

Hydrogen Atom Abstraction from Substituted Diphenylmethanes by Bromine Atoms

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The relative reactivities of a variety of *ortho*-, *meta*-, and *para*-substituted diphenylmethanes with N-bromosuccinimide in refluxing carbon tetrachloride have been determined by competition experiments. The reactivities of diphenylmethanes bearing nucleophilic *ortho* substituents, e.g., COOC₆H₅, NO₂, COSC₆H₅, OCSC₆H₅, and C₆H₅, are somewhat less than those of their *para* isomers, and the rate ratios for reaction of these isomeric pairs with bromine atoms are not significantly different from those of pairs in which the substituents are incapable of *ortho* participation. Possible reasons for the failure of the nucleophilic groups to function as intramolecular catalysts when located adjacent to the reaction center are discussed. On the basis of a consideration of the magnitude of the ρ value observed for bromine atom abstraction of benzylic hydrogen from *meta*- and *para*-substituted diphenylmethanes, it is suggested that the effectiveness of *ortho* substituents as participants in radical processes relates to the degree of polarization at the transition state.

This report is one of a series dealing with the influence of substrate substituents on the rate of abstraction of benzylic hydrogen by bromine atoms generated from N-bromosuccinimide.¹ The current investigation has been concerned with the influence of ring substituents on the rate of conversion of diphenylmethanes into benzhydryl bromides. The research was stimulated in part by the observation²⁻⁵ that certain nucleophilic *ortho* substituents (COOC₆H₅ and NO₂) function effectively as intramolecular catalysts in solvolysis reactions of benzhydryl halides. It has seemed of interest to determine whether or not these and other potentially nucleophilic *ortho* substituents may also participate in reactions proceeding by way of benzhydryl radical (as contrasted to benzhydryl cation) type intermediates.⁶ Accordingly, a number of pairs of *ortho* and *para* isomers of appropriately substituted diphenylmethanes have been included among the substrates used in the present study. The relative rates of reaction of the various substrates with N-bromosuccinimide in carbon tetrachloride have been determined by means of competition experiments. In correlating the experimental results the relative reactivities of certain *meta*- and *para*-substituted diphenylmethanes have been treated by the Hammett equation as a means of assessing the extent of polarization at the transition state of the reactions in question.

Experimental Section

Analytical Procedures.—Melting points and boiling points are uncorrected. Visible spectra were recorded on a Beckman DB instrument and infrared spectra were taken with a Perkin-Elmer Model 237B instrument. Nuclear magnetic resonance spectra were obtained using a Varian Associates Model A-60A instrument. Nmr proton chemical shifts are reported in parts per

million (δ) downfield from TMS. Microanalyses were performed by Mr. V. Tashinian and Associates, Berkeley, Calif.

Materials.—Commercial samples of toluene (Eastman Organic Chemicals), ethylbenzene, anisole (Matheson Coleman and Bell), benzyl chloride (Mallinckrodt), diphenylmethane (Aldrich Chemical Co., Inc.), and N-bromosuccinimide (Arapahoe Chemicals, Inc.) were used without further purification. J. T. Baker reagent grade carbon tetrachloride was used as the reaction medium in the competition experiments.

o- and *p*-methoxydiphenylmethane were prepared in 85% yield by the reaction of *o*- and *p*-benzylphenol (Columbia Organic Chemicals), respectively, with a slight excess of dimethyl sulfate in aqueous sodium hydroxide. The usual product recovery procedures were employed⁷ to obtain *o*-methoxydiphenylmethane, bp 104–105° (0.4 mm) [lit.⁸ b 159–160° (12 mm)], *n*_D²⁰ 1.5800, and *p*-methoxydiphenylmethane, bp 123–123.5° (1 mm) [lit.⁹ bp 133–135° (4 mm)].

o-Phenylbenzophenone was prepared from 2-bromobiphenyl (K & K Laboratories) by the procedure of Bradsher.¹⁰ *o*- and *p*-benzylbiphenyl^{11,12} were obtained through the Wolff-Kishner reduction of *o*- and *p*-phenylbenzophenone (*para* isomer from Eastman Organic Chemicals), respectively.

