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THE NITRENE INTERMEDIATE IN THE PHOTO-FORMATION OF CARBAZOLE FROM 2-AZIDOBIPHENYL

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The cyclization of 2-azidobiphenyls to carbazoles has attracted attention in recent years (1,2,3) as a model system to decide two questions: (a) Is the loss of nitrogen from the azide concerted with ring closure or is a discrete intermediate (nitrene) formed? (b) Is the reacting intermediate a biradical (triplet) or an electrophilic (singlet) species?

Smolinsky (4,5), Smith (6) and others (1) have made a strong case for the existence and biradical nature of the intermediate,* basing their argument on the close parallelism of many azide reactions with those of the carbenes (insertion into C-H bonds) and on the insensitivity of reaction rates to substitution in both aromatic rings. Their evidence, convincing as it is, remains, however, circumstantial. We now wish to report on an experiment which, we believe, directly demonstrates the appearance of an intermediate and identifies it as the nitrene.

2-Azidobiphenyl was incorporated at a concentration of about 10^{-4}M in an EPA matrix at 77°K. The absorption spectrum of the azide in these conditions appears as curve 1 in Fig.1. The system was irradiated with a Philips mercury arc (MBL/U, 125W), for increasing time intervals and the spectrum recorded with a Unicam SP800 spectrophotometer after each exposure (curves 2-4, Fig.1). The photometric curves show the appearance of a new absorption with a peak at 342mμ and a low intensity band ending at 400mμ; the (approximate) isosbestic point at 290mμ indicates that essentially a single product was being formed. After a total exposure time of 1 minute (corresponding to practically complete conversion of the azide) a filter transmitting only above 320mμ was interposed between the lamp and the cell. Further irradiation, limited now to the absorption bands of the intermediate "bleached" the peak at 342mμ and caused a strong absorption to appear at 293mμ (curves 1-6, Fig.2). The isosbestic point at 312mμ is again indicative of a single reaction path. After a total irradiation time of one hour the final spectrum settled down to curve 6 on Fig.2, which by comparison with an authentic sample identified the final product as carbazole.

There is no doubt that an intermediate is formed in the matrix reaction at 77°K. The identification of the intermediate rests on the similarity of its absorption spectrum with the spectra of a series of aromatic nitrenes which we hope to publish shortly. All these spectra show the general characteristics of aromatic structures with an

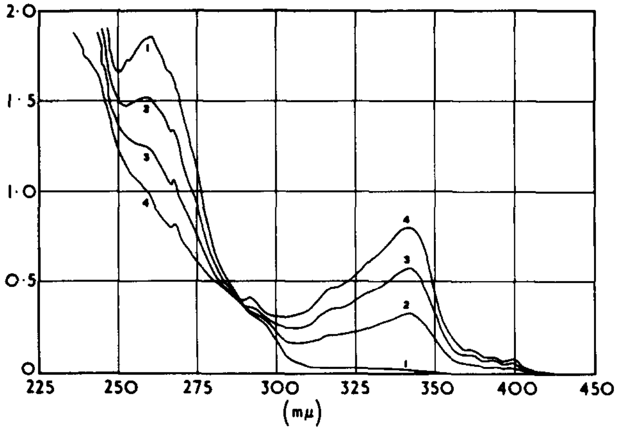
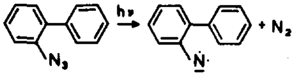


FIG.1. Photometric curves for the primary reaction



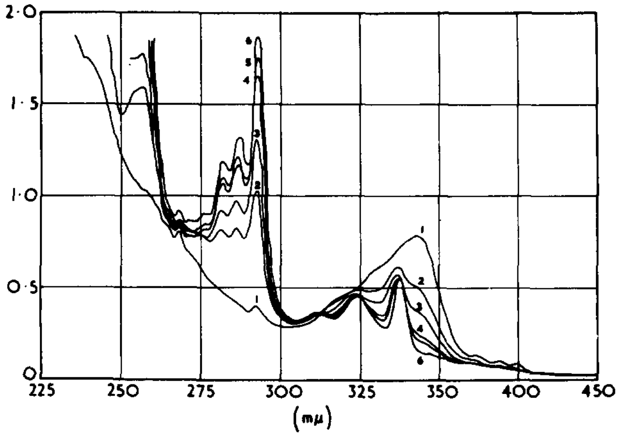
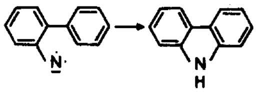


