

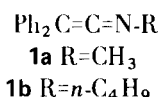
## Heterocycles from Ketenimines. V. 2-Iminoazetidines Through Thermolysis (1a)

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Staudinger (2) and Stevens (3) have reported that, when heated, ketenimines, and in some cases ketenimine precursors, yield polymeric materials. No structures have been proposed for these polymeric products although Stevens did state that dimers were produced during the preparation of diphenylketene-*N*-methylimine (**1a**) and diphenylketene-*N*-*n*-butylimine (**1b**) from the corresponding imino chlorides (3). Since other heterocumulenes such as ketenes and carbodiimides have been shown to yield



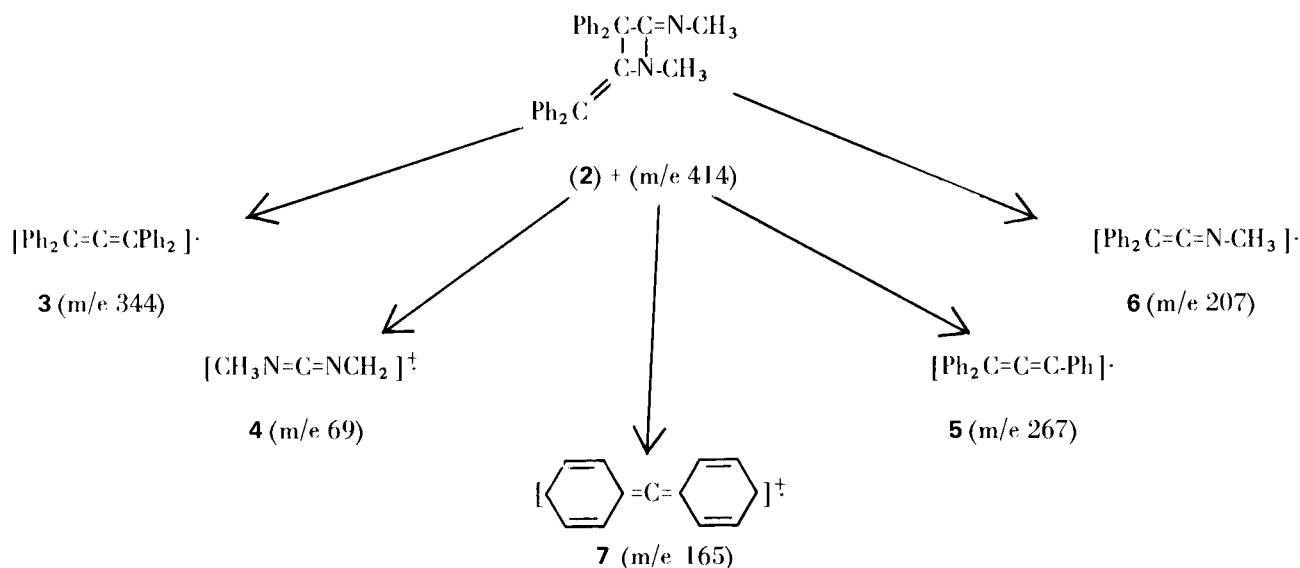
interesting heterocycles upon thermolysis (4) and since the ketenimine moiety has been shown to be reactive to thermolysis, we have undertaken a study of the thermolysis of the system with the goal of obtaining some novel substituted heterocyclic compounds.

The products obtained when ketenimines are heated seem to fall into three groups (1b). If the nitrogen atom

of the ketenimine contains an aryl substituent, dimerization through cyclization occurs to produce 3,4-dihydroquinazolines (this will be the subject of a later report). On the other hand, if the ketenimine moiety is fully substituted with alkyl groups, trimers are produced (1b). Ketenimine **1a** was studied as an example of the diarylketene-*N*-alkylimine system and constitutes this report.

If **1a** is heated for six weeks in a sealed ampoule at 125°, the contents of the ampoule triturated with hexane, and the residue crystallized from hexane-acetone, one obtains a colorless solid, m.p. 170-171°, which exhibits ir absorptions at 1745 cm<sup>-1</sup> and 1630 cm<sup>-1</sup>. The product has a slightly higher m.p. and the ir absorptions differ somewhat from Steven's compound (3); however, the product produced from Steven's directions is identical in all aspects to ours. The nmr of this product has absorptions at 2.67 δ (s, 3H), 2.94 δ (s, 3H), and 7.17 δ (20 H), and ms peaks at *m/e* = 414 (15%), 344 (74%), 267 (29%), 207 (100%), 165 (43%) and 69 (35%). The two nmr singlets are the N-CH<sub>3</sub> groups in which one is significantly

### SCHEME



more deshielded. This difference is most easily envisioned with an amine methyl and an imine methyl (5). Structure **2** accounts for both the necessity of nonequivalent methyls and for the ms data as shown in the SCHEME.

