BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN VOL. 43 2217—2222 (1970)

Studies on Fluorene Derivatives. XXVI.[1] Radical Reactions in the Copyrolysis of Thermally-reactive Tribiphenylenepropanes

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(Received January 30, 1970)

The pyrolyses of thermally-reactive tribiphenylenepropanes (mp 293°C (dec) or 257°C (dec)) in the presence of thermally-reactive 2,7,2′,7′,2″,7″-hexabromotribiphenylenepropane (mp 318—320°C (dec)) were investigated. Hydrocarbons, 2′,7′,2″,7″-tetrabromotribiphenylenepropane, 2,7-dibromo-9,9′-bifluorenyl, and -bifluorenylidene were obtained as pyrolysates from the respective thermal reactions, probably from intermolecular radical disproportionation reactions. In addition, 2,7,2′,7′-tetrabromo-9,9′-bifluorenyl, -bifluorenylidene, 2,7-dibromo-fluorene, and -fluorenone from hexabromotribiphenylenepropane, and 9,9′-bifluorenyl, -bifluorenylidene, fluorene, and fluorenone from tribiphenylenepropanes were formed by intramolecular reactions attributed to radical formation in the pyrolysis of each substrate. The pyrolyses of both tribiphenylenepropanes, 9,9′-bifluorenyl and 2,7,2′,7′,2″,7″-hexabromotribiphenylenepropane, were observed in a differential scanning calorimeter. The thermogram of tribiphenylenepropane (mp 257°C) is similar to that of 9,9′-bifluorenyl; the first endothermic peak corresponds to the melting point, and the second, broad one seems to be due to the slow formation of 9,9′-bifluorenylidene from 9,9′-bifluorenyl by means of a dehydrogenation process. In the thermogram of tribiphenylenepropane (mp 293°C), the first endothermic peak is the melting point, while the second, small one is probably caused by the overlapping of exothermic and endothermic peaks due to radical reactions during the formation and pyrolysis of tribiphenylenepropane (257°C). The thermal homolyses of solid tribiphenylenepropane isomers or those in a silicon oil solution were examined by ESR, which confirmed the radical formation in the pyrolyses.

Tribiphenylenepropanes were obtained by the Michael reaction[2] of 9,9′-bifluorenylidene (**3**) and

1) XXV of this series: K. Suzuki, M. Minabe, M. Fujimoto and N. Nohara, This Bulletin, **42**, 1609 (1969).

2) a) K. Suzuki, *Nippon Kagaku Zasshi*, **70**, 189 (1949). b) L. A. Pinck and G. E. Hilbert, *J. Amer. Chem. Soc.*, **68**, 2014 (1946).

fluorene (**13**), by the condensation of **13** with sodium amide, and by other reactions.[3] One of the isomers (mp 257°C (dec)), (**2**), is converted to the other (mp 293°C (dec)), (**1**), by the action of *N*-bromosuccinimide or Triton B.[4] We have found that the reverse process occurs during pyrolysis.

Compound **1** gave two isomers, **2** and **3**, and 9,9′-bifluorenyl (**4**) by pyrolysis, while **2** gave **3** and **4**.[2a] Additionally, 2,7,2′,7′,2″,7″-hexabromotribiphenylenepropane (**5**) yielded 2,7,2′,7′-tetrabromo-9,9′-bifluorenyl (**6**), -bifluorenylidene (**7**), and 2,7-dibromofluorenone (**12**) by pyrolysis.[5] Previously, homolytic fission was proposed as the mechanism for the formation of **2**, **3**, **4**, **6**, and **7**.[6]

The current investigation deals with the confirmation of the reaction products formed by intermolecular radical reactions during the thermolyses of tribiphenylenepropanes in the presence of **5**.

