The Radiolysis of Biphenyl by Gamma-rays[*]

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Polyphenyls are the most promising materials for use as organic moderators and coolants. Studies have been developed on the radiolytic and pyrolytic decomposition of these materials. Most of the papers published have, however, concerned the determination of the amount of gaseous products and of the residue with a high boiling point, or gross changes in the physical properties of such materials from engineering points of view.[1-3] Little work has been done on the mechanism of the radiolytic decomposition of polyphenyls.

For the radiolysis of benzene, Patrick and Burton[4] reported that the $G(C_6H_6 \rightarrow \text{polymer})$ value equals 0.75 and that the average polymer contains five molecules of a benzene ring. Gordon et al.[5] studied the reaction further; they identified biphenyl and several types of its partially hydrogenated compounds from the products by means of vapor phase chromatography and mass-spectrometric analysis.

For the identification of radiolytic products of biphenyl, Hellman et al.[6] and West[7]

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1) R. O. Bolt, J. G. Carroll, R. Harrington and R. C. Gilberson, "Proceedings of the Second United Nations International Conference on the Peaceful Uses of Atomic Energy," 29, 276 (1958).

2) C. A. Trilling, ibid., **9**, 468 (1958).

3) D. R. de Halas, *HW-56769* (1958).

4) W. N. Patrick and M. Burton, *J. Am. Chem. Soc.*, **76**, 2626 (1954).

5) S. Gordon, A. R. Van Dyken and T. F. Doumani, *J. Phys. Chem.*, **62**, 20 (1958).

6) M. Hellman, R. L. Alexander and C. F. Coyle, *Anal. Chem.*, **30**, 1206 (1958).

7) W. W. West, *AECU-4699* (1960).

adopted a technique of liquid chromatography, while Boxter and Keen[8] developed high temperature gas chromatography. Hall and Elder[9] and Keen et al.[10] determined mass-spectrometrically the yields of the products with a high molecular weight from the radiolysis of biphenyl, which include terphenyl, quaterphenyl, hexaphenyl and quinquephenyl. Meanwhile, Burr and Scarborough[11] and Rayroux and Baertschi[12] investigated the isotope effect on the radiolysis of biphenyl by using deuterated biphenyl.

From these previous investigations, it is clear that the non-volatile products from the radiolytic decomposition mainly consist of polyphenyls, partially-hydrogenated polyphenyls and condensed polynuclear aromatic compounds. Among these polyphenyls appear to be the major products, but few papers have been published on accurate *G*-values for them. Therefore, the present work will aim to obtain precise information concerning the radiolytic mechanism for biphenyl by determining the *G*-values of the non-volatile products. Here, reverse isotope dilution analysis by using a ^{14}C-labeled compound was applied to determine the isomer yields of the terphenyls and quaterphenyls produced by the radiolysis of biphenyl.

On the basis of the results, the mechanism for the present reaction will be discussed.

An abstract was published previously.[13]

Experimental

Preparation of Materials. — *Biphenyl and Terphenyls.*—Commercial products were recrystallized several times from alcohol or benzene until they reached the melting point indicated in the literature.[14]

o, o'-Quaterphenyl.—This substance was synthesized, starting from *o*-aminobiphenyl, by successive diazotization, Sandmeyer decomposition and Ullmann condensation. To improve the yields, slightly modified procedures were employed.

A sodium nitrite (9 g.) solution was vigorously stirred into a mixture of *o*-aminobiphenyl (22 g.) and 6.5% aqueous hydrochloric acid solution in an ice-bath. Then a potassium iodide (50 g.) solution was added to the mixture, the temperature being kept below 10°C. The reaction product was extracted with ether (150 ml.). The ether extract was washed with water and then with a 10% sodium bisulfite solution, and dried over calcium chloride. After the removal of the solvent, 2-iodobiphenyl (46.0 g.) was distilled at 177~178°C under 18 mmHg. Found: C, 51.35; H, 3.53; I, 45.34. Calcd. for $C_{12}H_9I$: C, 51.45; H, 3.24; I, 45.31%.

