the expression, $\Delta G^\circ = -RT \ln K$; where ΔG° is the free energy at 298°K; R is the ideal gas constant; i.e., 1.987×10^{-3} Kcal/mole°K; T is the absolute temperature of 298°K; and K is the value of the equilibrium constant obtained from the percentage of cis isomer divided by the percentage of trans isomer. The percentages were determined by nmr integration. The free energy difference from the trans to the cis isomer was found to be about 0.76 Kcal/mole for 19 and 0.50 Kcal/mole

from trans 9 to cis 9. The bisimines exist predominately in the trans configuration.⁵² The free energy difference between the trans and cis isomers would be expected to be lower for 9 than for 19. The free energy difference between isomers was also calculated for 10. A value of 0.41 Kcal/mole at 298°K was obtained. Resonance structures, imparting some single bond character to the azomethine linkage, would be expected to decrease the energy difference.

Attempts were made to calculate the Arrhenius activation energy for N,N'-dicyclohexyl-2,2,4,4-tetramethyl-1,3-cyclobutanediimine (19), and N,N'-diphenyl-2,2,4,4-tetramethyl-1,3-cyclobutanediimine (9) at their coalescence temperatures using the method of Isaacs.⁵³

$$E_A = (\text{slope of plot}) \times (2,303) \times (R)$$

$$E_A = \text{Arrhenius activation energy (Kcal/°K mole)}$$

$$R = \text{Ideal gas constant (1.987 cal°K}^{-1}\text{mole}^{-1}\text{)}$$

$$\text{Slope of plot} = \text{Derived from Arrhenius plot of log of rate constant, } k, \text{ versus } 1 \times 10^3 / \text{temperature in } ^\circ\text{K.}$$

$$k = \frac{2\pi\Delta}{\sqrt{2}} \text{ second}^{-1}$$

$$k = \text{Rate constant (see above)}$$

$$\Delta = \text{Separation between nmr signals of } \underline{\text{cis}} \text{ and } \underline{\text{trans}} \text{ isomers in cycles per second.}$$

The following values were obtained for N,N'-dicyclohexyl-2,2,4,4-tetramethyl-1,3-cyclobutanediimine (19): $E_A = 4.58 \times 10^{-3}$ Kcal/°K mole, $E_{AT} \text{ coalescence} = 2.01$ Kcal/mole.

The following values were obtained for N,N'-diphenyl-2,2,4,4-tetramethyl-1,3-cyclobutanediimine (9):

| <u>E_A (Kcal/°K mole)</u> | <u>E_{AT} coalescence (Kcal/mole)</u> |
|--|---|
| 3.92 x 10 ⁻³ | 1.46 |
| 2.29 x 10 ⁻³ | 0.85 |
| Average E _{AT} = $\frac{1.46 + 0.85}{2}$ (Kcal/mole) = 1.16 Kcal/mole | |

The phenyl bisimine 9 being more conjugated, has less double bond character between carbon and nitrogen than the cyclohexylbisimine 19. The lower Arrhenius energy of activation value for 9 compared to 19, agrees with the lower coalescence energy value of 9, compared to 19. The calculated values of E_{AT} are somewhat inaccurate due to the difficulty in determining the exact coalescence temperature, T(°K), and the exact separation (Δ) between cis and trans nmr signals on the A-60-A nmr spectrometer. More precise measurements can be made with a 100 MHz nmr spectrometer.

The use of cyclohexylamine, cycloheptylamine, and cyclooctylamine gave significant amounts of bisimines 19, 22, and 24, respectively. The nmr spectra of 19 and 22 in CCl₄, showed the presence of approximately 33 percent of the cis isomer and 67 percent of the trans isomer. The nmr spectrum of the octylbisimine 24 in CCl₄ showed less than one percent of the cis isomer and over 99 percent of the trans isomer. Apparently cyclooctylamine is the limiting factor toward formation of the cis isomer. No attempts were made to isolate the trans isomer

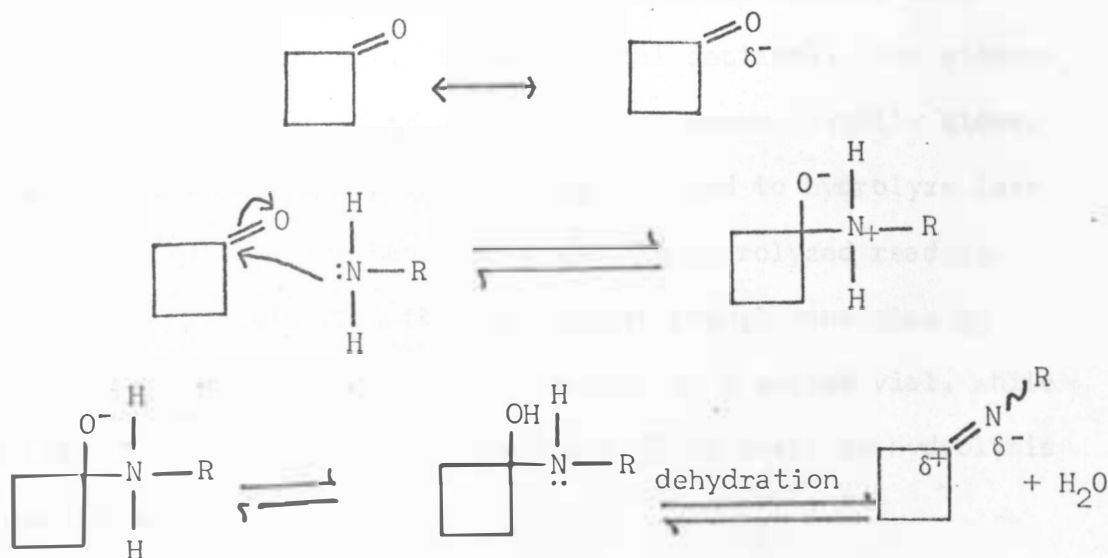
as a pure product. The preparation of cyclononylbisimine, using cyclononylamine, was not attempted.

A slight increase in the trans ratio was noted when N,N'-di(1-naphthyl)-2,2,4,4-tetramethyl-1,3-cyclobutanediimine (14) was prepared. Nmr integration showed the presence of approximately 75 percent of the trans isomer and approximately 25 percent of the cis isomer.

Ground State Reactions of Bisimines

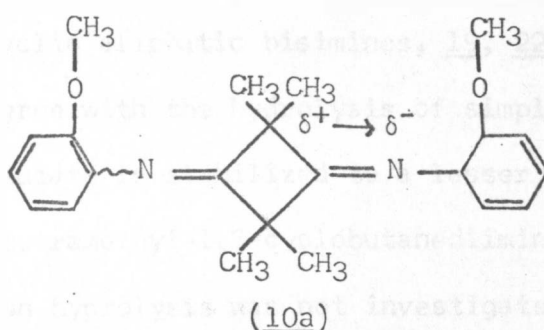
The reaction chemistry of bisimines of 2,2,4,4-tetramethylcyclobutanedione varies considerably from the reaction chemistry of simple imines.⁵⁰

The mechanism for imine formation from ketones and primary amines is believed to proceed in the following manner:⁵⁰



Since all steps in the mechanism are reversible, hydrolysis of imines to starting materials is possible.

Inspection of the mechanism indicates that hydrolysis could be accelerated when the R group increases the partial positive charge on C and the partial negative charge on N. The inductive effect of the methoxy group increases the polarization of the carbon nitrogen double bond, which increases the rate of hydrolysis. This is illustrated with structure 10a, showing inductive effects.



Bisimines of 2,2,4,4-tetramethylcyclobutanedione are susceptible to hydrolysis. The methoxyphenyl bisimine 10 decomposed to starting material during storage, even though elaborate precautions were taken to prevent hydrolysis (see experimental section). The ethoxyphenyl bisimine 11 appeared to darken and decompose slightly slower than 10. The o-chlorophenyl bisimine 12 appeared to hydrolyze less rapidly. In addition, the benzyl bisimine 13 hydrolyzed readily. Also of interest is the fact that the liquid phenyl monoimine 34 hydrolyzed after standing for several months in a sealed vial, while the solid, aliphatic, cyclohexyl monoimine 35 is inert to hydrolysis upon standing.