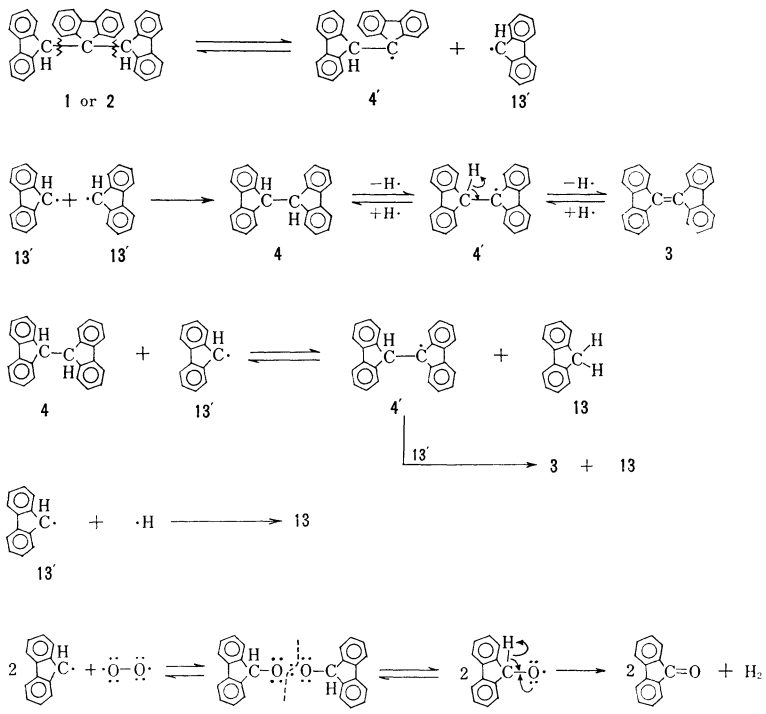
In a preliminary experiment,[2a] **13** and fluorenone (**14**) could not be isolated. A re-investigation of the pyrolysis of tribiphenylenepropane isomers showed that **1** gave **2**, **3**, **4**, **13**, and **14**, while **2** gave **3**,**4**, **13**, and **14**, as confirmed by gas-chromatographic analysis. The data are listed in Table 1.

Moreover, for the purpose of studying the thermal behavior, a differential scanning calorimeter (DSC) was employed which showed exothermic or endothermic peaks depending on the combination of physical and chemical changes proceeding at the reaction temperature. The formation of free radicals was confirmed by ESR.

Compounds **4**, **1**, **2**, and **5** are thermally-active species, each possessing two active methine groups. Under the pyrolytic conditions, the six carbon-bromine bonds in **5** are more stable than the 9-9′-9″ carbon-carbon covalent bonds in tribiphenylenepropanes.

Accordingly, the pyrolysates, **2**, 2′,7′,2″,7″-tetrabromotribiphenylenepropane (**8**), **6**, **7**, 2,7-dibromo-9,9′-bifluorenyl (**9**), -bifluorenylidene (**10**), **3**, 2,7-dibromofluorene (**11**), **12**, **13**, and **14** were observed by the copyrolysis of **1** and **5** at 320—330°C. Also, by the same process, **8**, **6**, **7**, **9**, **10**, **3**, **4**, **11**, **12**, **13**, **14**, and 2% of recovered **2** were obtained by the copyrolysis of **2** and **5** at 330—340°C.

In view of these results, it appears that all compounds participate in the fission of 9-9′-9″ carbon-carbon bonds in tribiphenylenepropanes. Moreover, the formation of the three structures, **8**, **9**, and **10**, can be explained in terms of intermolecular free radical reactions based on the thermal homolyses between the two different bromo- and nonbromo-tribiphenylenepropanes precursors. Schemes I and II summarize the pyrolytic pathways suggested for



