

made up to be slightly supersaturated at room temperature, was cooled to 0°, and before crystallization could occur, 4.2 g. of finely powdered 4-N-(*o*-methylaminophenyl)-iminopentanone-2 was rapidly added. An immediate deep red-orange coloration followed, and in a few minutes a salt crystallized out, which was filtered off after the addition of an equal volume of dry benzene;

yield, 5.8 g. Attempts to purify this orange-colored product by crystallization or sublimation resulted in decomposition. The material was washed with dry benzene, dried for 5 hr. at 106° (0.1 mm.) and analyzed.

Anal. Calcd. for C₂₆H₂₂N₆O₁₂: C, 51.15; H, 3.63; N, 13.77. Found: C, 50.52; H, 3.60; N, 13.99.

[CONTRIBUTION FROM THE RESEARCH DIVISION OF PHILLIPS PETROLEUM CO., BARTLESVILLE, OKLA.]

Relative Reactivities of Positions on Biphenyl in the Generation of Reactive Species by Electron Irradiation and in Subsequent Ring Substitution

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A model is proposed to separate the relative reactivities of the three different positions on biphenyl in the generation of reactive species by ionizing radiation and the relative reactivities of the same positions on biphenyl in its substitution by the reactive species. The method depends on quantitative analysis of the six isomeric quaterphenyl products. Relative yields of these products from irradiation of biphenyl with electrons at 80 and 300° have been obtained and used to check the model. The model fits the experimental data well. Results indicate that the net production of reactive species is not random; that most reactive species are free radicals but that some species more *para*- and less *ortho*-selective than free radicals are also formed; and that there is considerable hindrance to *ortho*-substitution at 300°

Introduction

Quantitative analyses have been made of the six isomeric quaterphenyls produced from biphenyl by ionizing radiation. The relative yields of the isomers are related here to the relative reactivities or partial rate factors of biphenyl both in the generation of reactive species by radiation and in substitution of biphenyl molecules by these species. To our knowledge, partial rate factors for the generation of reactive species by ionizing radiation have not been reported. These factors or reactivities should allude to the nature of the radiative generation processes. The partial rate factors for substitution of the molecule by reactive species are obtained simultaneously. These will be averages for substitution of biphenyl by its free radicals, ion-molecules, excited molecules, etc. Deviation of the averages from partial rate factors obtained with free radicals alone will depend on the frequency with which other reactive species occur and on their selectivity. The partial rate factors of biphenyl in its substitution by the three isomeric biphenyl free radicals were obtained by irradiation with ultraviolet light of dilute solutions of the respective iodobiphenyls in biphenyl.

The relative reactivities or partial rate factors of the three different positions on biphenyl to substitution by free radicals such as phenyl have been extensively investigated.¹ Substitution of the benzene ring by a free phenyl radical appears to proceed through an intermediate containing a tetrahedral carbon attached to its original hydrogen atom and to the entering group.² This intermediate, although it may be classed as a radical, does not appear active enough to substitute a benzene ring because no terphenyls are produced from benzene and phenyl free radicals. The main reaction of the intermediate is disproportionation into biphenyl and dihydrobiphenyl. The intermediate appears to a lesser extent to dimerize to form tetrahydroquaterphenyl. 1,1',4,4'-Tetrahydro-4,4'-diphenylbiphenyl and 1,4-dihydrobiphenyl have been isolated from the products of a reaction between benzene and benzoyl peroxide from which air was excluded.³ In the disproportionation reaction, deuterium appeared to be removed less readily than hydrogen from the

tetrahedral carbon.⁴ Orientation (*ortho*, *meta*, and *para*) of the entering group might similarly affect which intermediates were reduced and which were aromatized in the disproportionation reactions. This raised doubt⁴ that the isomer ratios of only the aromatic products represented the relative frequencies (partial rate factors) with which the initial additions occurred at the various positions on the aromatic ring. Indeed the use of isomer ratios for this purpose has been questioned.⁵ The yield of biphenyl (distinguished from dihydrobiphenyl) was increased by the presence of molecular oxygen.⁶ Dimerization of the intermediate was inhibited by cupric ions.⁷ The distribution of aromatic products from substitution of various aromatics by free radicals were found to be unaffected by the presence of oxygen.⁸ These authors⁸ were of the opinion that the entering aryl group would not affect the course of the disproportionation reactions and that the relative yields of isomeric aromatic products reflected the frequencies or partial rate factors of the addition reactions.

