BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN VOL. 42 766—772 (1969)

Photo-Aryl Coupling and Related Reactions. II. The Formation of Triphenylenes from Halogeno-*o*-terphenyls[1]

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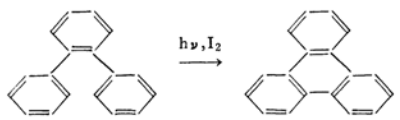
(Received July 9, 1968)

Electronic effects on the photochemical conversion of *o*-terphenyl to triphenylene were examined by comparing the ultraviolet irraiation reaction, carried out in a benzene solution using iodine as an oxidant, of three classes of *o*-terphenyl derivatives, 4- (**3**) and 4'-substituted (**4**) and 4,4''-disubstituted derivatives (**5**). While a strong electron-withdrawing group such as nitro group, hindered the cyclization reaction to occur, methoxy, fluoro, chloro and bromo compounds afforded the corresponding triphenylene derivatives. With bromo and iodo compounds, however, a complex mixture of the products resulted due to photochemical cleavage of a carbon-halogen bonding, which led to the formation of phenylation products and hence phenyltriphenylenes together with reduction products. Further, with iodo compounds, it was found that no oxidant was necessary to effect the cyclodehydrogenation reaction since iodine was liberated during the photolysis. Possible pathways for the formation of the photolysis products from bromo and iodo compounds were discussed in relation to the relative rates of carbon-halogen cleavage and cyclization reactions. Comparison among three classes of halogeno compounds indicated that, with the exception of iodides, the cyclization reaction occurred more readily with type **4** compound than type **3** compounds, while type **5** compounds reacted only with difficulty.

Recently, we have developed[2] an efficient, quite simple method for the preparation of triphenylene (**2**) employing a photo-aryl coupling reaction of *o*-terphenyl (**1**). By this procedure **2** was obtainable in an optimum yield of 88%. A similar observation has also been announced, in the form of a preliminary account, by Kharasch and co-workers.[3]

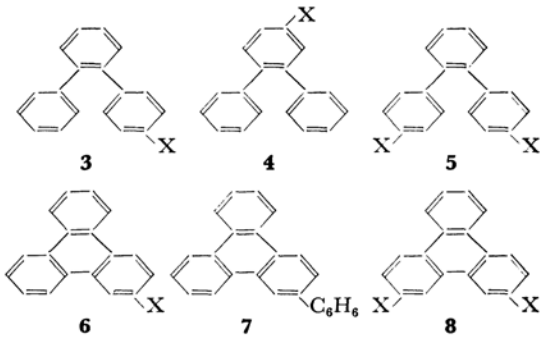


1 **2**

This cyclodehydrogenation reaction, induced by iodine, is regarded as an extention of thoroughly studied *cis*-stilbene - phenanthrene reactions,[4] representing a special case where the central unsaturated linkage of *cis*-stilbene is incorporated into an aromatic system. Mallory and co-workers,[5] during their extensive studies on the photochemistry of stilbenes, have been the first to irradiate **1** but to obtain negative results. Failure could be ascribed, in addition to the problem of a light source, to the choice of cyclohexane as a solvent, since the reaction had been shown to be much slower in this solvent[2] than in benzene in contrast to the *cis*-stilbene case where both solvents are equally suited.

Besides this solvent effect, it has been found[2] that oxygen is ineffective to bring about the cyclization reaction of **1**, thus showing a marked contrast again with the *cis*-stilbene case where iodine, oxygen or preferably a combination of these are employed as the oxidant.

In this paper, elcctronic effects on the photo-aryl coupling reaction were examined by choosing three representative classes of compounds **3**—**5**. Types **3** and **4** compounds are assumed to give the same product, 2-substituted triphenylene (**6**), whereas



3 **4** **5**

6 **7** **8**

1) For previous paper in this series see, T. Sato, Y. Goto, T. Tohyama, S. Hayashi and K. Hata, This Bulletin, **40**, 2975 (1967).

2) T. Sato, Y. Goto and K. Hata, *ibid.*, **40**, 1994 (1967).

3) N. Kharasch, T. G. Alston, H. B. Lewis and W. Wolf, *Chem. Commun.*, **1965**, 242.

4) F. R. Stermitz in O. L. Chapman ed. "Organic Photochemistry," Vol. 1, Mercel Dekker, Inc., New York (1967), p. 249.

5) F. B. Mallory, C. S. Wood and J. T. Gordon, *J. Am. Chem. Soc.*, **86**, 3094 (1964).