The mixed bisimine 37 darkened slightly in color after standing for several months. Other cyclic aliphatic bisimines, 19, 22, and 24, are also resistant to hydrolysis after standing for several months.

On the basis of hydrolysis observations, it appears that bisimines are susceptible to hydrolysis in the following order: aromatic bisimines with electron-donating substituents, 10, 11, > aromatic bisimines, 9, > cyclic aliphatic bisimines, 19, 22, and 24. These results tend to agree with the hydrolysis of simple imines.⁵⁰ The protonated intermediate is stabilized to a lesser extent in N,N'-diphenyl-2,2,4,4-tetramethyl-1,3-cyclobutanediimine (9). The role of steric factors upon hydrolysis was not investigated.

Just as aromatic bisimines are more susceptible toward hydrolysis than aliphatic bisimines, they are also more susceptible to catalytic hydrogenation which involves free radicals.

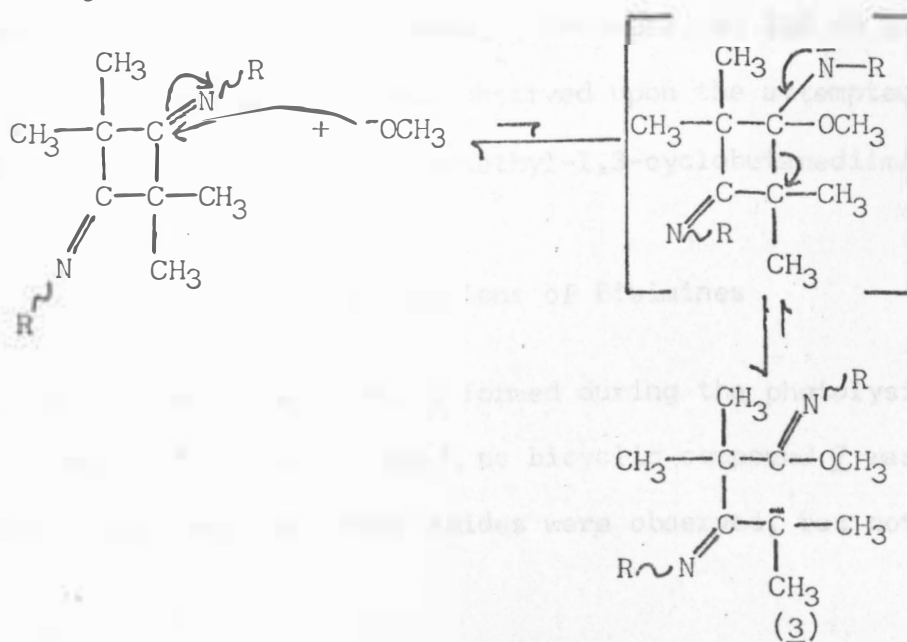
Phenyl bisimine 9 was reduced to the corresponding amine (see experimental section), while cyclohexyl bisimine 19 was not.

Simple imines, both aliphatic and aromatic, have been reduced catalytically and chemically,^{50,36} with slightly better yields sometimes reported with aromatic imines.⁵⁰ The chemical reduction of bisimines 9 and 19 was not undertaken. Although amines will undergo dehydrogenation reactions,⁵⁰ no attempt was made to dehydrogenate the diamine 41 to the starting bisimine 9.

Bisimines will react as bases and form immonium salts, with hydrogen chloride gas. The phenyl bisimine 9 as well as the cyclohexyl bisimine 19 readily formed the ionic salts 39 and 40.

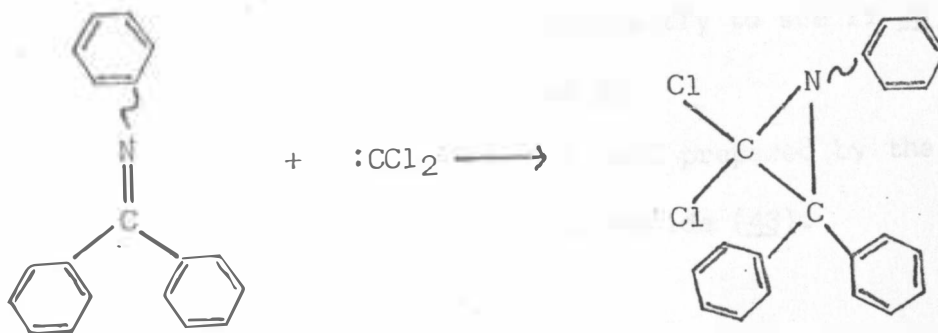
Although bisimines 9 and 19 reacted readily to form ionic salts with hydrogen chloride gas, they appear to be inert toward nucleophilic attack by the ionic reagents sodium hydride, sodium methoxide, and sodium amide. In each case quantitative recovery of starting material was accomplished. No ring opened products were obtained. The only variable appeared to be the presence of very weak open chain amide stretching frequencies in the infrared spectrum after reactions of 19 with sodium amide. These bands appeared at 3390, 1720, and 1565 cm^{-1} . Any amide present may have been formed as a result of hydrolysis, or it may have been an impurity present in 19.

The overall equilibrium of formation and hydrolysis of simple imine compounds changes little with the nature of the nucleophile. The rates of addition, unlike equilibria, however, are highly dependent on the basic nature of the attacking nucleophile (the rate of addition of the hydroxyl ion should be greater than that of the water molecule in the hydrolysis of simple imines).³⁶ An equilibrium may exist which favors ring closure. It is shown below:



No attempts were made to prove the existence of the ionic intermediate. Varying the reaction conditions could prove to be useful also.

Although bisimines do not appear to undergo all types of ionic reactions, they may undergo electrophilic addition reactions, such as with carbenes. The cyclohexyl bisimine 19 reacted with a carbene (see experimental section). Product identification was not made due to difficulty in purifying the product(s). The reaction should be rerun on a larger scale. Carbenes generated in several different ways^{50,36} will directly add to simple imines as shown.³⁶



Some simple imines will thermally decompose at 120 to 210°, giving nitriles.⁵⁰ No decomposition was observed upon the attempted pyrolysis of N,N'-dicyclohexyl-2,2,4,4-tetramethyl-1,3-cyclobutanediimine (19).

Photochemical Reactions of Bisimines

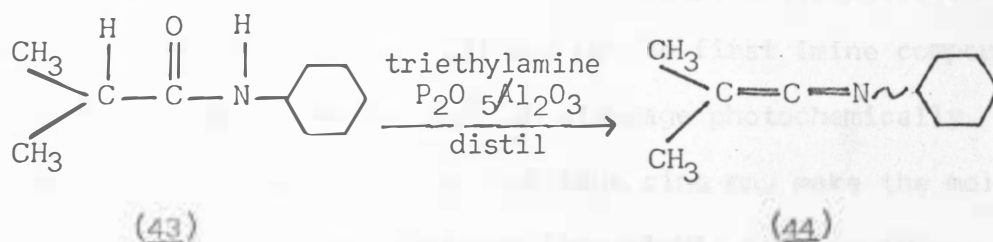
Although pinacol was readily formed during the photolysis of 19 in the presence of oxygen, Table 1, no bicyclic compound 7 was observed. Compounds resembling open chain amides were observed, but not completely

identified. It was found that the number of products obtained increased with the length of photolysis. In addition, acetone was detected.⁴²

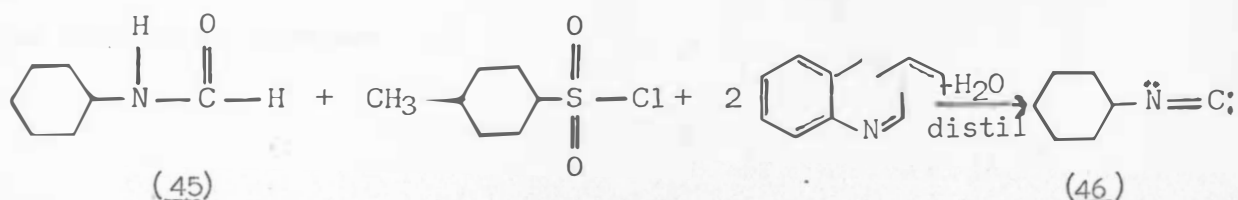
To simplify product identification, the photochemical reactions of the bisimine 19 were carried out under nitrogen, Table 2, instead of oxygen. This procedure eliminated the formation of pinacol and amide-like compounds, which were difficult to identify.

