lization. Chromatography of 1 g. of this mixture on alumina[24] and elution with ether and methylene chloride gave 0.75 g. of VI, m.p. 172–173° followed by[25] 0.18 g. of VII, m.p. 184–185°. Thus 24 g. of the mixture has roughly 4:1 composition of VI and VII giving an estimated net yield of 15.6 g. (37%) of VII and 18 g. (43%) of VI. The remaining crude reaction product was chromatographed to obtain 6 g. of a liquid, which lacked —OH and —C≡CH bands (infrared) and showed saturated and α,β-unsaturated carbonyl bands. This liquid has not been further examined.

While 1 g. of pure VII could be obtained from 4.2 g. of VI under conditions described in (b), the starting material was recovered unchanged when ethanol was omitted in another experiment. When 1 g. of 17α-ethynyltestosterone,[26] m.p. 264–266°, was treated as in (b) the starting material was recovered unchanged.

Epimerization of VII *to* VI. Treatment of 2.16 g. of pure VII, m.p. 184–185°, as in (b) above yielded 0.4 g. (18.5%) of VI, m.p. 172–173°, and 1.5 g. (69.4%) of VII, m.p. 184–185°, by crystallization and chromatography.

1-Ethynyl-1α,6-diacetoxy-8a-methyl-1,2,3,7,8,8a-hexahydronaphthalene, IX. Treatment of 2.3 g. of VII, m.p. 184–185°, at room temperature with 15 ml. of acetic anhydride containing 100 mg. of *p*-toluenesulfonic acid yielded 2.0 g. of product, m.p. 110–114° after a work up as above. One crystallization from ether-petroleum ether (b.p. 35–55°) afforded 1.8 g. (55.4%) of IX, m.p. 113–114°; λ_{max} 234 mμ (ε 19,950); infrared 3.04 (s), 4.80 (w), 5.70 (s), 5.76 (s), 6.00 (m), 6.10 (m) μ.

Anal. Calcd. for $C_{17}H_{20}O_4$: C, 70.8; H, 7.0. Found: C, 71.0, 71.0; H, 7.0, 7.1.

Conversion of IX *to* I. A solution of 1.43 g. of IX in 5 ml. of 90% formic acid was refluxed for 1.5 hr. and worked up as described in the preparation of I from VIII. Chromatography of the crude liquid yielded 330 mg. (32.6%) of I, m.p. and mixed m.p. with product from VIII, 97–98°.

1-Acetyl-6-oxo-8a-methyl-3,4,6,7,8,8a-hexahydronaphthalene-6-trimethylenethioketal, X. To a suspension of 1.8 g. of I in a mixture of 5 ml. of ether and 2 ml. of boron fluoride-etherate cooled in ice bath, 1 ml. of propane-1,3-dithiol was added dropwise. The suspension soon turned to a clear solution and in 2 hr. set to a mass of needles. The mixture was dissolved in ether, washed with 10% aqueous sodium bicarbonate and treated as usual. The crude liquid deposited 2.2 g. of crystals which on recrystallization from ether afforded 2.0 g. (75%) of X, m.p. 119.5–120.0°; λ_{max} 230 mμ (ε 12,300)[27]; infrared 6.00 (s), 6.18 (m) μ both of relatively diminished intensity as compared to same peaks in I.

Anal. Calcd. for $C_{16}H_{22}OS_2$: C, 65.3; H, 7.5; S, 21.8. Found[a]: C, 65.1, 65.3; H, 7.6, 7.6; S, 21.6, 21.8.

