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PHOTOCHEMICAL REACTIONS OF BIPHENYLENE I. FORMATION OF A PHOTODIMER

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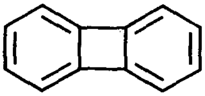
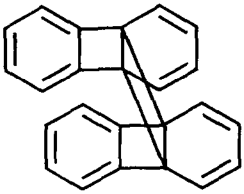
A study of possible photoaddition reactions of biphenylene I (1) led us to examine the reaction of this substance itself to ultraviolet irradiation. After our investigation began, a report appeared (2) indicating that a small amount of tetraphenylene is formed when a hexane solution of biphenylene is irradiated with either 2537 or 3500 angstrom light. Two other investigators have recently claimed that biphenylene is unreactive to ultraviolet light (3).

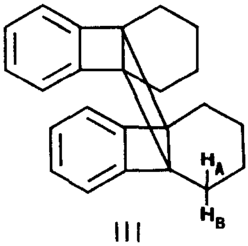
Our results are different from those cited. In a typical experiment, 30 ml. of a 1% solution of biphenylene in hexane is irradiated through pyrex, at reflux, with a 275-watt sunlamp. A single product is deposited, the reaction proceeding to near completion in three days. The product formed is a crystalline photodimer, molecular ion at m/e 304.1232 (calc. for $C_{24}H_{16}$: m/e 304.1252), m.p. 255-265°(dec.) after recrystallization from chloroform and sublimation at 120-130°/0.05 mm. Ir (KBr): 13.25, 13.80, 14.81μ. The assignment of structure II, syn-13,14,15,16-dibenzopentacyclo-$[6.4.2.2^{2,7}.0.0^{2,7}]$hexadeca-3,5,9,11,13,15-hexaene, to the photodimer


I


II

follows mainly from its nmr spectrum ($CDCl_3$, δ units) that is comprised of a singlet for the aromatic protons at 7.04 (8H) and an $A'_2B'_2$ system for the diene protons spanning 6.48-5.52 (8H). The anti-isomer would be expected to show a lower field aromatic resonance at about 7.28 (4) and a higher field position for the olefinic protons located over a shielding aromatic ring. An alternative structure based on the formation of tetraphenylene and subsequent cyclobutane closure between two opposed aromatic rings need not be considered for the photodimer. Tetraphenylene (2,5) is unreactive under the conditions of the photodimerization.

Catalytic hydrogenation of II with Pd/C in ethyl acetate proceeds with uptake of four equivalents of hydrogen to give the octahydrodimer III, syn-13,14,15,16-dibenzopentacyclo[6.4.2.$2^{2,7}$.0.$0^{2,7}$]hexadeca-13,15-diene, m.p. 179-180°, plates from benzene-ethanol, molecular ion at m/e 312. Calc. for $C_{24}H_{24}$: C, 92.29; H, 7.71. Found: C, 92.10; H, 7.88. Ir (KBr): 13.25, 13,70μ.



III

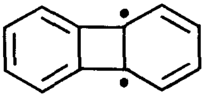
The nmr spectrum ($CDCl_3$, δ units) of III shows a singlet for the aromatic protons at 6.93 (8H), two multiplets centered at 2.80 (4H) and 2.12 (4H) for the H_A and H_B protons respectively, and a broad band centered at 1.57 (8H) for the remaining methylene protons. The chemical shift for the latter methylenes, excludes their placement in the shielding region of an aromatic ring.

Other derivatives of the dimer have not as yet been prepared. Attempted Diels-Alder reactions with maleic anhydride and dimethyl acetylenedicarboxylate have failed to take place in solution at temperatures up to 130°.

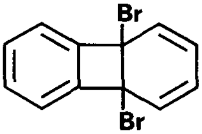
At 170° reaction occurs with maleic anhydride, but the product is not a simple adduct and has not been further characterized. It may be that normal Diels-Alder products are not obtained because of the large steric interactions that develop when the diene ring undergoing condensation is forced against the opposed diene ring.

The photodimerization can also be carried out in absolute ethanol, acetone, and without solvent in a sealed tube at 130°.

It appears from the structure of the photodimer that biphenylene is reacting in a form depicted as IV. Barton (6,7) has suggested the derivative structure V for the intermediate that gives rise to 3,8-dibromocyclooctatetraene in the photobromination of biphenylene.



IV



V

No definite conclusion has been reached at this time with regard to the singlet or triplet nature of biphenylene in the dimerization; experiments are being carried out currently to clarify this matter.

The mass spectrum of the photodimer deserves separate comment. At 70 ev the peaks at m/e 304, 303, and 302 have relative intensities of 66.8:100:74.8. Lowering the ionizing voltage to 13 ev changes the relative intensities to 85.5:100:44.5, with concurrent disappearance of the doubly charged ions seen in the 70 ev spectrum. Intense M-1 and M-2 peaks have also been observed in the mass spectrum of tetraphenylene in which case loss of two atoms of hydrogen has been taken to indicate bond formation between adjacent aromatic rings (7). A related transformation may be taking place in the syn-photodimer II.

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