In a small test tube, 2-iodobiphenyl was mixed with copper powder and placed in an oil-bath at 260°C for 20 min. The reaction mixture was extracted with benzene. Removal of the benzene, chromatography of the residue on activated aluminia with petroleum ether, and three recrystallizations from ethanol gave *o, o'*-quaterphenyl (3.9 g., 17.5% yield, m. p. 119.1~119.6°C). Found: C, 93.96; H, 5.89. Calcd. for $C_{24}H_{18}$: C, 94.08; H, 5.92%.

m, m'-Quaterphenyl.—The product was obtained, starting from *m*-aminobiphenyl, by a procedure similar to that used for *o, o'*-quaterphenyl (4.3 g., 16.3% yield, m. p. 86.6~87.2°C). Found: C, 94.25; H, 6.08. Calcd. for $C_{24}H_{18}$: C, 94.08; H, 5.92%.

p, p'-Quaterphenyl. — A product of the Pilot Chemical Co. Inc. was recrystallized, first from anisole and then from benzene (m. p. 320.0°C).

Triphenylene.—A product of the Aldrich Chemical Co. Inc. was recrystallized from ethanol (m. p. 200.4°C).

Biphenyl-(phenyl-^{14}C). — The synthesis has been described in previous papers.[15,16]

Procedure. — *Irradiation.* — Biphenyl-(phenyl-^{14}C) (33.2 mc./mol., 30~50 mg.) was placed in an irradiation tube of Hario glass (Fig. 1a) and degassed under 10^{-4}~10^{-5} mmHg in a dry ice-ethanol bath. After the sealing of the tube at the position of the dotted line (Fig. 1a), the glass tube, protected with an aluminum capsule, was heated with an electric furnace, the temperature being kept at 100±5°C. The irradiation was carried out by a Co-60 gamma-facility installed at the Japan Atomic

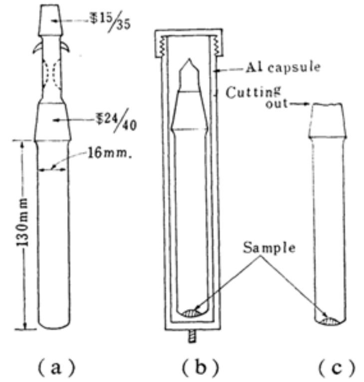

Fig. 1. Irrradiation tube.

(a) Irradiation tube
(b) Irradiation in aluminum capsule after degassing
(c) After irradiation

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[8] R. A. Boxter and R. T. Keen, *NAA-SR-3154* (1959).

[9] K. L. Hall and F. A. Elder, *J. Chem. Phys.*, **31**, 1420 (1959).

[10] R. T. Keen, R. A. Boxter, R. H. J. Gercke and W. L. Orr, *NAA-SR-4355* (1962).

[11] J. G. Burr and J. M. Scarborough, *J. Phys. Chem.*, **64**, 1367 (1960).

[12] J. M. Rayroux and P. Baertschi, *Helv. Chim. Acta.*, **43**, 484 (1960).

[13] H. Kōyama, G. Tsuchihashi and A. Danno, This Bulletin, **35**, 696 (1962).

[14] I. Heilbron and H. M. Bumbury, "Dictionary of Organic Compounds," Eyre & Spottiswoode, London (1953).

[15] H. Kōyama, N. Morikawa, T. Migita, R. Itō and G. Tsuchihashi, *Radioisotopes*, **9**, 112 (1960).

[16] H. Kōyama, N. Morikawa and G. Tsuchihashi, ibid., **11**, 107 (1962).

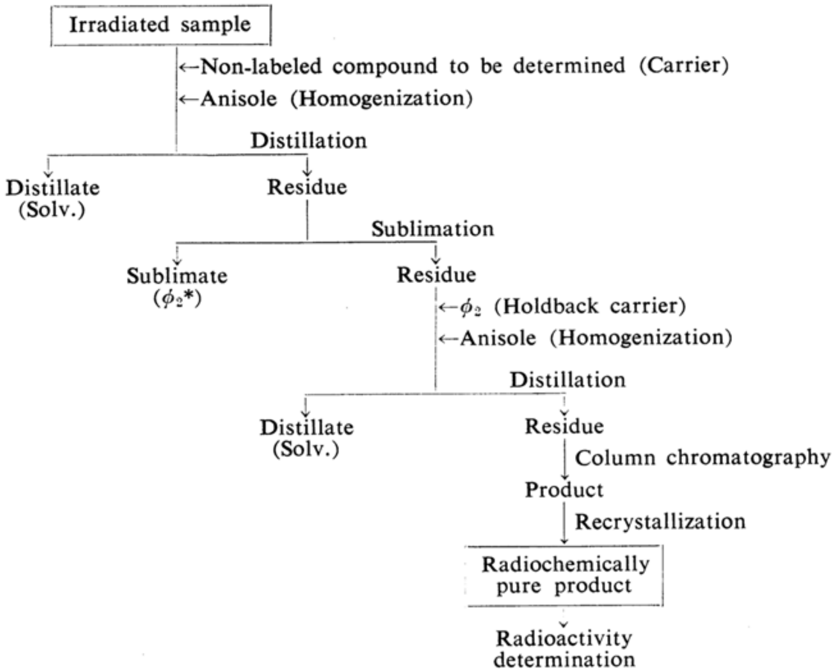

Fig. 2. Isolation process of the radiolytic product.

