

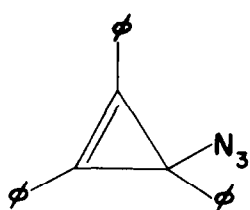
THE REARRANGEMENT OF 1-AZIDO-1,2,3-TRIPHENYLCYCLO-
PROPENE TO 4,5,6-TRIPHENYL-v-TRIAZINE

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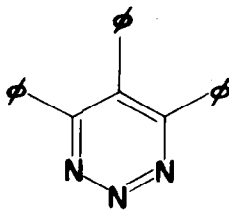
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(Received 13 May 1960)

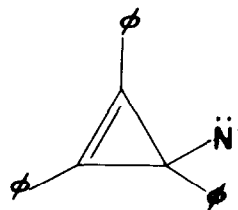
WE wish to report the preparation of 1-azido-1,2,3-triphenylcyclopropene (I) and its facile rearrangements to 4,5,6-triphenyl-v-triazine (II), a derivative of a hitherto unknown ring system.¹ This work was originally undertaken in order to attempt the conversion of I to the corresponding hypothetical nitrene (III),² an intermediate which appeared capable of undergoing several interesting rearrangements.



I



II



III

The addition of excess sodium azide to a solution of 1,2,3-triphenylcyclo-

¹J. G. Erickson in The Chemistry of Heterocyclic Compounds, Vol. X, Chap. I. Interscience, New York (1956).

²G. Smolinsky, J. Amer. Chem. Soc. In press, and references therein.

propenyl bromide³ in dimethylformamide followed by an aqueous workup gave a liquid which is assigned the structure of the azide I on the basis of the following evidence: (i) its I.R. spectrum contained a strong band at 4.75μ , characteristic of aliphatic azides,⁵ (ii) its U.V. spectrum was essentially identical to that of 1-methoxy-1,2,3-triphenylcyclopropene (IV),⁶ (iii) it was converted to IV on treatment with sodium methoxide in methanol. The azide I decomposed at a moderate rate at room temperature and rapidly in boiling xylene with the formation of two products. One of these, isolated in 45% yield, was a colorless, crystalline solid II (m.p. 276° dec.) isomeric with I (Found: C, 81.49; H, 4.98; N, 13.24; M.W. 306. Calc. for $C_{21}H_{15}N_3$: C, 81.53; H, 4.89; N, 13.58; M.W. 309.) The I.R. spectrum (KBr) of II had no band below 6μ other than aryl C-H; the U.V. spectrum showed λ_{\max}^{EtOH} 262μ (21,400), 278μ (shoulder, 15,500) and 297μ (shoulder, 8,100) and was unchanged in the presence of dilute HCl. II was converted to 3,4,5,-triphenylpyrazole (V)^{7,8} upon reduction in acetic acid solution with either zinc or hydrogen over palladium and was readily hydrolyzed to 1,2,3-triphenylpropane-1,3-dione (VI)⁷ by the action of hydrochloric acid in hot acetic acid.

³ This salt was prepared by the reaction of benzal chloride, potassium t-butyrate and diphenylacetylene in benzene followed by reaction of the resulting, unisolated 1-t-butoxy-1,2,3-triphenylcyclopropene with anhydrous hydrogen bromide, a method which, unknown to us, had previously been developed by Breslow.⁴

⁴ R. Breslow. Private communication.

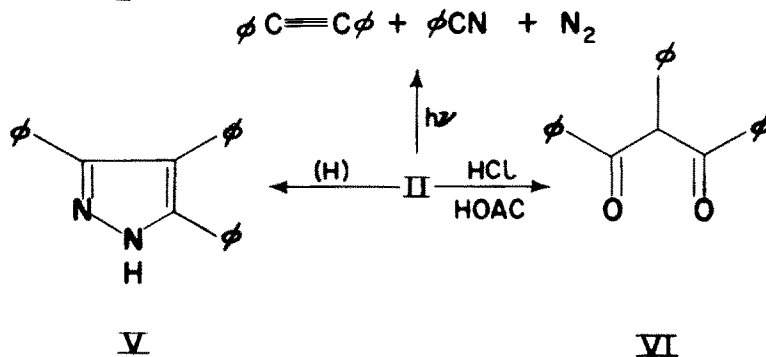
⁵ E. Lieber, C.N.R. Rao, T.S. Chao and C.W.W. Hoffman, Analyt. Chem. 29, 9161 (1957).