TABLE 1. PHYSICAL PROPERTIES OF SUBSTITUTED *o*-TERPHENYLS

Compound	X	Mp, °C	Formula	Calcd, %			Found, %		
				C	H	Halogen	C	H	Halogen
3	NO_2	112 — 113.5[a]							
3	NHAc	152.5—153[b]							
3	F	77.5 — 79	$C_{18}H_{13}F$	87.07	5.28		87.02	5.51	
3	Cl	82.5 — 83	$C_{18}H_{13}Cl$			13.39			13.78
3	Br	93 — 94[c]	$C_{18}H_{13}Br$	69.92	4.24	25.84	69.60	4.56	25.84
3	I	116 — 116.5	$C_{18}H_{13}I$	60.70	3.68	35.62	61.19	3.50	35.38
3	OCH_3	61.5 — 62.5	$C_{19}H_{16}O$	87.66	6.19		87.73	6.30	
4	NO_2	118.3—118.5[d]	$C_{18}H_{13}NO_2$			(5.09[h])			(5.10[h])
4	Br	103.5—104.5	$C_{18}H_{13}Br$	69.92	4.24	25.84	69.61	4.42	25.68
5	NO_2	213.5—214[e]							
5	Cl	136 — 136.5	$C_{18}H_{12}Cl_2$	72.26	4.04	23.70	72.48	4.25	24.35
5	Br	168 — 170[f]	$C_{18}H_{12}Br_2$	55.65	3.09	41.26	55.34	3.45	41.17
5	I	224 — 226				52.64			52.01
10		151 — 151.5	$C_{24}H_{17}Br$	74.82	4.44		74.18	4.49	
12		144 — 146	$C_{24}H_{17}I$			29.35			28.56
13		181 — 181.5[g]	$C_{30}H_{22}$	94.20	5.80		94.14	5.85	

a) Lit. 105—106°C,[6] 115.5—116.5°C.[7]
b) Lit. (D. H. Hey, M. J. Perkins and G. H. Williams, *J. Chem. Soc.*, **1961**, 749) 159.5—160.5°C.
c) Prepared by the direct bromination of *o*-terphenyl. Formerly, Woods and Scotti[25] prepared the compound from 2-phenyl-2-cyclohexane by the Grignard reaction (reported mp 89—90.5°C).
d) Lit. 118—119°C.[8] Allen and Burness[7] obtained the compound as a by-product on nitration of *o*-terphenyl, but did not determine the position of the nitro group (reported mp 119.5°C).
e) Lit. 218°C.[6]
f) Lit. 170°C.[6] Since 4,4',4''-tribromo derivative[6] also had a similar mp (170°C), the structure was confirmed by elemental analysis.
g) Lit. 182—184°C.[25]
h) Values for nitrogen.

3,6-disubstituted triphenylene (**8**) may be obtained from **5**. In view of difficulties in preparing triphenylene derivatives possessing a definite structure either by ring construction or by substitution method, the present attempt was designed to provide useful synthetic means for them.

o-Terphenyl derivatives used for the photochemical studies are listed in Table 1. Except for bromides (**3**, **5**/Br),*1 which were obtained by the vapor phase bromination[6] of **1**, other types **3** and **5** compounds were prepared by the diazo reaction of amines (**3**,**5**/NH_2).[6,7] 4'-Nitro-[8] and 4'-bromo-*o*-terphenyls (**4**/NO_2, Br) were prepared by the decomposition of 5-substituted 2-(*N*-nitrosoacetamido)biphenyls in benzene solutions.

The ultraviolet irradiation reactions were performed with a 1-kW high-pressure mercury arc lamp housed in a water bucket, into which a sample solution in a quartz tube was immersed. A typical example is illustrated by the case of fluoride (**3**/F): A dilute benzene solution, 1.67×10^{-2} M, containing an equimolar quantity of iodine was irradiated for 96 hr under nitrogen atmosphere. By column chromatography on alumina, there was obtained a 77% yield of 2-fluorotriphenylene (**6**/F).[9] Structural proof was achieved by UV, IR and analytical data. The results of the photochemical reactions are summarized in Table 2. Physical properties and UV data of the triphenylene derivatives are compiled in Table 3.

Whereas chloride (**3**/Cl) reacted similarly to the fluoride to give a 45% yield of 2-chlorotriphenylene (**6**/Cl), bromide (**3**/Br) was found to afford a complex mixture of the products, consisting of starting material (18%), triphenylene (**2**, 6%), 2-bromotriphenylene (**6**/Br, 26%)[10] and 2-phenyltriphenylene (**7**, 28%)[11] listed in the order of elution from alumina column (Exp. 4).

The photolytic cleavage of a carbon-halogen bond is also responsible for the formation of **2** and **7** from iodide (**3**/I). Total triphenylene fraction

*1 The notation means compounds **3** and **5**, where X=Br.

6) C. F. H. Allen and F. P. Pingert, *ibid.*, **64**, 2639 (1942).
7) C. F. H. Allen and D. M. Burness, *J. Org. Chem.*, **14**, 175 (1949).
8) F. H. Case, *ibid.*, **21**, 477 (1956).
9) P. M. G. Bavin and M. J. S. Dewar, *J. Chem. Soc.*, **1956**, 164.
10) C. C. Barker, R. G. Emmerson and J. D. Periam, *ibid.*, **1955**, 4482.
11) D. D. Lawson and C. M. Buess, *J. Org. Chem.*, **25**, 272 (1960).