TABLE I. CHROMATOGRAPHIC CONDITION IN THE ISOLATION OF THE RADIOLYTIC PRODUCTS OF BIPHENYL

Product	Chromato. column*		In maximum eluting power		Solvent for recryst.
	Diameter mm.	Length cm.	Solvent composition (Ratio of vol.)	Temp.	
o-Terphenyl	25	25~26	Pet. ether - benzene (9 : 1)	Room temp.	Methanol
m-Terphenyl	25	25~26	Pet. ether - benzene (4 : 1)	Room temp.	Ethanol
p-Terphenyl	20	25~26	Pet. ether - benzene (1 : 9)	Room temp.	Benzene
o, o'-Quaterphenyl	25	25~26	Pet. ether - benzene (3 : 2)	Room temp.	Ethanol
m, m'-Quaterphenyl	25	25~26	Pet. ether - benzene (2 : 3)	Room temp.	Ethanol
p, p'-Quaterphenyl	20	25~26	Chloroform	50°C	Benzene
Triphenylene	20	25~26	Pet. ether - benzene (1 : 1)	Room temp.	Ethanol

* Absorbent is activated alumina.

Energy Research Institute.17) The absorbed dose was measured by means of a Fricke dosimeter using a *G*-value of 15.5.

Isolation. — After the irradiation, the radiolytic product to be determined was isolated according to the process diagrammed in Fig. 2. The technique employed here has been described in a previous report.18) The composition of the eluting solvent in chromatography on activated alumina was gradually varied from petrolum ether to a benzene-rich solvent (Table I). For the isolation of *p, p'*-quaterphenyl, high-temperature chromatography was adopted. Namely, the column was equipped with a jacket and heated by circulating hot water. The recrystallization of the product was repeated to reach a constant specific activity. The radioactivities of all samples except *p, p'*-quaterphenyl were determined by using a Tri-Carb liquid scintillation spectrometer with a correction for the quenching effect. In the case of *p, p'*-quaterphenyl, the sample was oxidized to carbon dioxide by the Van Slyke-Folch method,19) and the resulting carbon dioxide was charged into an ionization chamber (Applied Physics Co.). Then the radioactivity was determined by the rate-of-charge method20) with a vibrating-reed electrometer (Cary Model 31).

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17) A. Danno, M. Omura, H. Hotta, H. Hirakawa, G. Tsuchihashi and I. Yamaguchi, The 7th Hot Laboratories and Equipent Conference, Cleveland (1959), p. 349.

18) A. Danno, G. Tsuchihashi and H. Kōyama, *JAERI-1040* Report of Japan Atomic Energy Research Institute (1963).

19) D. D. Van Slyke and Folch, *J. Biol. Chem.*, **136**, 509 (1940).

20) B. M. Tolbert, *UCRL-3499* (1956).

TABLE II. *G*-VALUES FOR THE PRODUCTS FROM THE RADIOLYSIS OF BIPHENYL

Product	Number of recryst.	Specific activity μc./mol.	*G*-Value	Ratio of *G*-value
o-Terphenyl	5 6	1.62 1.58	0.0063	7.6
m-Terphenyl	7 8	0.109 0.108	0.0012	1.4
p-Terphenyl	4 5	0.0194 0.0200	0.00083	1.0
o,*o*′-Quaterphenyl	4 5	0.348 0.350	0.0049	5.9
m,*m*′-Quaterphenyl	4 5	0.576 0.576	0.0051	6.1
p,*p*′-Quaterphenyl	4 5	1.30 1.60	0.0104	12.5
Triphenylene	4 5	0.00 0.00	0.0000	—