In the work reported herein, conversions were limited to very low levels, the hydroaromatic products were found to be rapidly aromatized in air, and little dimerization product or tar was detected. In the case of complete aromatization of all the radical substitution products, any influence of the entering group on disproportionation reactions would not appear to affect the isomer distribution unless some rearrangement or back reaction of the intermediate occurred. Back reaction is believed to be unlikely energetically. Rearrangement of the intermediate would not be detected by methods employed in the present work and could affect the net distribution of products. Such perturbations could be important in explanations of differences in reactivity of the various positions on an aromatic ring.

The Model.—The chemical processes occurring during the irradiation of biphenyl are divided into two independent events.

Event 1 (generation of reactive species)

(4) E. L. Eliel, S. Mayerson, Z. Welvart, and S. H. Wilen, *ibid.*, **82**, 2936 (1960).

(5) D. F. DeTar, *ibid.*, **83**, 1014 (1961).

(6) M. Eberhardt and E. L. Eliel, *J. Org. Chem.*, **27**, 2289 (1962).

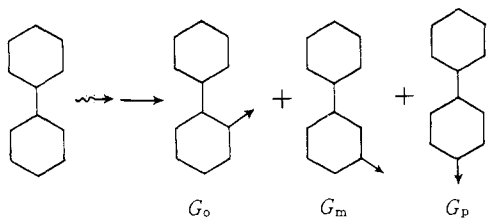
(7) S. C. Dickerman and G. B. Vermont, *J. Am. Chem. Soc.*, **84**, 4150 (1962).

(8) R. T. Morrison, J. Cazes, N. Samkoff, and C. A. Howe, *ibid.*, **84**, 4152 (1962).

(1) (a) D. R. Augood and G. H. Williams, *Chem. Rev.*, **57**, 123 (1957); (b) C. Walling, "Free Radicals in Solution," John Wiley and Sons, Inc., New York, N. Y., 1957, pp. 482-486.

(2) G. W. Wheland, *J. Am. Chem. Soc.*, **64**, 900 (1942).

(3) D. F. DeTar and R. A. J. Long, *ibid.*, **80**, 4742 (1958).



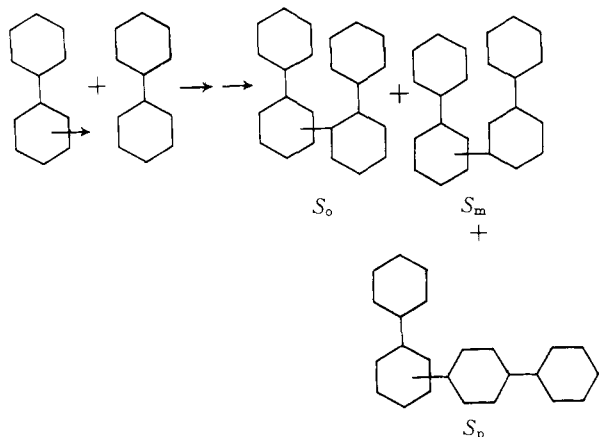
G_o = probability that if a reactive species is formed the ultimate reactive center will be at an *o*-position

G_m = similar conditional probability for generation of a *m*-centered reactive species

G_p = same for a *p*-reactive species

$G_o + G_m + G_p = \text{unity}$

Event 2 (substitution of a ring by reactive species)



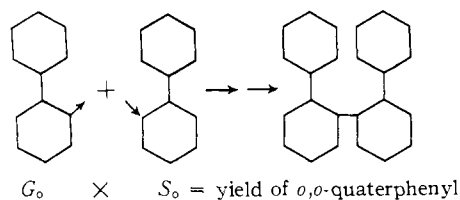
S_o = probability that if a biphenyl ring is substituted it will be substituted at an *o*-position

S_m = similar conditional probability for substitution at a *m*-position

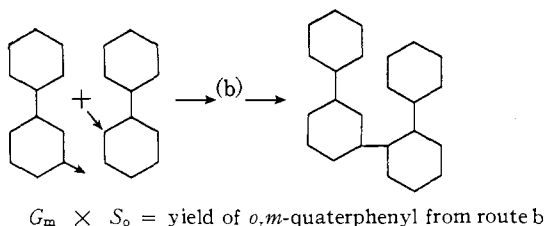
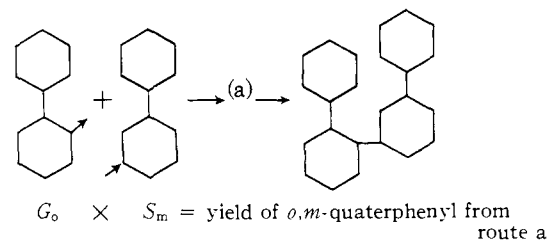
S_p = same for a *p*-position