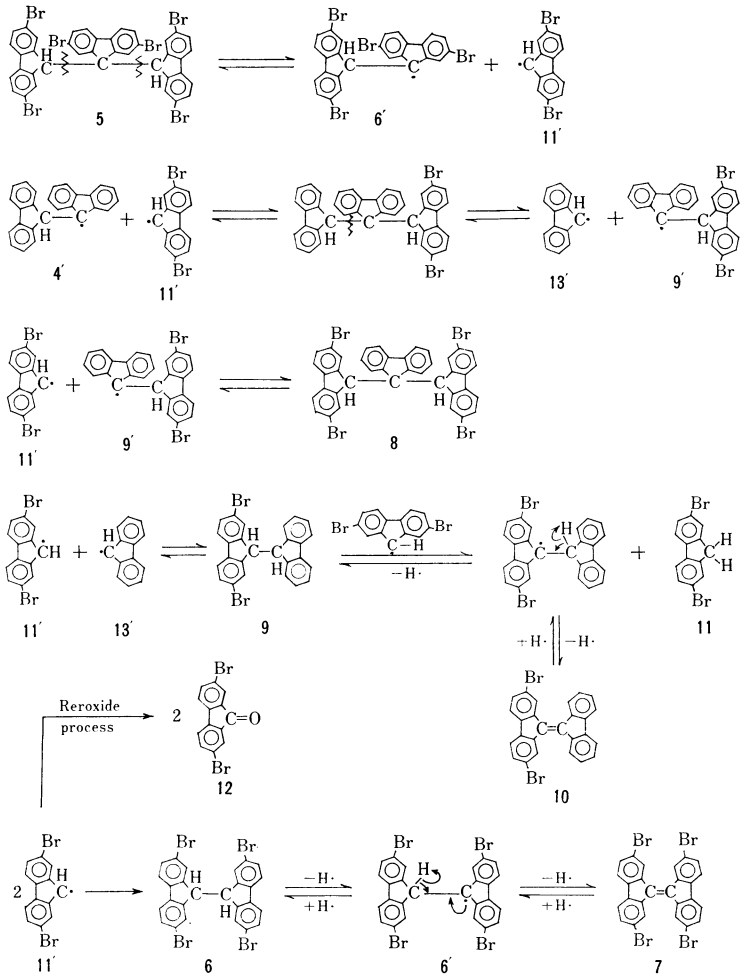
Scheme I. Pyrolyses of tribiphenylenepropanes.

3) a) K. Suzuki, *Nippon Kagaku Zasshi*, **72**, 825 (1951). b) K. Suzuki, *ibid.*, **72**, 827 (1951); **75**, 711 (1954); K. Suzuki and S. Kajigaeshi, This Bulletin, **35**, 408 (1962); K. Suzuki and M. Fujimoto, *ibid.*, **37**, 1833 (1964); K. Suzuki, M. Minabe, M. Fujimoto and N. Nohara, *ibid.*, **42**, 1609 (1969).

4) K. Suzuki and M. Minabe, unpublished.

5) K. Suzuki, *Nippon Kagaku Zasshi*, **75**, 795 (1954).

6) K. Suzuki, *Technol. Repts. Tohoku Univ.*, **19**, 63 (1955).



Scheme II. Pyrolyses of tribiphenylenepropanes in the presence of 2,7,2′,7′,2″,7″-hexabromotribiphenylenepropane (**5**).
(Compounds **6**, **7**, **8**, **9**, **10**, **11** and **12** were isolated.)

the formation of these compounds.

The 9-fluorenyl (**13′**) and 9-fluorenyl-9′-fluorenylidene (**4′**) radicals were presumably formed in the initial homolytic fission of **1** or **2**. A coupling reaction of **13′** could occur in the melt to give **4**, while the unsaturated hydrocarbon, **3**, may have been formed by dehydrogenation during the pyrolytic process.[2a] The formation of **13** can be explained by hydrogen abstraction from **4′** or **4** by **13′** during the formation of **3** and/or by reaction of **13′** with a hydrogen radical.

Tribiphenylenepropane (mp 257°C), (**2**), may be formed by a re-combination of the **4′** and **13′** radicals in a different steric configuration from that of the compound with a mp of 293°C (**1**). The coupling product of **4′** could not isolated; if this were formed, it might lead to the formation of **3** and **13′** by pyrolysis.

In addition, **14** was probably formed from **13′**, in the presence of trace amounts of air, *via* a peroxide mechanism by simple scission on the oxygen-oxygen bond to radicals analogous to that which would occur in peroxide, as is indicated in Scheme I.

