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

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Application of photo-aryl coupling reactions for the syntheses of triphenylene and dibenzo[*fg*,*op*]naphthacene was explored. Three types of reactions were developed: Photocyclodehydrogenation of polyphenyl compounds, photolytic reactions of iodoarenes, and photocyclodehydrohalogenation of halogenopolyaryls. The effects of solvent, oxidant, and wavelength on the photocyclization of *o*-terphenyl and 2,2′-diphenylbiphenyl to the triphenylene and naphthacene, respectively. were examined. The conversion was best achieved by the reaction carried out in an aromatic solvent in the presence of an equimolar amount of iodine using a quartz or a Vycor vessel. Versatility of the processes was shown by the formation of naphthacene starting from either 2,2′-diphenylbiphenyl (57% yield), 2,2′-bis(2-chlorophenyl)biphenyl (67%), 1,2,3-triphenylbenzene (21%), or 2,6-diiodobiphenyl.

Difficulties in obtaining pure samples of polycondensed aromatic compounds are largely overcome by utilizing the intramolecular photo-aryl coupling reaction.[2] Versatility of the process was examined by applying it to the synthesis of phenanthrene,[3] triphenylene,[4,5] pyrene,[6,7,8] and dibenzo[*fg*, *op*]naphthacene (I) ring systems.[1]

In this paper we wish to describe three types of photochemical processes, namely, a cyclodehydrogenation reaction of polyphenyls, a photolytic reaction of iodoarenes, and a cyclodehydrohalogenation reaction of halogenopolyphenyls, all aiming at the development of a synthetic means for triphenylene and dibenzonaphthacene I.

Results and Discussion

Photolytic Cyclodehydrogenation of Polyphenyls. Triphenylene was obtained in nearly quantitative yield by the irradiation of a dilute benzene solution of *o*-terphenyl (*ca.* 1.7×10^{-2}M) containing an equimolar amount of iodine (Scheme 1).[4] Similarly photocyclodehydrogenation of 2,2′-diphenylbiphenyl and 1,2,3-triphenylbenzene produced dibenzonaphthacene I in yields of 57% and 21%, respectively, as reported in a preliminary paper (Scheme 1)[1].

Representative examples for the preparation of triphenylene and I are shown in Tables 1 and 2, respectively. For comparison some of the previous data[4] are also included in Table 1.

The following generalization was deduced from a series of experiments: The reaction can be carried out under a stream of nitrogen but the presence of oxygen does not impede cyclization. Oxygen alone, however, is not effective as an oxidant. An equimolar amount of iodine is required to facilitate the reaction. As for solvent, aromatic solvents such as benzene or chlorobenzene are more suitable than cyclohexane. Use of a

Table 1. The photocyclodehydrogenation reaction of *o*-terphenyl to triphenylene[a]

o-Terphenyl mmol	Iodine mmol	Solvent	Lamp[c]	Filter	Atmosphere	Yield, %
1.04	none	C_6H_6 or C_6H_{12}	1000-H	quartz	air	0[d]
1.04	0.20	C_6H_{12}	1000-H	quartz	air	11.9
1.06	0.20	C_6H_{12}	1000-H	quartz	nitrogen	19.6
1.02	1.00	C_6H_{12}	1000-H	quartz	nitrogen	29.1
1.04	trace	C_6H_6	1000-H	quartz	nitrogen	26.2
1.00	1.01	C_6H_6–C_6H_{12}[b]	1000-H	quartz	nitrogen	45.4
1.02	1.01	C_6H_6	1000-H	quartz	nitrogen	87.9
1.01	1.01	C_6H_5Cl	1000-H	quartz	nitrogen	78
1.01	1.01	C_6H_6	100-L	Vycor	nitrogen	87
1.00	1.00	C_6H_6	1000-H	Pyrex	nitrogen	2
1.01	1.02	C_6H_6	1000-H	glass	nitrogen	0

a) Irradiation was carried out for 20 hr using 60-m*l* solutions.
b) A 1:1 solution was used.
c) 1000-H: a 1-kW high-pressure mercury lamp. 100-L: a 100-W low-pressure mercury lamp.
d) Irradiation was continued for 46 hr.

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[1] Photo-Aryl Coupling and Related Reactions. VII. Part VI: T. Sato, S. Shimada, and K. Hata, *Chem. Commun.*, **1970**, 766.

[2] T. Sato, *Yuki Gosei Kagaku Kyokai Shi*, **27**, 715 (1969).

[3] T. Sato, Y. Goto, T. Tohyama, S. Hayashi, and K. Hata, This Bulletin, **40**, 2975 (1967).

[4] T. Sato, Y. Goto, and K. Hata, *ibid.*, **40**, 1997 (1967); see also N. Kharasch, T. G. Alston, H. B. Lewis, and W. Wolf, *Chem. Commun.*, **1965**, 242.

[5] T. Sato, S. Shimada, and K. Hata, This Bulletin, **42**, 766 (1969).

[6] T. Sato, E. Yamada, Y. Okamura, T. Amada, and K. Hata, *ibid.*, **38**, 1049 (1965).

