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PHOTOCHEMISTRY OF 2-SUBSTITUTED BIARYLS. II.[1]
AZO COMPOUND FORMATION FROM 2-AZIDOBIPHENYL

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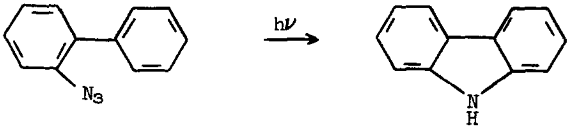
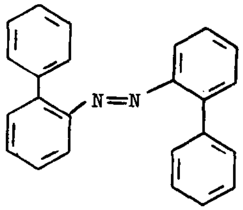
The thermal and photochemical generation of nitrenes from aryl and alkyl azides has been a major field of interest in organic chemistry for the last several years. In particular, extensive studies on the pyrolytic chemistry of azidobiaryls has been carried out by Smith, Abramovitch, and Smolinsky.[2] Initial photochemical studies by Smith and Brown[3] on 2-azidobiphenyl indicated the major pathway to be carbazole formation. Recent work has supported the intermediacy of a nitrene in this reaction.[4] In connection with our mechanistic studies on 2-biarylisocyanate photolysis, we were concerned with reaction pathways available to the 2-imidobiphenyl triplet. Toward this end we have found unexpected and unusual results in the sensitized photolysis of 2-azidobiphenyl.



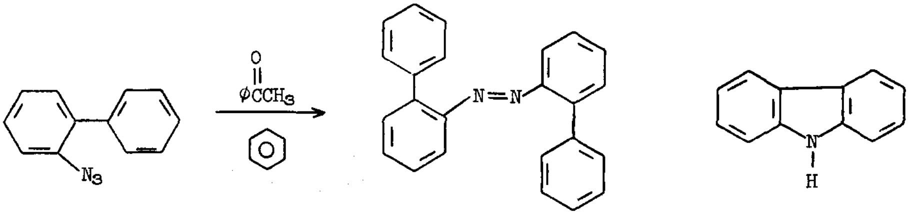
I II



III

Due to a lack of available information on the triplet energy of I and the possible dependence of this energy on conformation,[5] we have utilized the high energy sensitizers acetone ($E_T > 75$ kcal/mole) and acetophenone ($E_T = 72$-74 kcal/mole). Examination of the irradiation of I in neat acetone by TLC showed the presence of two major products and several minor ones. Chromatography of the reaction mixture on Silica Gel afforded two crystalline fractions: fraction I, 2% ether-hexane elution, consisted of yellow-orange needles (41%); fraction II, 10% ether-hexane elution, yielded white plates (28%). Fraction II was identified as carbazole by comparison with an authentic sample.

Fraction I, which proved to be homogeneous by TLC, was recrystallized from 95% ethanol to yield red crystals, m.p. 144.5-145.5°.[6] The IR spectrum (KBr) showed a number of sharp weak absorptions from 6.7-12.0 µ and strong bands at 13.08, 13.65, and 14.50 µ. The latter absorptions appear to be characteristic of 2-substituted biphenyls. The UV spectrum in 95% ethanol exhibited maxima at 458 mµ (ϵ = 410), 335 mµ (ϵ = 14,100), and 233 mµ (ϵ = 26,500). The mass spectral fragmentation pattern showed a parent mass at 334 (74% of base peak) and predominant peaks at 181 (21%), 153 (base peak) and 152 (76%). The 181 and 153 correspond to loss of $C_{12}H_9$ and $C_{12}H_9N_2$ processes well documented from the extensive investigations of Bowie, Lewis, and Cooks.[7] The 152 peak may arise from loss of $C_{12}N_{10}N_2$ to yield the biphenylene species, $C_{12}H_8^{+}$. Although the spectroscopic evidence supported the structure of the new compound as azo-2-biphenyl (III), chemical proof was desired. Unfortunately, the new product proved to be relatively inert to standard reduction procedures such as stannous chloride and HCl or sodium hydrosulfite. However, oxidation of 2-biphenylisocyanate with 90% hydrogen peroxide by the procedure of Esser, Rastädter, and Reuter[8] afforded a low yield of azo compound. This synthetic compound proved identical in all respects to the new photoproduct. Thus, the structure of the photoproduct is assigned as azo-2-biphenyl on the basis of spectroscopic evidence and comparison with synthetic material.