1-Acetyl-6β-hydroxy-8a-methyl-3,4,6,7,8,8a-hexahydronaphthalene, XI. A solution of 1 g. (5.0 mmoles) of I, 200 mg. (5.3 mmoles) of sodium borohydride and 1 ml. of water in 10 ml. of *t*-butyl alcohol was stirred for 1 hr. at room temperature. The excess borohydride was destroyed by adding a few drops of glacial acetic acid and the mixture evaporated to dryness. After the usual treatment the crude liquid gave 0.5 g. of crystals, m.p. 111–114°, and the mother liquor on chromatography afforded a further 120 mg. of crystals. Two crystallizations from ether-methanol yielded 0.58 g. (58%) of colorless XI, m.p. 115–117°, λ_{max} 231 mμ (ε 11,900)[27]; infrared 2.86 (s), 6.03 (s), 6.16 (m).

Anal. Calcd. for $C_{13}H_{18}O_2$: C, 75.7; H, 8.8. Found[a]: C, 75.8, 75.8; H, 8.9, 9.0.

Conversion of I *to* XIII. To a solution of 1.1 g. of I in 10 ml. of dry methanol was added 0.13 g. of sodium hydroxide. The initially colorless solution turned dark red instantaneously on adding the alkali. After 12 hr. at room temperature, the reaction mixture was acidified with a few drops of glacial acetic acid and evaporated to dryness under aspirator pressure. The residue dissolved in methylene chloride was treated as usual. The crude liquid was chromatographed on alumina and eluted with 1:1 ether-benzene mixture to obtain 490 mg. of crystals, m.p. 115.0–116.5°. Charcoal treatment of an ether solution furnished 370 mg. (33.6%) of colorless XIII, m.p. 116–117°; λ_{max} 279 mμ (ε 25,600); infrared 5.82 (s), 6.02 (s), 6.14 (v.s.), 6.26 (s) μ.

Anal. Calcd. for $C_{13}H_{16}O_2$: C, 76.4; H, 7.9. Found[a]: C, 76.3, 76.4; H, 7.7, 7.6.

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[24] When the commercial neutral Aluminum Oxide Woelm was used, extensive loss due to decomposition occurred.

[25] According to the generalization of D. H. R. Barton and R. C. Cookson, *Quart. Rev.*, **10**, 44 (1956) the ethynyl alcohol, m.p. 172–173°, eluted first, should have an axial hydroxyl group. This assignment would indicate structure VII for the 172° isomer as proposed by Nazarov.[11] However, as factors responsible for adsorption of the epimeric alcohols, VI and VII, might be complicated by the proximity of the α,β-unsaturated carbonyl function, a definite assignment cannot be made without further evidence. We have preferred the structures given for reasons mentioned.[12]

[26] We wish to thank the Upjohn Co., Kalamazoo, Mich., for this sample.

[27] We believe that the methyl ketonic function is free in X for two reasons: (a) the absorption maximum for XIV, VI, and VII is at 242 mμ; (b) the λ_{max} for 1-acetyl-1-cyclohexene types is at 232 mμ. See J. D. Chanley, *J. Am. Chem. Soc.*, **70**, 244 (1948).

[CONTRIBUTION FROM THE RESEARCH AND ENGINEERING DIVISION, MONSANTO CHEMICAL CO.]

Steric Effects in the Gomberg Reaction[1]

HAROLD WEINGARTEN

Received June 10, 1960

The influence of substitution *ortho* to the radical site in homolytic aromatic arylation was investigated. Steric effects were found to be insignificant.

Although the Gomberg reaction has been known in the literature[2] for nearly forty years, it has been investigated quantitatively only during the last ten.[3] The bulk of these quantitative studies describe the ratio of biphenyl products

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[1] Presented at the 135th Meeting of the American Chemical Society at Boston, Mass., April 1959, Abstr., p. 47-O.

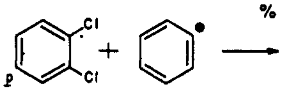
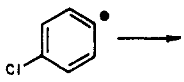
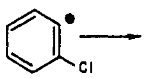
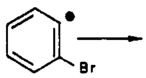
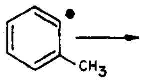
[2] M. Gomberg and W. E. Bachman, *J. Am. Chem. Soc.*, **46**, 2339 (1924).

derived from the phenylation of substituted aromatic solvents. A number of studies have also been reported in which *para*-substituted phenyl radicals were used rather than phenyl radicals.[4,5] Even fewer quantitative studies have been reported describing the effect of substitution *ortho* to the radical site.[6] In the present work we report the behavior of several *ortho*-substituted phenyl radicals. The results of this study have enabled us to describe the configuration of the product determining transition state in somewhat more detail.