TABLE 2. ULTRAVIOLET IRRADIATION REACTION OF SUBSTITUTED *o*-TERPHENYLS (**3**—**5**) AND 2-BROMOTRIPHENYLENE (**6**/Br)[a]

Exp.	Compd.	X	mmol	Iodine mmol	Irrad. time, hr	Triphenylenes, %			*o*-Terphenyls, %	
						6	**2**	**7**	**1**	Recovery
1	**3**	NO_2	1.00	1.01	96					94
2	**3**	F	1.01	1.01	96	77				15
3	**3**	Cl	0.51[f]	0.50	96	45				48
4	**3**	Br	1.03	1.02	96	26	6	28		18
5	**3**	Br	1.03		96					67
6	**3**	I	1.00	1.02	48		36	45		10
7	**3**	I[b]	0.52[f]		24		9	17		31
8	**3**	I[c]	0.50[f]		24		9	—	36	45
9	**3**	I[c]	0.50[f]		72		6	—	37	38
10	**3**	I	1.00		48		18	41		
11	**3**	I[d]	0.52[f]		24			—	37	6
12	**3**	OCH_3	1.00	1.02	48	65	1			
13	**4**	NO_2	1.00	1.02	72					88
14	**4**	Br	1.01	0.99	24	66	14	11		
15	**4**	Br	0.50[f]		24					81
16	**4**	Br[c]	1.00	1.00	46	27	27	—	20	11
17	**5**	NO_2	1.01	1.01	96					[g]
18	**5**	Cl	0.99	1.01	96					60
19	**5**	Cl	0.52[f]	0.52	120					81
20	**5**	Br	1.01	1.00	20					[g]
21	**5**	Br[e]	1.00	1.02	96					35
22	**5**	I[e]	1.01		48					1
23	**6**	Br	0.20[f]	0.25	24	91			—	—
24	**6**	Br	0.50		24	83			—	—

a) Unless otherwise stated, the photochemical reactions in a benzene solution (60 ml) were carried out in a quartz cell using a 1-kW high-pressure mercury lamp under a nitrogen atmosphere.
b) The reaction was carried out under oxygen.
c) Carried out in cyclohexane.
d) Carried out in toluene.
e) Other products are shown in the schemes in the text.
f) Less amount of benzene was used to adjust the concentration to 1.67×10^{-2} M.
g) Infrared spectrum of the product was completely superimposable with that of the starting material.

(**2** plus **7**) amounted to 81% even with shorter irradiation period compared with other halides (Exp. 6). The cleavage of the carbon-iodine bond was so extensive that only isolable iodo compound was a small amount of starting material and no 2-iodotriphenylene (**6**/I) was detected.

The extensive cleavage of the carbon-iodine bond suggested that the liberated iodine might serve as an oxidant to induce the oxidative aryl coupling reaction. That this was indeed the case was confirmed by the experiments carried out in the absence of iodine (Exp. 7—10). The reaction proceeded similarly with irradiation under oxygen (Exp. 7), which itself was ineffective as an oxidant to bring about the cyclization.[2] In contrast, no cyclization occurred when bromides (**3**, **4**/Br) were irradiated in the absence of iodine (Exp. 5, 15).

Although the studies on the photolysis of iodoaromatic compounds date back to 1924 when Job and Emschwiller[12] investigated bond strength of a carbon-iodine bonding, the mechanistic aspects and synthetic applicability have been explored only quite recently.[13] Lately, intermolecular as well as intramolecular aryl coupling reactions induced by the photolysis of iodoaromatics have found wide application not only for the formation of polyphenyls and phenanthrenes but also for the complex natural product[14] and heterocyclic compounds.[15-17]

12) A. Job and G. Emschwiller, *Compt. rend.*, **179**, 52 (1924).
13) W. Wolf and N. Kharasch, *J. Org. Chem.*, **30**, 2493 (1965). Refer to the literatures cited in this paper for earlier studies in this field.
14) S. M. Kupchan and H. C. Wormer, *Tetrahedron Letters*, **1965**, 359; S. M. Kupchan and H. C. Wormer, *J. Org. Chem.*, **30**, 3792 (1965).
15) P. W. Jeffs and J. F. Hansen, *J. Am. Chem. Soc.*, **89**, 2798 (1967).
16) H. S. Thyagarajan, N. Kharasch, H. B. Lewis and W. Wolf, *Chem. Commun.*, **1967**, 614.
17) S. M. Kupchan and R. M. Kanojia, *Tetrahedron Letters*, **1966**, 5353.