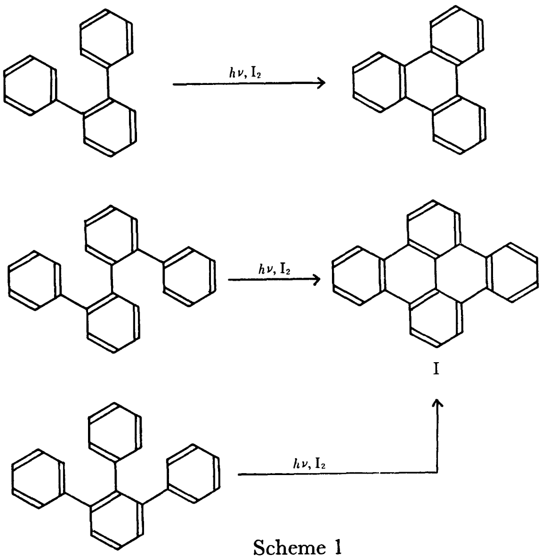
[7] T. Sato, M. Wakabayashi, S. Hayashi, and K. Hata, *ibid.*, **42**, 773 (1969).

[8] S. Hayashi and T. Sato, to be submitted to this Bulletin.

TABLE 2. THE PHOTOCYCLODEHYDROGENATION REACTION OF 2,2′-DIPHENYLBIPHENYL AND 1,2,3- TRIPHENYLBENZENE TO DIBENZO[*fg,op*]NAPHTHACENE (I)[a]

Compound mmol	Iodine mmol	Benzene m*l*	Lamp	Filter	Yield, %
2,2′-Diphenylbiphenyl					
1.01	1.04	80	100-L	Vycor	57
1.02	1.04	60	1000-H	quartz	34
0.52	0.52	30	1000-H	Pyrex	1
1,2,3-Triphenylbenzene					
0.19	0.20	60	100-L	Vycor	21

a) Irradiation was carried out for 72 hr under nitrogen.



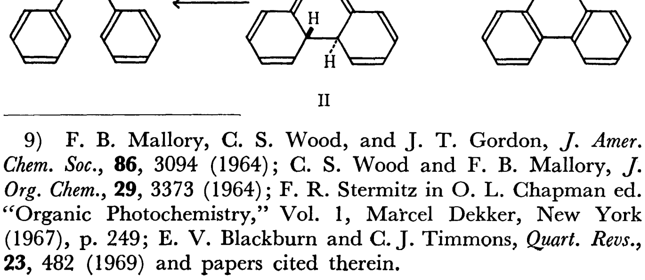
Scheme 1

benzene-cyclohexane mixture gave a medium result.

This is in a sharp contrast to the related photocyclization of *cis*-stilbene to phenanthrene, for which cyclohexane is a preferred solvent and both oxygen and iodine are equally effective.[9] Only a catalytic amount of iodine is enough to effect cyclization.

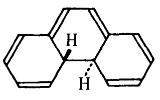
Wavelength effects were studied by carrying out photolysis using various filters. Although the reaction proceeded satisfactorily either with a quartz or a Vycor filter, it was suppressed by a Pyrex filter. No reaction occurred when a glass filter was inserted.

A possible pathway of the reaction is shown in the following equation for the case of *o*-terphenyl as an example. *o*-Terphenyl shows a UV maximum at 235 nm in ethanol. By photoexcitation, the molecules give dihydrotriphenylene II via a concerted process. Dehydrogenation of II generates triphenylene.



II

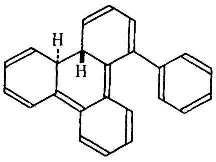
This sequence is formulated after the well-studied *cis*-stilbene - phenanthrene reaction,[9] for which the structure of the intermediate, 4a,4b-dihydrophenanthrene (III), was determined beyond doubt either by chemical and spectroscopic methods[10] or by direct trapping.[11] A *trans* relationship of the tertiary hydrogens as shown in II and III is based on the conrotatory photocyclization of 1,3,5-hexatriene systems.[12]



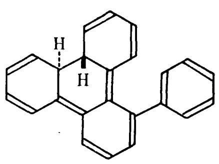
III

Spectral changes of a benzene solution of *o*-terphenyl during irradiation indicated the appearance of new bands at ~360, 375, and 400 nm, possibly due to II. Most peaks of triphenylene were masked by absorption due to the solvent. Detailed spectral and kinetic studies on the formation of II will be reported elsewhere.[13]

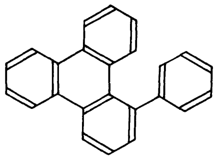
With 2,2′-diphenylbiphenyl and 1,2,3-triphenylbenzene the structure of the intermediate can be written as IV and V. Although a stepwise cyclization *via* IV or V is favored to a simultaneous double cyclization reaction, no 1-phenyltriphenylene (VI) was isolated from the reaction mixture. Even when the conversion was incomplete, the rest of the material was found to be the starting compound. It is highly probable that VI, once formed, is rapidly cyclized to I since the molecular arrangement becomes favorable for further ring closure.[14]



IV



V



VI

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9) F. B. Mallory, C. S. Wood, and J. T. Gordon, *J. Amer. Chem. Soc.*, **86**, 3094 (1964); C. S. Wood and F. B. Mallory, *J. Org. Chem.*, **29**, 3373 (1964); F. R. Stermitz in O. L. Chapman ed. "Organic Photochemistry," Vol. 1, Marcel Dekker, New York (1967), p. 249; E. V. Blackburn and C. J. Timmons, *Quart. Revs.*, **23**, 482 (1969) and papers cited therein.