TABLE III. *G*-VALUES OF *o*,*o*′-QUATERPHENYL PRODUCED FROM THE RADIOLYSIS OF BIPHENYL UNDER VARIOUS CONDITIONS

Temp., °C	Dose rate eV./g. min.	Time hr.	Absorbed dose eV./g.	*G*-Value
100	0.00	150	0.00	0.0000
Room temp.	2.25×10^{17}	168	2.27×10^{21}	0.0004
100	2.54×10^{17}	150	2.29×10^{21}	0.0049
100	2.54×10^{17}	452	6.89×10^{21}	0.0042
100	2.54×10^{17}	602	9.20×10^{21}	0.0048

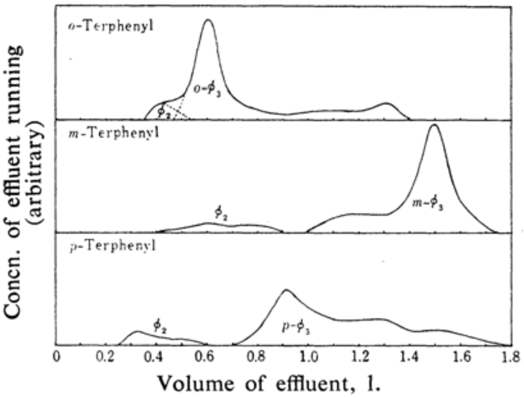

Fig. 3. Isolation of radiolytic terphenyls of biphenyl by liquid chromatography.

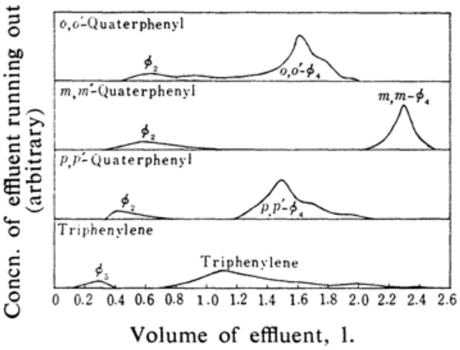

Fig. 4. Isolation of radiolytic quaterphenyls and triphenylene of biphenyl by liquid chromatography.

Results and Discussion

***G*-Values.**—Figures 3 and 4 show the isolation of the radiolytic products of biphenyl by liquid chromatography. The *G*-values of these products are tabulated in Table II. Table III illustrates the *G*-values for the *o*,*o*′-quaterphenyl produced from the radiolysis of biphenyl under various conditions. The following conclusions may be drawn from Table III; (1) the pyrolysis of biphenyl does not take place under such conditions (2) different reaction patterns were observed between the liquid and solid states, and (3) *G*-values are independent of the total absorbed dose in the range of our experiments.

Free Radical Substitution. — The primary process of radiation chemistry is conceived of as the ionization and excitation of molecules. In radiation chemistry of the liquid phase, the reactive entities which bring about most chemical changes are possibly free radicals, since the neutralization of the ions produced by the impact of secondary electrons will often enough to make very probable the production of highly-excited molecules.[21]

Deuterium isotope effects are reported from two different groups.[11,12] Rayroux and Baertschi studied the pile-irradiation of biphenyl and concluded that the deuterated

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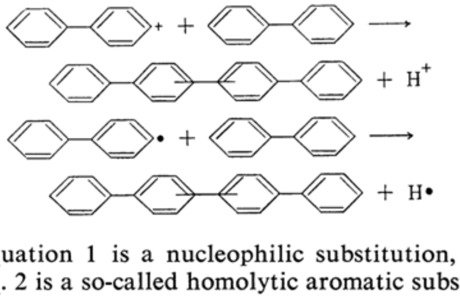
[21] A. J. Swallow, "Radiation Chemistry of Organic Compounds," Pergamon Press, Oxford (1960), p. 15.

compound decomposes more slowly than the ordinary biphenyl by a factor of two. Burr and Scarborough studied the mechanism of hydrogen gas formation in the radiolysis of biphenyl by gamma-rays. They found an isotope effect of 3.00 in the formation of radiolytic hydrogen and deuterium from the ordinary and from the deuterated biphenyls. These large isotope effects clearly indicate that the cleavage of the C–H bond in biphenyl plays an important role in the radiation decomposition, since the probability for the ionization or excitation of ordinary biphenyl should not differ greatly from that of deuterated biphenyl, according to the Frank-Condon principle.22) Accordingly, the observed isotope effects must be for those of the fragmentation of the ion or the excited molecule. The isotope effect on the fragmentation reaction may be satisfactorily explained in terms of the Frank-Condon principle.23) The explanation for the isotope effect should be applicable to the molecules which possess large π-electron systems, for example, benzene or biphenyl. For ionization or excitation, the structure change in these molecules will be little, since the promotion of an electron from the π-electron system will have little effect on the whole electronic structure. Therefore, the internuclear distance for the potential minimum point of the upper state will be close to that of the ground state.