Infrared spectra after photolyses,⁴⁶ Table 1, gave bands at 2080 and 2095 cm^{-1} indicating the possible presence of a keteneimine,⁴⁶ or an isonitrile.⁵⁴ Dimethylketene-N-cyclohexylimine (44) and cyclohexylisocyanide (46) were synthesized independently to see if 46 and 44 were products formed in the photolysis of 19.

Dimethylketene-N-cyclohexylimine (44) was prepared by the dehydration^{43,44} of N-cyclohexyl-2-methylpropionamide (43).

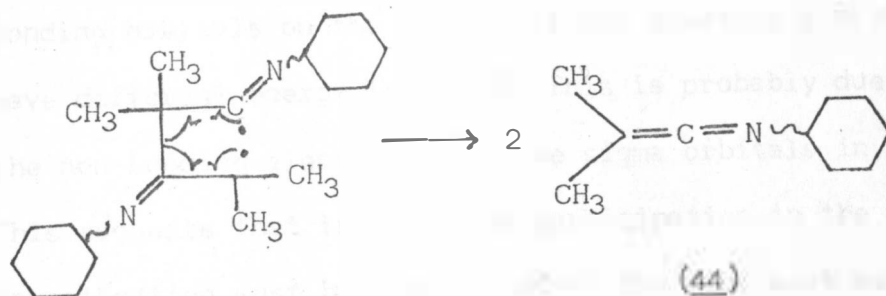
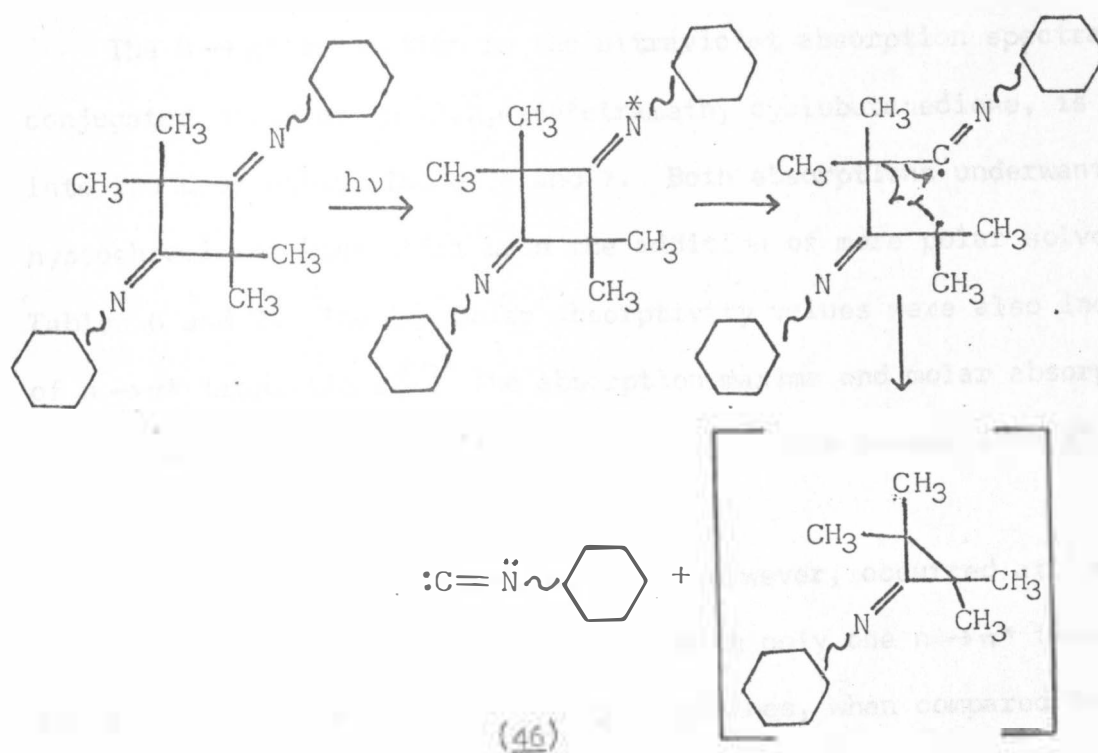


Cyclohexylisocyanide (46) was synthesized by the dehydration of N-cyclohexylformamide (45).⁴⁹



Gas chromatographic and mass spectral patterns of cyclohexylisocyanide (46) and mass spectral patterns of dimethylketene-N-cyclohexylimine (44) were similar to appropriate patterns found in the photolysis of N,N'-dicyclohexyl-2,2,4,4-tetramethylcyclobutanediimine (19) carried out under pure dry nitrogen, Table 2. It would appear that cyclohexylisocyanide (46) and dimethylketene-N-cyclohexylimine (44) are the first and second formed products, respectively, of the photolysis of the parent compound 19. The presence of many additional photoproducts with time is believed to result from further photolyses and reactions of these compounds.

The formation of the first two photoproducts may result from Norrish Type I cleavage, in a manner analogous to Type I cleavage observed in ketone photolysis.² As previously mentioned, page of this thesis, cyclic imines tend to undergo syn-anti isomerization rather than photochemical reactions. N,N'-Dicyclohexyl-2,2,4,4-tetramethylcyclobutanediimine (19) may be the first imine compound reported to undergo extensive Norrish cleavage photochemically. The inherent strain present in the cyclobutane ring may make the molecule more susceptible to Norrish cleavage than simple acyclic imines. Mechanisms of Type I Norrish cleavage, which may result in cyclohexylisocyanide (46) and dimethylketene-N-cyclohexylimine (44) are presented below: Additional studies are needed to further elucidate the mechanisms involved.



Ultraviolet Absorption Spectroscopy⁵⁵

The $n \rightarrow \pi^*$ transition in the ultraviolet absorption spectra of non-conjugated bisimines of 2,2,4,4-tetramethylcyclobutanedione, is split into two components, Tables 6 and 7. Both absorptions underwent a hypsochromic or blue shift upon the addition of more polar solvents,⁵⁵ Tables 6 and 7. The low molar absorptivity values were also indicative of $n \rightarrow \pi^*$ transitions.⁵⁵ The absorption maxima and molar absorptivity values were, in fact, similar to those of simple azomethines 47, Table 7.

Both transitions of the bisimines, however, occurred at lower energy than the simple azomethine 47, with only one $n \rightarrow \pi^*$ transition. The lower absorption energy for the bisimines, when compared to 47, can be explained by increased conjugation, which could result from $p-\pi$ type overlap between p -orbitals on the one and three carbon atoms. Due to recent experiments in photoelectron spectroscopy, the non-bonding orbitals on the oxygens of the diketone 4 have been shown to have different energy levels.²³ This is probably due to interaction of the non-bonding electrons with the sigma orbitals in the ring skeleton. This suggests that transannular participation in the system under investigation must be interpreted at the very most as a combination of $1,3-\pi$ and non-bonding sigma orbital interaction.

The energy level diagram in Figure 4 would suggest the presence of four $n \rightarrow \pi^*$ transitions when only two are observed for both the