Accordingly, the formation of compounds **6**, **7**, and **11** seems reasonable in these instances by combinations of free radical species; this is analogous with the reaction of tribiphenylenepropane, as is illustrated in Scheme II. Likewise, the formation of **12** may be similar to the case of **14**.

Our interpretation is that compound **8** is presumably formed by a combination of dissociation and coupling during the thermal reaction. The free radicals, **4′** and 2,7-dibromo-9-fluorenyl (**11′**), produce by coupling the intermediate, 2′,7′-dibromotribiphenylenepropane,[7] which may then

7) 2′,7′-Dibromotribiphenylenepropane led to 2′,7′,2″,7″-tetrabromotribiphenylenepropane (**8**) and other correlated compounds by pyrolytic reactions (see Ref. 3a).

dissociate into **13′** and 2,7-dibromo-9-fluorenyl-9′-fluorenylidene (**9′**) radicals. Thus, **8** is formed by the reaction of **11′** and **9′** radicals. In addition, **9** may have been formed by a radical reaction of **11′** and **13′**; further, **10** could conceivably result from **9** by a process analogous to that in the case of **3**.

The pyrolysates, **13**, **14**, **4**, and **3**, from **1** or **2**, in order of their retention times, were confirmed by gas-chromatographic analysis. Differential scanning calorimetry was employed to study the thermal behavior of the reactive **1**, **2**, **4**, and **5** on the basis of the pyrolyses described above. These results are illustrated in Fig. 1.

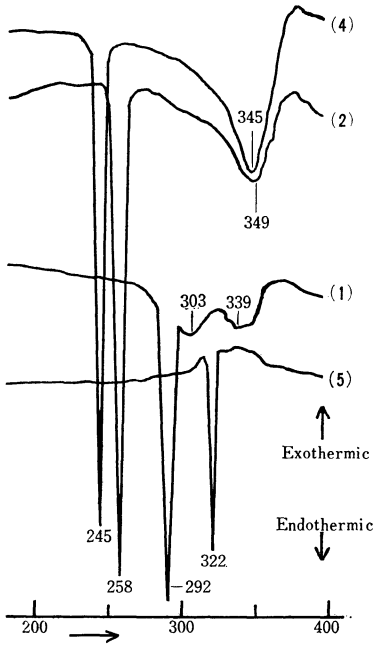


Fig. 1. Differential scanning calorimeter thermograms of **1**, **2**, **4** and **5**.

In the (4) thermogram, **4** (mp 246°C), one of the pyrolysates from **1** or **2**, can be seen to melt at the first endothermic peak (245°C), while the second, broad peak (345°C, dark red) is probably the major constituent due to the slow formation of **3** (red needles) from **4** by dehydrogenation. Moreover, the pyrolysis of **4** is known to form **3**.[2a] In this connection, the application of the DTA method to the pyrolysis of **4** has previously been reported by Lewis and Edstrom,[8] but the curves were not clear.

The two major endothermic peaks for the (2) thermogram are similar to those of **4**; the first peak corresponds to the melting point (red) at about 258°C, but a relatively slow pyrolysis[9] at the melting point was observed, unlike the case with **1**.

8) I. C. Lewis and T. Edstrom, *J. Org. Chem.*, **28**, 2050 (1963).

9) See Table 1, Run 3, for example.

