Heterocycles from Ketenimines. IV. 3-Iminosubstituted-1,2-oxazetidines (1)

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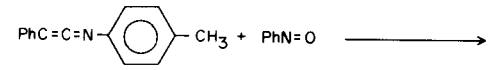
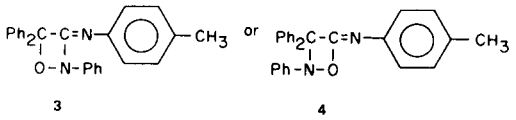
We have been investigating the ability of ketenimines (nitrogen analogs of ketenes) to serve as precursors to small ring heterocycles with exocyclic unsaturation (2). As part of our overall program, we have studied the reaction of ketenimines with nitrosobenzenes.

Equimolar amounts of nitrosobenzene (**1**) and diphenylketene-*N*-(*p*-tolyl)imine (**2**) were dissolved in the minimum amount of ether and the solution was allowed to stand overnight. An infrared spectrum of the reaction mixture showed the absence of the strong ketenimine absorption at 2000 cm^{-1}. The addition of hexane to the cold ether solution caused the precipitation of a colorless product which melted at 95-96° and which showed a strong infrared absorption at 1710 cm^{-1}. This absorption is characteristic of an imine on a four membered ring (2). Elemental analysis indicated a one to one adduct and led us to postulate **3** or **4** as the product (Eq. 1).

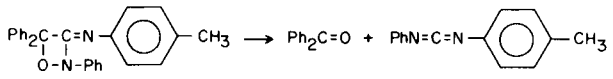


2 **1**



3 **4**

(Eq. 1)



(Eq. 2)

The adduct undergoes smooth thermal decomposition to yield a distillable product which has a strong infrared absorption at 2150 cm^{-1}. This absorption is characteristic of carbodiimides and is about 100 cm^{-1} lower than the isocyanate absorption (3). Therefore the adduct must be **3** and the decomposition is illustrated by Equation 2. Further proof was obtained by (a) hydrolyzing the carbodiimide to phenyl *p*-tolylurea which was identical in all respects to an authentic sample and by (b) monitoring the decomposition by GC for the benzophenone. Analysis by this latter method gave us a quantitative yield of benzophenone. The reaction appears to be general for ketenimines and aromatic nitroso compounds.

The production of only one of the two possible adducts surprised us as the similar addition of nitrosobenzene to ketenes gives both products (4, 5) and the product we obtained is the reverse of that predicted from polar effects. Extended HMO calculations were made on nitrosobenzene and the ketenimine to determine if an excited state of either was involved in the reaction. The results show that the ketenimine moiety must be in the ground state and the nitrosobenzene must be in the first excited state to give orbital overlap consistent with the mode of addition we observe experimentally. Obviously, this excited level can be reached by thermal means at room temperature. However, we were interested in the possibility of photochemically producing the adduct and, therefore, we have made some rate studies to this end. At 0° an appreciable enhancement in rate of disappearance of ketenimine is observed in an irradiated sample over a dark sample. We are currently continuing our studies on the mechanism of this reaction.

EXPERIMENTAL

Melting points were determined on Fisher-Johns and Mel-Temp apparatuses and are corrected. Infrared spectra were determined in carbon tetrachloride and potassium bromide on Perkin-Elmer Model 137 and 137G Infracords. The gas chromatography measurements were made on the Aerograph Auto-Prep instrument and analyses were performed by Galbraith Laboratories, Inc., Knoxville, Tennessee.

3-*N*-(*p*-Bromophenyl)imino-2,4,4-triphenyl-1,2-oxazetidine.

To a solution of 15.0 g. (0.044 mole) of diphenylketene-*N*-(*p*-bromophenyl)imine in 100 ml. of anhydrous ether was added a solution of 5.0 g. (0.046 mole) of nitrosobenzene in 100 ml. of anhydrous ether. The mixture was allowed to stand two days (until the loss of the ketenimine infrared absorption at 2000 cm^{-1} was complete) and then the solvent was concentrated without heating to about 25 ml. The addition of hexane to the cold solution caused the precipitation of 15 g. (76% yield) of the product, m.p. 86-87°. Recrystallization of the product from hexane gave an analytically pure sample as colorless crystals, m.p. 86-87°.

Anal. Calcd. for $C_{26}H_{19}BrN_2O$: C, 68.58; H, 4.20; N, 6.15. Found: C, 68.52; H, 4.22; N, 6.18.

3-*N*-(*p*-Tolyl)imino-2,4,4-triphenyl-1,2-oxazetidine (**3**).

The same procedure was followed using 5.0 g. (0.017 mole) of diphenylketene-*N*-(*p*-tolyl)imine and 1.89 g. (0.017 mole) of nitrosobenzene to yield 4.2 g. (60%) of an analytically pure product as colorless crystals, m.p. 95-96°.

Anal. Calcd. for $C_{27}H_{22}N_2O$: C, 83.05; H, 5.68; N, 7.16. Found: C, 83.13; H, 5.64; N, 7.23.

3-*N*-(*p*-Tolyl)imino-4,4-diphenyl-2-*p*-tolyl-1,2-oxazetidine.

The same procedure was followed with 5.0 g. (0.014 mole) of diphenylketene-*N*-(*p*-tolyl)imine and 1.74 g. (0.017 mole) of *p*-nitrosotoluene to yield 3.0 g. (41%) of analytically pure product as colorless crystals, m.p. 102-103°.

Anal. Calcd. for $C_{28}H_{24}N_2O$: C, 83.14; H, 5.97; N, 6.92. Found: C, 83.22; H, 6.03; N, 6.89.