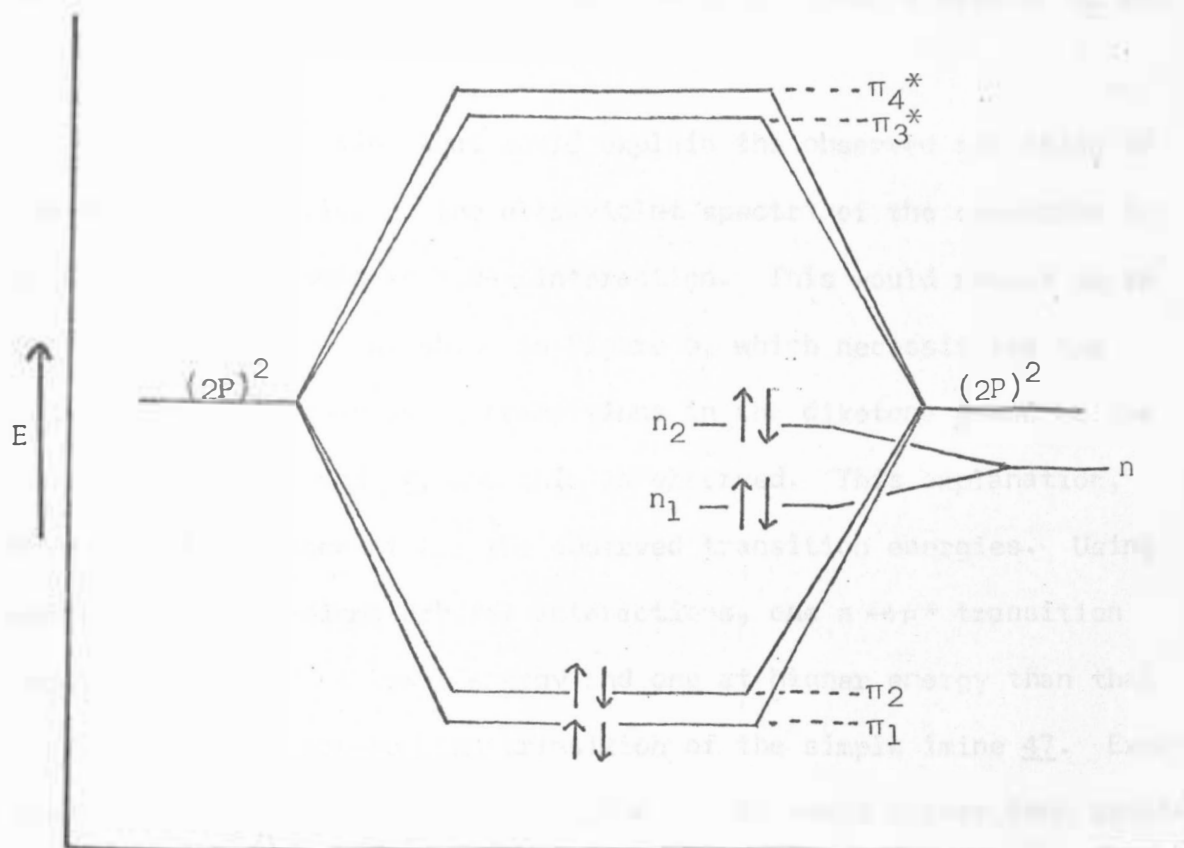


Figure 4. Energy level diagram for 2,2,4,4-tetramethylcyclobutanedione (4), or the bisimine 3, using π and non-bonding orbitals and assuming 1,3- π type overlap, and non-bonding-sigma orbital interaction, but eliminating the very small non-bonding- π interaction.

diketone 4 and the bisimines, 19, 22, and 24 in Table 6. This is reasonable, provided the difference in energy between π_3^* and π_4^* is not significant when compared to the energy difference between n_2 and n_1 .

One alternate view that would explain the observed splitting of the $n \rightarrow \pi^*$ transition in the ultraviolet spectra of the compounds in question is to assume no 1,3- π interaction. This would result in an energy level diagram as shown in Figure 5, which necessitates the presence of two non-bonding transitions in the diketone 4 and in the bisimines 19, 22, and 24, and this is observed. This explanation, however, cannot account for the observed transition energies. Using only non-bonding-sigma orbital interactions, one $n \rightarrow \pi^*$ transition would be expected at lower energy and one at higher energy than that observed for the non-bonding transition of the simple imine 47. Experimentally, this is not observed, Table 7. It would appear from existing experimental data that Figure 4 would best represent the compounds under examination.

In addition, no splitting of the $n \rightarrow \pi^*$ transition for 1,3-dimethylenecyclobutane was observed,¹⁵ indicating that π^* orbitals



are not as readily split as orbitals containing non-bonding electrons. The suggestion is made that the splitting of $n \rightarrow \pi^*$ transitions in 4

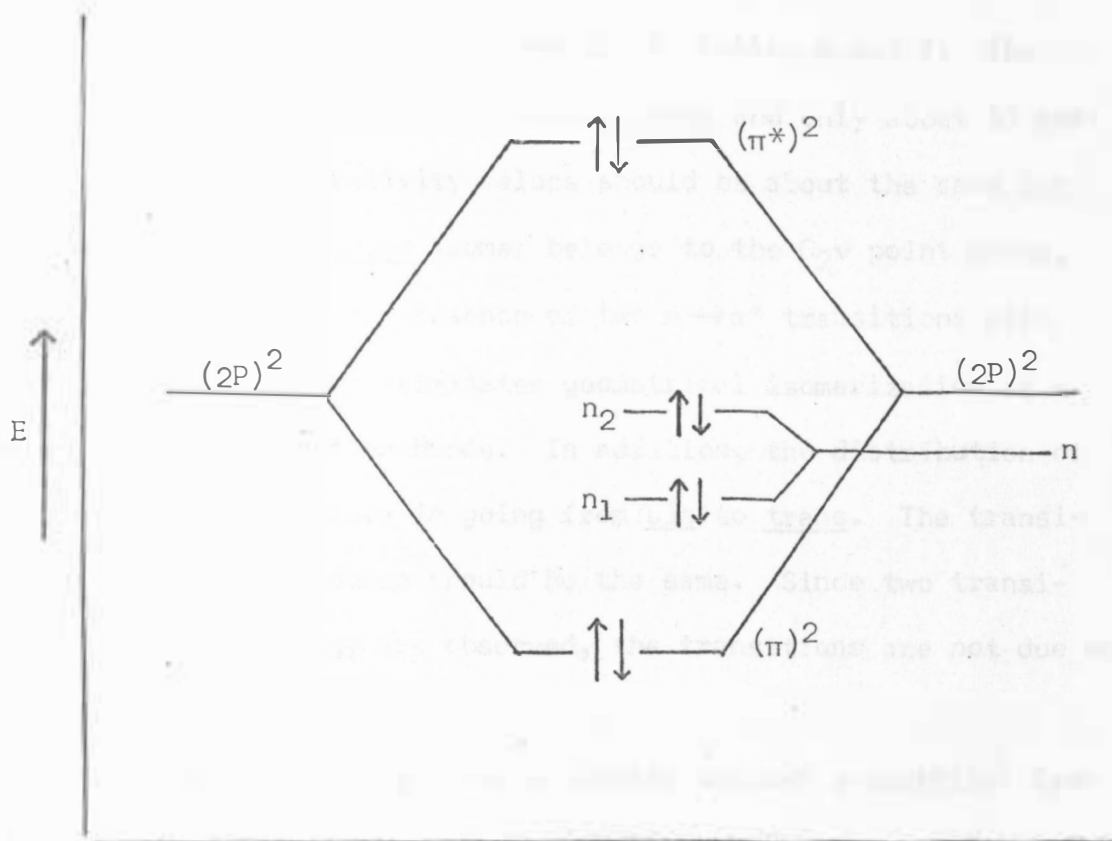


Figure 5. Energy level diagram for 2,2,4,4-tetramethylcyclobutanedione (4) and the bisimines 19, 22, and 24, using π and non-bonding orbitals and assuming non-bonding-sigma orbital interaction, but no 1,3- π type overlap.

and 19 is caused mainly by splitting of the orbitals containing non-bonding electrons, rather than by splitting of the π^* orbitals.

The possibility of geometrical isomerism as a cause of the two $n \rightarrow \pi^*$ absorption bands may be eliminated. Molar absorptivity values are very similar for both transitions of 19, Tables 6 and 7. The equilibrium solution is about 67 percent trans and only about 33 percent cis.⁵² Molar absorptivity values should be about the same for each isomer, since the trans isomer belongs to the C_{2v} point group, while the cis is C_{2h} . The presence of two $n \rightarrow \pi^*$ transitions with similar absorption maxima eliminates geometrical isomerization as a cause of the two absorption bands. In addition, the distribution of π electrons does not change in going from cis to trans. The transition energy for both isomers should be the same. Since two transitions of different energy are observed, the transitions are not due to geometrical isomerization.