FIG.2. Photometric curves for the secondary reaction



odd electron, as exemplified by the benzyl radical and its iso-electronic analogs (7). Also the bands at 342mμ and 400mμ are near the corresponding bands of biphenyl-3-nitrene (331mμ and 408mμ). The intermediate is therefore in all probability the expected biphenyl-2-nitrene.

How relevant are these observations on a rigid matrix at 77°K to the reaction in a liquid medium at normal temperature? In answer to this question it will be observed firstly, that the final product is the same in both cases. Secondly, we have measured the quantum yield of carbazole formation in ethanol at 25°C. It is 0.36± 0.02 and corresponds to a quantum yield for nitrene formation of 0.44 ± 0.02. (The yield of carbazole from the initial amount of azide present is 81%, incidentally very close to the yield of 77% found by Smith and Brown (3)). The quantum yield of nitrene formation in the matrix at 77°K is 0.43 ± 0.05. The agreement between the quantum yield in both conditions indicates an identical first step and a separate intermediate even at normal temperature. Thirdly, the quantum yield of the second step at 77°K, assuming all the absorbed light to be effective, is between 0.01 and 0.02. This value is surprisingly low in view of the high efficiency of ring closure at 25°C. The secondary reaction must therefore be an activated process.

An estimate of the activation energy of the secondary reaction may be obtained by the following argument: in our experiment the nitrene was kept at 77°K for about 15 minutes before initiating the second stage of the reaction, and can therefore be assumed to have returned to its ground state. Smolinsky, Wasserman and Yager (8) have shown by ESR spectroscopy that the ground state of phenyl nitrene and several related molecules is a triplet. The absorption band of biphenyl-2-nitrene at 342mμ corresponds to an allowed transition ($\varepsilon = 5500$). According to the interpretation of aromatic radical spectra by Dewar and Longuet-Higgins (9), and Longuet-Higgins and Pople (10) the band at 400mμ belongs to the same symmetry and spin species, its low intensity being due to the approximate cancellation of transition moments. Irradiation of the nitrene in either of these bands can populate in the first instance only triplet excited states. With a triplet as the ground state the first excited triplet state will have a lifetime of the order of 10^{-8}sec. or less. On the assumption that this excited state is responsible for ring closure the rate constant at normal temperature must be at least $k = 10^{8}$ sec $^{-1}$ if the reaction is to occur during the life of the excited species. With a (monomolecular) frequency factor of 10^{14} the activation energy is found to be about 8 Kcal/mol. (This is a reasonable value, close to the activation energy for hydrogen abstraction by methyl radicals.) At 77°K the reaction cannot proceed unless this activation energy is provided in some form. In the conditions of our experiment it is provided through the excitation of higher vibrational levels. The successful completion of the reaction depends however on this energy appearing in a particular vibrational mode: ring closure thus competes with the (fast) redistribution of energy within the molecule and with its dissipation to the matrix. Hence the low efficiency of the second step in the matrix photolysis.

The experimental facts so far are fully compatible with an excited triplet as the reactive species both in the matrix at 77^{o}K as well as in solution at normal temperature and this is in agreement with previous suggestions (4,6). However, it must be emphasized that a singlet intermediate cannot be excluded as partly or even entirely responsible for ring closure. The transition from the ground T^{o}-state to the first excited singlet state S* is forbidden and will give rise only to a low intensity absorption, but S* could be efficiently populated via T* and once formed would have a relatively long lifetime with all its chemical consequences. We conclude that while the existence of the nitrene intermediate seems established, its spin state in the reaction must still remain in doubt. A study of the luminescence emission of the nitrene may be of interest in this connection. Experiments to this effect are in preparation.

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