RESULTS

The influence of substitution *ortho* to the radical site was investigated by generating *ortho*-substituted phenyl radicals in the presence of *o*-dichlorobenzene. The use of *o*-dichlorobenzene greatly simplified the product analysis since only two biphenyls can be formed. The experimental results are recorded in Table I.[7]

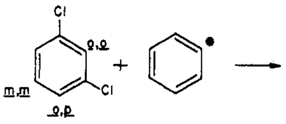
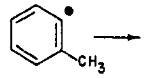
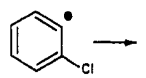
TABLE I
o-DICHLOROBENZENE RESULTS

		% ortho	% para	%
1.		67±3	33±3	2.0
2.		66±3	34±3	1.9
3		55±3	45±3	1.2
4.		54±4	46±4	1.2
5		66±3	34±3	1.9

Phenyl and *p*-chlorophenyl radicals were used as controls (Reactions 1 and 2) and found not to vary significantly in product ratio from each other. Furthermore, their *o/p* ratio agrees with that recorded for the phenylation of chlorobenzene.[3,8] *ortho*-Chloro and *ortho*-bromo substitution are seen to lower measurably the *o/p* ratio (Reactions 3 and 4) while *o*-methyl substitution (Reaction 5) remains at the control value. These results have led us to the conclusion that while *ortho*-halo substitution may give rise to unfavorable dipolar repulsions in the transition state, steric effects are relatively unimportant.

To convince ourselves of the lack of importance of steric effects several experiments were carried out with *m*-dichlorobenzene (Table II). A control experiment with phenyl radicals revealed an *o,o/o,p* ratio equivalent to that obtained with *o*-dichlorobenzene in close adherence to the principle of additivity. The use of *o*-methylphenyl radicals showed a small steric effect, but even here the *o,o*-position is the most reactive. *Ortho*-chloro substitution causes a more marked decrease in *o,o*-product as would be expected.

TABLE II
m-DICHLOROBENZENE RESULTS

		% o,o	% o,p	% m,m
		46±2	44±2	10±2
2.		40±3	48±3	12±3
3.		25±3	59±3	16±3

Product structural assignments were made by one of three methods depending on the compound: (1) independent synthesis, (2) isolation from the reaction mixture followed by oxidation to the substituted benzoic acids, and (3) comparison of structure to relative vapor phase chromatographic retention time[9] (*para* isomers always had higher retention times than *ortho*). The products of Reaction 1 (Table I), 2,3-(*ortho*) and 3,4-dichlorobiphenyl (*para*), were independently synthesized and the *para* isomer shown to have the higher retention time. Two crystalline compounds were isolated from the product of Reaction 2. Oxida-

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(3) D. H. Hey and G. H. Williams, *Discussions Faraday Soc.*, 14, 216 (1953).

(4) C. Shih, D. H. Hey, and G. H. Williams, *J. Chem. Soc.*, 4403 (1958).

(5) R. L. Dannley and M. Sternfeld, *J. Am. Chem. Soc.*, 76, 4543 (1954).

(6) D. H. Hey, in *Theoretical Organic Chemistry*—The Kekule Symposium, Butterworths, London, 1959, p. 257.