The *o*- and *p*-benzoyloxydiphenylmethane were synthesized from the corresponding *o*- and *p*-benzylphenol and benzoyl chloride as described previously.²

To prepare *o*-thionbenzoyloxydiphenylmethane, 6.3 g of thiobenzoyl chloride¹³ was added dropwise to a solution of 7.4 g of *o*-benzylphenol in 30 ml of pyridine as the mixture was stirred. The reaction mixture was warmed on a steam bath for ca. 2 hr and then stirred at room temperature for an additional 12 hr. The reaction was carried out under a nitrogen atmosphere. The mixture was separated into two layers by the addition of ether and water. The ether phase was washed successively with dilute hydrochloric acid and sodium hydroxide solutions and dried over anhydrous magnesium sulfate. The ether solvent was then removed, and the residual oil was purified by alumina column chromatography. A yellow band was removed from the column by use of a 3:1 *n*-pentane-anhydrous ether mixture. On evaporation of the solvent from the eluent, an orange-yellow oil was obtained which solidified upon standing at room temperature. Recrystallization of this material from mixed hexanes yielded 4.8 g (39%) of *o*-thionbenzoyloxydiphenylmethane as yellow crystals: mp 86–88°; visible max (C₂H₅OH) 435 m μ (ϵ 116); ir (Nujol) 1270 cm⁻¹ (ester C=S); nmr (CCl₄) δ 3.85 (s, 2, CH₂), 7.25 (br, 12, aromatic), and 8.20 ppm (m, 2, *ortho* to C=S).

Anal. Calcd for C₂₀H₁₆OS: C, 78.90; H, 5.31; S, 10.53. Found: C, 78.64; H, 5.45; S, 10.44.

p-Thionbenzoyloxydiphenylmethane was prepared from 4.9 g of *p*-benzylphenol and 4.3 g of thiobenzoyl chloride by much the same procedure described for the synthesis of the *ortho* isomer.

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(6) The influences of neighboring groups on the rates of polar displacement processes have been subject to extensive investigation, but relatively few examples have been reported of homolytic processes which are accelerated through participation by a group adjacent to the reaction center. Notable in this connection are the decompositions of certain perbenzoates as investigated by J. C. Martin and his associates; see T. H. Fisher and J. C. Martin, *J. Amer. Chem. Soc.*, **88**, 3882 (1966), and preceding papers.

Purification was accomplished by alumina column chromatography. Recrystallization of the crude product from *n*-hexane yielded 3.0 g (37%) of *p*-thionbenzoyloxydiphenylmethane as yellow needles: mp 67–69.5°; visible max (C₂H₅OH) 435 mμ (ϵ 118); ir (Nujol) 1270 cm⁻¹ (ester C=S); nmr (CCl₄) δ 4.00 (s, 2, CH₂), 7.25 (br, 12, aromatic), and 8.35 ppm (m, 2, *ortho* to C=S).

Anal. Calcd for C₂₀H₁₆OS: C, 78.90; H, 5.31; S, 10.53. Found: C, 78.74; H, 5.43; S, 10.35.

o-Bromobenzophenone was obtained from *o*-bromobenzoyl chloride by a procedure described previously.¹⁴

o- and *p*-bromodiphenylmethane^{15,16} were prepared by reduction of *o*- and *p*-bromobenzophenone (*para* isomer from Aldrich Chemical Co., Inc.) in a mixture of 47% hydriodic acid and red phosphorus as described elsewhere.¹⁵

The preparation of *o*- and *p*-benzylbenzoic acid and *o*- and *p*-carbophenoxydiphenylmethane has been described previously.²