$S_o + S_m + S_p = \text{unity}$

The yield of a symmetrical quaterphenyl relative to the sum of isomeric quaterphenyl yields is equal to the product of the probabilities of the two independent events; *i.e.*



Unsymmetrical quaterphenyls are formed by two reaction routes. The relative yield of an unsymmetrical isomer is the sum of the probabilities of the two routes; *i.e.*



In summary

$$\text{Yield of } o,o\text{-quaterphenyl (2,2'-diphenylbiphenyl)} = Y_{o,o} = G_o S_o \quad (1)$$

$$\text{Yield of } o,m\text{-quaterphenyl (2,3'-diphenylbiphenyl)} = Y_{o,m} = G_o S_m + G_m S_o \quad (2)$$

$$\text{Yield of } o,p\text{-quaterphenyl (2,4'-diphenylbiphenyl)} = Y_{o,p} = G_o S_p + G_p S_o \quad (3)$$

$$\text{Yield of } m,m\text{-quaterphenyl (3,3'-diphenylbiphenyl)} = Y_{m,m} = G_m S_m \quad (4)$$

$$\text{Yield of } m,p\text{-quaterphenyl (3,4'-diphenylbiphenyl)} = Y_{m,p} = G_m S_p + G_p S_m \quad (5)$$

$$\text{Yield of } p,p\text{-quaterphenyl (4,4'-diphenylbiphenyl)} = Y_{p,p} = G_p S_p \quad (6)$$

The following equations are dependent but convenient in the solution of the other equations

$$G_o + G_m + G_p = \text{unity} \quad (7)$$

$$S_o + S_m + S_p = \text{unity} \quad (8)$$

The conditional probabilities G and S are related to partial rate factors (relative reactivities) by the number of equivalent positions on biphenyl available for reaction. The factors given here are relative to the *m*-position ($r_m = \text{unity} = k_m$)

r_o = partial rate factor of *o*-positions in generation of reactive species = $G_o/4 \div G_m/4 = G_o/G_m$

r_p = partial rate factor of *p*-positions in generation of reactive species = $G_p/2 \div G_m/4 = 2G_p/G_m$

k_o = partial rate factor of *o*-positions in substitution = $S_o/4 \div S_m/4 = S_o/S_m$

k_p = partial rate factor of *p*-positions in substitution = $S_p/2 \div S_m/4 = 2S_p/S_m$

Equations 1, 4, and 6 are single term and relate corresponding G - and S -values (such as G_o and S_o). They can be substituted into eq. 2, 3, and 5 to solve for G and S . Equation 1 is solved for S_o in terms of G_o and $Y_{o,o}$. Equation 4 is solved for S_m in terms of G_m and $Y_{m,m}$. When these two expressions are substituted for S_o and S_m in eq. 2, eq. 2' quadratic in G_o and G_m is obtained.

$$Y_{o,m} = G_o \left(\frac{Y_{m,m}}{G_m} \right) + G_m \left(\frac{Y_{o,o}}{G_o} \right) \quad (2')$$

Multiplying through by $G_o G_m$ gives

$$Y_{o,m}(G_o)^2 - Y_{o,m}G_o G_m + Y_{o,o}(G_m)^2 = 0 \quad (2'')$$

Similarly

$$Y_{o,p} = G_o \left(\frac{Y_{p,p}}{G_p} \right) + G_p \left(\frac{Y_{o,o}}{G_o} \right) \quad (3')$$

$$Y_{p,p}(G_o)^2 - Y_{o,p}G_o G_p + Y_{o,o}(G_p)^2 = 0 \quad (3'')$$

$$Y_{m,p} = G_m \left(\frac{Y_{p,p}}{G_p} \right) + G_p \left(\frac{Y_{m,m}}{G_m} \right) \quad (5')$$

$$Y_{p,p}(G_m)^2 - Y_{m,p}G_m G_p + Y_{m,m}(G_p)^2 = 0 \quad (5'')$$

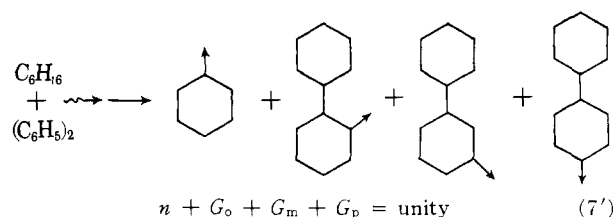
Equations 2'', 3'', and 5'' are simultaneous quadratics with three unknowns, G_o , G_m , and G_p .