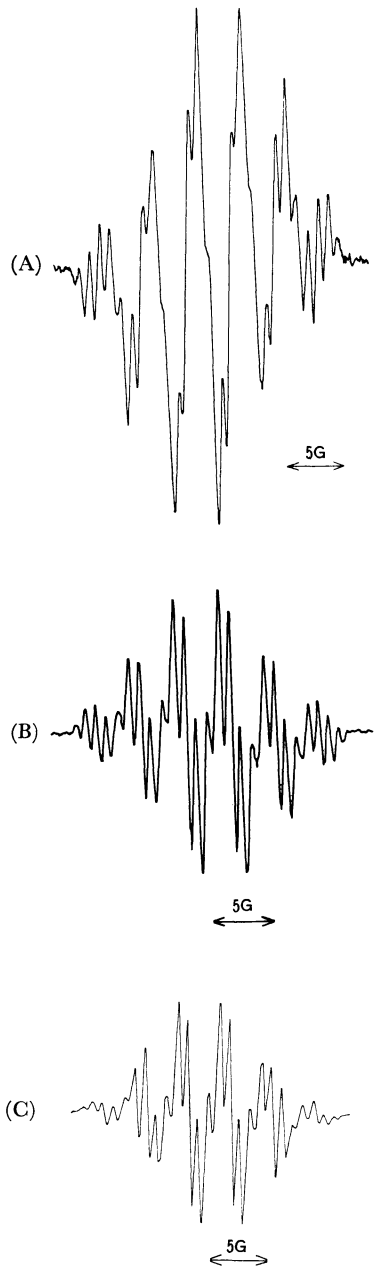
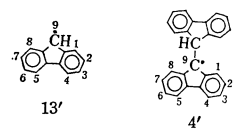


Fig. 2. Experimental spectra generated from the tribiphenylenepropane (**1**).
(A): 280°C
(B): 286°C in silicon oil solution
(C): Simulated pattern of **4′** or **13′**; 5H (1, 3, 6, 8 and 9)=3.67 gauss; 4H (2, 4, 5 and 7)=0.82 gauss; line width=0.65 gauss



Subsequently, the slope curves suggest that the melting depression can be attributed to the progressive formation of compounds **3**, **4**, **13**, and **14** with an elevation of the temperature after the melting peaks. In addition, the broader endothermic peak (349°C) suggests that the **4**→**3** transformation is taking place.

In the thermogram of **1**, the slope curves at 200—280°C as the thermolyses increase with an elevation in the temperature. Indeed, the pyrolysis was accompanied by a readily observable red color change in addition to the temperature rise. Thus, the melting peak (292°C) is relatively small compared with that of **2**, although equal weights of the **1** and **2** isomers were used. The results of ESR show that the pyrolyses of tribiphenylenepropane isomers begin at about 200°C. The first, small peak (303°C) after the melting point suggests the formation of **2** from **1** with a consequent pyrolysis of **2** (mp 257°C), as has been described above. Accordingly, the peaks overlap as a result of compensation by exothermic and endothermic peaks. The endothermic peak (339°C) might correspond to the formation of **3** from **4**.

Although the sample weight of **5** used was roughly equal to those of **1** or **2**, the melting peak (322°C) of **5** is comparatively small; **5**, therefore, corresponds to double the molecular weight.

The solid compounds, **1**, **2**, and **4**, were degassed and their ESR spectra were measured in the range from about 200°C to near their melting points. The signals obtained from each sample were very similar. A typical pattern of **1** is shown in Fig. 2. The signal measured in a silicon oil solution is in sharp contrast to that observed in a solid sample. The same results were observed in a squalane solution instead of in the silicon oil.

As is shown by the simulation calculations, these spectra can be explained in terms of the hyperfine interaction with five equivalent protons with a large splitting constant and four equivalent protons with a small splitting constant. These splitting constants may be attributed to the two radicals, **4′** and/or **13′** (see Fig. 2). Previously Dalton and Liebman[10] observed the fluorenyl radical, **13′**, generated from 9-diazofluorene in decalin at 170°C. The ESR spectra observed in the present work are, however, in poor agreement with those observed by Dalton *et al.* Therefore, the radical is conceivably **4′** rather than **13′**.

Experimental

All the melting points are uncorrected.

The gc data were obtained with a JGC-810FP apparatus (Japan Electron Optics Lab. Co., Ltd.), using a column containing 10% Silicone SE-30 on Chromosorb W-AW. During analysis, the column temperature was programmed at 304°C, while the detector and injector temperatures were maintained at 340°C and 400°C respectively. Samples **1** and **2** were used as 2% chloroform solutions.