Now, on the basis of the isotope-effect studies, the rupture of the C–H bond should take place at the first step in the radiolysis of biphenyl. The intermediate formed as a result may be a biphenylyl cation or radical and a hydrogen atom. The former two species are capable of reacting with a biphenyl molecule to produce the quaterphenyls which are identified as major products in the present work.



(1)

(2)

Equation 1 is a nucleophilic substitution, and Eq. 2 is a so-called homolytic aromatic substitution. The distribution of quaterphenyl isomers should be quite different in the two mechanisms. In order to establish the orientation of the reaction, it is necessary to determine the amount of all the isomers of quaterphenyls. However, it is impossible to derive the origin of quaterphenyls from these yields. For example, from the G-value of o,p'-quaterphenyl, it is impossible to know whether a o-biphenylyl radical is substituting the para-position of the biphenyl molecule or whether a p-biphenylyl radical is substituting the ortho-position of the biphenyl molecule.

If we assume (1) that the chemical selectivity for the cleavage of the C–H bond by radiation is so small that o-, m- and p-biphenylyl radicals will be produced with equal probability and (2) that the reactivities of the attacking radical are nearly equal, the product ratio for symmetrical quaterphenyls will represent the orientation of the substitution reaction. From our observed values, the ratio of the partial rate factors for ortho-, meta- and para-substitution reactions in the radiolysis of biphenyl are reduced to 1.0 : 1.0 : 8.4.

The partial rate factors for a typical nucleophilic reaction, nitration, were reported by Simamura and Mizuno as 41 and 38 for the ortho- and para-positions respectively.24) Other types of nucleophilic substitution reactions, such as bromination, chlorination or detritiation reactions, have been tabulated in a reviewing article.25) These experimental results indicate that biphenyl is a strongly ortho-, para-orienting substrate with relation to nucleophilic substitutions. Our present reaction seems to be different from the nucleophilic substitution mechanism, since the yield for the meta-isomer is rather larger.

As an alternative mechanism, the possibility of free radical substitution remains. Hey and his co-workers published the ratio of o-, m- and p-terphenyls from the free radical phenylation of biphenyl as 48.5 : 23.0 : 28.5.26) (The ratio of partial rate factors is 2.1 : 1.0 : 2.5.) Although there remains some doubt about the mechanism of homolytic aromatic substitution by the decomposition of benzoyl peroxide,27) the above value could be used to indicate the characteristic behavior of biphenyl toward radical substitution reactions. In Hey's experiment, phenyl is the attacking radical, whereas in the present work, the biphenylyl radical is proposed as the substituting entity. The formation of o,o'-quaterphenyl is the result of the ortho-substitution of the

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22) F. H. Field and J. L. Franklin, "Electron Impact Phenomena," Academic Press Inc., New York (1957), p. 57.

23) Ref. 22, p. 204.

24) O. Simamura and Y. Mizuno, This Bulletin, **30**, 196, (1957).

25) V. Gold (editor), "Advances in Physical Organic Chemistry," Vol. I, Academic Press Inc., London (1963), p. 67.

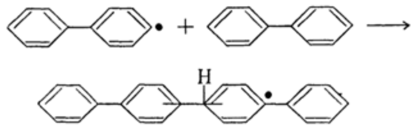
26) J. I. G. Cadogan, D. H. Hey and G. H. Williams, *J. Chem. Soc.*, **1954**, 794.

27) D. F. DeTar and R. A. J. Long, *J. Am. Chem. Soc.*, **80**, 4742, (1958).

o-biphenylyl radical; hence, considerable steric hindrance of the substitution is to be expected. If the differences in the reactivities of substituting radicals by the steric hindrance are taken into account, we may conclude that the orientation of the reaction roughly agrees with that of the free radical mechanism.

The same examination for the product ratio of terphenyls leads to the conclusion that the phenyl cation should not be the intermediate, but the phenyl radical is likely to give terphenyl by substituting biphenyl molecule.