(7) The laboratory method we used to generate phenyl and substituted phenyl radicals involved treatment of the diazonium chloride with sodium acetate. Yields were between 30 and 60%. We do not feel these low yields reflect a fractionation of products or preproduct intermediates since the work of D. F. DeTar and H. J. Scheifele, Jr., *J. Am. Chem. Soc.*, 73, 1442 (1951); R. Huisgen and R. Grashey, *Ann.*, 607, 49 (1957); D. R. Angood, D. H. Hey, and G. H. Williams, *J. Chem. Soc.*, 2094 (1952); and D. H. Hey, A. Nechvatal, and T. S. Robinson, *J. Chem. Soc.*, 2892 (1951) demonstrates that biphenyl product ratios are nearly unchanged over a yield range between 15 to above 80% using various radical sources under a wide range of conditions. Nevertheless, it should be pointed out that the ArAr'H· intermediate has been shown by D. F. DeTar and R. A. Long, *J. Am. Chem. Soc.*, 80, 4742 (1958) to yield products other than biphenyls where Ar'H is unsubstituted.

(8) R. Huisgen and R. Grashey, *Ann.*, 607, 46 (1957).

(9) Gas chromatography was our principal analytical tool and the chromatographic areas were shown to be proportional to mole per cent.

TABLE III

BIPHENYL DERIVATIVES

Compound	M.P. (Lit. M.P.)	Carbon, %		Hydrogen, %		Halogen, %	
		Found	Calcd.	Found	Calcd.	Found	Calcd.
2,3-Dichlorobiphenyl[a]	27.7–28.2°	64.5	64.6	3.7	3.6	31.8	31.8
3,4-Dichlorobiphenyl[a]	48.0–49.0° (46°[b])						
2,4-Dichlorobiphenyl[a]	24.1–24.4°	64.7	64.6	3.6	3.6	31.6	31.8
3,5-Dichlorobiphenyl[a]	31.0–32.0° (36°[c])						
2,3,4′-Trichlorobiphenyl[d]	73.0–73.2°	55.7	56.0	2.7	2.7	41.1	41.3
3,4,4′-Trichlorobiphenyl[d]	86.8–87.8°	56.2	56.0	3.2	2.7	41.0	41.3
2,3,2′-Trichlorobiphenyl[e]	28.1–28.8°	55.9	56.0	2.7	2.7	41.2	41.3
3,4,2′-Trichlorobiphenyl[e]	60.1–60.4° (66°[f])	55.9	56.0	2.8	2.7	41.3	41.3
						m. eq. hal./g.	
3,4-Dichloro-2′-bromobiphenyl[g]	66.3–66.5°	47.9	47.7	2.5	2.3	9.92	9.93

[a] Independently synthesized *via* Gomberg reaction. [b] W. Blakely and H. A. Scarborough, *J. Chem. Soc.*, 3007 (1927). [c] L. E. Hinkel and D. H. Hey, *J. Chem. Soc.*, 2786 (1928). [d] Isolated from Reaction 2, Table I. [e] Isolated from Reaction 3, Table I. [f] L. Mascarelli, D. Gatti, and B. Longo, *Gazz.*, **63**, 654 (1933). [g] Isolated from Reaction 4, Table I.

tion of the component with the higher retention time yielded a mixture of 3,4-dichlorobenzoic and 4-chlorobenzoic acids proving it to be the *para* isomer. In a similar way the component with the higher retention time was shown to be the *para* isomer in Reactions 3 and 4. By analogy with the preceding examples the component with the higher retention time from Reaction 5 was assumed to be the *para* isomer.

The products of Reaction 1 (Table II) are 2,6-dichlorobiphenyl (*o,o*), 2,4-dichlorobiphenyl (*o,p*), and 3,5-dichlorobiphenyl (*m,m*). 2,4- and 3,5-Dichlorobiphenyl were independently synthesized and used to assign structures to the chromatographic peaks. The structural assignments for Reactions 2 and 3 were made by analogy with Reaction 1.