The infrared spectra were recorded as KBr pellets using a JASCO model IR-G spectrophotometer (Japan Spectroscopic Co., Ltd.).

Differential scanning calorimeter. The instrument used in this investigation was of the Desktop type, 8001-CS (Rigaku Denki Co., Ltd.), was equipped with α-aluminum oxide as a standard sample, and had a sensitivity of ±4 mcal/sec. The experiments were run at atmospheric pressure in air at a heating rate of 10°C per minute. Samples **4** (13.3 mg), **1** (18.1 mg), **2** (18.1 mg), and **5** (18.2 mg) were pyrolyzed in sealed aluminum pans (o.d., 5.0 mm; height, 2.0 mm; thickness, 5/100 mm) with aluminum covers (5/100 mm) which were packed with a sample clipper.

The ESR spectrometer used was an X-band JES-3BSX-type apparatus (Japan Electron Optics Lab. Co., Ltd.) with a 100-KHz-field modulation and a variable-temperature insert dewar.

Pyrolysis of Tribiphenylenepropane (1). Finely-powdered **1** (4.94 g or 0.01 mol) was placed in a 300-m*l* Erlenmeyer flask attached to an air condenser. The flask was then heated in a salt-bath to 305—308°C with shaking for 5 min. After 3—4 min, the reactant was a red melt.

After the content of the flask had resolidified, it was ground to a fine powder; this powder was then extracted with 50 m*l* of boiling cyclohexane. The residual portion (mp 245—270°C) was recrystallized from benzene to give 3.52 g (71%) of **2** (mp 257°C (dec)). Upon the evaporation of the benzene mother liquor to a small volume, 0.53 g (11%) of **1** (mp 292—293°C (dec)) was recovered.

The dilution of the last benzene mother liquor with ethanol afforded a yellow precipitate, which was recrystallized from benzene to give 0.14 g (3%) of **4** (mp 243—244°C). The residue from the evaporation of the benzene-ethanol mother solution to dryness was recrystallized from ethanol to give 0.06 g of **3** (mp 185—186°C).

The concentration of the cyclohexane extract to a small volume afforded 0.35 g of **3** (mp 184—185°C). Then the cyclohexane mother solution was evaporated to dryness and the residue was sublimed *in vacuo* at a bath temperature of 140°C, yielding 0.02 g (0.4%) of **13** (mp 110—112°C) and 0.02 g (0.4%) of **14** (mp 77—79°C), which were separated by column chromatography in benzene on alumina. The unsublimable material was recrystallized from benzene to give 0.13 g (total 0.54 g, 11%) of **3** (mp 183—185°C).

Pyrolyses of Tribiphenylenepropane (1) in the Presence of 2,7,2′,7′,2″,7″-Hexabromotribiphenylenepropane (5). Finely-powdered **1** (3.00 g; 0.006 mol) and 2.90 g (0.003 mol) of **5** were placed in a 300-m*l* Erlenmeyer flask attached to an upright air condenser. When the mixture was heated at 320—330°C for 5 min, it yielded a red pyrolysate after a few minutes.

The powdered product was extracted with 80 m*l* of boiling cyclohexane. The fractional recrystallization of the residue part from 130 m*l* of refluxing benzene yielded 0.06 g of **7** (mp 423—424°C (dec)), 0.05 g of **6** (mp 318—319°C), 0.06 g of **8** (mp 313—314°C (dec)), 0.04 g

10) D. R. Dalton and S. A. Liebman, *J. Amer. Chem. Soc.*, **91**, 1194 (1969).

