A New Route to Polycondensed Aromatics: Photolytic Formation of Dibenzo[*fg*,*op*]naphthacene[1]

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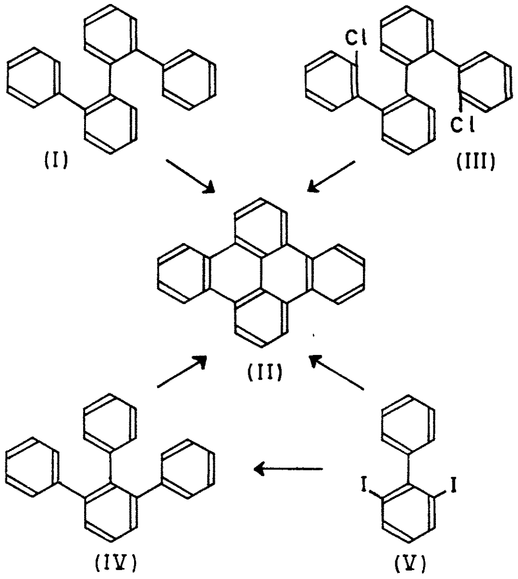
Summary The versatility of the photo-aryl coupling reaction is shown by the synthesis of the title compound starting from any of the four compounds; 2,2′-diphenylbiphenyl, 2,2′-bis-(2-chlorophenyl)biphenyl, 1,2,3-triphenylbenzene, or 2,6-di-iodobiphenyl.

THE versatility and applicability of photo-aryl coupling reactions[2,3] are demonstrated by the successful synthesis of the title compound starting from any of the following four compounds; 2,2′-diphenylbiphenyl (I), 2,2′-bis-(2-chlorophenyl)biphenyl (III), 1,2,3-triphenylbenzene (IV), or 2,6-di-iodobiphenyl (V).

Irradiation reactions were carried out in benzene solutions using a 1 kw high-pressure mercury lamp or a 100 w low-pressure lamp. Representative results are summarized in the Table.

Irradiation of (I) in the presence of an equimolar amount of iodine produced a crystalline deposit, which, on recrystallization from xylene, was obtained as pale yellow prisms, m.p. 351—352°, and was identified to be dibenzo[*fg*,*op*]-naphthacene based on the u.v. spectrum[4] and correct analytical results: u.v. λ_{max} (C_6H_6) 373 (log ϵ 2·36), 363 (2·76), 354 (2·85), 328·5 (4·21), 315 (4·26), and 288 nm (4·73). With 72 h irradiation the yield reached 57%, which was much higher than that from any other method leading to (II).[5,6] The importance of 253·7 nm light was clearly demonstrated by the experiments using a Pyrex filter with which essentially no cyclization reaction occurred. In cyclohexane the reaction proceeded rather slowly. Oxygen alone was not effective as the oxidant. These features are in accord with those found for *o*-terphenyl–triphenylene reactions[3] rather than for *cis*-stilbene–phenanthrene reactions[7] for which oxygen is equally effective as iodine.



A double cyclodehydrogenation reaction induced by iodine occurred also with (IV), though less efficiently, producing 21% of (II), the rest of the material being recovered as (IV). The formation of (II) is also possible starting from a simple biphenyl derivative (V), which on photolytic bis-phenylation would generate (IV). On irradiation with the low-pressure lamp, (V) disappeared completely after 120 h. The reaction mixture consisted of 24% of (IV) and a small amount of (II) together with 42% of triphenylene. 2,2′-Di-iodobiphenyl did not, however, produce (I) or (II) but led to the formation of dibenziodolium iodide, which on thermal decomposition regenerated 2,2′-di-iodobiphenyl.[8]

A third mode of cyclization occurred with (III), which on brief irradiation of 20 h, afforded up to a 67% yield of (II). No added oxidant is necessary for the double cyclization reaction. Stabilization of a radical species through conjugation with a halogen atom is assumed to be the driving force of the reaction coupled with ready extrusion of hydrogen chloride.[9]

Photolytic formation of dibenzo[fg,op]*naphthacene* (II)

Compound	mmol	Iodine mmol	Benzene mmol	Lamp[a]	Filter	Irradiation time (h)	Yield (%)
(I)	1·01	1·04	80	100-L	Vycor	72	57
(I)	1·02	1·04	60	1000-H	quartz	72	34
(I)	0·52	0·52	30	1000-H	Pyrex	72	1
(III)	0·98	—	60	100-L	Vycor	20	67
(IV)	0·19	0·20	60	100-L	Vycor	72	21

[a] 100-L; a 100 w low-pressure lamp. 1000-H; a 1 kw high-pressure lamp.

Lastly, the dehydrohalogenative cyclization reaction was also successfully used for the synthesis of triphenylene. The irradiation of 2-chloro- and 2-bromo-2′-iodobiphenyl in benzene produced 37 and 25% yields, respectively, of triphenylene. No 1-halogenotriphenylene was formed although oxidative cyclization leading to it was possible. It is not likely, at least with the chloride, that the reaction was initiated by C–X homolysis.[10]

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[5] A possible alternative method leading to (II) from (I) may be thermal cyclodehydrogenation over metal catalyst. The thermal reaction of (I) with chromia-on-alumina has, however, been shown to afford only 2-phenyltriphenylene *via* phenyl migration, C. H. Hansch and C. F. Geiger, *J. Org. Chem.*, 1958, **23**, 477.

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