Actually, the symmetry of eq. 1, 4, and 6 does not allow G and S to be distinguished (or a choice to be made on which to eliminate). The same coefficients in eq. 1, 4, and 6 and in 2'', 3'', and 5'' result when S is substituted for G as when G is substituted for S . Equations 2'', 3'', and 5'' give two sets of real solutions. One of the real sets correspond to solutions for G and the other for S . Solutions for both G and S are simultaneously obtained because a true choice between elimination of G or S from eq. 2, 3, and 5 by the use of eq. 1, 4, and 6 is not allowed by the symmetry of the latter. The same sets of solutions are obtained whichever is eliminated. One real set can be converted into the other by substitution into eq. 1, 4, and 6. However, this is duplication and the solutions are not independent. Substitution of the solutions into eq. 1-6

to calculate yields of quaterphenyls does not serve to distinguish between G and S because of symmetry. The two terms in eq. 2, 3, and 5 switch in value as assignment of G and S labels to the real solutions are switched, but the sum of the two terms (the yield) does not change.

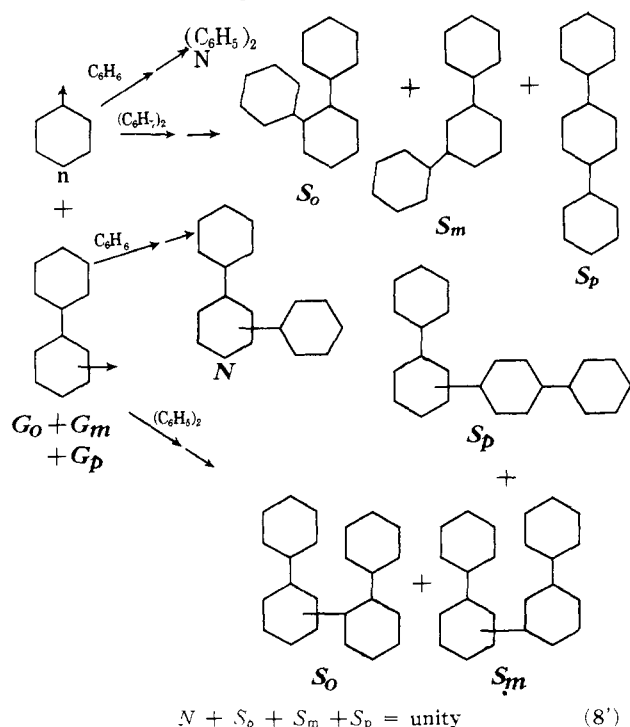
The solutions to these equations were first obtained by hand calculations. The solutions for " G " and " S " were converted into " r " and " k " values and compared with k values obtained from the substitution of biphenyl by free radicals. Unequivocal assignment of r and k labels to the solutions could be made because of the similarity of the latter to the partial rate factors obtained with free radicals. This allowed unambiguous assignments of G and S .

When a program was designed for machine calculations, the model was broadened to include the case for irradiation of mixtures of benzene and biphenyl. Event 1 now included the generation of reactive species from benzene as well as from biphenyl



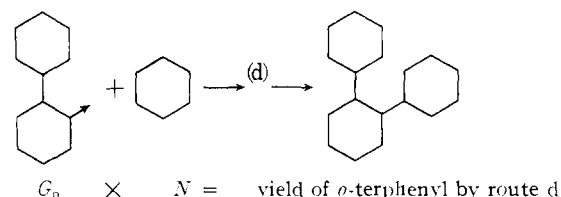
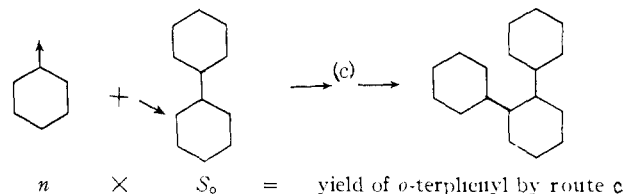
where n is the relative probability of a phenyl reactive species being formed from benzene by ionizing radiation and G_o , G_m , and G_p are the probabilities of o -, m -, and p -centered reactive species being formed from biphenyl by the same irradiation.

