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Heterocycles from Ketenimines. I.

Imino Substituted 1,2-Diazetidines

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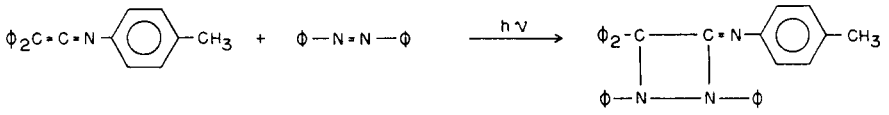
As part of an overall investigation of the preparation and reactions of heterocycles with exocyclic unsaturation from ketenimines (nitrogen analogs of ketenes), we have studied the condensation of diphenylketene *p*-tolylimine (I) with various symmetrically substituted azobenzenes. An analogous ketene reaction appears to occur through a nucleophilic attack by *cis*-azobenzenes on the ketene with the formation of 1,2-diazetidinones (2-4).

Work in this laboratory (5) has shown that the nucleophilic addition of alkoxide ions to the ketenimine structure produces imidates and, hence, that nucleophilic attack involves the carbon-carbon double bond of the ketenimine. Therefore, the reaction of a ketenimine and an azobenzene should produce a 1,2-diazetidine with an exocyclic imine function (II).

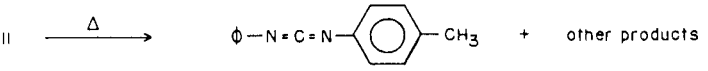
A solution of diphenylketene *p*-tolylimine and azobenzene in ether was irradiated with a sunlamp, which maintained the azobenzene in the *cis* form and supplied heat for the reaction. An infrared spectrum of the precipitated product exhibited a strong absorption at 1705 cm^{-1}, the expected area of absorption for the imine linkage on a strained ring (II).

Chemical proof of structure II was obtained through thermal degradation studies. When the adduct was heated at 197°, immediate decomposition occurred. An infrared spectrum of the decomposition mixture was complex but did contain a strong absorption at 2150 cm^{-1} attributable to the carbodiimide structure III (6). Vacuum distillation of the mixture gave a small amount of pure carbodiimide which was hydrolyzed in dilute hydrochloric acid to the corresponding urea. This product was found to be identical to synthetic phenyl *p*-tolylurea. Had the addition of azobenzene taken place at the carbon-nitrogen double bond of the ketenimine, the product, a triazetidine, would not be expected to yield a carbodiimide when thermally degraded.

In order to establish the utility of this reaction and with the hope of obtaining more insight into the mechanism, we studied the condensation of I with several symmetrically substituted azobenzenes. The reaction with *p*,*p*'-dihydroxyazobenzene was somewhat faster than with azobenzene as determined by the rate of disappearance of the ketenimine absorption at 2000 cm^{-1}. However, no product could be isolated from this reaction, probably because the 1,2-diazetidine formed decomposed thermally in the refluxing benzene solution. The disappearance of the ketenimine absorption was accompanied by the appearance of the carbodiimide absorption at



I II



III

2150 cm^{-1}. *o,o'*-Dihydroxyazobenzene did not react, but *p,p'*-dimethylazobenzene reacted at about the same rate as the unsubstituted system whereas *m,m'*-dimethyl- and *p,p'*-dichloroazobenzene reacted much more slowly. Thus, some electron-donating substituents on the azobenzene nucleus do increase the rate of reaction while electron-withdrawing substituents decrease the rate as would be expected for a nucleophilic mode of attack. However, the electronic effect of a ring substituent does not appear to be nearly as important as the position of the substituent. We are now trying to determine if this apparent steric hindrance is caused by difficulties in producing the *cis*-azobenzenes or if it is an aspect of the condensation mechanism.

EXPERIMENTAL

All melting points were determined on a calibrated Fisher-Johns apparatus. Infrared spectra were obtained on the Perkin-Elmer Infracord using either potassium bromide wafers or carbon tetrachloride solutions. Analyses were by Galbraith Laboratories, Inc., Knoxville, Tennessee.

1,2,4,4-Tetraphenyl-3-*p*-tolylimino-1,2-diazetidine.

A solution of 5.00 g. (0.017 mole) of I and 3.23 g. (0.018 mole) of azobenzene in 40 ml. of anhydrous ether was refluxed under a sunlamp. A white precipitate began to appear after 4 days. Collection of the solid gave 6.93 g. (83%) of colorless needles which upon crystallization from acetone afforded an analytical sample as colorless needles, m.p. 175-176°.

Anal. Calcd. for $C_{33}N_{27}N_3$: C, 85.12; H, 5.85; N, 9.03. Found: C, 85.11; H, 6.00; N, 8.90.

