Azirines. IV. The Photolysis of β-Azidovinyl Ketones[*1]

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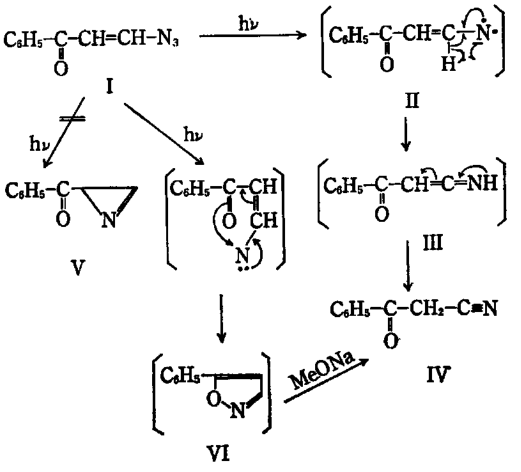
Although the pyrolysis[1] and photolysis[2-4] of vinyl azides as a method of preparing azirine have already reported on, there has been no report with regard to the photolysis of azidovinyl ketones. Therefore, we have been trying to obtain the functional derivatives of azirine by means of the photolysis of azidovinyl ketones. During the course of our work, Maiorana[5] reported the photolysis of azidovinyl phenyl ketone. Since, however, we tried the photolysis under slightly different conditions from his, we want here to report our results with this compound and with a cyclic azidovinyl ketone which has not hitherto been reported.

First, β-azidovinyl phenyl ketone[6] (I) was chosen as the azidovinyl ketone. The photolysis of I in benzene gave, with the evolution of nitrogen, benzoylacetonitrile (IV) in a 20% yield instead of 3-benzoylazirine (V). When the residual solution was treated with sodium methoxide, another crop of IV was obtained in a 17% yield. The formation of the second crop of IV may most reasonably be explained in terms of the alkaline hydrolysis of 5-phenylisoxazole (VI). The ready ring cleavage of isoxazoles unsubstituted at the 3-position with sodium methoxide has been known.[7] The results thus show that the nitrene II formed by the photolysis of I does not add to the double bond, but rather attacks the carbonyl group to give the VI or rearranges to the IV by the migration of a hydrogen atom, as is shown in the chart.



It is known[6] that β-azidovinyl ketones are decomposed on contact with acids to give substituted isoxazoles and nitriles, presumably through a vinyl nitrene intermediate.

When the photolysis of I was carried out in aqueous tetrahydrofuran instead of benzene in order to detect the III, Compound IV was obtained in a 27% yield instead of the desired benzoylacetamide. However, the v.p.c. analysis of the residual oil showed the presence of three other components (A, B and C). Component A was identified as methyl benzoate by a comparison of their v.p.c. retention times and infrared absorption spectra. The mechanism of the formation of this compound is not clear. The structure of Component B has not yet been elucidated, but it may be presumed to be a carbonyl compound because its IR spectrum exhibits a band at 1690 cm^{-1}. Component C was solidified on cooling, mp 31—33°C; the infrared spectrum of this compound has no characteric absorption bands except for that of phenyl group. These spectral data and the melting point suggest that it may be presumed to be a 5-phenyloxazole or its isomer.

Next, we attempted the irradiation of 5,5-dimethyl-3-azido-2-cyclohexene-1-one, prepared by the reaction of 5,5-dimethyl-3-chloro-2-cyclohexene-1-one and sodium azide, as a cyclic azidovinyl ketone, in benzene, but no nitrogen evolved. When this photolysis was carried out in aqueous tetrahydrofuran, the evolution of nitrogen was observed and colorless plates with a composition of $C_8H_{13}NO_2$ were obtained. This product was assigned as 6,6-dimethylhexahydroazepine-2,4-dione (XI) on the basis of the spectral data described below. The infrared spectrum of this compound exhibits bands at 3090 and 3200 cm^{-1} for the cyclic lactam NH group, 1710 cm^{-1} for the carbonyl group, and 1670 cm^{-1} for the amido-carbonyl group. The NMR spectrum shows a singlet at

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[*1] Part III. S. Sato, This Bulletin, **41**, 1440 (1968).

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2) L. Horner, A. Christman and A. Gross, *Chem. Ber.*, **96**, 399 (1963).

3) A. Hassner and F. W. Fowler, *Tetrahedron Letters*, **1967**, 1545.

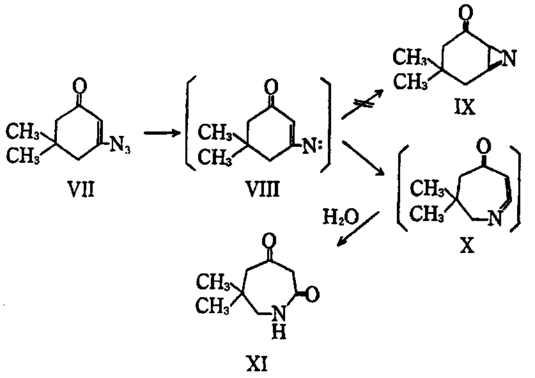
4) F. W. Fowler, A. Hassner and L. A. Levy, *J. Am. Chem. Soc.*, **89**, 2077 (1967).