The production of 2-iminoazetidines by the thermolysis of ketenimines appears to be specific for diarylketene-*N*-alkylimines as none of the other ketenimines systems studied yielded this adduct (1b).

#### EXPERIMENTAL

Melting points were determined on Fisher-Johns and Mel-Temp apparatuses and are corrected. Infrared spectra were determined in carbon tetrachloride and Nujol on Perkin-Elmer Model 137 and 137 G Infracords. The gas chromatography measurements were made on the Aerograph Auto-Prep Instrument using a Carbowax 20M, a DC-200, or a SE-30 column. The mass spectra were recorded on a Perkin-Elmer Model 270 mass spectrometer and the nuclear magnetic resonance spectra on a Varian A-60 spectrometer in carbon tetrachloride. Analyses were performed by Galbraith Laboratories, Inc., Knoxville, Tennessee. 3,3-Diphenyl-4-diphenylmethyldiene-1-methyl-2-(*N*-methyl)iminoazetidine (**2**).

##### Method A.

Into an ampoule was placed 3.69 g. (0.018 mole) of diphenylketene *N*-methylimine (3). The sealed ampoule was heated at 125° for two weeks. After cooling, a small portion of the contents of the ampoule was analyzed by vpc. The chromatograph showed the reaction product to be a mixture of two main products. Forty-six percent of the mixture was found to be unreacted ketenimine; while 36% of the mixture was diphenylketene *N*-methylimine dimer by comparison of retention times with those of authentic samples (see Method B). Several other products of undetermined structure were also present in low yield.

The ampoule was resealed and heated for an additional four weeks. After cooling, the contents of the ampoule were triturated with hexane. The resultant residue was recrystallized from hexane-acetone. There was obtained 2.10 g. (57%) of **2** m.p. 170-171°. Mixture melting point with Steven's dimer (3) (m.p. 170-171°) was unchanged (m.m.p. 170-171°). The solid was assigned structure **2** on the basis of the following spectral data: ir 1745 (s), 1630 (s), 1600 (m), 1495 (m), 1465 (m), 1450 (m), 1370 (m), 1040 (m), 1025 (m), 760 (s), 740 (m), 700 cm<sup>-1</sup> (s). Uv 213 nm (35,600), 395 nm (16,600). Nmr  $\delta$  2.67 (s, 3H, NCH<sub>3</sub>), 2.94 (s, 3H, C-NCH<sub>3</sub>), 7.17 (s, 20 H, ArH). Molecular weight 414 by vpc-ms with m/e values of 69 (35), 165 (43), 207 (100), 267 (29), 344 (74) and 414 (15) parent ion.

*Anal.* Calcd. for C<sub>30</sub>H<sub>26</sub>N<sub>2</sub>: C, 86.92; H, 6.32; N, 6.76. Found: C, 87.08; H, 6.27; N, 6.88.

##### Method B.

The procedure followed was similar to that previously described (3). In a 250 ml. flask equipped with a condenser and a calcium chloride drying tube were placed 22.5 g. (0.1 mole) of diphenyl-*N*-methylacetamide, 20.8 g. (0.1 mole) of phosphorus pentachloride, and 150 ml. of dry benzene. The mixture was heated at reflux until evolution of hydrogen chloride ceased (ca. 1 hour). The reaction mixture was concentrated on the rotatory evaporator under reduced pressure and the residual oil co-distilled with three portions (20 ml.) of dry benzene on the rotatory evaporator to remove any residual phosphorus oxychloride. The remaining yellow oily residue was transferred to a 500 ml. flask equipped with a condenser, a stirrer, and a nitrogen atmosphere containing 60.7 g. (0.6 mole) of triethylamine and 150 ml. of dry benzene. The stirred reaction mixture was refluxed under nitrogen for 6 hours. After cooling, 13.5 g. (98%) of triethylamine hydrochloride was collected by filtration and washed with dry ether. The filtrate and ether washings were combined and concentrated on the rotatory evaporator. Distillation of the residue afforded two fractions: (1) 6.0 g. (29%), b.p. 121-150° (0.17 mm); (2) 4.6 g. (22%), b.p. 215-217° (0.17 mm) (lit. (3) 215-225° (0.1 mm)). The first fraction was impure ketenimine contaminated with dimer. The second fraction readily crystallized. Several recrystallizations from hexane-acetone afforded a white solid, m.p. 170-171° (lit. (3) m.p. 166-167.5°).

##### Acknowledgement.

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