10) F. B. Mallory, C. S. Wood, J. T. Gordon, L. C. Lindquist, and M. L. Savitz, *J. Amer. Chem. Soc.*, **84**, 4362 (1962); W. M. Moore, D. D. Morgan, and F. R. Stermitz, *ibid.*, **85**, 829 (1963); M. V. Sargent and C. J. Timmons, *ibid.*, **85**, 2186 (1963); M. V. Sargent and C.J. Timmons, *J. Chem. Soc.*, **1964**, 5544; K.A. Muszkat and E. Fischer, *ibid.*, *B*, **1967**, 663; E. V. Blackburn, C. E. Loader, and C. J. Timmons, *ibid.*, *C*, **1970**, 163.

11) T. D. Doyle, N. Filipescu, W. R. Benson, and D. Banes, *J. Amer. Chem. Soc.*, **92**, 637 (1970).

12) R. B. Woodward and R. Hoffmann, "The Conservation of Orbital Symmetry," Verlag Chemie Gmbh (1970).

13) Upon irradiation benzene solutions of *o*-terphenyl exhibit spectral changes under both oxygen and deaerated conditions. On the other hand, no spectral changes occur in cyclohexane.

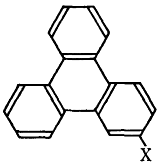
14) As a measure of photocyclization, the sum of the free valence numbers in the first excited state of atoms undergoing cyclization is calculated by the HMO method. The values found for 2,2′-diphenylbiphenyl, 1,2,3-triphenylbenzene, and 1-phenyltriphenylene VI are 0.962, 1.003, and 0.962, respectively. For details, see T. Sato and T. Morita, This Bulletin, in press.

Inability of oxygen to enter into a hydrogen abstraction step seems to reflect either an essential difference in the ability of hydrogen abstraction between oxygen and iodine or a factor concerning concentration. The latter possibility is indicated by experiments using a varying amount of iodine. Presumably tertiary hydrogens of II are less reactive than those of III, since rather higher concentration of II can be expected in the photoequilibrium when a favorable geometry for cyclization and extra conjugation extending over four rings are considered.

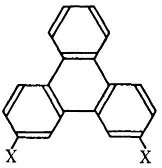
Incident light will be largely absorbed by solvent benzene. Enhancement of the reaction rate by the aromatic solvent indicates the possibility of sensitization. Action of iodine through complexation with the aromatic ring must also be considered.

The photocyclization of polyphenyl is proved to be an efficient synthetic method for certain polycondensed aromatics and may be further applied in various fields. Besides involving high yields and simple procedures the process has a simplified isolation technique. With triphenylene pure material was obtainable merely by concentrating the benzene solution after it was washed with sodium thiosulfate. It is more simple in the case of I, since the material separates out of the solution during the course of formation resulting from irradiation. Single recrystallization of the collected material from xylene gave pure I, mp 351—352°C.

Starting from substituted *o*-terpehnyls a number of triphenylene derivatives such as VII and VIII, were prepared.[5]



VII



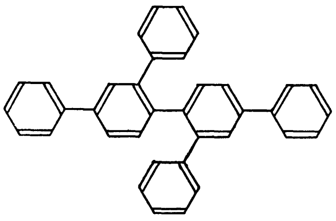
VIII

Substituents include CH_3, C_6H_5, Br, Cl, F, $COOC_2H_5$, and CN. The preparation of 2-cyanotriphenyelne, (VII/CN) and ethyl triphenylene-2-carboxylate (VII/$COOC_2H_5$) are described in Experimental. Most of the available synthetic methods known for triphenylene and its derivatives[15] can not be modified to allow introduction of such a variety of functional groups. Syntheses via trimerization are used to give some sym.-trisubstituted triphenylenes.[16] The electrophilic substitution reaction of triphenylene results in the formation of both 1- and 2-substituted compounds and it is difficult to control and direct the orientation.[17]

Only synthetic method reported for I is that of Sako,[18] who obtained I in 35—40% yield by decomposition of the bis-diazonium salt derived from 2,2′-diamino-6,6′-diphenylbiphenyl. There are several reports on the formation of I though not suitable for synthetic purposes.[19]

A possible alternative synthesis after Scheme 1 would be a thermal cyclodehydrogenation reaction over metal catalysts. The thermal conversion of *o*-terphenyl to triphenylene required high temperatures of 625°C with chromia-on-alumina (10% yield)[20] or 490°C with palladium-platinum-charcoal (63% yield).[21] Most substituents would not survive such severe reaction conditions. Attempted cyclodehydrogenation of 2,2′-diphenylbiphenyl using the metal catalyst produced a phenyl migration product, 2-phenyltriphenylene (VII/C_6H_5). Neither 1-phenyltriphenylene (VI) nor I was produced.

