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Photolysis of 2,3-Diphenylcycloprop-2-enecarboxylic Acid Azide and its Homologue[†]

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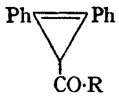
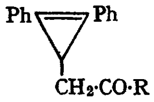
THE photochemical behaviour of the two diazoketones (I) and (II) corresponding to the title compounds is remarkably different.[1] The α-keto-carbene photochemically generated from (I), but not from (II), adds intramolecularly to the double bond, competing with a Wolff-type rearrangement. In spite of several recent reports of the intramolecular C–H insertion reaction[2] of α-keto-nitrene, the intramolecular addition to double bonds is apparently unprecedented[3] and we have further investigated the photolyses of acid azides (III) and (IV).

Compound (III) underwent a normal Curtius rearrangement at 70° in inert solvents to provide quantitatively an isocyanate (V)[4] which was converted into the corresponding urethane (ethyl), m.p. 141—142°[‡] [*cf.* compound (VII)]. Irradiation of an ethereal solution (0·2%) of (III) with a low-pressure mercury lamp at −30° provided, in addition to (V) in 50—60% yield and diphenylacetylene (4%), an amide, m.p. 162—163° (15%) to which structure (VI) was assigned on the basis of the following spectral data: λ_{max}(EtOH) 310 mμ (log ε 4·1) 326 (4·00): λ_{max}($CHCl_3$) 2·96 μ, 6·02, 6·65, 6·91; n.m.r., τ 8·95 (t, 3H), 8·80 (d, 3), 7·25 (s, 1), 6·58 (q, 2), 4·50 (m, 2), 2·25—2·84 (m, 10). These results are in contrast with those observed for (I) which led to the formation of an extremely strained tricyclo[2,1,0,$0^{2,5}$]pentanone derivative. While other interpretations§ are available, we feel that the photochemically generated keto-nitrene apparently does not contain a large excess of vibrational energy, compared with the keto-carbene, and underwent only intermolecular insertion reaction.

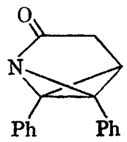
Thermolysis of (IV), as reported previously,[1b] provides the corresponding isocyanate (VII) which was found to be stable to boiling carbon tetra-



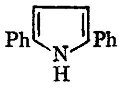
(I) R=CHN_2
(III) R=N_3
(VI) R=NH·CHMe·OEt



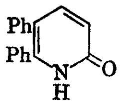
(II) R=CHN_2
(IV) R=N_3



(XII)



(X)



(XI)

[†] This work was included in lectures given in December, 1966, at the National Research Council, (Ottawa), Iowa State University, and Indiana University. An early portion of this work was carried out at Mellon Institute, Pittsburgh, Pa.

[‡] Upon silicic acid chromatography, (eluent: chloroform containing 0·75% ethanol), this compound was partially transformed into 3-ethoxy-1,2-diphenylcyclopropene.

§ Problems concerning the multiplicity of the nitrene are under investigation.

chloride.¶ In ethanol, the protonation of isocyanate (VII) readily occurs and the resulting cation reacts with solvent or the double bond of the cyclopropene to afford the corresponding urethane (VIII) and 3,4-diphenylpyridone (IX). The ratio of (VIII) to (IX) was temperature-dependent, being 2·5 at room temperature, and 0·3—0·5 at 78°.

Photolysis of (IV) under similar conditions to those for (III) (−30°), followed by treatment with ethanol at 55° afforded 2,5-diphenylpyrrole (X)[5] m.p. 140·5—141·5° (6%), 5,6-diphenylpyridone (XI)[6] (5%), m.p. 272—273°, diphenylacetylene (1%), (VIII) (15%), and (IX) (21%). It is attractive to postulate the nitrene addition product (XII)** as a common intermediate in the formation of (X)†† and (XI), although several other pathways to the latter compound are conceivable. Since photolysis of isocyanate (VII) gave neither (X) nor (XI), the ground-state isocyanate (VII) was at least excluded as a possibility. The acid azides derived from cyclopent-3-eneacetic acid and cyclopent-3-enecarboxylic acid upon irradiation (solvent: CH_2Cl_2) showed carbonyl absorption at 5·80 and 5·60 μ, respectively, indicating the presence of resonance-prohibited amide groups,[8] but we failed to isolate these unstable products. Dr. O. E. Edwards informed us that his group had carried out similar photolyses of other systems and successfully isolated hydroxy-lactams derived from a keto-nitrene addition product. All these results strongly suggest that (XII) is an intermediate in the formation of (X) and possibly of (XI) as well.

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¶ The corresponding keten readily underwent the intramolecular cycloaddition to the double bond (see ref. 1b).

** The initial formation of a triazoline derivative prior to the loss of nitrogen has not been excluded in the present case. See ref. 7.

†† The cleavage of the N—CO bond of (XII) is expected to occur readily due to the destabilized amide group and the strain involved in this system.

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[2] J. W. ApSimon and O. E. Edwards first made this observation: *Proc. Chem. Soc.*, 1961, **461**; *Canad. J. Chem.*, 1962, **40**, 896.

[3] R. A. Abramovitch and B. A. Davis, *Chem. Rev.*, 1964, **64**, 149; W. Lwowski and G. T. Tisue, *J. Amer. Chem. Soc.*, 1965, **87**, 4022 (these authors showed that pivaloylnitrene added to cyclohexene).

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