TABLE 3. PHYSICAL PROPERTIES OF 2-SUBSTITUTED AND 3,6-DISUBSTITUTED TRIPHENYLENES

Compound	X	Mp, °C	Formula		Anal, % Calcd	Anal, % Found	λ_{max} (log ε)
6	F	181.5[a]	$C_{18}H_{11}F$	C H	87.80 4.49	88.05 4.49	248(4.85), 257(5.08), 271(4.10),[f] 283(4.08), 303(3.32), 313.5(2.83), 320.5(2.67), 328.5(2.87), 335(2.60), 344(2.84)
6	Cl	143.5—144.5	$C_{18}H_{11}Cl$	C H	82.30 4.22	82.59 4.28	250.5(4.56), 259(4.79), 274.5(3.38), 286(3.83), 305(3.02), 314.5(2.46),[f] 322.5(2.32), 330.5(2.10),337.5(2.19), 346.5(1.97)
6	Br	129—131[b]	$C_{18}H_{11}Br$				252(5.18), 260.5(5.41), 275(4.56), 287(4.57), 307.5(3.80), 316(3.10),[f] 323.5(2.96), 331(2.91), 338(2.82), 347(2.48)
6	OCH_3	110—111[c]	$C_{19}H_{14}O$	C H	88.34 5.46	88.07 5.25	254(4.86), 262(5.04), 277(4.20),[f] 287.5(4.16), 320(3.16), 327(2.94), 335(3.26), 343(2.84), 351(3.25)
7		180.5—181[d]	$C_{24}H_{16}$	C H	94.70 5.30	94.62 5.33	260(4.78),[f] 267.5(4.86), 287.5(4.39),[f] 301(4.29)[f]
8	Cl	172—179	$C_{18}H_{10}Cl_2$[e]				
8	Br	232—234	$C_{18}H_{10}Br_2$	C H	56.00 2.61	56.61 2.79	253(3.89), 263(4.12), 277(3.30),[f] 287(3.21),[f] 309.5(2.47),[f] 319(1.94),[f] 326(1.75), 334.5(1.71), 341(1.56), 350(1.43)
11		153—155	$C_{24}H_{15}Br$	C H	75.22 3.93	75.66 4.01	271, 298,[f] 307[f]
14		262—263	$C_{30}H_{20}$	C H	94.70 5.30	94.52 5.17	276, 307[f]

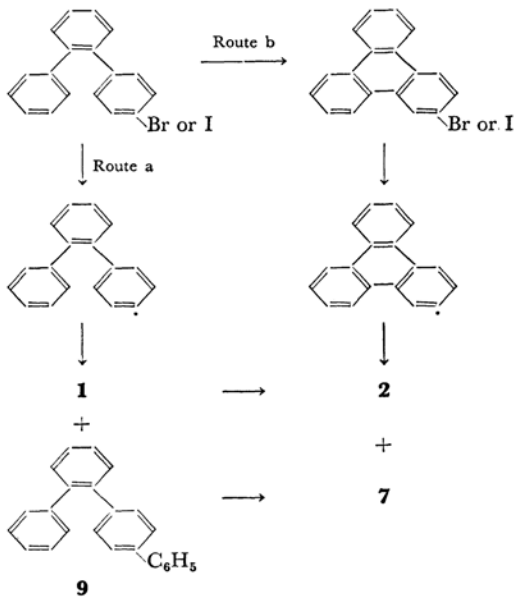
a) Lit. 185—185.5°C.[9]
b) Lit. 131—132°C.[10] No mp depression on admixture with the authentic material obtained by the bromination[10] of **2**.
c) Lit. (W. S. Rapson, *J. Chem. Soc.*, **1941**, 15) 97—98°C.
d) Lit. 183—184°C.[11]
e) Determined by mass spectroscopy, *m/e* 296.
f) Shoulders.

These arylation reactions are assumed[13] to be initiated by the formation of an aryl radical which attacks a benzene nucleus to give an arylcyclohexadienyl radical, dehydrogenation of which with iodine then terminates the reaction. The formation of phenylation products from halogeno-*o*-terphenyls may follow similar steps.

As more closely related studies, Kampmeier and Hoffmeister[18] have shown that the photolysis of 1,2-diiodobenzene in a benzene solution leads to the formation of a small amount of **2** (4% after 175 hr). Similarly irradiation of 2-iodobiphenyl for 60 hr also led to **2** in a small yield.[13,18] The cyclization step leading to **2** and **7** in the present cases would be similar with these.

There are two routes which may account for the formation of **2** and **7**, namely routes a and b:

Route a is initiated by the homolysis of a carbon-halogen bond to give *o*-terphenyl radical, which, *via* *o*-terphenyl (**1**) and 1,1′ : 2′,1″ : 4″,1‴-quaterphenyl (**9**),[3] cyclizes to **2** and **7**. In the alternative route b, cyclization reaction occurs first to afford 2-halogenotriphenylenes (**6**), which then loses a halogen atom by the homolytic cleavage.