Concerning the limitations of the photocyclodehydrogenation reaction, no cyclization occurred with nitro-*o*-terphenyls.[5] Iodo-*o*-terphenyls underwent extensive C–I homolysis.[5] A similar limitation was also found for stilbenes, for which the effect of substituents on the quantum yields was studied.[22] No cyclization occurred with diphenylquaterphenyl (IX).



IX

Photolytic Reactions of Iodoarenes. Due to low bond dissociation energies ($\sim$55 kcal/mol) of the C–I bond, iodoarenes undergo a facile photolysis reaction to give aryl and iodo radicals.[23,24] Application to biaryl syntheses was described by Wolf *et al.*[25]

Polyphenylation is expected when polyiodoarenes are photolyzed in benzene. Several examples are shown in Table 3. Liberated iodine can effect photocyclization when an *o*-terphenyl structure is present. Such an example is illustrated in the accompanying equation.[5]

The photolysis reactions of polyiodoarenes are summarized in Table 4. The construction of highly con-

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15) H. Heaney and I. T. Miller, *Org. Synth.*, **40**, 105 (1960) and references cited therein.

16) R. C. Hinton, F. G. Mann, and I. T. Miller, *J. Chem. Soc.*, **1958**, 4704; F. H. Marquardt, *ibid.*, **1965**, 1517; I. M. Matheson, O. C. Musgrave, and C. J. Webster, *Chem. Commun.*, **1965**, 278; P. Canonne and A. Regnault, *Tetrahedron Lett.*, **1969**, 243.

17) Ng. Ph. Buu-Hoi and P. Jaquignori, *J. Chem. Soc.*, **1953**, 941; C. C. Barker, R. G. Emmerson, and J. D. Periam, *ibid.*. **1955**, 4482; P. M. G. Bavin and M. J. S. Dewar, *ibid.*, **1955**, 4486, **1956**, 164; M. J. S. Dewar, T. Mole, and E. W. T. Warfard, *ibid.*, **1956**, 3581; M. J. S. Dewar and T. Mole, *ibid.*, **1957**, 342; R. Bolton and P. B. D. de la Mare, *ibid.*, *B*, **1969**, 170.

18) S. Sako, This Bulletin, **9**, 55 (1934).

19) G. Wittig and G. Lehmann, *Chem. Ber.*, **90**, 875 (1957); G. Wittig, E. Hahn, and W. Tochterman, *ibid.*, **95**, 439 (1962); I. B. Goldberg., R. F. Borch, and J. B. Bolton, *Chem. Commun.*, **1969**, 223.

20) C. H. Hansch and C. F. Geiger, *J. Org. Chem.*, **23**, 477 (1958).

21) P. G. Copeland, R. E. Dean, and D. McNeil, *J. Chem. Soc.*, **1960**, 1687.

22) H. Jungmann, H. Güsten, and D. Schulte-Frohlinde, *Chem. Ber.*, **101**, 2690 (1968).

23) J. M. Blair, D. Bryce-Smith, and B. W. Pengilly, *J. Chem. Soc.*, **1959**, 3174; A. Job and G. Emschwiller, *Compt, rend.*, **179**, 52 (1924).

24) R. K. Sharma and N. Kharasch, *Angew. Chem.*, **80**, 69 (1968).

25) W. Wolf. T. Erpelding, P. G. Naylor, and L. Tokes, *Chem. and Ind.*, **1962**, 1720; W. Wolf and N. Kharasch, *J. Org. Chem.*, **30**, 2493 (1965).

Table 3. The photolytic phenylation of polyiodoarenes[a]

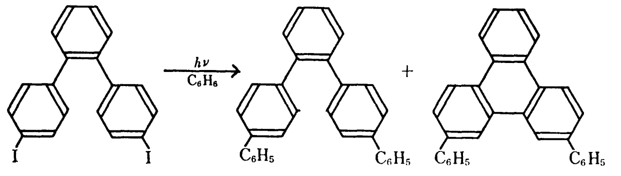
Compound	Irrad. time, hr	Product	Yield, %
p-Diiodobenzene	95	*p*-Terphenyl	52
4,4′-Diiodobiphenyl	71	1,1′:4′,1″:4″,1‴-Quaterphenyl	63
1,3,5-Triiodobenzene	147	1,3,5-Triiodobenzene	79

a) Benzene solutions (1.7×10^{-2}M) were irradiated using a 1-kW high-pressure lamp.