⁶ R. Breslow and C. Yuan, J. Amer. Chem. Soc. 80, 5990 (1958).

⁷ Identified by comparison with an authentic sample.

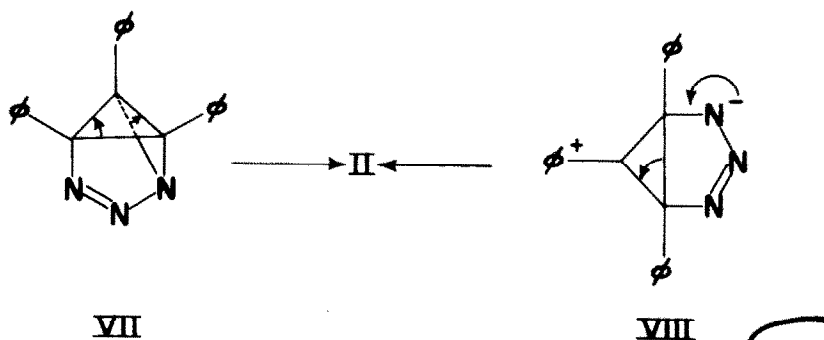
⁸ Cf. The behavior of the related 1,2,4-triazines upon reduction, R. Metzke, G. Rolle and G. Scherowsky, Chem. Ber. 92, 2481 (1959).

Furthermore, II is sensitive to light and was destroyed by irradiating a stirred suspension in benzene with a sunlamp for 12 hr. The crude product smelled strongly of benzonitrile and an examination of the I.R. spectrum suggested the presence of benzonitrile (4.45μ) and diphenylacetylene; the latter was isolated in 72% yield.⁷ These transformations and the spectral and analytical data can be rationalized only on the basis of the structure 4,5,6-triphenyl- γ -triazine (II). The ready hydrolysis and photolysis of



II are indicative of a loss in aromatic character of this ring system, probably a consequence of the presence of the γ -triazine linkage.

The formation of II may be explained by the intramolecular addition of the azide group to the double bond⁹ present in I, forming VII, followed by



⁹ J.H. Boyer and F.C. Canter, Chem. Rev. 54, 1 (1954).

collapse of this highly strained species to II. Alternatively, one may postulate electrophilic attack on the cyclopropene double bond by the azide group with the formation of VIII, a valence tautomer of II. These paths are closely related and cannot be distinguished on the basis of the data now available.

A yellow solid, m.p. 235° dec., $C_{42}H_{30}N_2$ (Found: C, 90.07; H, 5.46; N, 4.90; M.W. 480) was also isolated (13%) from the pyrolysis of I in xylene. It had no band in the I.R. below 6μ other than aryl C-H and showed λ_{\max}^{EtOH} 247μ (49,000), shifting to 263μ (25,000) in dilute HCl. It did not arise by the decomposition of II since the triazine was recovered unchanged when subjected to the pyrolysis conditions. This compound may arise via loss of N_2 from I accompanied by rearrangement and dimerization; the simple dimerization of the nitrene III is precluded as the resulting azo compound would be thermally labile and would probably decompose with loss of nitrogen. We have not as yet been able to establish the structure of this product and further work is in progress.

Note added in proof: Professor Breslow has informed us that he has isolated a product corresponding to II from the reaction of sodium azide with 1,2,3-triphenylcyclopropenyl bromide in boiling tetrahydrofuran.