18) J. A. Kampmeier and E. Hoffmeister, *J. Am. Chem. Soc.*, **84**, 3788 (1962).

Hydrogen abstraction and phenylation of triphenylene radical thus formed yield **2** and **7**. Whether a given halogeno-*o*-terphenyl decays after either the two competitive routes a or b is determined by the bond energies of the carbon-halogen linkage and the rate of aryl coupling reaction.

The fact that the ease with which the cyclization occurs is related to the electron density on the terminal benzene rings is illustrated by the extreme cases of three nitro derivatives (**3**—**5**/NO_2), which have been recovered unchanged even after 77—96 hr irradiation (Exp. 1, 13, 17). The results could be compared with a facile reaction of methoxy derivative (**3**/OCH_3), which afforded the expected 2-methoxytriphenylene (**6**/OCH_3) in a 65% yield together with a small amount of triphenylene[19] (Exp. 12). This electronic effect is assumed to be operated among halides **3**, although in a less degree. Another factor, carbon-halogen bond cleavage, however, becomes important only with bromides[23,24] and especially with iodides.[13]

Bond energy considerations favor route a over route b, since a halogen atom is more firmly attached to the resonance-stabilized triphenylene ring than to *o*-terphenyl moiety. Evidence indicated that **2** and **7** arose *via* route a were obtained in the following manner: i) 2-Bromotriphenylene (**6**/Br), the intermediate for route b, was shown to be quite stable (Exp. 23, 24). ii) Obviously, the cyclization of iodide (**3**/I) in the absence of iodine requires the carbon-iodine cleavage as the initial reaction. Further, the fact that the efficiency of the cyclization of the iodide was comparable to **1** itself and was much more rapid than other halides, suggested the loss of iodine in an earlier stage of the reaction.

These results showed that, whereas bromide (**3**/Br) decayed in both ways, the ratio of route a and route b in 3 : 4, iodide (**3**/I) followed most probably after route a and that the cleavage of the carbon-iodine bond ocurred much more rapidly than the cyclization reaction. Comparing between isomeric bromides (**3**, **4**/Br), 4-isomer afforded **6**/Br in a higher yield (66% compared with 26%) even with shorter reaction time (Exp. 4 *vs.* 14).

The reactions in cyclohexane or toluene afforded a reduction product. Thus *o*-terphenyl was isolated in a 36—37% yield by the irradiation of iodide (**3**/I) in a cyclohexane solution (Exp. 8, 9), in which the photo-aryl coupling reaction proceeds more slowly than in benzene (Exp. 10). The photolysis in toluene also afforded a 37% yield of **1** (Exp. 11). Similarly **1** was obtainable in a 20% yield by the irradiation of bromide (**4**/Br) in cyclohexane (Exp. 16).

Ultraviolet irradiation of dihalides (**5**/Cl, Br) revealed that the reactions were even difficult compared with monohalides as evidenced by the higher rates in the starting material recovery (Exp. 18, 19, 20, 21). Dichloride (**5**/Cl) afforded only a trace amount of **8**/Cl, which was characterized by the mass spectrum (parent peak had *m/e* 296).

If the cleavage of a carbon-halogen bond is to occur as above, then, a complex mixture of the products would be expected from the dihalides **5**. The replacement of the halogen atom by a hydrogen or phenyl group would give rise to five *o*-terphenyl structures. They include those *o*-terphenyls **1**, **3**, and **9** of which cyclization and transformation products would be similar to those of the monohalides. New types of *o*-terphenyl derivatives are 4-halogeno-4''-phenyl-*o*-terphenyl (such as **10** and **12**) and 1,1' : 4',1'' : 2'',1''' : 4''',1''''-quinquephenyl (**13**).[25]

Chromatography on alumina of the reaction mixture obtained from dibromide (**5**/Br) afforded four compounds (Exp. 21), among which the starting material was shown to be present in the largest amount (35%). Other compounds, identified by IR, UV and analytical data, were shown in the accompanying scheme (in the order of elution from the column). Diiodide (**5**/I) afforded five compounds which were separated by column chromatography on alumina (Exp. 22). Small amounts of the starting material (1%) and monoiodide (**3**/I, 1%) were eluted first, followed by three compounds as were shown in the scheme. When the reaction was further continued for 7 days, iodo compounds were found to be completely transformed into phenylation and reduction products. Thus only three hydrocarbons were isolated; they were 32% of the quinquephenyl (**13**), 5% of 2-phenyltriphenylene (**7**) and 37% of 3,6-diphenyltriphenylene (**14**). By an independent experiment, the irradiation of **13**, in the presence of iodine, was shown to yield **14** (9% after 92 hr). All the compounds had IR and UV spectra consistent with the assigned structures. Spectral

19) The formation of triphenylene was clearly demonstrated by gas chromatography. It could possibly be formed by carbon-oxygen cleavage of either **3**/OCH_3 or **6**/OCH_3. A small amount of phenolic material was also detected. Photolytic cleavage of ether linkage was noticed by several authors.[20-22] As another model compound having electron-releasing group 4-acetamido-*o*-terphenyl (**3**/$NHCOCH_3$) was irradiated, but soon after the start of the reaction, the compound began to separate out on the wall of the vessel and the reaction had to be discontinued.