5) Maiorana, *Ann. Chim.*, (Rome) **56**, 1531 (1966); *Chem. Abstr.*, **67**, 32420 (1967).

6) A. N. Nesmeyanov and M. I. Rybinskaya, *Izv. Akad. Nauk. SSSR, Otd. Khim. Nauk.*, 816 (1962); *Chem. Abstr.*, **58**, 3408 (1963).

7) L. Claisen and R. Sock, *Ber.*, **24**, 130 (1891).

τ 9.1 (6H) for the *gem*-dimethyl group, a singlet at τ 7.6 (2H) for the methylene on the 5-position of the ring, a multiplet at τ 6.8—6.9 (2H) for the methylene on the 7-position of the ring, a singlet at τ 6.6 (2H) for the methylene on the 3-position of the ring, and a multiplet at τ 2.0 (1H for the hydrogen on the nitrogen.



These results show that the migration of the methylene group to the nitrene occurs, giving a cyclic seven-membered keteneimine X, in preference to the intramolecular addition of the nitrene, giving condensed azirine IX.

Experimental

All the melting points were determined on a micro hot stage and are not corrected. The infrared spectra were taken on KBr tablets or neat liquid films.

Photolysis of β-azidovinyl Phenyl Ketone. a) A solution of 3.4 g (0.02 mol) of β-azidovinyl phenyl ketone[6] in 100 m*l* of dry benzene was irradiated through a Pyrex filter with a high-pressure mercury lamp under a nitrogen atmosphere for 20 hr, until nitrogen evolution ceased. The solution was then concentrated, and the residual oil was dissolved in ether and extracted with 10% sodium hydroxide, after which the extract was acidified with 10% hydrochloric acid. The solid which separated out was collected and recrystallized from water to give benzoylacetonitrile as colorless needles, mp 76—78°C (lit. 80.5°C).[8] (Found: C, 73.96; H, 4.88; N, 9.80%.) IR: 2200 ($C\equiv N$) and 1690 cm^{-1} ($C=O$). To the residual ethereal solution, a solution of excess sodium methoxide in 10 m*l* of methanol was added with cooling and stirring. The mixture was then stirred for one hour, after which 20 m*l* of water was added; the resulting mixture was washed with ether, and then the aqueous layer was acidified with 10% hydrochloric acid to give 0.3 g of colorless needles melting at 76—78°C. The melting point of this substance was undepressed on admixture with the benzoylacetonitrile obtained previously.

b) A solution of 2.2 g of I in 100 m*l* of tetrahydrofuran and 15 m*l* of water was irradiated through a Pyrex filter with a high-pressure mercury lamp under a nitrogen atmosphere for 16 hr, until nitrogen evolution ceased. When the solution was then treated by the method described above, 0.8 g of benzoylacetonitrile was obtained. The v.p.c. analysis of the residual oil showed the presence of three components; one of them was identified as methyl benzoate by a comparison of the retention times and the IR spectrum.

5,5-Dimethyl-3-azido-2-cyclohexene-1-one (VII). To a solution of 10 g (0.063 mol) of 5,5-dimethyl-3-chloro-2-cyclohexene-1-one[9] in 40 m*l* of methanol, a solution of 4.5 g (0.069 mol) of sodium azide in 70 m*l* of methanol and 5 m*l* of water was added with cooling and stirring. The mixture was then stirred for two hours at room temperature. To the reaction mixture, 100 m*l* of water was added, and the resulting mixture was extracted with ether; the extract was then washed thoroughly with water and dried over sodium sulfate. The solvent was removed by distillation; the IR spectrum of this residual oil exhibits a band at 2100 cm^{-1} for the azido group, 150 m*l* of tetrahydrofuran was added to the residue and the resulting solution was used for the photolysis without purification.

Photolysis of VII. To a solution of VII in THF, 30 m*l* of water was added. The mixture was irradiated with a high-pressure mercury lamp for 18 hr, until nitrogen evolution ceased. The solution was then concentrated by distillation under reduced pressure. The residual aqueous layer was washed with ether to remove any unreacted material, and then concentrated on a rotary evaporator. The solid which separated out was collected and recrystallized from *n*-pentane-ethanol to give 1 g of colorless plates, mp 148—149°C. Found: C, 61.91; H, 8.39; N, 8.92%. Mol wt, 142.8. Calcd for $C_8H_{13}NO_2$: C, 61.91; H, 8.44; N, 9.30%. Mol wt, 155.1.

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