Event 2 now included the substitution of both biphenyl and benzene by phenyl reactive species as well as the substitution of both biphenyl and benzene by biphenyl reactive species



where N is the relative probability of a benzene molecule being substituted by a reactive species (either phenyl or biphenyl type); and S_o , S_m , and S_p are the probabilities of a biphenyl molecule being substituted at the o -, m -, and p -positions by a reactive species (either phenyl or biphenyl type).

Irradiation of mixtures of benzene and biphenyl thus results in four additional products: biphenyl, o -, m -, and p -terphenyl. o -Terphenyl is formed by substitution at the o -position of biphenyl by phenyl reactive species and also by substitution of benzene by o -biphenyl reactive species. The yield of o -terphenyl relative to the other products (biphenyl, the six quaterphenyls, and the other two terphenyls) is the sum of the probabilities of the two routes



Thus,

$$\text{Yield of } o\text{-terphenyl} = nS_o + G_oN \quad (9)$$

Similarly

$$\text{Yield of } m\text{-terphenyl} = nS_m + G_mN \quad (10)$$

$$\text{Yield of } p\text{-terphenyl} = nS_p + G_pN \quad (11)$$

$$\text{Yield of biphenyl} = nN \quad (12)$$

Equations 9, 10, and 11 are not symmetrical and serve to relate G and S unambiguously; that is, different coefficients are obtained when G is solved for in terms of S and when S is solved for in terms of G . When the program including eq. 1-6, 7', 8', and 9-12, which is a system containing the original eq. 1-8 as a subsystem, is calculated using data from irradiation of pure biphenyl, the yields of biphenyl and the terphenyls are necessarily set at zero. Because the unsymmetrical larger system contains the symmetrical system as a subsystem, consistency with continuity requires the correct assignment of G and S to solutions of the equations in the limit as n and N go to zero. Thus G and S solutions are distinguished without recourse to free-radical data.

The partial rate factors obtained from this model are very sensitive to errors in the relative yields of isomeric quaterphenyls. Perturbations of various yields have caused perturbations in the factors that ranged up to three times the originating perturbations. It should be kept in mind that the G and S values and the corresponding r and k values obtained with this model are averages of values that are dissimilar because of isomerism as well as types of reactive species generated by radiolysis. This does not affect the accuracy of the solutions but does complicate interpretation of results.

Experimental

The biphenyl used was Eastman White Label grade found to contain no impurities detectable by our gas chromatographic method. All but two of the reference quaterphenyls were prepared from pure xenyl bromides and phenylcyclohexan-(*o* or *n*)-ones by the unambiguous method of Woods.⁹ These quaterphenyls were purified by adsorption chromatography (Alcoa F21 alumina, *n*-hexane-benzene gradient elution). A sample of *m,m*-quaterphenyl was supplied by the U. S. Bureau of Standards and was also later synthesized. *p,p*-Quaterphenyl was obtained from Eastman (*o,o*- and *m,m*-quaterphenyl are now available from K and K Laboratories, Inc.). All six reference quater-

(9) (a) G. F. Woods, "Preparation and Properties of Some Polyphenyls," WADC-TR 59-496 (1959); AD-233873; (b) G. F. Woods and P. Scotti, *J. Org. Chem.*, **26**, 312 (1961).

TABLE I
 ANALYSES OF ISOMERIC QUATERPHENYLS FROM IRRADIATION OF BIPHENYL WITH ELECTRONS

Sample	Temp., °C.	Analysis	Isomer content of product, %						Av. dev., %	Sum - 100, %
			<i>o,o</i> -	<i>o,m</i> -	<i>o,p</i> -	<i>m,m</i> -	<i>m,p</i> -	<i>p,p</i> -		
A	80	1	12.7	26.4	21.8	10.8	21.0	7.3	2.7	+0.2
		2	11.8	26.0	22.1	11.1	22.2	6.8	5.1	0
B	80	1	14.1	25.7	20.4	10.7	21.5	7.6	5.1	+ .2
		2	13.1	25.8	21.4	10.8	21.1	7.8	3.6	+ .1
C	300	1	5.4	20.1	17.4	18.3	29.9	8.9	1.7	+ .6
		2	4.5	17.8	15.9	19.9	32.0	9.9	4.4	+ .1
D	300	1	4.0	18.7	16.9	19.5	31.6	9.3	4.1	+ .2
		2	5.3	18.7	15.9	18.9	31.7	9.5	5.7	+ .4