To prepare *o*-thiolcarbophenoxydiphenylmethane, 8.4 g of thionyl chloride was added slowly to a solution of 13.4 g of *o*-benzylbenzoic acid² in 35 ml of dry pyridine. When the reaction mixture had cooled to room temperature, 7.9 g of thiophenol was added and the mixture was heated on a steam bath for 2.5 hr. Approximately 150 ml each of ether and water were added, and the ether layer was washed successively with dilute hydrochloric acid, 3 *N* sodium hydroxide, and water. The ether solution was dried (MgSO₄) and concentrated. The residual oil crystallized upon standing at room temperature. Recrystallization of the crude product from 110 ml of mixed hexanes provided 13.7 g (71.5%) of *o*-thiolcarbophenoxydiphenylmethane as white crystals: mp 63–64°; ir (Nujol) 1680 cm⁻¹ (ester C=O); nmr (CCl₄) δ 4.19 (s, 2, CH₂), 7.29 (m, 13, aromatic), and 7.84 ppm (m, 1, *ortho* to C=O).

Anal. Calcd for C₂₀H₁₆OS: C, 78.90; H, 5.31; S, 10.53. Found: C, 79.17; H, 5.24; S, 10.56.

p-Thiolcarbophenoxydiphenylmethane was prepared in 65% yield from 10.8 g of *p*-benzylbenzoic acid,² 7.00 g of thionyl chloride, and 6.5 g of thiophenol in 40 ml of pyridine by much the same procedure described for the synthesis of the *ortho* isomer. Recrystallization of the crude product from *n*-hexane gave 10 g of white crystals: mp 84–84.5°; ir (Nujol) 1660 cm⁻¹ (ester C=O); nmr (CCl₄) δ 3.97 (s, 2, CH₂), 7.24 (br, 12, aromatic), and 7.90 ppm (m, 2, *ortho* to C=O).

Anal. Calcd for C₂₀H₁₆OS: C, 78.90; H, 5.31; S, 10.53. Found: C, 78.79; H, 5.21; S, 10.71.

o-Nitrodiphenylmethane was prepared from *o*-nitrobenzyl bromide according to the procedure described previously,³ bp 130–131° (0.4 mm) [lit.³ bp 156–157° (1.3 mm)], *n*^{25D} 1.5966.

p-Nitrodiphenylmethane¹⁷ was synthesized by the reaction of *p*-nitrobenzyl bromide¹⁸ with benzene in the presence of aluminum chloride.

p-Methyldiphenylmethane was prepared in 91% yield by the Wolff-Kishner reduction of *p*-methylbenzophenone (Eastman Organic Chemicals), bp 96–97° (0.9 mm) [lit.¹⁹ bp 144° (16 mm)].

m-Methoxybenzophenone was prepared by the reaction of *m*-methoxybenzoyl chloride with benzene in the presence of anhydrous aluminum chloride, bp 142–143° (0.2 mm), mp 37–38° [lit.²⁰ bp 342–343° (730 mm), mp 37°].

m-Methoxydiphenylmethane²¹ was obtained in low yield (19.5%) by the Wolff-Kishner reduction of *m*-methoxybenzophenone.

p-Fluorodiphenylmethane²² and *p*-chlorodiphenylmethane²³ were prepared in ca. 90% yield by reduction of *p*-fluorobenzophenone (Aldrich Chemical Co., Inc.) and *p*-chlorobenzophenone (Matheson Coleman and Bell), respectively, in a mixture of red phosphorus and 47% hydriodic acid. The procedure was

similar to that employed by Bradsher¹⁵ in the synthesis of *o*-bromodiphenylmethane.

p-Carbomethoxydiphenylmethane was prepared in 91.5% yield by the sulfuric acid catalyzed reaction of *p*-benzylbenzoic acid² and methanol: bp 149–150° (1 mm); *n*^{25D} 1.5746; nmr (CCl₄) δ 3.87 (s, 3, CH₃), 4.01 (s, 2, CH₂), 7.21 (br, 7, aromatic), and 7.90 ppm (m, 2, *ortho* to C=O).