Table 4. Photoreactions of iodoarenes

Compound	mmol	Benzene m*l*	Irrad. time, hr	Product, %			
				Biphenyl	*o*-Iodo-biphenyl	Tri-phenylene	I
o-Diiodobenzene[a]	1.02	100	48	trace	28	2	
2-Iodobiphenyl[a]	1.04	100	24	11	11	11	
2,6-Diiodobiphenyl[a,b]	1.01	100	120	trace	2	42	trace
2,2′-Diiodobiphenyl[c,d]	0.52	30	21		1	3	

a) 100-L lamp
b) 1000-H lamp
c) 1,2,3-Triphenylbenzene was formed in 24% yield.
d) Dibenziodolium iodide was formed in 21% yield. Recovery of the starting material was 23%.

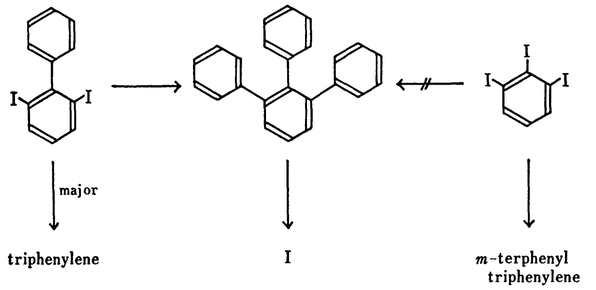


X XI

densed ring systems would become possible *via* polyphenylation-cyclization scheme.

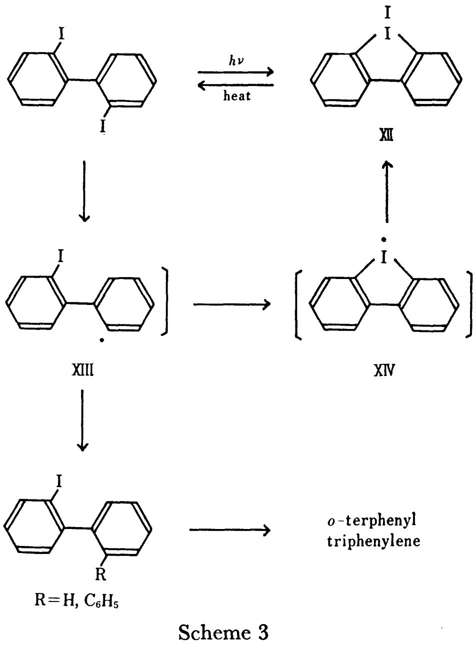
The photolysis of *o*-diiodobenzene in benzene produced triphenylene in addition to 2-iodobiphenyl and *o*-terphenyl. Similar results have been reported[26] and the formation of a benzyne intermediate was postulated.[26,27] The yield of triphenylene was improved by starting from 2-iodobiphenyl.

The photolysis of 1,2,3-triiodobenzene gave *m*-terphenyl and triphenylene but no 1,2,3-triphenylbenzene and/or its cyclization products. 2,6-Diiodobiphenyl produced I in a low yield, but again an alternative route leading to triphenylene was the major one (Scheme 2).



Scheme 2

As a possible precursor to I, 2,2′-diiodobiphenyl was photolyzed in benzene. However, a solid material was produced which was identified as dibenziodolium iodide (XII), mp 213—214°C decomp.[28] 2,2′-Diiodobiphenyl was regenerated from compound XII either by heating alone or by refluxing in xylene.[28] Formation of XII is explained by assuming an intermediacy of iodobiphenylyl radical XIII. An intramolecular radical attack on iodine to give XIV is followed by a radical recombination step (Scheme 3). That an aryl



Scheme 3

radical has a very high affinity to iodine has been noticed earlier.[29] Other products of the reaction include *o*-iodobiphenyl, *o*-terphenyl and triphenylene, the formation of which can also be explained by assuming XIII. *o*-Terphenyl radical XVII derived from 2-iodo-*o*-

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[26] J. A. Kampmeier and E. Hoffmeister, *J. Amer. Chem. Soc.*, **84**, 3787 (1962).

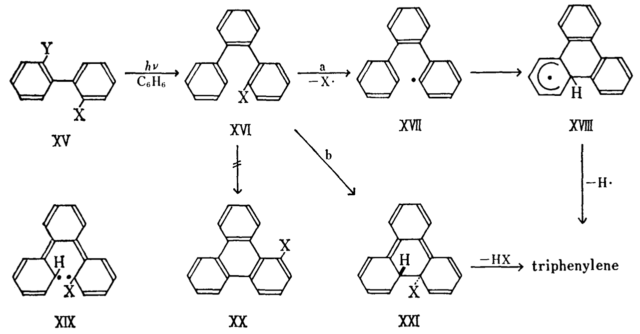
[27] N. Kharasch and R. K. Sharma, *Chem. Commun.*, **1967**, 492.

[28] H. Irving and R. W. Reid, *J. Chem. Soc.*, **1960**, 2078.

[29] D. L. Brydon and J. I. G. Cadogan, *Chem. Commun.*, **1966**, 744; D. L. Brydon and J. I. G. Cadogan, *J. Chem. Soc., C*, **1968**, 819; J. F. Bunnett and C. C. Wamser, *J. Amer. Chem. Soc.*, **88**, 5534 (1966).