 TABLE II
 PARTIAL RATE FACTORS FOR THE SUBSTITUTION OF BIPHENYL AT $80 \pm 5^\circ$ BY BIPHENYLYL FREE RADICALS FROM ULTRAVIOLET IRRADIATION OF IODOBIPHENYLS

Source of radicals, biphenyl	Isomer content of product, %						Av. dev., %	Factors ^a	
	<i>o,o</i> -	<i>o,m</i> -	<i>o,p</i> -	<i>m,m</i> -	<i>m,p</i> -	<i>p,p</i> -		k_o	k_p
2-Iodo-	41.1	23.9	35.0	0.0	0.0	0.0	2.8	1.7	2.9
3-Iodo-	0.0	44.7	0.0	26.4	28.9	0.0	0.6	1.7	2.2
4-Iodo-	0.0	0.0	49.0	0.0	24.5	26.5	0.6	2.0	2.2

^a Relative to the *m*-position ($k_m = \text{unity}$).

phenyls were 99+ % pure by gas chromatography. Their infrared spectra and melting points were consistent with the literature.

2- and 3-iodobiphenyl were prepared from the corresponding aminobiphenyls by diazotization and reaction with potassium iodide.¹⁰

2-Aminobiphenyl was obtained from Eastman. 3-Aminobiphenyl was obtained from 3-nitrobiphenyl (Aldrich Chemical Co.) by reduction with stannous chloride.¹¹ 4-Iodobiphenyl was obtained from Eastman.

Irradiations of biphenyl were made with a linear electron accelerator (Linac) built by Applied Radiation Corporation. The maximum power is rated at 4 kw. at 6 Mev., which corresponds to a maximum dose rate of 10^{10} rads per hour. Dose rate was reduced by diffusion of the beam and by operating at reduced rep rate. Duration of the irradiations was limited to 12 min. to obtain about 1% conversion. Irradiations were made at 80 ± 5 and $300 \pm 30^\circ$. Sample holders were glass ampoules and aluminum tubes for irradiations at 80 and 300° and contained 15 and 30 g. of biphenyl, respectively. Two samples were irradiated separately at each temperature after outgassing.

The irradiated samples were transferred to a batch sublimation apparatus where biphenyl was removed at $80-90^\circ$ (1 mm.) until the residues contained from about 10 to 50% products. The samples were deliberately exposed to air to aromatize hydroaromatic products. The sublimates were found free of higher boiling components. The residues were analyzed with a F and M Model 500 gas chromatograph fitted with a column 4 mm. i.d. by 300 mm. long packed with Chromosorb P containing 20% lithium chloride fused on at 700° . The column was operated from 200 to 425° at 15°/min.

The quaterphenyls in the radiation products were identified by separation on a preparatory-size gas chromatograph. Distinctive infrared and n.m.r. spectra were obtained and compared with the reference samples.

Two sets of known mixtures of the six quaterphenyls matched the composition of the radiation products within 2% of each quaterphenyl component. Precision of weighing the components in preparation of the known mixtures was 0.1%. Unknown samples and their companion knowns were chromatographed repetitively with care taken to match the amount of quaterphenyls charged. The order of elution of isomers was the same as the order in eq. 1-6.

Peak value was taken as the product of peak height times peak width at one-half height, as measured with a ruler and a low-power microscopic scale with precisions of about 0.2 and 0.5%, respectively. The mean peak values obtained from each set of chromatograms of the known mixtures were divided into the respective concentrations of components in the knowns to obtain correction factors. These ranged from 0.95 to 1.05 for the individual isomers and were only slightly dependent on the total quaterphenyl charged (about 0.3-1.0 mg). Scatter of the peak values among chromatograms in a set were obtained as percentage deviation from the mean averaged over-all quaterphenyls. The larger of the average deviations of unknown and companion known of each set is given in column 10 of Table I. Errors in correction factors would tend to make the sum of qua-

terphenyl analyses deviate from unity (or 100%). The relative concentrations or yields obtained from each set of analyses of an unknown were summed to determine this deviation which is given in the last column of Table I. The yields were then normalized to sum to 100% in every case.