20) M. S. Kharasch, G. Stampa and W. Nudenberg, *Science*, **116**, 309 (1952).

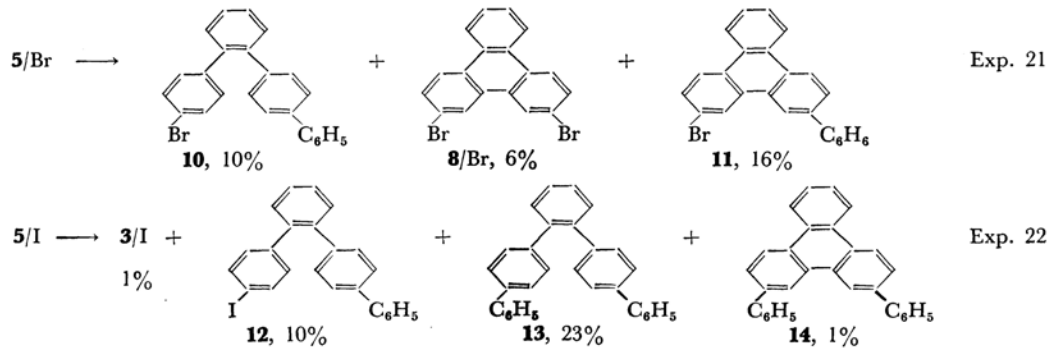
21) J. D. Margerum, J. N. Pitts, Jr., J. G. Rutgers and S. Searles, *J. Am. Chem. Soc.*, **81**, 1549 (1959).

22) C. S. Wood and J. B. Mallory, *J. Org. Chem.*, **29**, 3373 (1964).

23) S. M. Kupchan and H. C. Wormer, *Tetrahedron Letters*, **1965**, 359.

24) T. Matsuura and K. Omura, This Bulletin, **39**, 944 (1966).

25) G. F. Woods and F. Scotti, *J. Org. Chem.*, **26**, 312 (1961).



data and analytical figures are compiled in Tables 1 and 3. The formation of **13** and **14** suggested the potential utility of the present method for the synthesis of polyphenyls and their condensation products, such as phenyltriphenylenes.[26]

Of the triphenylene derivatives here obtained, the UV spectra of 2-fluoro- (**6**/F)[8] and 2-phenyltriphenylenes (**7**)[11] were recorded previously. Triphenylene and its derivatives usually display up to ten absorption bands (or shoulders) in the UV region. Slight bathochromic shifts, amounting 2—3 mμ, of each bands occurred with chloride (**6**/Cl) and bromide (**6**/Br) compared with the fluoride. 3,6-Dibromotriphenylene (**8**) showed a quite similar spectrum with the monohalides with slightly more bathochromic shifts (3—6 mμ from **6**/F). Attachment of a phenyl group simplified the spectrum enormously; thus only one peak at 268 mμ, together with three shoulders, were observed for **7**. Similarly, the absorption curves for 3-bromo-6-phenyl- (**11**) and 3,6-diphenyltriphenylenes (**14**) were similar to that of **7**, except that the absorption maximum was shifted to a long wavelength by 3 and 8.5 mμ respectively.

In conclusion, it was found that, with the exception of the iodides, introduction of two halogen substituents at the terminal benzene rings of *o*-terphenyl moiety retards the cyclization reaction significantly, whereas, introduction of one halogen substituent does it only moderately. On the other hand, the presence of a bromine substituent on the central benzene ring does not affect the reaction rate. The fact that benzene is superior over cyclohexane as the solvent for the photo-aryl coupling reaction strongly suggested the importance of the aromatic solvent as a good sensitizer.[13,27,28]

Experimental[29]

Materials. *o*-Terphenyl derivatives subjected to photochemical studies are tabulated in Table 1. Of these, six are known compounds. New syntheses and modifications of known methods will be briefly described.

4-Fluoro-*o*-terphenyl (3/F). To a diazonium chloride solution prepared from 4-amino-*o*-terphenyl (**3**/NH_2),[6] a 42% solution of fluoroboric acid was added. The resulting diazonium fluoroborate was decomposed thermally[30] and the reaction mixture was extracted with benzene. The fluoride (**3**/F) was obtained as colorless prisms, mp 77.5—79°C (recrystallized from *n*-hexane).