Anal. Calcd for C₁₈H₁₄O₂: C, 79.61; H, 6.25. Found: C, 79.55; H, 6.39.

p-Cyanobenzyl bromide²⁴ was obtained through the light-induced reaction of equimolar quantities of *N*-bromosuccinimide and *p*-cyanotoluene (Eastman Organic Chemicals) in carbon tetrachloride solution. From the product of reaction of *p*-cyanobenzyl bromide and anhydrous aluminum chloride in dry benzene, *p*-cyanodiphenylmethane²⁵ was obtained. Alternatively, this material was isolated in 76% yield from the crude products obtained by refluxing a mixture of *p*-benzylbenzamide,²⁵ thionyl chloride, and dry benzene.

m-Nitrobenzyl bromide¹⁸ was prepared through the light-induced reaction of equimolar quantities of *m*-nitrotoluene (Eastman Organic Chemicals) and *N*-bromosuccinimide. From products of the Friedel-Crafts reaction of 30 g of *m*-nitrobenzyl bromide and 18.5 g of anhydrous aluminum chloride in 300 ml of benzene, 18.2 g (61.5% yield) of *m*-nitrodiphenylmethane was isolated as a yellow liquid: bp 143–144° (0.5 mm); *n*^{25D} 1.5980; nmr (CCl₄) δ 4.02 (s, 2, CH₂), 7.25 (br, 7, aromatic), and 8.95 ppm (br, 2, *ortho* to NO₂).

Anal. Calcd for C₁₈H₁₁NO₂: C, 73.21; H, 5.21; N, 6.57. Found: C, 73.28; H, 5.18; N, 6.79.

Competition Experiments.—The particular pair of compounds used in an individual competition reaction were chosen such that they were relatively similar in their rates of reaction with *N*-bromosuccinimide (NBS) and their nmr proton absorption positions were well separated. For each determination the two competing compounds were weighed into a 50-ml flask containing a weighed quantity of NBS. This mixture was diluted to ca. 20–25 ml with carbon tetrachloride, treated with 0.1 g of benzoyl peroxide, stirred vigorously, and heated under reflux (measured pot temperature 77°) until the brominating agent had disappeared completely from the bottom of the flask (15–30 min).

After the reactions were complete, the cooled mixtures were treated with weighed samples of an appropriate internal standard and the amounts of the unreacted starting materials and their bromides in the liquid portion of the product mixture were determined using a Varian Associates Model A-60A instrument as described elsewhere.^{1a} The relative reactivities, k_A/k_B , of the competing pairs of compounds were calculated using the usual²⁶ integrated rate equation $k_A/k_B = \log(A_0/A_t)/\log(B_0/B_t)$, where A_0 and B_0 are the initial and A_t and B_t are the final quantities of the compounds competing for the brominating agent.

The results of the analyses of the various reaction mixtures are summarized in Table I. The quantities of the substituted diphenylmethane bromination products, ABr and BBr, were usually determined directly from the appropriate integrated proton peak areas. In some instances, and always when the bromide products did not have any benzylic or other nonaromatic protons, ABr and BBr were calculated as $(A_0 - A_t)$ and $(B_0 - B_t)$, respectively. In such cases, and also in those cases in which A_t or B_t were calculated as the difference between the amounts of starting materials and the products, the numerical values are reported in parentheses.

In most of the experiments summarized in Table I, the agreement between the amounts of bromide products formed, the amounts of competing substrates consumed, and the quantity of NBS initially present in the reaction mixture is very good. Notable among the exceptions are the results of experiments with diphenylmethanes bearing *o*-COSC₆H₅ and *o*-OCSC₆H₅ substituents.