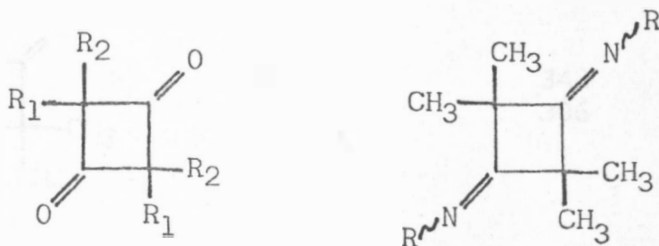
An even more convincing argument exists against geometrical isomerism causing the two $n \rightarrow \pi^*$ absorption bands. The nmr spectrum of N,N'-dicyclooctyl-2,2,4,4-tetramethyl-1,3-cyclobutanediimine (24) shows less than one percent of the cis isomer; the remainder is trans. The ultraviolet absorption spectrum shows two transitions of the same intensity (same molar absorptivity values, Table 6), and very similar to the molar absorptivity values of N,N'-dicyclohexyl-2,2,4,4-tetramethyl-1,3-cyclobutanediimine (19), Tables 6 and 7. If cis-trans isomerization were responsible for the two absorptions, then only one

major absorption band corresponding to the trans isomer should appear in the uv absorption spectrum of 24. This is distinctly not the case.

Comparison of the ultraviolet spectra of 2,2,4,4-tetramethylcyclobutanedione 4, the bisimines, 19, 22, and 24, and the dithione 48, shows that the $n \rightarrow \pi^*$ transitions of the bisimines absorb at highest energy, those of the diketone 4 next, and those of the dithione 48 at lowest energy. This is consistent with earlier studies in which arguments based on hybridization and symmetry explain the observed data quite satisfactorily.⁵⁶ In addition to the energy differences, the $n \rightarrow \pi^*$ transitions of the diketone 4 show a separation of 0.47 ev, those of the bisimine 19, 0.17 ev, and those of the dithione 48, 0.00 ev, Table 8. Self-consistent field molecular orbital calculations to determine the π energy levels for the compounds in question gave consistent trends, although the absolute magnitude of the calculated splitting in the $\pi \rightarrow \pi^*$ region is different from that observed in the $n \rightarrow \pi^*$ region. This is as expected, since the configurational interaction would be different for each state. A Pariser, Parr, and Pople self consistent field computer program containing a configurational interaction subroutine was used.^{57,58} This P^3 -CI SCF program suggested that two $\pi \rightarrow \pi^*$ transitions should be observed for the diketone 4; the difference in energy was calculated to be 0.50 ev. The bisimine 19 and the dithione 48 gave calculated differences of 0.30 ev and 0.24 ev, respectively.⁵⁷ As a final attempt to verify 1,3- π type interaction, the far ultraviolet spectrum of the cyclohexylbisimine 19 was examined. A transition was observed at 197 nm which, via molar absorptivity values

and solvent studies, was assigned as a $n \rightarrow \pi^*$ transition. There was no evidence for two electronic transitions down to the limit of the instrument, 185 nm.⁵⁷ If two transitions were present, they were too close to observe. It is apparent from these data, however, that the $\pi \rightarrow \pi^*$ transitions are not split to the same degree as are the $n \rightarrow \pi^*$. This means that the main feature in the energy difference of the $n \rightarrow \pi^*$ transitions is due to the nondegenerate non-bonding orbitals interacting with the sigma electrons of the cyclobutane ring, and not mainly due to 1,3- π type transannular interaction, which was a long held concept.

It has been reported that the extent of transannular participation is enhanced by large R groups,¹⁵ where R is CH_3 , C_2H_5 , or $n\text{-C}_3\text{H}_7$, in diketone systems of the type shown below. In the bisimines,



relationships between the size of R and the extent of transannular participation are not obvious. In the alicyclic bisimine compounds, however, the amount of splitting appears to be independent of the ring of the cyclic imine. Bisimines where R is a six, seven, or eight membered cyclic ring, Table 7, have similar absorption maxima and molar absorptivity values. An attempt to prepare the bisimine where R is a five membered cyclic ring was unsuccessful.

Table 7. Ultraviolet Absorption Spectral Data.


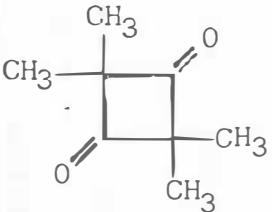
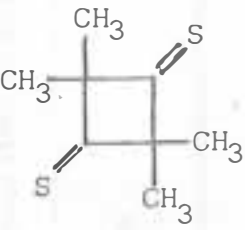
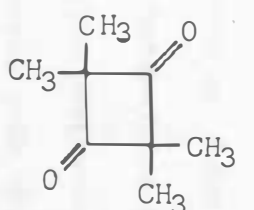
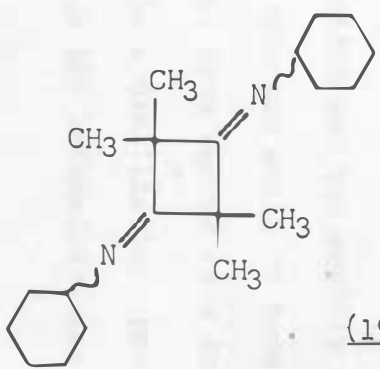
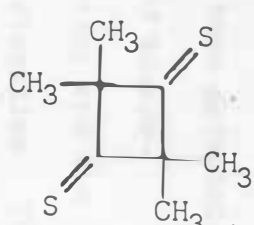
| Compound | Cyclohexane λ_{\max} (nm) | 95% Ethanol λ_{\max} (nm) | Molar Absorptivity (ϵ) (liters mole ⁻¹ cm ⁻¹) |
|--|--------------------------------------|--------------------------------------|--|
| (19) | 273 263 | 265 249 | 145 157 |
| (22) | 274 260 | 268 247 | 144 142 |
| (24) | 274 260 | 264 248 | 134 128 |
|  $\text{N} \sim \text{n-butyl}$ (47) | 250 | 240 | 290 |
|  (4) | 350 309 | 343 306 | 25 57 |
|  (48) | 500 | 490 | 22 |

Table 8. Amount of 1,3- π Interaction Indicated by the Magnitude of the $n \rightarrow \pi^*$ Ultraviolet Band Separation in Electron Volts*.

| Compound | Absorption max in cyclohexane (nm) | Absorption max in cyclohexane (ev) | Energy difference between $n \rightarrow \pi^*$ transitions (ev) |
|--|--|--|--|
|  (4) | 350 | 3.54 | 0.47 |
| | 309 | 4.01 | |
|  (19) | 273 | 4.54 | .0.17 |
| | 263 | 4.72 | |
|  (48) | 0 | 0 | 0 |

*Values calculated using the conversion factor $1.24 \times 10^{-4} \text{ ev cm}^{-1.58}$

Biological Activity of Dimethylketene-N-Cyclohexylimine (44) and the Corresponding Amide, N-Cyclohexyl-2-methylpropionamide (43)

After a period of several weeks, the presence of mold was observed growing in glassware used in the preparation of dimethylketene-N-cyclohexylimine (44) and N-cyclohexyl-2-methylpropionamide (43). It is suggested here that these compounds serve as a media for this mold. The mold was found growing in unsealed and sealed containers containing a limited amount of air. Growth was observed in containers kept in the light at room temperature which contained various amounts of the amide and certain impurities such as isobutyric acid, triethylamine, aluminum oxide, possible traces of keteneimine, and diphosphorus pentoxide and various decomposition products.

It is noteworthy that growth was observed after about five weeks in a sealed vial of the pure amide compound. The amide had been recrystallized twice from aqueous ethanol, and once from n-hexane, but had not been dried. If moisture was required for growth, the most likely sources would be: water vapor in the limited air supply; a possible trace of moisture in the compound itself; or dehydration of the amide by the organism itself, resulting in the formation of the keteneimine. Keteneimine formation was not readily observed; if formed, its presence may have been too small to have been detected. In addition, the keteneimine may have served as a food source.

Growth was also observed in a distillation apparatus and the attached small flasks into which the keteneimine was distilled. The

keteneimine was removed, and the vessel was sealed and stored in a refrigerator for about six weeks at a temperature of about 50°C, under a very limited amount of light. The vessel appeared to contain only a trace of keteneimine, with a possible slight contamination of amide and air.

The growth appeared to be both somewhat round, white colonies or long, filamentous, white colonies. The growth was streaked onto agar slants and in petri dishes containing agar blocks consisting of BHI (Brain Heart Infusion) agar. The blocks were supported above the bottom water level by means of glass tubing. As growth was poor on BHI agar blocks, growth was transferred to Sabourds Dextrose agar which resulted in much better growth, as well as sporulation, for purposes of identification.⁵⁹ Gross morphological characteristics indicating the probable identity of the organism, Pencillium frequentans, are given in Table 9.⁶⁰

It is significant that no growth had been observed in other compounds mentioned in this thesis. No growth had been observed in very dilute solutions of the keteneimine in isopropyl alcohol before and after photolysis. Also of interest is the observation that the dimer of dimethylketene-N-cyclohexylimine, the bisimine 19, was sent to the National Institute of Health for screening as a possible cancer chemotherapeutic agent and showed limited activity. Results have not been correlated with the chemotherapeutic value of the keteneimine 44.