Table 1. Reaction products in pyrolyses of tribiphenylenepropanes under different conditions

Run	Substrates		Reaction conditions °C×min	Products, g (%)					Recvd. g (%)
	Compds.	g (mol)		**2**	**4**	**3**	**13**	**14**	
1	**1**	4.94 (0.01)	295—300×3.5	0.94 (18)	0.04 (1)	0.11 (2)	0.01 (0.2)	0.12 (2)	3.58 (73)
2	**1**	4.94 (0.01)	305—308×5	3.52 (71)	0.14 (3)	0.54 (11)	0.02 (0.4)	0.02 (0.4)	0.53 (11)
3	**2**	4.94 (0.01)	265—267×5		0.02 (0.4)	0.02 (0.4)	trace	0.01 (0.2)	4.55 (92)
4	**2**	4.94 (0.01)	280—285×10		0.07 (1)	0.09 (2)	0.0014	0.04 (0.7)	4.45 (90)
5	**2**	4.94 (0.01)	260—290×20		2.33 (47)	0.61 (12)	0.20 (4)	0.28 (5)	1.11 (23)
6	**4**	6.6 (0.02)	Rm. temp.→390 (for 40) 390×5			0.66 (10)	1.90 (29)	0.38 (5)	0.80 (12)

of **9** (mp 265—266°C), and 0.10 g of recovered **5** (mp 318—320°C (dec)). These substances were deposited in the order of their decreasing solubilities by the removal of the benzene.

The cyclohexane extract was concentrated to a small volume. The following orange-red crystalline crops were filtered off: 0.19 g (total 0.25 g) of **8** (mp 313—314°C (dec)), 0.51 g (total 0.55 g) of **9** (mp 267—268°C), 0.08 g of **2** (mp 255—257°C (dec)), (no halogen), 0.24 g of **10** (mp 243—244°C), 1.57 g of **3** (mp 182—185°C), 0.17 g of **12** (mp 201—202°C), and a recovered 0.04 g (total 0.14 g) of **5** (mp 315—317°C (dec)). Fractional recrystallization from ethyl acetate was also employed.

The last cyclohexane mother solution was chromatographed on an alumina column. The eluant was evaporated to dryness, and the residue was fractionaly sublimed to 160°C under reduced pressure; 0.03 g of **13** (mp 108—110°C) and 0.01 g of **11** (mp 158—161°C) were thus separated. Fractions of 0.36 g of **14** (mp 79—80°C), (no halogen) and 0.05 g (total 0.22 g) of **12** (mp 195—197°C) were isolated from the yellow-absorbed band on the alumina column by established methods.

Pyrolyses of Tribiphenylenepropane (2) in the Presence of 2,7,2′,7′,2″,7″-Hexabromotribiphenylenepropane (5). A mixture of 3.00 g (0.006 mol) of **2** and **5** (2.90 g, 0.003 mol) was pyrolyzed at 330—340°C for 3 min in an atmosphere of nitrogen. The reaction products were then worked up in a manner similar to those employed in the **1** and **5** reactions. Thus 0.13 g of **7** (mp 428°C (dec)), 0.18 g of **8** (mp 312—314°C (dec)), 0.35 g of **6** (mp 316—317°C), 1.28 g of **9** (mp 268—270°C), 0.33 g of **4** (mp 240—241°C), 0.04 g of **10** (mp 238—240°C), 0.03 g of **13** (mp 111°C), 0.33 g of **14** (mp 79—80°C), 0.04 g of **11** (mp 161—163°C), 0.05 g of **12** (mp 199—201°C), and 0.11 g of **3** (mp 180—182°C) were isolated. In addition, 0.08 g of **5** and 0.64 g of **2** were recovered.

All the pyrolysates were known compounds which were identified by a comparison of their melting points, mixed melting points, and infrared absorption spectra with those of authentic samples.

The authors wish to express their gratitude to Drs. John and Elizabeth Weisburger of the National Institutes of Health, U. S. A., for supplying editorial assistance. Thanks are also due to Mr. Koichi Kubo for measurements of the electron spin resonance, Mr. Fumio Funatani of the Japan Electron Optics Lab. Co., Ltd., for his gas chromatographic analyses, and to Mr. Kimio Satoh of the Rigaku Denki Co., Ltd., for his measurements with the differential scanning calorimeter.

This work was supported in part by a grant-in-aid from the Ministry of Education, for which the authors wish to express their appreciation.