DISCUSSION

Althouth it has been suggested that bond formation in the transition state has progressed almost to sp^3 hybridization,[10] we consider this hypothesis untenable. The lack of contrast shown in Gomberg reaction relative rates, particularly the factor of only twenty-fold between benzene and naphthalene,[11] and the high proportion of *meta*- substitution argue strongly for a long, "π-like" bond in the transition state. Furthermore, the transition state picture must permit us to rationalize the dipolar repulsions we believe we have observed and the lack of significant steric effects. The transition state most consistent with the above requirements is described in Fig. 1. In this representation the direction of the forming C—C bond is nearly perpendicular to the plane of the *o*-dichlorobenzene ring. The plane of the radical bearing ring approximately bisects the *o*-dichlorobenzene ring at the carbon to which it is becoming attached. The direction of the C—H bond at the carbon undergoing substitution is only slightly modified.

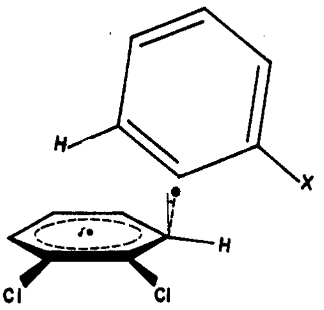

FIGURE 1

In this transition state the carbon-halogen dipoles are able to interact, while steric pressures between the substituent groups are minimal. The substituent X is pictured as being away from the *o*-dichlorobenzene ring since an examination of models shows significant steric repulsions are possible between X and the ring if H and X are interchanged.

EXPERIMENTAL[12]

Gomberg reaction. General method. To 0.1 mole of aniline or substituted aniline was added 30 ml. of concd. hydrochloric acid and the mixture was cooled in an ice bath. To this mixture was slowly added a solution of 10 g. (0.15 mole) of sodium nitrite in 15 ml. of water, keeping the temperature below 5°. If all of the solid did not dissolve it was filtered out before the next step. This solution of diazonium salt was added to 300 ml. of cold solvent–substrate (*o*- or *m*-dichlorobenzene or benzene) with vigorous stirring, followed by the addition of an aqueous solution of 50 g. of sodium acetate trihydrate. The ice bath was removed and the reaction mixture allowed to stir at room temperature until the evolution of nitrogen subsided. The temperature of the reaction was gradually raised until no more nitrogen was evolved. Between 90 and 100% of the theoretical nitrogen was collected.

The organic phase was washed several times with water, dried over magnesium sulfate, and the excess of solvent removed by reduced pressure distillation. The desired product was collected by distillation through a simple Claisen

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(10) D. R. Augood and G. H. Williams, *Chem. Revs.*, **57**, 183 (1957).

(11) R. Huisgen and G. Sorge, *Ann.*, **566**, 162 (1950).

(12) Melting points are corrected. Analyses were performed by the Analytical Department, Monsanto Chemical Co., Dayton, Ohio.

distilling head. The product was analyzed by gas chromatography without further purification. Yields were generally between 30 and 60%. Table III summarizes the analyses and melting points of the biphenyl products.

Vapor phase chromatographic method. The gas chromatography was carried out with either a Perkin-Elmer Model 154C or a Pye Argon instrument. The Perkin-Elmer was equipped with a 2-m. stainless steel column packed with fire brick C-22 (mesh 40–60) impregnated with Dow Corning Silicone Fluid 550 (10%). The eluent was helium and the column temperature was in the range of 180–200°. The Pye Argon was equipped with a 4.5-foot column packed with Celite (mesh 80–100) impregnated with Dow Corning Silicone Fluid 550 (5%). The eluent was argon and the column temperature was in the range of 150–160°.

Oxidation of biphenyl derivatives. General method. One gram of biphenyl derivative was dissolved in 20 ml. of acetic acid (gl.). Three grams of chromic anhydride was added to a solution of 1 ml. of water in 20 ml. of acetic acid. The two preparations were combined and heated on a steam bath for 2 hr. The reaction mixture was then poured into excess ice water and the precipitate collected and recrystallized from benzene. The benzoic acid product was then identified by mixed melting point with authentic sample or by infrared analysis.