Table 9. Morphology of Penicillium frequentans.

| Gross morphologic trait | <u>Penicillium frequentans</u> |
|-------------------------|---|
| Growth rate | Rapid |
| Topography | Flat |
| Texture | Powdery |
| Surface pigment | Green to blue-green |
| Reverse pigment | Yellow-brown |
| Microscopic morphology | <u>Penicillium frequentans</u> (see Figure 6). |
| Conidiophore | Simple |

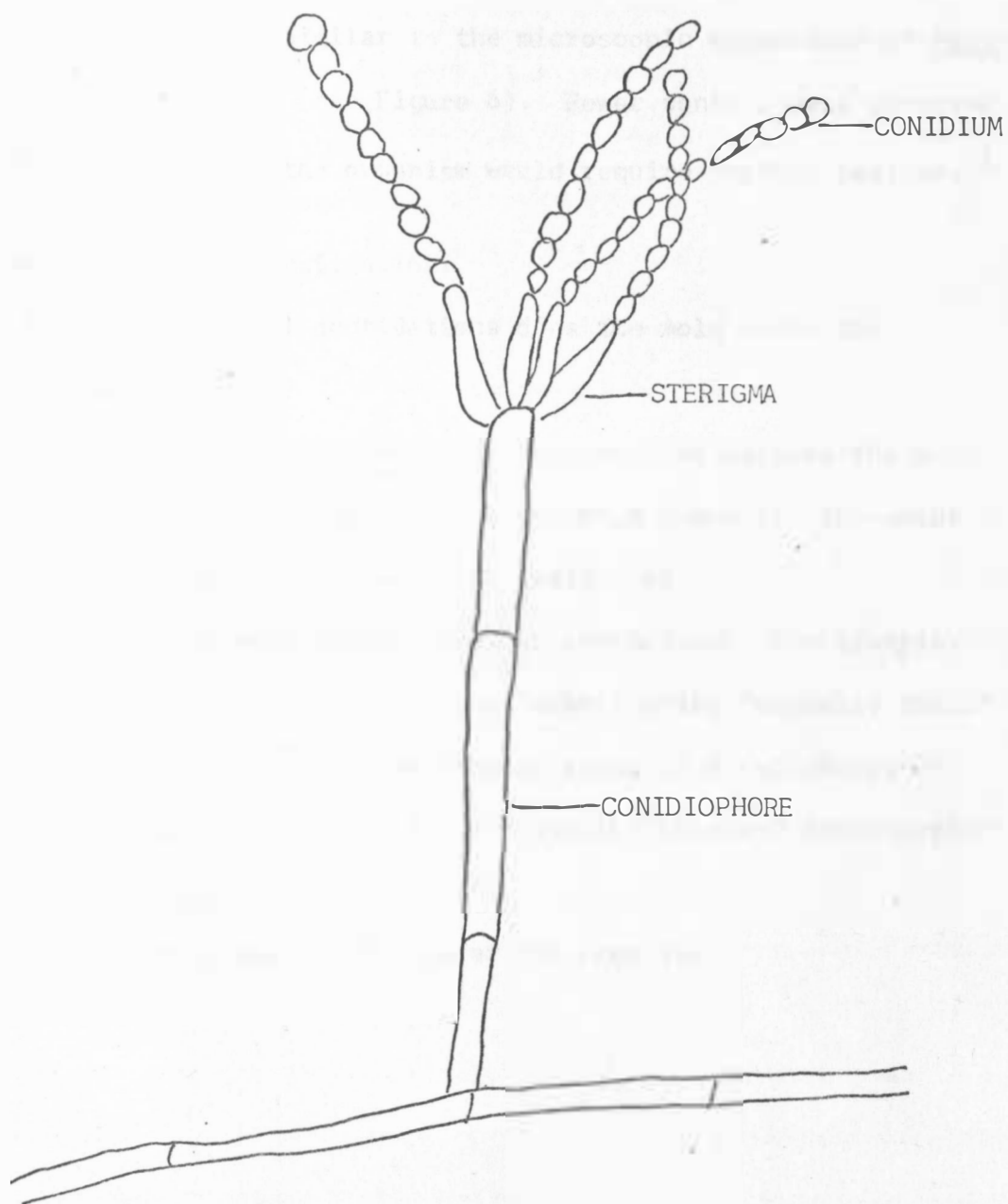


Figure 6. Penicillium frequentans.⁶⁰

The organism was stained with lactophenol cotton blue and examined under a microscope. The microscopic appearance of the organism (1000X) was similar to the microscopic appearance of Penicillium frequentans⁶⁰ (see Figure 6). Fewer conidia were observed. Absolute identity of the organism would require further testing.⁶¹

Future Topics for Investigation:

1. What chemical degradations does the mold do to the substrate(s)?
2. Under what conditions will the organism degrade the substrate? For example, will the mold dehydrate the amide when insufficient water is available?
3. Will the mold dehydrate other substrates? For example, what would be the result of substituting "normally toxic" phenyl rings⁵⁹ for cyclohexyl rings in N-cyclohexyl-2-methylpropionamide (43) and dimethylketene-N-cyclohexylimine (44)?
4. Positive identification of the organism.

CONCLUSIONS

The preparation, spectral properties, and reactions of bisimines of 2,2,4,4-tetramethylcyclobutanedione were examined.

The formation of monoimines and open chain amides was observed in the preparation of the bisimines. Two moles of starting amine favor the formation of bisimines, 3; one mole of strongly basic aliphatic amine favors the formation of the monoimine and open chain amide; and when one mole of weakly basic aromatic amine is used, monoimines are the major product and bisimines the minor product. Formation of monoimines is not observed when two moles of amine are used.

Basicity studies indicate that the use of weakly basic primary amines, such as aromatic amines, facilitates bisimine formation, and the product is formed quantitatively. In general, decreasing the basicity of the amines results in faster and more complete reactions (see pK_b values, Table 3).

Another factor in product distribution is steric considerations, Table 4. The use of *o*-isopropylaniline resulted in the bisimine 17, while the use of the larger, bulkier amine, 2,6-diisopropylaniline gave the monoimine 18. The isopropyl groups of the formed monoimine may repel the methyl groups of the cyclobutane ring sufficiently to prevent further attack by the amine; hence, no bisimine was formed.

The effect of reactant concentration was also investigated. Less concentrated solutions, using two moles of basic amine, result in the

formation of bisimines and open chain amides. More concentrated solutions result in the formation of imino open chain amides and bisimines.

The amount of available thermal energy also affects product formation. The diketone 4 does not react using solvents and amines with low boiling points.

The bisimines appear to be inert under reaction conditions using strong nucleophiles. They do, however, react with hydrogen chloride gas to form immonium salts. Aromatic bisimines can be catalytically reduced under high pressure to give amines. Aromatic bisimines containing electron donating groups tend to hydrolyze on standing to the starting amine and diketone 4. The cyclohexylbisimine 19 appears to undergo electrophilic addition reactions with carbenes, also.

Two new photochemical reactions of bisimines were observed. Complete spectrum irradiation of the cyclohexylbisimine 19 in the presence of oxygen, gave pinacol, acetone, and unidentified products resembling open chain amides. Complete spectrum irradiation in the presence of nitrogen gave dimethylketene-N-cyclohexylimine (44) and cyclohexylisocyanide (46). The Norrish cleavage resulting in the formation of 44 and 46 has not been extensively observed before in the simple azomethines.

The presence of cis-trans isomerism in the bisimines was established by nmr spectroscopy. The equilibrium consisted of approximately 67 percent of the trans isomer and 33 percent of the cis isomer. When cyclooctylamine was used as the primary amine, less than one percent of

the cis isomer was obtained and over 99 percent of the bisimine compound was trans.