Results

In Table II the relative reactivities of various isomeric pairs of *ortho*- and *para*-substituted diphenylmethanes with *N*-bromosuccinimide are compared. Included in this tabulation are $k(\textit{ortho})/k(\textit{para})$ values for several systems in which the substituents are

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TABLE I
 COMPETITIVE BROMINATIONS OF SOME SUBSTITUTED DIPHENYLMETHANES WITH N-BROMOSUCCINIMIDE (CCl₄, 77°)

C ₆ H ₅ CH ₂ C ₆ H ₄ X (A), X	B	Registry no.	A ₀ , mmol	A _f , mmol	B ₀ , mmol	B _f , mmol	ABr, mmol	BBr, mmol	NBS, ^a mmol	k _A /k _B	k _A /k _{toluene} (per H)	
<i>o</i> -COOC ₆ H ₅	(A), X = <i>o</i> -COOC ₆ H ₅	A, 23450-10-4 B, 23450-11-5	8.02	4.46	8.02	4.08	(3.56)	(3.94)	7.78	0.865	5.54 ^b	
<i>o</i> -COOC ₆ H ₅	A, X = Br		6.11	2.02	5.89	2.28	(4.09)	3.56	7.64	1.17	5.40 ^b	
<i>o</i> -COOC ₆ H ₅	A, X = <i>p</i> -COOC ₆ H ₅	B, 23450-12-6	5.01	2.37	4.49	1.56	(2.64)	2.85	5.65	0.710	5.56 ^b	
<i>p</i> -COOC ₆ H ₅	C ₆ H ₅ CH ₃	B, 108-88-3	7.74	3.78	25.18	2.73	(21.96)	(3.96)	3.22	7.41	5.18	7.77 ^c
<i>p</i> -COOC ₆ H ₅	C ₆ H ₅ CH ₃		8.20	4.78	32.59	2.82	(29.32)	(3.42)	3.27	6.87	5.09	7.64 ^c
<i>p</i> -COOC ₆ H ₅	C ₆ H ₅ CH ₂ CH ₃ ^d	B, 100-41-4	6.05	3.71	4.25	0.926	2.82	3.31	5.90	0.320	8.06 ^c	
<i>o</i> -NO ₂ ^e	C ₆ H ₅ CH ₃	A, 5840-40-4	6.00	2.53	6.28	2.73	(3.47)	(3.53)	7.20	1.04	1.56 ^f	
<i>o</i> -NO ₂ ^g	C ₆ H ₅ CH ₃		4.94	2.34	5.77	2.82	(2.60)	(2.95)	5.70	1.04	1.56 ^f	
<i>p</i> -NO ₂	C ₆ H ₅ CH ₃	A, 1817-77-2	7.25	2.38	6.48	4.34	4.53	(2.14)	7.36	2.78	4.17 ^f	
<i>p</i> -NO ₂	C ₆ H ₅ CH ₃		7.11	2.46	5.70	3.79	4.55	6.70	2.61	3.92 ^f		
<i>o</i> -OCOC ₆ H ₅	C ₆ H ₅ CH ₃		7.08	4.46	25.19	2.73	(22.68)	(2.62)	2.51	5.10	4.35	6.53 ^c
<i>o</i> -OCOC ₆ H ₅	C ₆ H ₅ CH ₃		7.89	5.16	33.79	2.73	(30.51)	(2.73)	3.28	6.08	4.18	6.27 ^c
<i>p</i> -OCOC ₆ H ₅	C ₆ H ₅ CH ₃	A, 23450-15-9	7.02	3.65	24.41	2.73	(22.89)	(3.37)	1.52	5.00	10.1	15.2 ^c