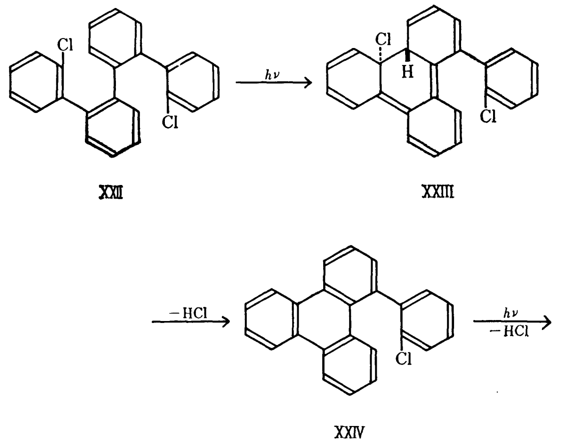
terphenyl undergoes an intramolecular arylation to give XVIII, from which triphenylene produced (Scheme 4, route a, X=Y=I).

Photolytic Cyclodehydrohalogenation of o-*Halogenopolyphenyl.* Photolytic reactions of iodoarenes were further examined using 2,2′-dihalogenobiphenyls (XV). Irradiation of 2-chloro- and 2-bromo-2′-iodobiphenyls (XV: X=Cl, Br; Y=I) for 79 hr using a 1-kW high-pressure lamp gave triphenylene in 37 and 25% yields respectively. The course of the reaction is illustrated in Scheme 4, route b. 2-Halogeno-*o*-terphenyl (XVI) formed by photolytic phenylation of XV will cyclize to XXI, dehydrohalogenation of which affords triphenylene. A higher electron density at the carbon atom carrying a halogen by its conjugation effect (*e.g.* XIX) is assumed to promote reaction coupled with ready extrusion of hydrogen halide. 2,2′-Dibromobiphenyl (XV, X=Y=Br) was recovered unchanged on irradiation with a high-pressure lamp but was converted to triphenylene (20%) by using a 100-W low-pressure lamp.



Scheme 4

An alternative way of cyclization to give 1-halogenotriphenylenes (XX) was not observed although oxidative cyclization leading to them was possible. At least with the chloride it is not likely that triphenylene is formed by the homolysis of C–X bonds after route a. The photolysis proceeds with increasing difficulties as the strength of the C–X bond increases.[24] Under the conditions studied no C–Cl cleavage occurred through C–Br bonds were partially photolyzed particularly when a low-pressure lamp was used.[5] Under conditions where extensive cleavage of the C–Br bond occurs triphenylene formation is possible by both routes a and b.



Scheme 5

In contrast to the oxidative cyclizations stated in the preceding sections, the cyclodehydrohalogenation reaction requires no added oxidant. When a benzene solution of 2,2′-bis(2-chlorophenyl)biphenyl (XXII) was irradiated for 20 hr under a stream of nitrogen I was obtained in 67% yield. The course of the reaction assuming an intermediacy of XXIII is shown in Scheme 5. No triphenylene derivative XXIV was detected. The reaction mechanism is in agreement with recent findings on the photolysis of certain *o*-halogenoarenes.[30]

Experimental

Starting Materials. Most compounds were purchased or prepared by the methods described in literature. Several new syntheses and modified procedures will be given below.

1,2,3- and 1,3,5-Triiodobenzene. By reductive deamination[31] of 3,4,5-triiodoaniline[31] 1,2,3- and 1,3,5-triiodobenzenes were produced, and then separated by column chromatography on alumina.

1,2,3-Triiodobenzene was recrystallized from ethanol as colorless plates, mp 110—113°C.[32]

Found: C, 16.07; H, 0.83%. Calcd for $C_6H_3I_3$: C, 15.81; H, 0.66%.

1,3,5-Triiodobenzene was recrystallized from ethanol as colorless needles, mp 177—179°C.[32] IR (KBr): 1735, 1700, 840 cm^{-1}.

Found: C, 16.02; H, 0.70%. Calcd for $C_6H_3I_3$: C, 15.81; H, 0.66%.

Dihalogenobiphenyls. They were prepared by the thermal decomposition of dibenziodolium halides[33] prepared from 2-iodosylbiphenyl by treatment with sulfuric acid followed by anion exchange.

Thermal reactions of dibenziodolium chloride, bromide, and iodide were carried out at 295, 290, and 210°C respectively.[34,35] From each reaction mixture the corresponding 2-halogeno-2′-iodobiphenyls were obtained as the major product. Each halide was purified by column chromatography on alumina: 2-chloro-2′-iodobiphenyl, mp 60—62°C; 2-bromo-2′-iodobiphenyl, mp 87.5—88°C; 2,2′-diiodobiphenyl, mp 108.5—110°C.

2,6-Diiodobiphenyl. 2,6-Diaminobiphenyl prepared by the reduction of 2,6-dinitrobiphenyl[36] was bis-diazotized and then decomposed with potassium iodide. After purification by column chromatography on alumina, it was recrystallized from *n*-hexane as prisms, mp 80—81°C. IR (KBr): 760, 720, 690, and 680 cm^{-1}.

