

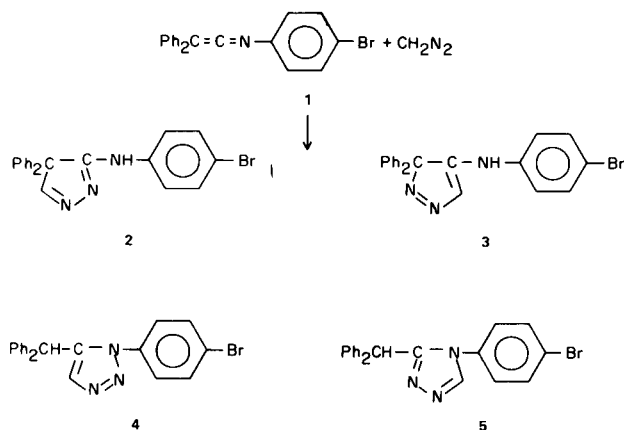
Heterocycles from Ketenimines. III. 1,2,3-Triazoles (1a-c)

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All reported reactions involving the production of heterocycles from ketenimines (nitrogen analogs of ketenes) yield products utilizing the carbon-carbon double bond of the ketenimine moiety. Such reactions include the addition of azobenzenes to produce 1,2-diazetidines (2), the addition of nitrones to produce isoxazolidines (1a), and the addition of ketones to produce oxetanes (3,4). We wish to report the first preparation of a heterocyclic system from ketenimines which utilizes the carbon-nitrogen double bond.

When diphenylketene-*N*-(*p*-bromophenyl)imine (1) is treated with cold diazomethane in the dark, a 1:1 adduct is obtained. The incorporation of the whole diazomethane molecule into the adduct is indicative of a 1,3-dipolar cycloaddition reaction. In postulating structures for the adduct all possible modes of addition must be considered (5). The simple addition of diazomethane to either double bond should result in an exocyclic unsaturated heterocycle with a methylene unit discernible by nmr. The absence of this group in the nmr spectrum indicates that isomerization of the exocyclic unsaturated center into the heterocycle has occurred. Thus, the adduct has structures 2,3,4, or 5.



The nmr spectrum of the adduct (determined in deuterated acetone) exhibits absorptions for fifteen protons from δ 6.14 to 7.2 and for one proton at δ 5.14. If the

adduct is structure 2 or 3, the 5.14 absorption would have to be assigned to the proton on the exocyclic nitrogen. Such a proton should undergo deuterium exchange and its position of resonance should be affected by varying the substituent in the adjoining phenyl ring. Since neither of these effects is observed, the adduct must have structure 4 or 5, and the 5.14 absorption is due to the methynyl hydrogen.

The ir spectrum of the adduct contains strong bands at 1077, 1022, and 980 cm^{-1} , characteristic of a 1,2,3-triazole ring, and the uv spectrum exhibits a single maximum at 210 $\text{m}\mu$, also indicative of the 1,2,3-triazole structure (6). These data plus the known production of 1,2,3-triazoles and not 1,2,4-triazoles from the reaction of diazomethane and Schiff's bases (7,8,9) establishes structure 4 for the adduct.

Similar results were obtained with diazomethane and diphenylketene-*N*-*p*-tolylimine. However diazoethane, diazopropane, phenyldiazomethane, and diphenyldiazomethane did not yield adducts with these ketenimines. The 1,2,3-triazoles obtained are colorless solids which are unreactive toward strong acid, vigorous oxidation, and catalytic hydrogenation. This lack of reactivity is attributed to the low solubility of the adducts in all common solvents except dimethyl sulfoxide.

The 1,3-dipolar cycloaddition of nitrones to ketenimines at elevated temperatures produces heterocycles involving the carbon-carbon double bond (1a) while the corresponding addition of diazomethane to ketenimines in the cold involves the carbon-nitrogen double bond. One can speculate that the double bond of the ketenimine moiety that is to be utilized in a cycloaddition of a 1,3-dipole can be controlled by temperature selection. We are investigating the addition of other 1,3-dipoles to ketenimines to test the generality of this observation.