<i>p</i> -OCOC ₆ H ₅	C ₆ H ₅ CH ₃		7.35	3.60	31.59	2.73	(29.43)	(3.75)	2.16	6.12	10.3	15.5 ^c
<i>p</i> -OCOC ₆ H ₅	C ₆ H ₅ CH ₃		8.89	5.00	28.43	2.73	(26.89)	(3.89)	1.54	5.57	10.4	15.6 ^c
<i>p</i> -OCOC ₆ H ₅	C ₆ H ₅ CH ₂ CH ₃ ^d		5.97	2.91	6.21	2.05	3.08	(4.16)	7.24	0.646	16.3 ^c	
<i>o</i> -OCH ₃	C ₆ H ₅ CH ₂ CH ₃ ^d	A, 883-90-9	4.80	2.13	4.41	1.91	(2.67)	(2.50)	5.80	0.970	24.4 ^c	
<i>o</i> -OCH ₃	C ₆ H ₅ CH ₂ CH ₃ ^d		4.44	2.07	5.19	2.21	(2.37)	3.02	6.02	0.897	22.6 ^c	
<i>o</i> -OCH ₃	C ₆ H ₅ CH ₂ CH ₃ ^d		3.84	1.77	4.71	1.93	(2.07)	2.70	5.40	0.866	21.8 ^c	
<i>p</i> -OCH ₃	C ₆ H ₅ CH ₂ CH ₃ ^d	A, 834-14-0	8.19	4.03	6.79	4.23	4.14	(2.56)	7.55	1.50	37.8 ^c	
<i>p</i> -OCH ₃	C ₆ H ₅ CH ₂ CH ₃ ^d		7.95	2.92	6.10	3.34	4.84	(2.76)	8.22	1.66	41.9 ^c	
<i>p</i> -OCH ₃	C ₆ H ₅ CF ₃ CH ₃ ^d		7.26	2.90	5.21	3.04	4.34	2.18	6.79	1.70	42.9 ^c	
<i>o</i> -Br	C ₆ H ₅ CH ₃	A, 23450-18-2	8.04	5.11	22.39	1.91	(19.37)	(2.93)	3.02	5.74	3.13	4.70 ^c
<i>o</i> -Br	C ₆ H ₅ CH ₃		15.72	8.31	30.05	1.91	(24.39)	(7.41)	5.66	13.10	3.01	4.52 ^c
<i>p</i> -Br	C ₆ H ₅ CH ₃	A, 2116-36-1	9.03	4.68	33.18	1.91	(30.51)	(4.35)	2.67	7.05	7.92	11.9 ^c
<i>p</i> -Br	C ₆ H ₅ CH ₃		9.06	4.93	42.90	1.91	(39.96)	(4.13)	2.94	7.22	8.28	12.4 ^c
<i>p</i> -Br	C ₆ H ₅ CH ₂ CH ₃ ^d		6.85	3.97	5.53	1.91	2.84	3.65	6.56	0.512	12.9 ^c	
<i>o</i> -COSC ₆ H ₅	C ₆ H ₅ CH ₃	A, 23450-20-6	5.29	3.56	5.14	1.91	(3.93)	(1.73)	1.21	7.69	1.48	2.22 ^c
<i>o</i> -COSC ₆ H ₅	C ₆ H ₅ CH ₃		4.45	2.46	5.70	1.91	(4.23)	(1.99)	1.47	7.74	1.98	2.97 ^c
<i>o</i> -COSC ₆ H ₅	C ₆ H ₅ CH ₃		6.11	4.09	5.85	1.91	(2.02)	(1.42)	7.67	1.45	2.18 ^c	
<i>o</i> -COSC ₆ H ₅	C ₆ H ₅ CH ₂ CH ₃ ^d		7.92	7.45	5.76	3.38	(0.47)	(2.38)	4.72	0.116	2.04 ^c	
<i>p</i> -COSC ₆ H ₅	C ₆ H ₅ CH ₃	A, 23450-21-7	7.30	4.32	34.41	1.91	(30.76)	(2.98)	3.65	6.60	4.60	6.90 ^c
<i>p</i> -COSC ₆ H ₅	C ₆ H ₅ CH ₃		6.95	3.51	21.68	1.91	(18.81)	(3.44)	2.87	6.40	4.79	7.19 ^c
