Interaction of Aromatic Hydrocarbon Excited Singlet States with 2-Azidobiphenyl

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Summary Markedly different results are reported for ketone- and aromatic hydrocarbon-sensitized decomposition of 2-azidobiphenyl: the ketones transfer triplet excitation to the azide, and the aromatic hydrocarbons singlet energy.

INTERMEDIATES in the direct and photosensitized decomposition of azides have been studied.[1] From the photochemistry of triarylmethyl azides it was concluded that the same intermediate was formed from the excited singlet and triplet states of the azide.[1g] The conclusion was based on identical product distributions from the direct and hydrocarbon sensitized decompositions of a variety of triarylmethyl azides. We report that the sensitized decomposition of 2-azidobiphenyl (**1**) by ketone sensitizers leads to remarkably different results from those obtained by hydrocarbon sensitizers. The results in this system indicate that aromatic hydrocarbons transfer singlet energy not triplet energy to the ground state azide.

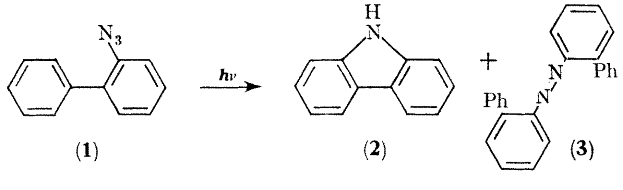
Direct irradiation of 10^{-2}M-solutions of 2-azidobiphenyl in ether, benzene, or isopropyl alcohol leads to the formation of carbazole (68—71%) and 2-azobiphenyl (8—11%).[2] The formation of azo-compound is quenched in the presence of piperylene or oxygen. Sensitized decomposition of (**1**) in benzene at 3500 Å by acetophenone (E_T 74·6 kcal./mole), *m*-methoxyacetophenone (E_T 72·4 kcal./mole), or benzophenone (E_T 68·5 kcal./mole) gave the azo-compound (**3**) with nearly complete exclusion of carbazole. In marked contrast, photosensitized decomposition of (**1**) by triphenylene, naphthalene, or pyrene led to the production of carbazole as the major product. When the triphenylene sensitized decomposition of (**1**) was carried out in the presence of 0·2M-piperylene, no reduction in the rate of azide disappearance was noted. Since piperylene (E_T *ca.* 60 kcal./mole) would be an effective quencher of triphenylene triplets (E_T 66·6 kcal./mole), the triplet state of

Irradiation of 2-azidobiphenyl[a]

Irradiation	% Carbazole	% Azo-compound
Direct irradiation	68—71	8—11
Acetophenone (1·7 M)	<2	40
m-Methoxyacetophenone (1·4 M)	<2	39
Benzophenone (0·9 M)	<2	41
Triphenylene (0·12 M)	72	14
Naphthalene (0·2 M)[b]	67	6
Pyrene (0·02 M)	95	<1

[a] Solutions 10^{-3} M in benzene; [b] 3000 Å source.

triphenylene is not responsible for the sensitized decomposition of (**1**).



The ketone-sensitized decomposition of (**1**) is without complication because the low concentration of acceptor employed (10^{-2}M) and the short lifetime of the ketone singlet state ($<10^{-10}$ sec.)[3] permit only triplet-energy transfer from sensitizer to azide. The high yield of carbazole in the hydrocarbon sensitized runs must be due to singlet-energy transfer to the ground-state azide. Caution should be exercised in employing aromatic hydrocarbons as sensitizers.[4] The observations recorded with pyrene are especially interesting since excited pyrene is functioning as a singlet sensitizer while ground-state pyrene acts as a quencher for azo-compound formation.

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