Heterocycles from Ketenimines. VI. A Perhydro-s-triazine through Thermolysis (1a,b)

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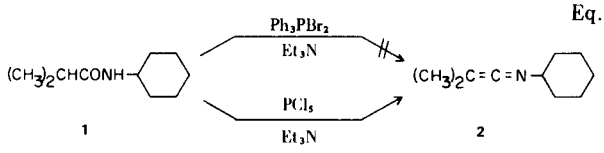
During an attempt to prepare dimethylketene *N*-cyclohexylimine (**2**) by the action of triphenylphosphine dibromide and triethylamine on *N*-cyclohexylisobutyramide (Eq. 1) (2), it was observed that the ir band at

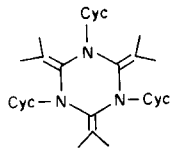
Eq. 1



1 2

2020 cm^{-1} (C=C=N absorption) of an aliquot of the reaction mixture increased in intensity until about one hour of reaction time had elapsed, whereupon it steadily decreased in intenisty. After 30 hours of reaction time the band at 2020 cm^{-1} was almost indiscernible. Apparently the ketenimine was generated initially and then consumed by a second reaction. The reaction mixture was filtered, the filtrate was evaporated to dryness, and the residue was extracted with hexane. Concentration of the hexane extracts yielded a white solid whose elemental analysis is the same as the ketenimine and whose ms showed major peaks at m/e = 453, 151, and smaller fragments. This data shows the white solid to be a trimer of the desired ketenimine. Pure ketenimine was prepared by the dehydrochlorination of the corresponding imino chloride (Eq. 1) (3) and then heated in a sealed tube. The same ketenimine trimer was obtained from this thermolysis reaction.

An ir spectrum of the trimer showed weak absorptions in the unsaturated range at 1680 and 1660 cm^{-1}, and the nmr spectrum exhibited a multiplet from δ 0.9-2.3 containing a strong singlet at δ 1.72 and a second multiplet at δ 2.9-3.3. The ratio of hydrogens under the two multiplets was 16 to 1. Thus the first multiplet with the protruding singlet must by the cyclohexyl protons and the methyl protons (48H) while the second multiplet is due to the single proton on the cyclohexyl carbon attached to nitrogen (3H). This interpretation would require all six methyls to be in identical environments and would limit the possible structures for the trimer to **3** and **4**.



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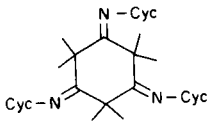

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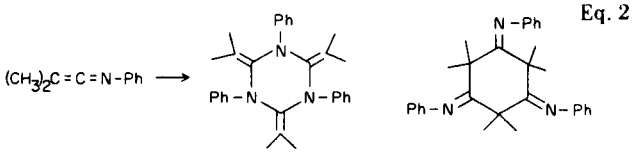
It was recently reported (4) that during the photolysis of dimethylketene *N*-phenylimine in acetone (Eq. 2) a trace of trimer is produced. This trimer has a strong ir absorption at 1675 cm^{-1} and an nmr singlet for the methyls at δ 1.44. The authors proposed the structure of this trimer (which could not be produced by direct photolysis or thermolysis of the ketenimine alone) to be **5** or **6**.

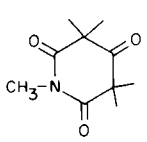
Eq. 2



5 6

Although the obvious differentiation of structure **3** and **4** or **5** and **6** would be through ozonolysis and a subsequent search for acetone, we found the trimer of dimethylketene *N*-cyclohexylimine to be too insoluble at low temperatures for ozonolysis and no reaction of the trimer of dimethylkene *N*-phenylimine was reported (4). Thus, attention was directed toward model compounds for spectroscopic indications of structure.

Martin, *et al.* (5) in 1966 published the spectroscopic data for three heterocycles which are somewhat analogous to the systems proposed for the trimers.



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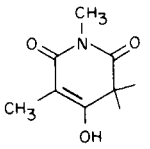

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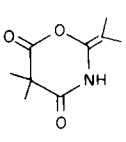

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Two of these compounds (**7** and **8**) contain only the *gem* dimethyl group and these methyls absorb in the nmr as singlets at δ 1.41 and 1.51, respectively. Compound **9** contains both the *gem* dimethyl and the isopropylidene group. The *gem* dimethyl protons absorb as a singlet at δ 1.43 and the isopropylidene methyl protons absorb as a singlet at δ 1.76. Later work by Pratt, Taylor, and Proctor (6) gave similar results for compounds containing both the *gem* dimethyls and isopropylidene methyls. This data would lend support to structure **3** for the trimer of dimethylketene *N*-cyclohexylimine (nmr absorption for methyl protons is a singlet at δ 1.72) and suggest structure **6** for the trimer of dimethylketene *N*-phenylimine (nmr absorption for methyl protons is a singlet at δ 1.44).

