A New Synthesis of Triphenylene by the Photochemical Aryl Coupling Reaction of *o*-Terphenyl[1]

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Triphenylene (II) has previously been prepared by the condensation of three molecules of cyclohexanone, followed by cyclodehydrogenation with copper or selenium,[2] and by the trimerization of the benzyne generated from *o*-bromoiodobenzene.[3] Several other methods are also available which utilize phenanthrene derivatives as the starting material.[4] In view of the continued interest in the triphenylene ring system, an attractive way of synthesizing II, its derivatives, and such heterocyclic analogs as azatriphenylenes may be sought in the oxidative aryl coupling reaction of *o*-terphenyl (I) or related compounds. Allen and Pingert[5] have already observed that the condensation of I to II in a low yield occurs as a frequent side reaction by the use of such dehydrogenating and condensing reagents as ozone, nitric acid, bromine, and aluminum chloride. These reactions, however, are devoid of any practical value. This note will describe an efficient yet simple way of synthesizing II, starting from I by using a photochemical process.

In Table 1 the irradiation reaction of I in a benzene or cyclohexane solution (1.6×10^{-2} M) under various conditions is summarized. While the reactions carried out by passing air through the solution resulted in the recovery of the starting material, iodine was found to effect the cyclization reaction. The reaction conditions were examined using varying amounts of iodine in a benzene solution. An optimum yield of 87.9% was achieved with an irradiation reaction of 20 hr in the presence of an equimolar iodine. Triphenylene (II) was isolated by the simple recrystallization of the reaction product as colorless needles, mp 194—195°C (picrate, mp 219—220°C). The infrared and ultraviolet spectra and elemental analyses were entirely consistent with the assigned structure. The same reactions carried out in a cyclohexane solution did not proceed satisfactorily, the best yield being only 47.6% and that attained only after 90 hr irradiation. No reaction occurred when I was refluxed with chloranil in *t*-butyl alcohol.

Related reactions of considerable interest include the photo-transannular reaction of [2.2]metacyclophane (III),[6] which, on irradiation in the presence of iodine, afforded 4, 5, 9, 10-tetrahydropyrene (IV) in a good yield, and the similar photo-aryl coupling reaction of *cis*-stilbenes[7] and the analogs,[8] which lead to the formation of phenanthrene structures. The mechanistic consideration of the former reaction comes from the ESR spectral evidence that the cyclophane-iodine charge-transfer complex is participated in the initial stage of the photochemical processes. On the other hand, Mallory and his co-workers[7b] have established that the latter reaction proceeds through the 4a, 4b-dihydrophenanthrene (VI) (or equivalent structures) resulting from the biradical V. The oxidation of the allylic position with iodine or oxygen (or preferably by both) in the dark reaction has been accounted for the formation of the phenanthrene ring system.

The cyclization reaction of I to II seems to be related to that of *cis*-stilbene to phenanthrene, since the mechanism requires the presence of an unsaturated linkage between the two aryl groups. According to Mallory *et al.*,[7b,9] when the olefinic bond of stilbene is incorporated in an aromatic system, no cyclization reaction is to be observed. In view of the present success in synthesizing II, however, this structural feature may not constitute a serious limitation of the photo-aryl coupling reaction. Moreover, the mechanistic implications that only an appreciable amount of iodine serves

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[1] Medium-Sized Cyclophanes, Part V. For part IV, see T. Sato, M. Wakabayashi, Y. Okamura, T. Amada and K. Hata, This Bulletin, in press.

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[9] Examples of failure include the attempted photocyclization of *o*-terphenyl, 9, 10-diphenylphenanthrene and the related compounds. In these compounds, it is assumed that the electron distribution in the excited state may not allow to provide enough electron availability at the two *o*-positions between which a new bond is formed.

TABLE 1. THE PHOTO-ARYL COUPLING REACTION OF *o*-TERPHENYL (I) TO TRIPHENYLENE (II)[a]

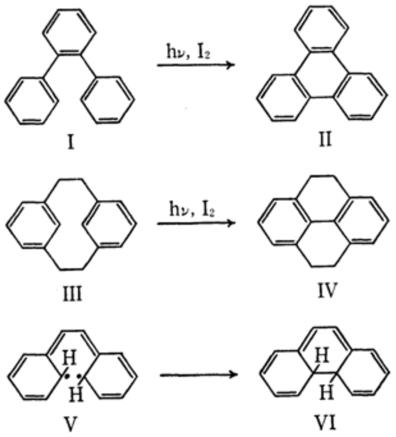
Compound I mmol	Iodine mmol	Solvent	Atmosphere	Irrad. time, hr	Yield of II, %	Recovery %
1.04	—	Benzene	Air	46	—	81.4
1.02	0.21	Benzene	N_2	5	24.8	
1.01	1.00	Benzene	N_2	5	61.2	
1.04	(3.5 mg)	Benzene	N_2	20	26.2	
1.02	0.22	Benzene	N_2	20	80.7	
1.02	1.01	Benzene	N_2	20	87.9	
0.32	—	Cyclohexane[b]	Air	20	—	64.8
1.04	0.20	Cyclohexane	Air	20	11.9	
1.06	0.20	Cyclohexane	N_2	20	19.6	
1.02	1.00	Cyclohexane	N_2	20	29.1	60.8
1.02	1.02	Cyclohexane[c]	N_2	20	15.6	56.9
1.05	0.21	Cyclohexane	N_2	64	25.0	
1.05	1.04	Cyclohexane	N_2	90	47.6	

[a] The photochemical reaction was carried out in a quartz cell containing 60 m*l* of the solvent using a 1000 W high-pressure mercury lamp.

[b] Forty-four milliliters of cyclohexane were used.

[c] Sodium bicarbonate (1.7 g) was added.

as an oxidant, not oxygen, and that benzene is superior to cyclohexane as a solvent, are in sharp contrast to the well-established stilbene-phenanthrene reaction and strongly suggest the participation of iodine in the initial stage of the photochemistry, as has been observed in the photolysis of [2.2]metacyclophane.



Experimental

***o*-Terphenyl (I).** A commercial material was used. It was also prepared by the nitrosation of *o*-acetamidobiphenyl, followed by decomposition in a benzene solution; colorless prisms, mp 57°C.

Found: C, 93.55; H, 6.14%. Calcd for $C_{18}H_{14}$: C, 93.87; H, 6.13%.

Triphenylene (II). The irradiation reactions of *o*-terphenyl under various conditions are summarized in Table 1. A typical reaction was carried out in the following way. A mixture of 235 mg (1.02 mmol) of I and 257 mg (1.01 mmol) of iodine in 60 m*l* of benzene was irradiated in a quartz cell under a current of nitrogen, using a 1000 W high-pressure mercury arc lamp (Wako HBC-1000) immersed in a circulated water jacket for a period of 20 hr. By the recrystallization of the product from ethanol, 205 mg (87.9%) of II, mp 194—195°C (lit. 198°C) were obtained as colorless needles; picrate, mp 219—220°C (lit. 223°C). The IR and UV spectra were consistent with the structure.

Found; C, 94.37; H, 5.01%. Calcd for $C_{18}H_{12}$; C, 94.70; H, 5.30%.

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