I III II (minor amounts)

Since in acetone some direct excitation of the azide occurs along with sensitization, energy transfer from excited acetophenone to I was studied in benzene. Photolysis of a benzene solution 1.7M in acetophenone and 1.5 x 10^{-2}M in I followed by chromatography on Silica Gel afforded the azo compound III in 40-43% yield. Although carbazole could be detected by TLC, the small amount present prevented its isolation in pure form.

Table I. Irradiations of 2-Azidobiphenyl[a]

Run	Solvent	Reactants	Time	% Yield Carbazole (II)	% Yield Azo compound (III)
1	Acetone[d]	1.5×10^{-2}M (I)	1 hr.	28	41
2	Benzene[b]	1.5×10^{-2}M (I) 1.7M acetophenone	0.5 hr.	<8%[e]	40
3	Benzene[b]	1.5×10^{-2}M (I) 1.7M acetophenone	1.0 hr.	<8%[e]	43
4	Ether[b]	1.5×10^{-2}M (I)	1.5 hr.	71	7[f]
5	Ether[c]	1.1×10^{-2}M (I)	0.5 hr.	71	9[f]
6	Ether[b]	1.5×10^{-2}M (I) 2M piperylene	1.5 hr.	89	4[f]
7	Ether[b]	1.5×10^{-2}M (I) 3.6M piperylene	1.5 hr.	84	4[f]

(a) All irradiations carried out with 450 watt Hanovia High Pressure Source under nitrogen in 150 ml. of solvent. (b) Pyrex filter. (c) Vycor filter. (d) Corex filter. (e) Carbazole could be detected by TLC but due to small amounts could not be separated from impurities by chromatography. (f) Yields may be subject to large error due to small quantities isolated.

The marked change in product ratio from sensitized irradiation of I suggested a reinvestigation of the direct photolysis of the azide at higher concentrations than those employed in earlier work.[3,4] Irradiation of 10^{-2}M solutions of I in ether through either Vycor or Pyrex afforded the results shown in Table I. Thus, in these direct irradiations the azo compound is formed to a minor extent. Since azo compound formation is necessarily a bimolecular process, experiments designed to intercept the reactive intermediate were investigated. Piperylene appeared as a good choice since it would not only serve as a potential trap for the possible nitrene or nitrogen radical intermediate, but also could serve to quench a higher energy excited triplet. Use of piperylene at 100 times the concentration of starting azide did not lead to complete quenching of azo compound formation. The fact that piperylene exerted some effect, however, was noted from the cleaner appearance of the irradiation mixture and the higher isolated yields of carbazole.

From these results it is apparent that sensitized photolysis of this aryl azide leads to markedly different results than those obtained by direct irradiation. The bimolecular nature of the reaction, excluding ground state complexation, indicates a rather long-lived species. Whether this species is a low energy 2-azidobiphenyl triplet or a triplet nitrene so complexed with the adjacent aromatic ring as to make it unreactive towards piperylene remains to be established. The data thus far favor the low energy triplet azide intermediate. In this connection it is interesting to note that the reluctance of the triplet azide to lose nitrogen directly parallels behavior observed for the isoelectronic 2-biphenylisocyanate.[1] Here the singlet affords carbazole and the triplet cyclizes to phenanthridone. Presently we are exploring the effect of solvent, light intensity, and sensitizers on this and other aryl and alkyl azides.

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References

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4. A. Reiser, H. Wagner, G. Bowes, Tetrahedron Letters, No. 23, 2635 (1966).
5. P. G. Wagner, J. Am. Chem. Soc., 89, 2820 (1967).
6. The compound apparently exists in two crystalline modifications. A yellow-orange form, which is obtained directly from the column, begins softening and turning red at 120° and completely melts at 143-144°. Slow recrystallization of this material from ethanol gives red crystals melting sharply at 144.5-145.5°. The two forms show identical TLC retention times, IR (CS_2), and UV spectra making it unlikely that they are *cis*- and *trans*-isomers.
7. J. H. Bowie, G. E. Lewis, and R. G. Cooks, J. Chem. Soc. (B), 621 (1967).
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