4-Chloro- and 4,4''-Dichloro-*o*-terphenyls (3, 5/Cl). They were prepared by the Sandmeyer reaction[31] of amines (**3,5**/NH_2).[6,7] The mono- and dichloride were obtained respectively as colorless plates, mp 82.5—83°C and 136—136.5°C (each recrystallized from *n*-hexane).

4-Bromo- and 4,4''-Dibromo-*o*-terphenyl (3, 5/Br). *o*-Terphenyl was brominated with bromine vapor after the method of Allen and Pingert.[6]

The dibromide was obtained as colorless plates, mp 168—170°C (recrystallized from *n*-hexane). Since 4,4',4''-tribromo-*o*-terphenyl was reported to have a similar mp (170°C), the structure was confirmed by elemental analysis.

The above bromination reaction was stopped when the reaction mixture started to solidify after remaining a viscous liquid. The reaction product in that case was found to be mainly the monobromide, colorless plates, mp 93—94°C (recrystallized from *n*-hexane). The monobromide was formely prepared[25] from 2-phenyl-2-cyclohexanone by the Grignard reaction.

4-Iodo- and 4,4''-Diiodo-*o*-terphenyl (3, 5/I). They were prepared in the usual way by the decomposition of diazonium or bis(diazonium) chloride with potassium iodide.

The monoiodide was obtained as colorless plates, mp 116—116.5°C (recrystallized from *n*-hexane).

The diiodide was obtained as nearly colorless plates, which discolored on standing, mp 224—226°C (recrystallized from benzene).

4-Methoxy-*o*-terphenyl (3/OCH_3). 4-Hydroxy-*o*-terphenyl was prepared by the decomposition of the diazonium sulfate made from **3**/NH_2. Without further

26) The photolytic bisphenylation of diiodopolyphenyls would become a general synthetic method of polyphenyls having two more benzene rings. Studies on this matter will be reported elsewhere.

27) H. Morrison, *J. Am. Chem. Soc.*, **87**, 932 (1965).

28) F. Wilkinson, *J. Phys. Chem.*, **66**, 2569 (1962).

29) All melting points are uncorrected. UV spectra were recorded on a Cary 15 spectrophotometer. The authors are grateful to Mr. H. Kohashi of Osaka University for providing us with the data. Gas chromatography was performed with Hitachi K 53 chromatograph using 5% silicone gum XE-60 on Chromosorb W. column.

30) A. Roe, *Organic Reactions*, **5**, 193 (1957).

purification, it was methylated with dimethyl sulfate, colorless plates, mp 61.5—62.5°C (recrystallized from *n*-hexane).

4'-Bromo-*o*-terphenyl (4/Br). 2-Acetamido-5-bromobiphenyl,[32] mp 130°C, was nitrosated with nitrosyl chloride and was decomposed in a benzene solution in the usual manner.[33] The bromide was purified by passing through alumina column as a benzene solution, and was obtained as colorless plates, mp 103.5—104.5°C (recrystallized from *n*-hexane).

4'-Nitro-*o*-terphenyl (4/NO_2). It was prepared by the decomposition of 5-nitro-2-(*N*-nitrosoacetamido)-biphenyl,[8,34] mp 133°C, in a benzene solution following the method of Case,[8] colorless plates, mp 118.3—118.5°C (recrystallized from *n*-hexane). The compound was reported to be obtainable as a minor product by the direct nitration of *o*-terphenyl and once was referred to as *x*-nitro-*o*-terphenyl, mp 119.5°C.[7]

Photochemical Reactions. *General Procedure.* A sample solution (1.67×10^{-2} M) in a quartz vessel equipped with gas inlet and outlet tubes, was irradiated externally with a 1-kW high-pressure mercury arc lamp (Wako HBC-1000) immersed in a bucket. Cooling was given by running water. During the irradiation a stream of nitrogen (or air) was bubbled through the solution.

The results of photolysis studies are summarized in Table 2. Analysis of the reaction products were performed by column chromatography on alumina, which was eluted with a mixture of *n*-hexane and benzene of varying ratio. A fraction of approximately 100 m*l* was collected. Identification of *o*-terphenyl and triphenylene were also achieved by gas chromatography, though the use of which was limited to a few cases.

The physical properties and UV data of triphenylene derivatives prepared in this study are summarized in Table 3. Since the reaction conditions are given in Table 2, and the work-up procedure of the reaction mixtures from nitro-, fluoro-, chloro-, and methoxy-*o*-terphenyls are straight-forward, only representative experiments on bromides and iodides are briefly mentioned.