The concentrations of quaterphenyls in the irradiation mixtures corresponded to about 0.5 and 1.0% conversions of biphenyl at 80 and 300° . Products from irradiation at 300° contained about 2% each of *m*- and *p*-terphenyl. Other smaller peaks were observed in the chromatograms of irradiated biphenyl. Less than 5% of the irradiation products were nonvolatile at 285° (0.1 mm.). This would include any octaphenyls produced by dimerization of the reaction intermediates.

The *m*- and *p*-terphenyl are believed to be due to inter-ring scission followed by substitution of biphenyl by the resultant phenyl radicals. Constituents causing the minor peaks are not known but their concentrations would not affect the distribution of quaterphenyl yields in excess of the over-all precision of the analyses.

Partial rate factors of biphenyl in substitution by biphenylyl (xenyl) free radicals were desired for comparison with radiolytic results. Generation of aryl free radicals by irradiation of aryl iodides with ultraviolet light had been reported by Blair and Bryce-Smith¹² and by Kharasch and Wolf.¹³ The former irradiated iodobenzene and obtained a distribution of isomeric iodobiphenyl yields that was the same as that obtained by decomposing benzoyl peroxide in iodobenzene.

Irradiations of iodobiphenyls in biphenyl by ultraviolet light were used to obtain partial rate factors for substitution of biphenyl by biphenylyl free radicals. A solution of 0.6% of 2-iodobiphenyl in biphenyl (70 ml.) was irradiated at $80 \pm 5^\circ$ with ultraviolet light from a 100-watt lamp (Hanovia high pressure mercury arc, Type SOL) for 2 hr. The experiment was repeated with 3-iodobiphenyl and with 4-iodobiphenyl. The reaction products were analyzed consecutively with known reference mixtures. Compositions of the reaction products and partial rate factors obtained from them are given in Table II.

Partial rate factors for the substitution of biphenyl by phenyl free radicals were obtained by irradiation of a 1% solution of iodobenzene in biphenyl with ultraviolet light. Chromatograms of the resulting *o*-, *m*-, and *p*-terphenyl mixture were evaluated by comparing with consecutive chromatograms of a known mixture. The partial rates obtained are given in the first line of Table III. Corresponding literature¹⁴ values obtained by decomposition of benzoyl peroxide in biphenyl at 80° and analysis by infrared spectroscopy are given in the last line of Table III.

 TABLE III
 COMPARISON OF PARTIAL RATE FACTORS FOR PHENYLATION OF BIPHENYL AT 80° OBTAINED WITH DIFFERENT SOURCES OF RADICALS

Source of radicals	Factors ^a	
	k_o	k_p
Iodobenzene	1.9	2.4
Benzoyl peroxide ¹⁴	2.1	2.5

^a Relative to the *m*-position ($k_m = \text{unity}$).

(10) D. R. Augood, J. I. G. Cadogan, D. H. Hey, and G. H. Williams, *J. Chem. Soc.*, 3412 (1953).

(11) S. T. Bowden, *J. Chem. Soc.*, 1111 (1931).

(12) J. M. Blair and D. Bryce-Smith, *ibid.*, 1788 (1960).

(13) N. Kharasch and W. Wolf, *J. Org. Chem.*, **26**, 283 (1961);

The agreement between the literature values¹⁴ and ours is not exact but sufficiently good to verify further the usefulness of the aryl iodide method. Care must be exercised with aryl iodides as radical sources to use only low concentrations and low degrees of irradiation with ultraviolet light. The most serious complication encountered was the conversion of *o,p*-quaterphenyl into a material (presumed to be 2-phenyltriphenylene) eluting after *p,p*-quaterphenyl. Only approximate corrections could be made for this when more concentrated solutions were extensively irradiated. This conversion was imperceptible in the ultraviolet irradiations reported here and did not need to be corrected for.

Results

The eight sets of relative yields of isomeric quaterphenyls given in Table I were separately substituted into the unsymmetrical set of eq. 1-6, 7', 8', 9-12. The solutions of G and S values were obtained by machine calculations (they can also be obtained by hand). The G and S values were repetitively substituted back into this set of equations to obtain deviations of calculated yields from experimental yields. The arithmetic sum of the deviations was taken to a practical minimum. The final G and S values were converted into r and k partial rate factors which are given in Table IV. The values given in the last column of this table are differences between yields of quaterphenyls calculated from G and S values and the experimental yields divided by the latter. These deviations should be less than the experimental scatter given in Table I (column 9). Agreement between experiment and model was reasonably good.