EXPERIMENTAL

Melting points were determined on a Fisher-Johns apparatus and are corrected. Infrared spectra were determined in potassium bromide on Perkin-Elmer Model 137 and 137 G Infracords. The ultraviolet spectrum was determined in an ethanol solution on a

Perkin-Elmer 202 spectrophotometer. The nuclear magnetic resonance spectra were determined in deuterated acetone and deuterated dimethyl sulfoxide solutions on a Varian A-60 instrument. Analyses were performed by Galbraith Laboratories, Inc., Knoxville, Tennessee.

1-*p*-Bromophenyl-5-benzhydryl-1,2,3-triazole (4).

Diazomethane, prepared by the method of McKay (10) from 15 g. (0.10 mole) of 1-methyl-1-nitroso-3-nitroguanidine, was purified by distillation, and was dried over potassium hydroxide for three hours. The ether solution of diazomethane (150 ml.) was decanted into a 500 ml. Erlenmeyer flask and a solution of 3.48 g. (0.01 mole) of diphenylketene-*N*-(*p*-bromophenyl)imine (11) in 50 ml. of anhydrous ether was added. The solution was held at a temperature below 0° for three days in a dry ice-isopropyl alcohol bath in the dark. The mixture was removed from the cold bath and the ether solution was decanted from the white solid that had precipitated. The solid was recrystallized from aqueous acetone to yield 1.68 g. (43%) of pure 1-*p*-bromophenyl-5-benzhydryl-1,2,3-triazole (4), m.p. 172-173°. The adduct was not affected by strong uv irradiation. It showed strong ir absorptions at 1590 and 1480 cm^{-1} as well as 1077, 1022, and 980 cm^{-1} . Its uv spectrum showed only one absorption band, λ max 210 ($\epsilon = 400,000$). Nuclear magnetic resonance absorptions (deuterated acetone) occurred at δ 5.14 (1H) and from δ 6.14 to 7.2 (15 H) (TMS standard) and the spectrum in deuterated dimethyl sulfoxide was not affected by the introduction of deuterium oxide.

Anal. Calcd. for $\text{C}_{21}\text{H}_{16}\text{N}_3\text{Br}$: C, 64.62; H, 4.13; N, 10.77; mol. wt., 390.28. Found: C, 64.75; H, 4.26; N, 10.95; mol. wt., 389.

1-*p*-Tolyl-5-benzhydryl-1,2,3-triazole.

An ether solution of diazomethane (100 ml.) prepared as described was added to a solution of 0.46 g. (0.0016 mole) of diphenylketene-*N*-*p*-tolylimine (11) in 10 ml. of anhydrous ether. The solution was held at room temperature to allow the ether to evaporate. Evaporation of the ether left 0.48 g. of a yellow oil. The oil was triturated with ether which dissolved 0.32 g. of the material. The remaining 0.16 g. (31%) melted at 143-146°. Recrystallization of the product from aqueous acetone gave an analytically pure compound, m.p. 146.5-148.5°.

Anal. Calcd. for $\text{C}_{22}\text{H}_{19}\text{N}_3$: C, 81.20; H, 5.88; N, 12.91. Found: C, 81.21; H, 5.91; N, 12.89.

Attempted 1,2,3-Triazole Formation with Other Diazocompounds.

Treatment of diphenylketene-*N*-(*p*-bromophenyl)imine and diphenylketene-*N*-*p*-tolylimine with diazoethane, diazopropane, 1-phenyldiazoethane and diphenyldiazomethane under a variety of conditions did not result in the production of any 1,2,3-triazoles.

Attempted Reactions of 4.

Compound 4 was found to be inert to hydrogenation over Adams Catalyst in a Parr hydrogenation apparatus at 35 psi, to hydrolysis by concentrated hydrochloric or sulfuric acid, and to oxidation by permanganate or dichromate.

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