4-Bromo-*o*-terphenyl (3/Br). *Exp. 4.* A solution of 319 mg (1.03 mmol) of **3**/Br, 260 mg (1.02 mmol) of iodine in 60 m*l* of benzene was irradiated under nitrogen for 96 hr. After the irradiation reaction was over, the solution was successively washed with sodium thiosulfate solution and water, and was dried over magnesium sulfate. The product was then subjected to column chromatography on alumina using a 10 : 1 mixture of *n*-hexane - benzene as an eluent. By checking the elutes with IR spectra, the products were separated into the following four fractions; 56.5 mg (18%) of **3**/Br, mp 93—94°C (colorless plates from *n*-hexane), 14.2 mg (6%) of **2**, mp 193—194°C (colorless needles from ethanol), 81.3 mg (26%) of **6**/Br,[10] mp 129—131°C (colorless needles from acetone) and 88.2 mg (28%) of **7**,[11] mp 180.5—181°C (colorless needles from ethanol).

Exp. 5. When irradiated in the absence of iodine, the starting material was completely recovered.

4-Iodo-*o*-terphenyl (3/I). *Exp. 10.* A benzene solution of 356 mg (1.00 mmol) of **3**/I was irradiated for 48 hr. By chromatography on alumina, eluted with a 4 : 1 *n*-hexane - benzene mixture, there were obtained 37.1 mg (18%) of **2** (fractions 14—20) and 113 mg (41%) of **7** (fraction 30~).

Exp. 8, 9 and 11. The photolysis in cyclohexane or toluene yielded *o*-terphenyl, which was eluted first from alumina column.

4'-Bromo-*o*-terphenyl (4/Br). *Exp. 14.* A solution of 311 mg (1.01 mmol) of **4**/Br, 250 mg (0.99 mmol) of iodine in 60 m*l* of benzene was irradiated under nitrogen for 24 hr. By chromatography on alumina, eluted with a 9 : 1 *n*-hexane - benzene mixture, there were obtained 31.3 mg (14%) of **2** (fractions 70—76), 204.5 mg (66%) of **6**/Br (fractions 77—120) and 34.2 mg (11%) of **7** (fractions 126—132).

Exp. 16. The irradiation reaction products were first eluted with *n*-hexane, which afforded 44.9 mg (20%) of **1** (fractions 20—30) and 34.9 mg (11%) of **4**/Br (fractions 32—42). The solvent was switched to a 9 : 1 *n*-hexane - benzene mixture to obtain 61.5 mg (27%) of **2** (fractions 61—80) and 83.0 mg (27%) of **6**/Br (fractions 82~).

4,4''-Dibromo-*o*-terphenyl (5/Br). *Exp. 21.* A solution of 388 mg (1.00 mmol) of **5**/Br, 259 mg (1.02 mmol) of iodine in 60 m*l* of benzene was irradiated under nitrogen for 96 hr. The reaction product was analyzed by column chromatography on alumina. After elution with *ca.* 1400 m*l* *n*-hexane, the eluent was changed to a 9 : 1 *n*-hexane - benzene mixture. Starting material (135.2 mg, 35%) came out first (fractions 20—25) which was followed by 39.6 mg (10%) of **10**, mp 151—151.5°C as colorless plates from *n*-hexane (fractions 43—44), 21.8 mg (6%) of **8**/Br, mp 232—234°C as colorless needles from *n*-hexane (fractions 46—48) and 63.0 mg (16%) of **11**, mp 153—155°C, as colorless amorphous material from ethanol (fractions 64—75).

4,4''-Diiodo-*o*-terphenyl (5/I). *Exp. 22.* A solution of 484 mg (1.01 mmol) of **5**/I in 60 m*l* of benzene was irradiated under nitrogen for 48 hr. Since the reaction mixture discolored considerably due to liberated iodine after about 26 hr, it was necessary to remove it by washing the reaction mixture with sodium thiosulfate solution. By column chromatography on alumina, there were obtained five fractions by elution with a 9 : 1 *n*-hexane - benzene mixture; 5.5 mg (2%) of **3**/I (fractions 8—10), 7.2 mg (1%) of **5**/I (fractions 15—19), 42.1 mg (10%) of **12**, mp 144—146°C as colorless plates from *n*-hexane (fractions 39—55), 88.9 mg (23%) of **13**, mp 181—182°C as colorless plates from *n*-hexane (fractions 65—115) and 5.5 mg (1%) of **14** as colorless needles (fractions 116~).

Photochemical conversion of **13** to **14** was confirmed by an independent experiment, in which 50 mg of **13** and 35 mg of iodine in a benzene solution (15 m*l*) was irradiated for 92 hr. By chromatography on alumina, **14**, mp 262—263°C, was isolated in a 9% yield. Quinquephenyl **13** was recovered in 71% yield.

The authors are indebted to the members of the analytical section of the Institute of Physical and Chemical Research for carrying out microanalyses.

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32) H. A. Scarborough and W. A. Waters, *J. Chem. Soc.*, **1927**, 94.

33) W. E. Bachmann and R. A. Hoffman, *Org. Reactions*, **2**, 224 (1957).

34) F. Bell, *J. Chem. Soc.*, **1928**, 2773.