The weak ir absorptions at 1680 and 1660 cm^{-1} for the trimer **3** or **4** and the strong ir absorption at 1675 cm^{-1} for the trimer **5** or **6** would suggest the same structures as the nmr results. Trimer **3** with an enamine structure would be expected to absorb weakly while trimer **6** with an imine structure would be expected to absorb strongly in the unsaturated range of the ir.

Final spectroscopic support comes from the uv spectrum. The trimer represented by **3** or **4** absorbs at 214 nm (ϵ = 17,300). Stork (7) has reported that enamines exhibit a uv max at 230 ± 10 nm (ϵ = 5000-8000) and Benzing (8) has observed similar results. On the other hand imines have been shown to exhibit uv max at 250 ± 10 nm (9,10). The absorption observed for the trimer of dimethylketene *N*-cyclohexylimine of 214 nm with an ϵ value of approximately three times that reported by Stork as a normal enamine absorption supports structure **3** for the trimer.

Since **3** and **4** should differ spectroscopically and since the perhydro *s*-triazine **3** is the only structure that agrees with the nmr, ir and uv data, one concludes that the trimer of **2** is **3**. Similarly the nmr and ir data reported by Singer (4) when compared with the model compounds **7**, **8**, and **9** would suggest the presence of ring *gem* dimethyls and an imine functional group. Only structure **6** would fit this data.

Other work in this laboratory (1a) indicates that the only ketenimines which trimerize to any extent upon thermolysis are the fully aliphatic substituted ketenimines. Systems with aromatic substituents yield dimers as the major thermolysis product. This trimerization reaction appears to be a good route to perhydro- *s*-triazines.

EXPERIMENTAL

Infrared spectra were determined with a Perkin-Elmer Model 137 or 137G spectrometer. Nuclear magnetic resonance spectra were taken on a Varian A-60 instrument in carbon tetrachloride solvent and peak positions are reported in ppm from internal tetramethylsilane. Ultraviolet spectra were recorded on a Perkin-Elmer Model 202 spectrometer and hexane was employed as the solvent. Analyses were performed by Galbraith Laboratories, Incorporated, Knoxville, Tennessee.

1,3,5-Tricyclohexyl-2,4,6-trisopropylideneperhydro-*s*-triazine. Method A.

In a 2-l. flask equipped with a stirrer, a condenser, and a nitrogen atmosphere were placed 800 ml. of methylene chloride and 101.5 g. (0.387 mole) of triphenylphosphine. The flask was cooled in an ice bath and 61.85 g. (0.387 mole) of bromine was added at such a rate that the solution did not boil. To the resultant suspension was added 120 ml. of triethylamine followed by 65.5 g. (0.387 mole) of *N*-cyclohexylisobutyramide. The ice bath was removed and the stirred contents of the flask were refluxed under nitrogen. The progress of the reaction was monitored by observing the change in the intensity of the absorption band in the ir at 2020 cm^{-1} (C=C=N). The intensity of the absorption band at 2020 cm^{-1} increased steadily up until an hour of reaction time had elapsed, whereupon it began a gradual decrease in intensity. After 30 hours of reaction time the band at 2020 cm^{-1} was almost indiscernible; whereupon, the reaction mixture was cooled in ice and filtered with suction. The filtrate was evaporated to dryness on the rotatory evaporator and extracted with five 100 ml. portions of hot hexane. Concentration of the hexane solution to *ca.* 100 ml. resulted in the precipitation of 34.7 g. (59%) of crude trimer, white solid, m.p. 168-170°. Several recrystallizations from hexane-acetone afforded an analytical sample, m.p. 170-171°. [Ir 1680 and 1660 cm^{-1} in the unsaturated range. Nmr δ 0.9-2.3 (multiplet containing a singlet at δ 1.72, 48H) and 2.9-3.3 (3H). Molecular weight 453 by ms with principal m/e values of 151 and less].

Anal. Calcd. for $C_{30}H_{51}N_3$: C, 79.41; H, 11.33; N, 9.26. Found: C, 79.68; H, 11.14; N, 8.91.

Method B.

Into an ampoule was placed 3.20 g. (21 mmoles) fo dimethylketene *N*-cyclohexylimine. The sealed ampoule was heated at 125° for two weeks. A small amount of white solid was deposited after the ampoule stood at room temperature for several days. The supernatant liquid was removed with an eye dropper and sealed in an ampoule for further heating; while the precipitate was collected and recrystallized from hexane-acetone. There was obtained 0.2 g. (6%) of the trimer of dimethylketene *N*-cyclohexylimine, white solid, m.p. 170-171°. The ir and nmr spectra of the material were identical with those of the material obtained in Method A.

There was subsequently obtained 1.1 additional grams (41% total yield) from the supernatant liquid after heating eight additional weeks.

Acknowledgment.

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