The formation of polyphenyls by the free radical mechanism probably proceeds according to DeTar's mechanism.[27)]



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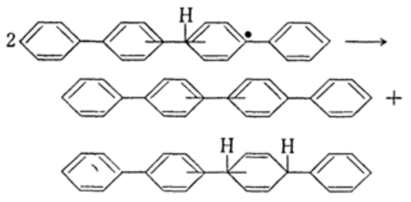
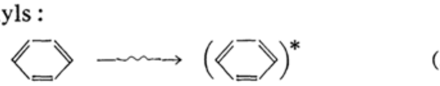


(4)

Equation 4 is a disproportionation reaction of radicals. The plausibility of this mechanism has been discussed in the summary by Walling, together with other possible mechanisms.[28)] DeTar and Long actually obtained 1, 4-dihydrobiphenyl from the reaction of the phenyl radical with benzene; the amount nearly equals that of biphenyl.

Gordon, Van Dyken and Doumani carried out the gamma-irradiation of benzene and found a mixture of phenyl cyclohexene and phenyl cyclohexadiene in the C_{12} fraction, together with biphenyl.[5)] They proposed a molecular-mechanism to account for the formation of these partially-hydrogenated biphenyls:



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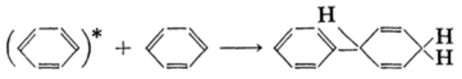

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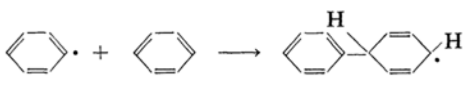
However, the formation of phenylhexadiene is alternatively explained by the free radical mechanism:



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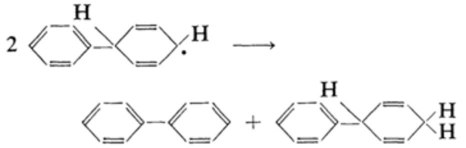
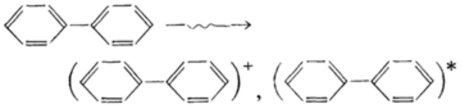


(8)

A Comparison of the Formation of Terphenyls and Quaterphenyls.—The production of phenyl and biphenylyl radicals as the intermediates which bring about the formation of polyphenyls may be presented by the following equations:



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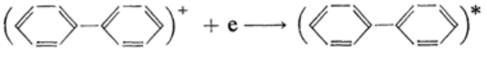

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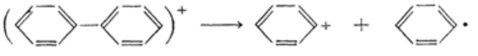

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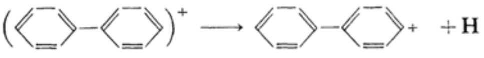

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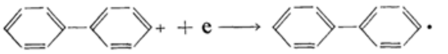

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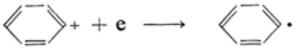

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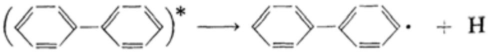

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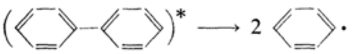
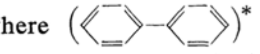
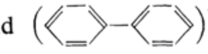
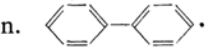
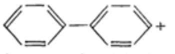
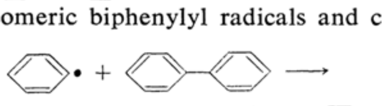


(16)

where  and  represent an excited biphenyl molecule and a biphenyl cation.  and  are, respectively, one of three isomeric biphenylyl radicals and cations.



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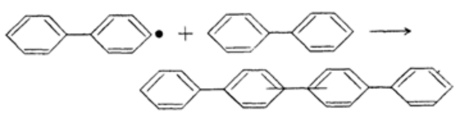

(18)

Each molecule of terphenyl or quaterphenyl is presumed to be formed by the attack of a phenyl radical or a biphenylyl radical respectively on the biphenyl molecule, while radicals are undoubtedly produced directly in the primary process of the irradiation. Although we did not determine *G*-values for the formation of the three remaining unsymmetrical

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28) C. Walling, "Free Radicals in Solution," John Wiley & Sons, Inc., New York (1957), p. 482.

quaterphenyls, they would probably be of the same magnitude as those for the symmetrical quaterphenyls. Therefore, the G-value of the unsymmetrical quaterphenyl could be calculated as an arithmetical average of the symmetrical ones; for example, the G-value of m, p'-quaterphenyl is 0.0078. The sums of the G-values for terphenyls and quaterphenyls are 0.0083 and 0.041 respectively; the latter is about five times as large as the former. This relation is different from Hall's report.9)

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