

COMPETITIVE CYCLIZATIONS IN THE PHOTOCHEMISTRY OF 2-BIPHENYLISOCYANATE

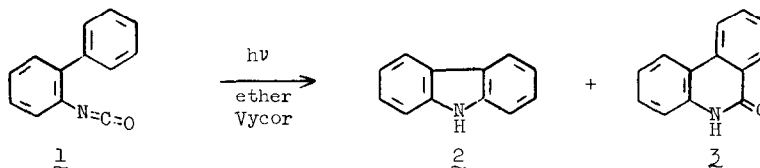
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While the photolysis of ketenes has been extensively studied;¹ the photochemistry of the related isocyanates has received relatively little attention.² In initiating our studies of isocyanate photochemistry it appeared appropriate to utilize a system which would minimize potential reaction pathways. Having noted the efficiency with which the nitrene generated from pyrolysis of 2-azidobiphenyl is trapped internally to afford carbazole, it was deemed worthwhile to begin our studies with the related isocyanate. Hopefully this system would have available intermolecular reaction pathways for intermediates formed in primary photochemical steps.

The photolysis of 2-biphenylisocyanate, 1, with a 450 watt Hanovia medium pressure source utilizing a Vycor filter afforded two major products as detected by thin layer chromatography (TLC). In a typical run 1.112 g. of 1 in 400 ml. of anhydrous ether was irradiated for 3 hrs. in a nitrogen atmosphere. The light yellow oily solid was triturated



with 3 ml. of cold hexane and the residue chromatographed on silica gel. Four fractions were obtained: 3% ether-hexane, 0.100 g. of starting isocyanate; 7% ether-hexane, 0.1467 g. white plates, m.p. 237-241°; 20% ether-hexane, 0.0786 g.; and 100% ether, 0.1090 g, m.p. 288-295°.

The material from 7% ether-hexane elution was judged homogenous by TLC and recrystallized from ethanol to afford 0.0974 g. of white platelets, m.p. 242.5-243.5°. The identity of the fraction as carbazole was established by I.R. and mixed m.p. comparison with authentic material.

The 20% ether-hexane fraction was identical in all respects with urea derived from starting isocyanate. Careful inspection of the photolysis mixture by TLC prior to workup indicated only a trace of urea to be present. Thus the major portion of the compound must arise during workup and chromatography.

The last chromatographic fraction was recrystallized from acetone-ethanol to afford 0.075 g. of white needles, m.p. 297.0-298.5°. The I.R. (KBr) of this material showed the strong absorptions at 6.00, 6.12, 6.21, 13.30, 13.38 and 13.78 μ . The mass spectrum at 70 ev. consisted of a strong parent peak at $m/e = 195$. The mass spectrum together with the analysis indicated a compound isomeric with starting isocyanate. Thus our analytical data suggested the structure of this photoproduct to be the phenanthridone 2. This assignment was confirmed by I.R. and mixed melting point comparison with phenanthridone prepared by the recently reported method of Yang, Shani, and Lenz.⁴

Inspection of Table I shows that the carbazole and phenanthridone account for the major photochemical products in this system. Furthermore, the photoreaction is subject to

Table I
Photolysis of 2-Biphenylisocyanate in Ether^a

Run	Time	Starting Isocyanate	Recovered Isocyanate ^{b,c}	Carbazole ^b	Phenanthridone ^b
1	1 hr.	0.5345 g.	0.3752 g.	0.0671 g.	0.0532 g.
2	1.5 hr.	0.9001 g.	----- ^d	0.1350 g.	----- ^d
3	3.0 hr.	1.112 g.	0.7820 g.	0.1467 g.	0.1100 g.

^aAll irradiations in 400 ml. of solvent

^bCrude yields, fractions showing I.R. identical with respective pure components

^cConsisting of both isocyanate and its derived urea

^dNot determined

a severe retardation in rate by product. Whether this is totally a result of starting isocyanate capturing a smaller fraction of incident irradiation with increasing time due to light absorption by product, or whether quenching via an energy transfer mechanism is partially operative remains to be established.

Since 2-aminobiphenyl and N,N'-diphenylurea, 4, were potential transient intermediates from photolysis of 1, we wished to exclude these compounds as precursors of 2 and 3. Irradiation of 0.7740 g. of 2-aminobiphenyl in 400 ml. of ether for 1 hr. afforded neither 2 or 3 (TLC). However, photolysis of 0.3928 g. of the urea, 4, for 1 hr. through Vycor did produce small amounts of 3 as detected by thin layer. Chromatography of the reaction mixture afforded less than 0.014 g. of 3. Thus the efficiency of this reaction precludes a major portion of the isocyanate reaction proceeding via some two-photon process involving the urea as an intermediate.

Experiments aimed at supplying evidence on the multiplicity of the reacting excited state have been only partially successful thus far. From acetophenone sensitization experiments at least four products are formed. At present we have been unable to detect carbazole by either TLC or chromatography, however, the phenanthridone is readily isolable. We are currently investigating solvent effects and exploring better sensitization procedures for this system.

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References

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- (2) ibid., p. 486.
- (3) For leading references see R. A. Abramovitch and B. A. Davis, Chemical Reviews, 64, 149 (1964).
- (4) N. C. Yang, A. Shani, G. R. Lenz, J. Am. Chem. Soc., 88, 5369 (1966).