Found: C, 35.62; H, 2.02%. Calcd for $C_{12}H_8I_2$: C, 35.49; H, 2.00%.

*4′-Iodo-*m*-terphenyl.* This was prepared from 4′-amino-*m*-terphenyl by diazotization followed by decomposition with potassium iodide, bp 183—187°C/0.2—0.3 mmHg. IR (KBr): 1000, 890, 820, 750, and 690 cm^{-1}.

Found: C, 60.72; H, 3.58%. Calcd for $C_{18}H_{13}I$: C, 60.70;

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H, 3.68%.

*4-Cyano-*o*-terphenyl.* a) 4-Amino-*o*-terphenyl⁵⁾ was diazotized and treated with cuprous cyanide solution in the usual manner. Vacuum distillation at 158—160°C/1 mmHg produced colorless needles, mp 122.5—123.5°C, recrystallization from *n*-hexane. IR (KBr): 2220 cm^{-1}.

b) A mixture of 17 g (0.055 mol) of 4-bromo-*o*-terphenyl⁵⁾ 5.2 g (0.058 mol) of cuprous cyanide in 9 m*l* of pyridine was refluxed for 8 hr.³⁸⁾ After washing with aqeous ammonia the mixture was extracted with benzene. Extraction with *n*-hexane gave 8.2 g of 4-cyano-*o*-terphenyl.

Found: C, 89.37; H, 5.20; N, 5.31%. Calcd for $C_{19}H_{13}N$: C, 89.38; H, 5.13; N, 5.49%.

Ethyl o*-Terphenyl-4-carboxylate.* A solution of 10 g (0.039 mol) of 4-cyano-*o*-terphenyl, 80 m*l* of ethanol and 28 m*l* of concentrated sulfuric acid was refluxed for 7 hr was obtained 3.8 g (32%) of the ethyl ester by chromatographical purification. IR (KBr): 1720 cm^{-1} as colorless needles, mp 81—81.5°C. IR (KBr): 1720 cm^{-1}.

Found: C, 83.69; H, 6.02%. Calcd for $C_{21}H_{18}O_2$: C, 83.42; H, 6.00%.

1,2,3-Triphenylbenzene. This was prepared by photolysis of 2,6-diiodobiphenyl in benzene in a 24% yield, mp 156—157°C. IR (KBr): 750, and 690 cm^{-1}.

Found: C, 93.75; H, 6.00%. Calcd for $C_{24}H_{18}$: C, 94.08; H, 5.92%.

2,2′-Bis(2-chlorophenyl)biphenyl (XXII). This was prepared from 2-chloro-2′-iodobiphenyl by the Ullmann reaction carried out at 250—260°C for 20 min, colorless plates from *n*-hexane, mp 129.5—130.5°C. IR (KBr): 760 and 735 cm^{-1}.

Found: C, 76.26; H, 4.30%. Calcd for $C_{24}H_{16}Cl_2$: C, 76.81; H, 4.30%.

3′,2″-Diphenyl-1,1′:4′,1″:4″,1‴-quaterphenyl (X). This was prepared by the Ullmann reaction of 4′-iodo-*m*-terphenyl at 280—300°C, mp>350°C. IR (KBr): 890, 830, 755, and 690 cm^{-1}.

Found: C, 93.71; H, 5.64%. Calcd for $C_{36}H_{26}$; C, 94.28; H, 5.72%.

Photochemical Reactions. Either a 1-kW high-pressure lamp (Wako HBC-1000) or a 100-W low-pressure lamp (Ushio UL2-1HQ) was used as a light source for the external irradiation of sample solutions. For experiments using the high-pressure lamp the set-up was immersed in a bucket kept cool with running water. The spiral-shaped low-pressure lamp was used in combination with a quartz cooling unit into which a reaction vessel made of Vycor was inserted.

Photolyses were carried out under a nitrogen current unless otherwise stated using sample solutions with concentration of *ca.* 1.7×10^{-2} M in appropriate solvents.

The analysis of the reaction mixture was performed by column chromatography on alumina by eluting with *n*-hexane or benzene, or a mixture of the two. Materials were characterized by comparing their physical properties and spectral data with those of the authentic compounds. For a qualitative study gas chromatographical analysis was also employed using a Hitachi K-53 machine in combination with XE-60 silicone gum rubber on chromosorb W column.

Representative results are summarized in Tables 1—4. The preparation of triphenylene and I by the photolytic cyclodehydrogenation reaction of polyphenyl compounds are compiled in Tables 1 and 2. Application of photolytic phenylation reaction is summarized in Tables 3 and 4. Typical examples are given.

1,1′:4′,1″:4″,1‴-Quaterphenyl. The irradiation of a benzene solution (60 m*l*) containing 403 mg (0.99 mmol) of 4,4′-diiodobiphenyl for 71 hr produced the quaterphenyl in 63% yield, recrystallized from benzene, mp 304—305°C.³⁹⁾ IR (KBr): 820, 750, and 680 cm^{-1}. UV ($CHCl_3$): 298 nm (log ε 4.75).