3-*N*-(*p*-Bromophenyl)imino-4,4-diphenyl-2-(*p*-bromophenyl)-1,2-oxazetidine.

The same procedure was followed with 5.6 g. (0.015 mole) of diphenylketene-*N*-(*p*-bromophenyl)imine and 3.0 g. (0.016 mole) of *p*-bromonitrosobenzene to yield 5.2 g. (60%) of analytically pure product as colorless crystals, m.p. 103-104°.

Anal. Calcd. for $C_{26}H_{18}Br_2N_2O$: C, 58.44; H, 3.39; N, 5.24. Found: C, 58.46; H, 3.35; N, 5.33.

3-*N*-(*p*-Tolyl)imino-4,4-diphenyl-2-*p*-bromophenyl-1,2-oxazetidine.

The same procedure was followed with 4.5 g. (0.016 mole) of diphenylketene-*N*-(*p*-tolyl)imine and 3.0 g. (0.016 mole) of *p*-bromonitrosobenzene to yield 3.0 g. (39.5%) of analytically pure product as colorless crystals, m.p. 88-88.5°.

Anal. Calcd. for $C_{27}H_{21}BrN_2O$: C, 69.08; H, 4.51; N, 5.97. Found: C, 69.15; H, 4.48; N, 6.05.

3-*N*-(*p*-Tolyl)imino-4,4-diphenyl-2-*p*-chlorophenyl-1,2-oxazetidine.

The same procedure was followed with 3.6 g. (0.012 mole) of diphenylketene-*N*-(*p*-tolyl)imine and 1.8 g. (0.012 mole) of *p*-chloronitrosobenzene to yield 1.7 g. (31%) of analytically pure product as colorless crystals, m.p. 71-72°.

Anal. Calcd. for $C_{27}H_{21}ClN_2O$: C, 76.31; H, 4.98; N, 6.59. Found: C, 76.59; H, 4.90; N, 6.60.

3-*N*-(*p*-Tolyl)imino-4,4-diphenyl-2-*p*-nitrophenyl-1,2-oxazetidine.

To a solution of 1.0 g. (0.003 mole) of diphenylketene-*N*-(*p*-tolyl)imine in 50 ml. of chloroform was added a solution of 0.54 g. (0.003 mole) of *p*-nitronitrosobenzene in 50 ml. of chloroform. The mixture was allowed to stand for four hours (until the loss of the ketenimine infrared absorption at 2000 cm^{-1} was complete), and then the solvent was evaporated. The residue was crystallized from hexane to yield 1.10 g. (71%) of analytically pure colorless crystals, m.p. 135-137°.

Anal. Calcd. for $C_{27}H_{21}N_3O_3$: C, 74.46; H, 4.86; N, 9.64. Found: C, 74.70; H, 4.75; N, 9.65.

3-*N*-(*p*-Bromophenyl)imino-4,4-diphenyl-2-*p*-nitrophenyl-1,2-oxazetidine.

The same procedure was followed with 1.5 g. (0.004 mole) of diphenylketene-*N*-(*p*-bromophenyl)imine and 0.66 g. (0.004 mole) of *p*-nitronitrosobenzene to yield 1.1 g. (51%) of analytically pure product as colorless crystals, m.p. 143-144°.

Anal. Calcd. for $C_{26}H_{18}BrN_3O_3$: C, 62.38; H, 3.62; N, 8.39. Found: C, 62.56; H, 3.48; N, 8.34.

Preparation of Phenyl-*p*-tolylurea by Thermal Degradation of **3**.

One gram of 3-*N*-(*p*-tolyl)imino-2,4,4-triphenyl-1,2-oxazetidine was heated in a vacuum distillation apparatus at atmospheric pressure until extensive decomposition was apparent. The residue was then vacuum distilled to give a yellow liquid which had a strong infrared absorption at 2150 cm^{-1}. To a solution of the distillate in 20 ml. of tetrahydrofuran was added 10 ml. of 3 *N* hydrochloric acid and the mixture was stirred for two days. The mixture was then extracted with ether (3x with 30 ml.) and the combined extracts were washed acid free with water. After the combined ether extracts were dried over anhydrous magnesium sulfate, the ether was removed to leave a small amount of white crystalline compound identical in all respects to synthetic phenyl *p*-tolylurea. A melting point of a mixture of the two compounds was not depressed. No spectral or other evidence was obtained for *p*-tolylisocyanate.

Gas Chromatographic Analysis for Benzophenone in the Decomposition of the Adducts.

Samples of the various adducts were introduced in a solution in carbon tetrachloride directly onto a 5 foot column packed with 15% SE-30 on Kromat CE and had been preheated to 300°. Before and after each sample of adduct, a known amount of benzophenone was put through the column. Retention times allowed us to identify benzophenone from our adducts and relative peak areas allowed us to determine its concentration. In all cases the benzophenone concentration was between 94.5 and 99.5% of the theoretical amount possible from the adducts analogous to **3**.

Acknowledgment.

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REFERENCES

(1) Part III: M. W. Barker and J. H. Gardner, *J. Heterocyclic Chem.*, **6**, 251 (1969).

(2) M. W. Barker and M. E. Coker, *ibid.*, **4**, 155 (1967).

(3) L. J. Bellamy, "The Infra-red Spectra of Complex Molecules," John Wiley and Sons, Inc., New York, N. Y., 1959, p. 267.

(4) H. Staudinger and S. Jelagin, *Ber.*, **44**, 365 (1911).

(5) G. Kresze and A. Trede, *Tetrahedron*, **19**, 133 (1963).

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