TABLE IV
PARTIAL RATE FACTORS^a OF BIPHENYL UNDER ELECTRON IRRADIATION

Sample	Temp., °C.	Analysis	r_o	r_p	k_o	k_p	Av. dev., %
A	80	1	0.9	0.9	1.4	2.9	3.4
		2	.9	.8	1.2	3.0	3.7
B	80	1	.80	.90	1.6	2.8	1.8
		2	.80	1.0	1.5	2.9	1.4
C	300	1	.61	0.78	0.49	2.5	0.2
		2	.53	.83	.39	2.4	2.1
D	300	1	.59	.78	.36	2.5	0.9
		2	.48	.78	.51	2.6	2.3

^a Relative to *m*-position ($k_m = \text{unity}$, $r_m = \text{unity}$).

The S_o , S_m , and S_p and the corresponding k_o , k_m , and k_p values (Table IV) obtained from the model are each averages of reactivities of positions on the biphenyl molecule to reactive species that may differ not only in isomeric structure but type of reactive site (radical, ion, etc.). For comparison with k values obtained with free radicals generated from iodobiphenyls (Table II), the latter must be averaged by weighting each individual k value with the appropriate G value which represents the probability of that radical being formed. This is done in Table V. It will be noted that the radiolytic k_o value is smaller and that the radiolytic k_p value is larger than the corresponding weighted averaged of k_o and k_p obtained with free radicals. Only the k_p value obtained with 2-biphenyl free radicals was as high as the radiolytic k_p value.

It should be noted that *o,o*-, *o,m*-, and *o,p*-quaterphenyl were the only isomers formed from the irradiation of 2-iodobiphenyl in biphenyl. Similarly, *o,m*-,

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

TABLE V
COMPARISON OF REACTIVITIES^a OF BIPHENYL TO FREE RADICALS AND TO RADIOLYTIC SPECIES AT 80°

Reactive site	Reactive species		Free radical data			
	Probability of formation, G		k_o	k_p	Gk_o	Gk_p
2- (<i>ortho</i>)	0.370		1.7	2.9	0.63	1.07
3- (<i>meta</i>)	.435		1.7	2.2	.74	0.96
4- (<i>para</i>)	.195		2.0	2.2	.39	0.43
Average free radical k values weighted by G					1.8	2.5
Average radiolytic k values					1.5	2.9

^a Relative to *m*-position ($k_m = \text{unity}$).

m,m-, and *m,p*-quaterphenyl were the sole products from 3-iodobiphenyl and biphenyl, and only *o,p*-, *m,p*-, and *p,p*-quaterphenyl were formed from 4-iodobiphenyl and biphenyl. This is strong indication that hydrogen abstraction or isomerization of free radicals or products did not occur at 80°. However, conclusions cannot be made regarding possible rearrangement or back reaction of the reaction intermediates.

Conclusions

1. The proposed model is believed to be a good method for obtaining partial rate factors for both the radiolytic generation of reactive species and the substitution reactions. The model should be applicable to the study of other compounds and other types of ionizing radiation. The approximate yields of dimers from irradiation of other polyphenyls by electrons (and γ -rays) should be predictable by the use of r and k factors of biphenyl modified by the additivity principle.

2. The low r_p and particularly the low r_o values obtained from electron irradiations at 300° indicate that either the radiolytic generation processes are non-random or that some reactive species are selectively destroyed. The r values obtained at 80° may not differ enough from unity to support a definite conclusion.

3. The radiolytic k_p values are larger and the k_o values are smaller than the average obtained with biphenyl free radicals. This indicates that one or more reactive species more *p*-selective and less *o*-selective than the free radicals is also generated by electron irradiation of biphenyl.

4. The low k_o value obtained at 300° may be due to hindrance caused by increased amplitude of oscillation of the rings of biphenyl about their common bond, but could be due to back reaction or rearrangement of the radical-ring addition intermediate.

5. Since only three quaterphenyl isomers were formed from ultraviolet irradiation of each iodobiphenyl in biphenyl at 80°, it is concluded that hydrogen abstraction, isomerization of the free radicals, or isomerization of final products did not occur.

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