Acknowledgment. The author wishes to thank William D. Ross and James M. Schlater for their excellent work on the gas chromatographic analyses.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, FLORIDA STATE UNIVERSITY]

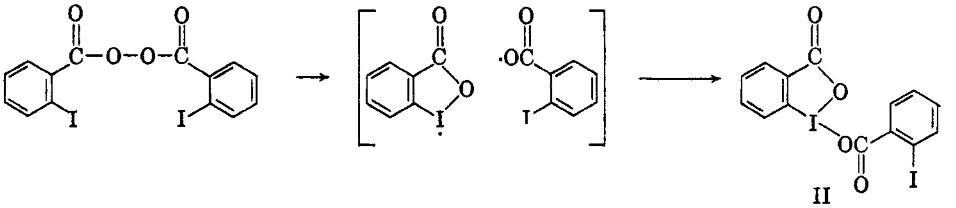
o-Iodo-p'-nitrobenzoyl Peroxide[1]

WOLFGANG HONSBERG AND J. E. LEFFLER

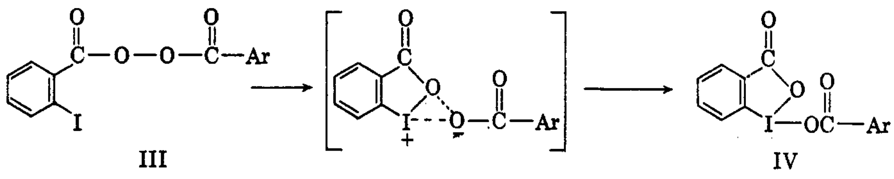
Received June 13, 1960

Bis(o-iodobenzoyl) peroxide and o-iodo-p'-nitrobenzoyl peroxide decompose by a concerted free radical mechanism leading to heterocyclic iodo radicals. The change from an o'-iodo to a p'-nitro substituent markedly decelerates the decomposition rather than accelerating it as would be expected for an ionic mechanism. The decomposition of o-iodo-p'-nitrobenzoyl peroxide is not subject to acid catalysis but is accelerated to an unusual extent by polar solvents. Vinyl chain polymerization is initiated by the peroxide even in polar solvents.

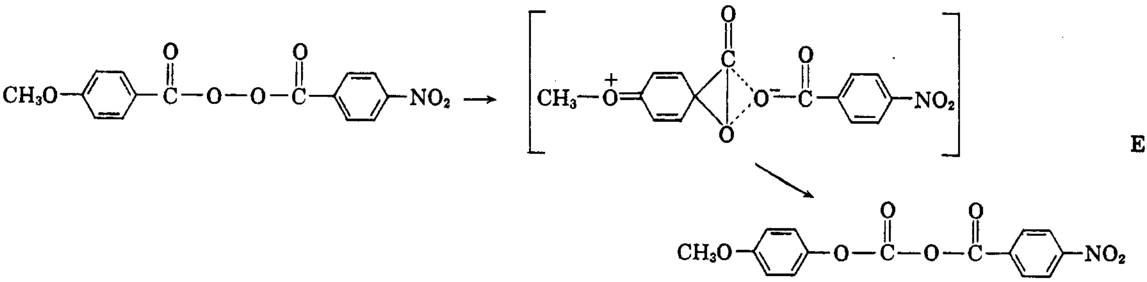
The decomposition of bis(o-iodobenzoyl) peroxide (I) is a fast reaction involving participation of the *ortho* iodo substituent in the cleavage of the peroxide bond.[2] The main product is a cyclic compound (II), presumably arising from the recombination of free radicals. However, the initiation of polymerization by the peroxide (I) is inefficient, probably because of primary recombination of the radicals, but leaving open the possibility of some concurrent, nonradical decomposition.



Eq. 1



Eq. 2



Eq. 3

The most likely nonradical reaction path would be decomposition into ion pairs (Equation 2) analogous

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(1) This investigation was supported by a grant from the National Science Foundation.

(2) J. E. Leffler, R. D. Faulkner, and C. C. Petropoulos *J. Am. Chem. Soc.*, 80, 5435 (1958).