1,2-Di(*m*-tolyl)-4,4-diphenyl-3-*p*-tolylimino-1,2-diazetidine.

A solution of 1.27 g. (0.005 mole) of I in 30 ml. of anhydrous benzene to which was added 0.96 g. (0.004 mole) of *m,m'*-dimethylazobenzene was refluxed under a sunlamp for 25 days. The solvent was removed under reduced pressure (aspirator) and the residue dissolved in methanol, charcoaled, and concentrated. Cooling of the methanol solution gave 0.41 g. (20.8%) of solid which crystallized from methanol as colorless needles, m.p. 168-169°.

Anal. Calcd. for $C_{35}H_{31}N_3$: C, 85.16; H, 6.33; N, 8.51. Found: C, 85.02; H, 6.05; N, 8.65.

1,2-Di(*p*-tolyl)-4,4-diphenyl-3-*p*-tolylimino-1,2-diazetidine.

A solution of 0.78 g. (0.002 mole) of I and 0.42 g. (0.002 mole) of *p,p'*-dimethylazobenzene (7) in 130 ml. of anhydrous ether was refluxed under a sunlamp for 6 days. The solvent was removed under reduced pressure (aspirator), and the residue was crystallized from acetone to afford 0.37 g. (37.6%) of white solid, m.p. 158-159°. Successive recrystallizations of the solid from acetone gave the analytical sample as colorless needles, m.p. 177-178°.

Anal. Calcd. for $C_{35}H_{31}N_3$: C, 85.16; H, 6.33; N, 8.51. Found: C, 85.09; H, 6.21; N, 8.45.

1,2-Di(*p*-chlorophenyl)-4,4-diphenyl-3-*p*-tolylimino-1,2-diazetidine.

A solution of 1.30 g. (0.004 mole) of I and 0.92 g. (0.003 mole) of *p,p'*-dichloroazobenzene (8) in 130 ml. of anhydrous ether was refluxed under a sunlamp for 14 days. The solvent was removed under reduced pressure (aspirator). Crystallization of the residue from aqueous acetone gave 0.49 g. (30.6%) of solid which when recrystallized from acetone afforded the analytical sample as colorless needles, m.p. 183-185°.

Anal. Calcd. for $C_{33}H_{25}N_3Cl_2$: C, 74.15; H, 4.71; N, 7.86. Found: C, 74.34; H, 4.83; N, 7.37.

Attempted Preparation of 1,2-Di(*p*-hydroxyphenyl)-4,4-diphenyl-3-*p*-tolylimino-1,2-diazetidine.

A solution of 0.43 g. (0.002 mole) of *p,p'*-dihydroxyazobenzene and 0.56 g. (0.002 mole) of I in 30 ml. of anhydrous benzene was allowed to reflux under a sunlamp for 15 days. The solvent was removed under reduced pressure (aspirator), and the residue, a red-brown oil, was crystallized from ethanol. An infrared spectrum of the yellow crystals (m.p. 110-120°) obtained from the ethanol crystallization contained absorption bands at 2150 cm^{-1} (carbodiimide) and at 2000 cm^{-1} (ketenimine). The reaction was not studied further.

Attempted Preparation of 1,2-Di(*o*-hydroxyphenyl)-4,4-diphenyl-3-*p*-tolylimino-1,2-diazetidine.

After *o,o'*-dihydroxyazobenzene was treated with I in the above manner for 14 days, a quantitative recovery of the azobenzene was made.

Thermal Decomposition of 1,2,4,4-Tetraphenyl-3-*p*-tolylimino-1,2-diazetidine.

A sealed pyrex test tube containing 0.50 g. of II was heated for 1 hour and 10 minutes at 197° (refluxing benzoyl chloride). Distillation of the residue at 125° and 2.5 mm. pressure gave a small amount of yellow liquid whose infrared spectrum exhibited a strong absorption at 2150 cm^{-1}, indicative of the N=C=N group of the carbodiimide III. This yellow liquid was suspended in dilute hydrochloric acid at room temperature for three days, and then the solid present was collected. Crystallization of this precipitate from ethanol gave a colorless solid whose infrared spectrum was identical to that of phenyl *p*-tolylurea prepared from phenyl isocyanate and *p*-toluidine.

Acid Hydrolysis of 1,2,4,4-Tetraphenyl-3-*p*-tolylimino-1,2-diazetidine.

An attempt was made to hydrolyze the exocyclic imine function of II to the known diazetidinone (2) with hydrochloric acid. However, once the hydrochloric acid concentration was high enough to attack the imine, it was too high for the existence of the β-lactam system and only further degradation products were found.

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