Ultraviolet studies indicated the presence of three transitions between 185 and 360 nm. These two $n \rightarrow \pi^*$ transitions and one $\pi \rightarrow \pi^*$ transition have been interpreted as resulting from a combination of, mainly, interaction of non-bonding electrons on nitrogen with the sigma orbitals of the cyclobutane ring, and 1,3- π transannular participation across the ring.

Biological activity was observed in dimethylketene-N-cyclohexylimine (44) and N-cyclohexyl-2-methylpropionamide (43). These compounds appear to act as substrates for Penicillium frequentans.

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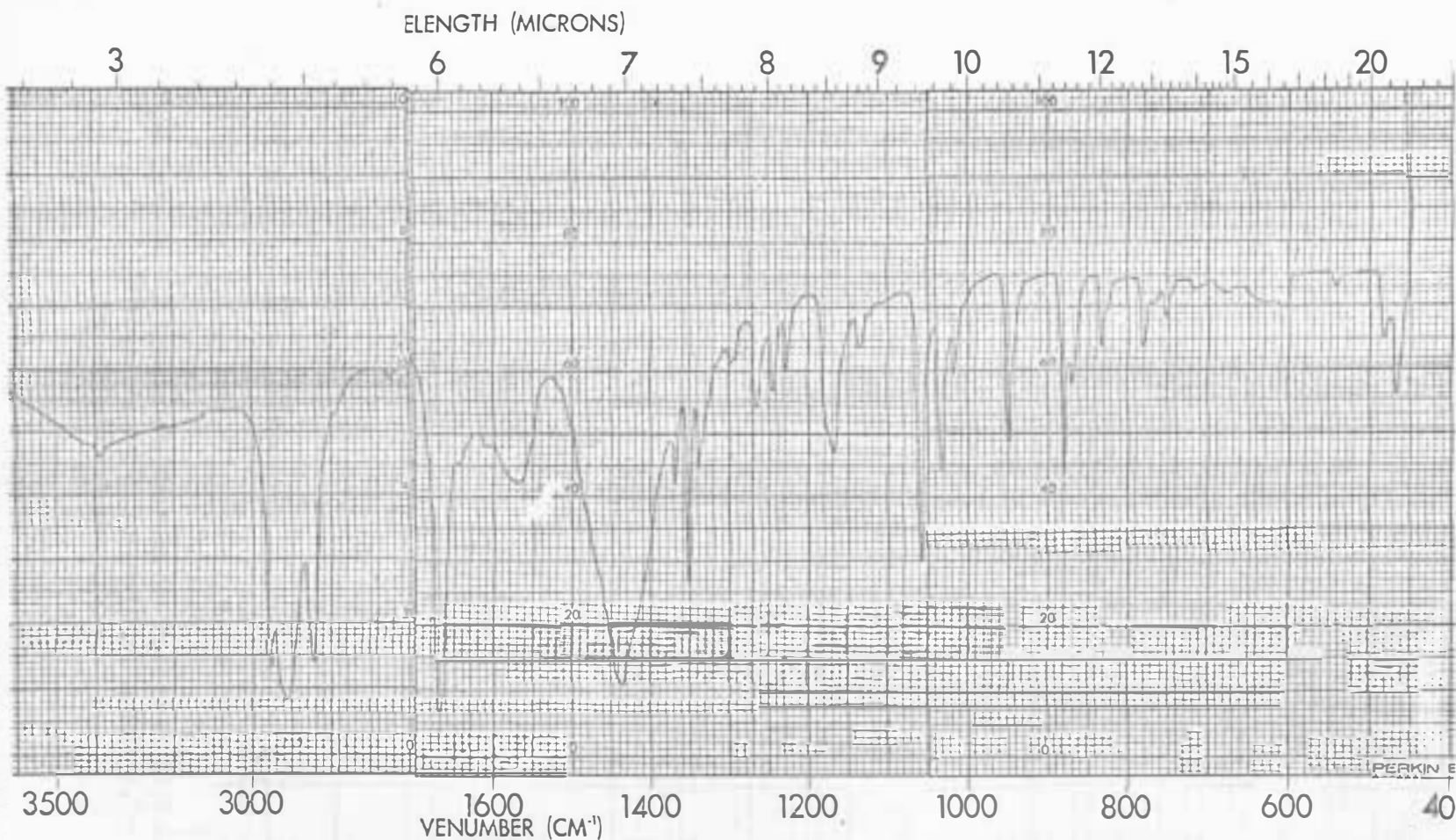
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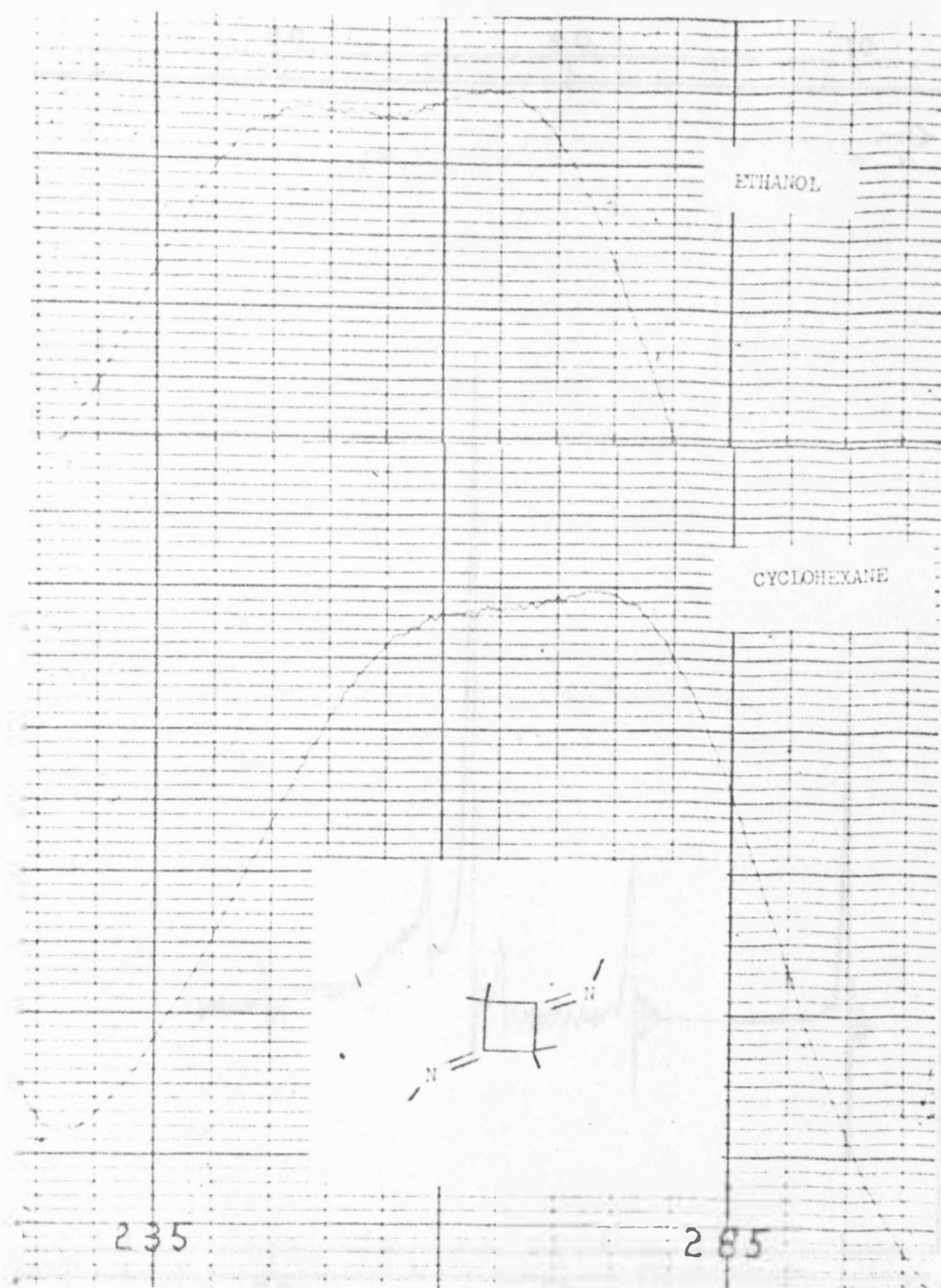
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APPENDIX