Found: C, 94.37; H, 6.08%. Calcd for $C_{24}H_{18}$: C, 94.08; H, 5.92%.

1,3,5-Triphenylbenzene. A solution of 481 mg (1.06 mmol) of 1,3,5-triiodobenzene in 60 m*l* of benzene was irradiated for 147 hr. 1,3,5-Triphenylbenzene was obtained in 79% yield, recrystallized from ethanol as colorless needles, mp 168—170°C.³²⁾ IR (KBr): 870, 740, and 690 cm^{-1}.

Found: C, 93.91; H, 5.90%. Calcd for $C_{24}H_{18}$: C, 94.08, H, 5.92%.

*Photolysis of 4′-Iodo-*m*-terphenyl.* A benzene solution (60 m*l*) containing 362.7 mg (1.02 mmol) of 4′-iodo-*m*-terphenyl was irradiated for 48 hr. The product was separated by column chromatography on alumina to give *m*-terphenyl (29%), 2′-phenyl-*p*-terphenyl (5%) and 2-phenyl-triphenylene (28%), mp 180.5—181°C.⁵⁾ Recovery of the starting material was 25%.

2′-Phenyl-*p*-terphenyl was characterized by elemental analysis.

Found: C, 93.32; H, 5.88%. Calcd for $C_{24}H_{18}$: C, 94.08; H, 5.92%.

Photolysis of 2,2′-Diiodobiphenyl. Irradiation of 2,2′-diiodobiphenyl resulted in the formation of an insoluble matter which began to separate immediately after the reaction. It was identified as dibenziodolium iodide, mp 210°C dec.,²⁸⁾ and was obtained in 21% yield.

Gas chromatography analysis of the benzene solution identified 2-iodobiphenyl (1%), *o*-terphenyl (1%), starting material (23%), and triphenylene (3%) in the order of the retention times (Table 4).

Triphenylene. *a) From* o*-Terphenyl.* Triphenylene was obtained in an almost 90% yield by the photolysis of *o*-terphenyl and iodine in benzene (Table 1). The experimental procedures are essentially the same as before.⁴⁾

b) From 2-Chloro- and -bromo-2′-iodobiphenyls: A solution of 287 mg (0.91 mmol) of 2-chloro-2′-iodobiphenyl in 60 m*l* of benzene was irradiated with the high-pressure lamp for 79 hr. Triphenylene (37%) and the starting material (14%) were isolated.

From 2-bromo-2′-iodobiphenyl 25% of triphenylene was produced, 16% of the starting material being recovered.

Upon irradiation with the low-pressure lamp for 65 hr 2,2′-dibromobiphenyl afforded 20% yield of triphenylene.

2-Cyanotriphenylene (VII, R=CN). A benzene solution (60 m*l*) of 256 mg (1.0 mmol) of 4-cyano-*o*-terphenyl and 258 mg (1.01 mmol) of iodine was irradiated in a quartz vessel using the high-pressure lamp for 96 hr. By repeated recrystallizations from ethanol and chromatography on Florisil 28 mg of colorless needles was obtained, mp 220—221°C. IR (KBr): 2220 cm^{-1}.

Found: C, 89.14; H, 4.39%. Calcd for $C_{19}H_{11}N$: C,90.09; H, 4.38%.

Ethyl Triphenylene-2-carboxylate (VII, R=$COOC_2H_5$*).* A benzene solution (60 m*l*) of 305 mg (1.01 mmol) of ethyl *o*-terphenyl-4-carboxylate and 256 mg (1.01 mmol) of iodine was irradiated as above. Colorless needles were obtained, mp 129.5—130.5°C, from ethanol. IR (KBr): 1700 cm^{-1}.

Found: C, 83.70; H, 5.34%. Calcd for $C_{21}H_{16}O_2$: C,

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83.98; H, 5.37%.

Dibenzo[fg,op]*naphthacene (I).* *a) From 2,2′-Diphenylbiphenyl*: A solution of 310 mg (1.0 mmol) of 2,2′-diphenylbiphenyl, mp 116—117°C,[39] $\lambda_{\max}$ 228 nm (log ε 4.54), and 265 mg (1.0 mmol) of iodine in 60 m*l* of benzene was irradiated with a low-pressure lamp through a Vycor vessel. After 72 hr, a crystalline deposit was collected and was recrystallized from xylene, pale yellow prisms, mp 351—352°C,[18] yield 57%. UV (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). Found: C, 95.66; H, 4.71%. Calcd for $C_{24}H_{14}$: C, 95.33; H, 4.67%.

b) From 1,3,5-Triphenylbenzene: Compound I was obtained in 21% yield (Table 2).

c) From 2,2′-Bis(2-chlorophenyl)biphenyl (XXII): A solution of 366 mg (0.98 mmol) of XXII in 60 m*l* of benzene was irradiated with the low-pressure lamp for 20 hr to give 67% of I.

d) From 2,6-Diiodobiphenyl: Among other products compound I was obtained in a low yield (Table 4).