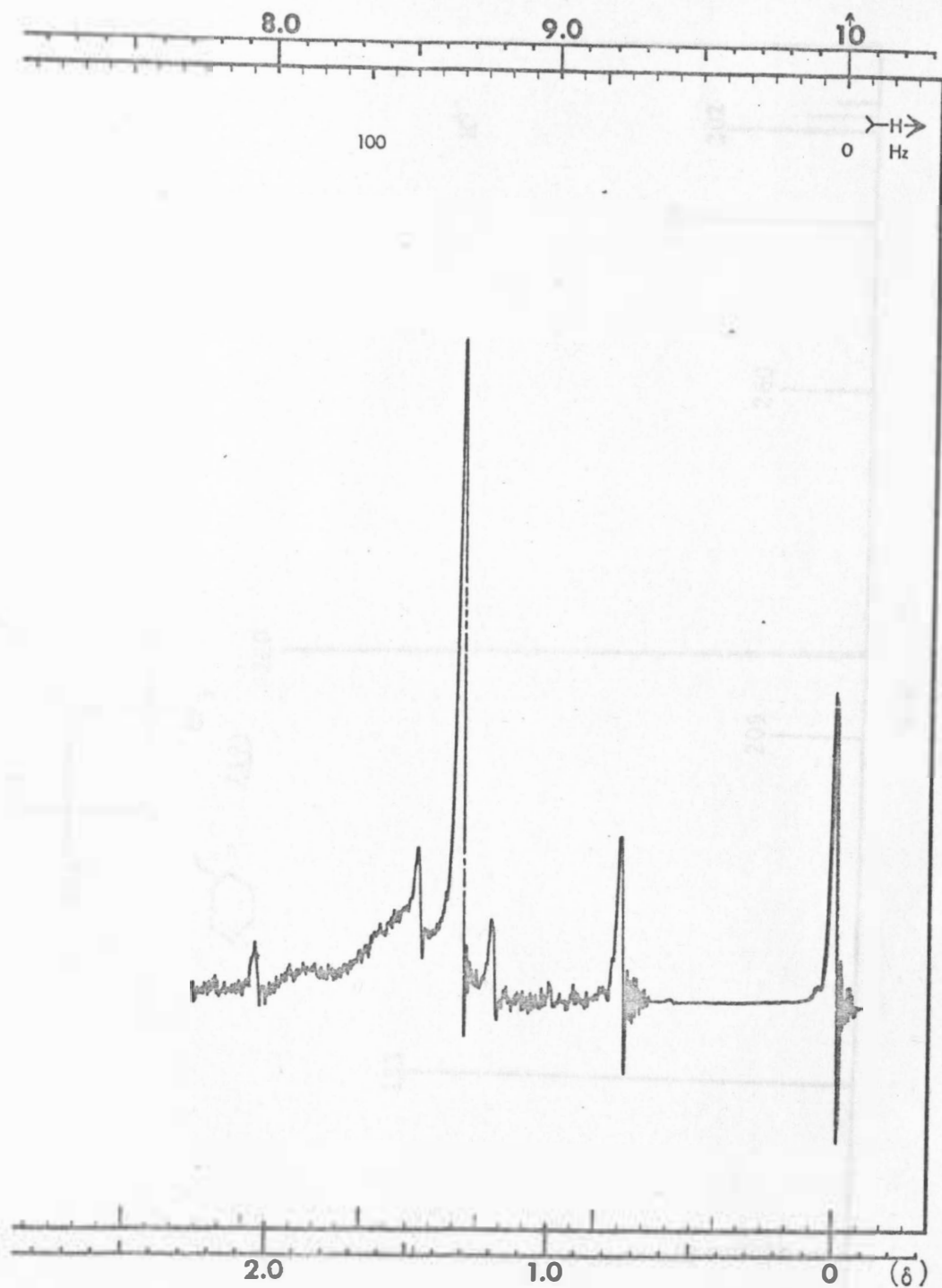
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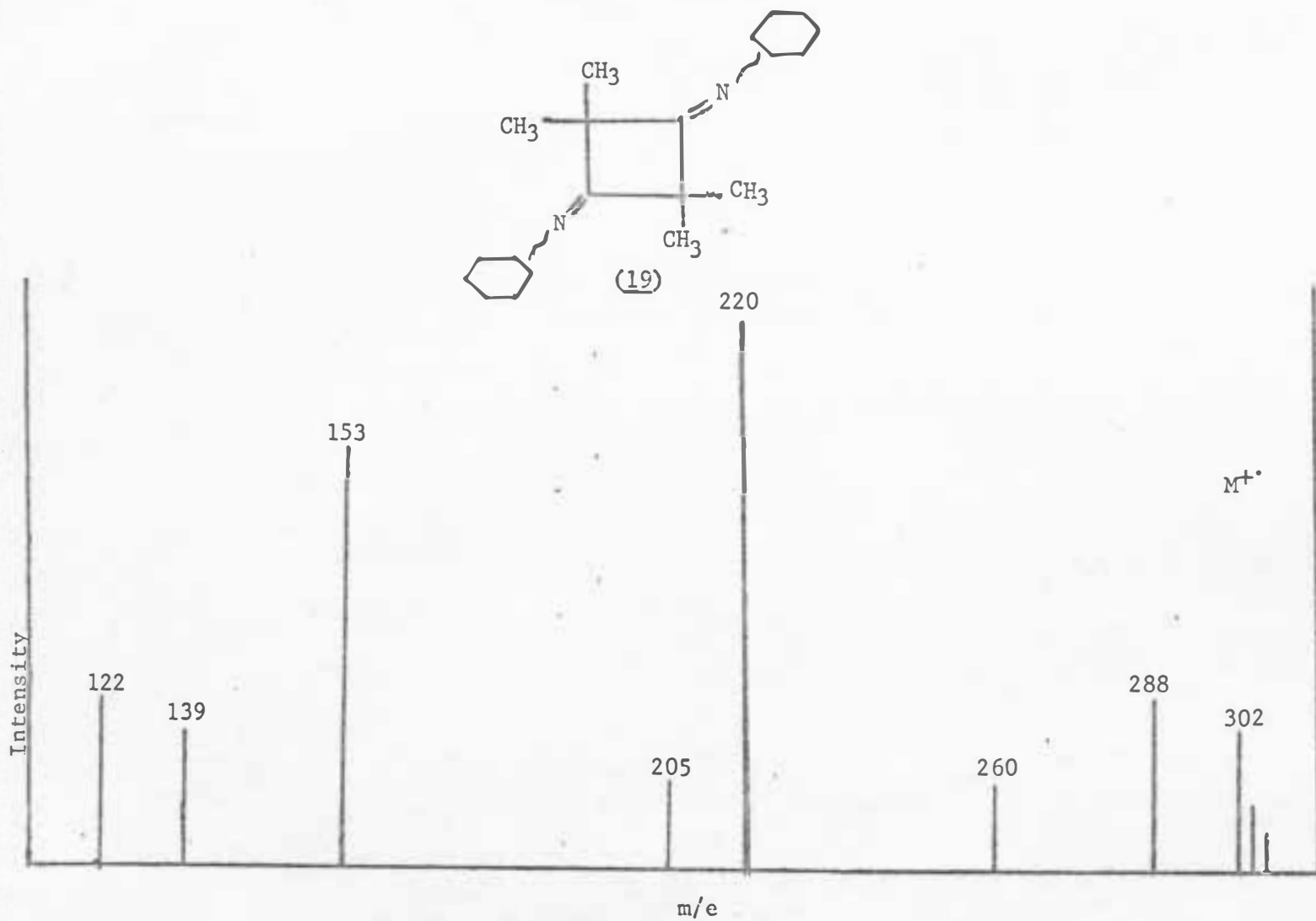
Spectrum 1. Infrared Spectrum of N,N'-Dicyclohexyl-2,2,4,4-tetramethyl-1,3-cyclobutanediimine (19).



Spectrum 2. Ultraviolet Absorption Spectrum of N,N'-Dicyclohexyl-2,2,4,4-tetramethyl-1,3-cyclobutanediimine (19).



Spectrum 3. Nuclear Magnetic Resonance Spectrum of N,N'-Dicyclohexyl-2,2,4,4-tetramethyl-1,3-cyclobutanediimine (19).



Spectrum 4. Mass Spectrum of N,N'-Dicyclohexyl-2,2,4,4-tetramethyl-1,3-cyclobutanediimine. (19).