<i>p</i> -COSC ₆ H ₅	C ₆ H ₅ CH ₂ CH ₃ ^d		6.35	4.60	5.16	1.74	1.82	3.44	5.36	0.296	7.45 ^c	
<i>o</i> -OCSC ₆ H ₅	C ₆ H ₅ CH ₂ CH ₃ ^d	A, 23450-22-8	3.42	2.43	3.56	1.48	(0.99)	2.02	4.84	0.388	9.78 ^c	
<i>o</i> -OCSC ₆ H ₅	C ₆ H ₅ CH ₂ CH ₃ ^d		4.04	2.90	4.35	1.74	(1.14)	2.26	5.18	0.362	9.11 ^c	
<i>p</i> -OCSC ₆ H ₅	C ₆ H ₅ CH ₃	A, 23450-23-9	4.56	2.20	20.10	1.91	(18.50)	(2.36)	1.60	4.16	8.80	13.2 ^c
<i>p</i> -OCSC ₆ H ₅	C ₆ H ₅ CH ₂ CH ₃ ^d		4.65	3.03	3.34	1.53	1.64	1.79	3.93	0.546	13.8 ^c	
<i>o</i> -C ₆ H ₅	C ₆ H ₅ CH ₃	A, 606-97-3	6.90	2.75	29.60	1.91	(26.86)	(4.15)	2.74	6.90	9.40	14.1 ^c
<i>o</i> -C ₆ H ₅	C ₆ H ₅ CH ₃		6.54	2.74	21.50	1.91	(19.55)	(3.80)	1.95	5.81	9.21	13.8 ^c
<i>o</i> -C ₆ H ₅	C ₆ H ₅ CH ₂ CH ₃ ^d		5.12	2.20	3.92	1.91	(0.97)	2.93	2.92	5.95	0.605	15.2 ^c
<i>p</i> -C ₆ H ₅	C ₆ H ₅ CH ₃	A, 613-42-3	7.31	2.70	28.20	1.91	(26.71)	(4.61)	1.49	6.32	18.0	27.0 ^c
<i>p</i> -C ₆ H ₅	C ₆ H ₅ CH ₃		7.24	2.72	32.65	1.91	(30.76)	(4.52)	1.89	6.63	16.3	24.5 ^c
<i>p</i> -C ₆ H ₅	C ₆ H ₅ CH ₂ CH ₃ ^d		7.31	3.04	6.34	2.65	4.24	3.78	8.16	1.01	25.4 ^c	
<i>p</i> -CH ₃	C ₆ H ₅ CH ₂ CH ₃ ^d	A, 620-83-7	8.14	4.42	7.16	4.15	3.59 ^b	(3.01)	7.44	1.11	28.0 ^c	
<i>p</i> -CH ₃	C ₆ H ₅ CH ₂ CH ₃ ^d		6.86	3.11	5.82	2.88	3.70 ^b	2.99	7.39	1.12	28.2 ^c	
<i>m</i> -OCH ₃	C ₆ H ₅ CH ₂ CH ₃ ^d	A, 23450-27-3	5.74	2.40	5.76	1.60	3.36	4.13	7.91	0.679	17.1 ^c	
<i>m</i> -OCH ₃	C ₆ H ₅ CH ₂ CH ₃ ^d		5.80	3.41	6.30	2.94	2.44	3.32	5.95	0.699	17.6 ^c	
<i>p</i> -F	C ₆ H ₅ CH ₂ CH ₃ ^d	A, 587-79-1	6.06	2.63	5.95	1.62	3.40	4.38	8.04	0.642	16.2 ^c	
<i>p</i> -F	C ₆ H ₅ CH ₂ CH ₃ ^d		7.32	4.90	6.60	3.46	2.45	3.19	5.79	0.621	15.7 ^c	
<i>p</i> -Cl	C ₆ H ₅ CH ₂ CH ₃ ^d	A, 831-81-2	9.26	5.36	7.21	2.48	3.81	(4.73)	8.96	0.514	12.9 ^c	
<i>p</i> -Cl	C ₆ H ₅ CH ₂ CH ₃ ^d		8.00	4.61	7.40	2.63	3.33	4.74	8.25	0.532	13.4 ^c	
<i>p</i> -COOCH ₃	C ₆ H ₅ CH ₂ CH ₃ ^d	A, 23450-30-8	6.89	4.50	4.85	1.31	2.29	3.43	5.97	0.324	8.17 ^c	
<i>p</i> -COOCH ₃	C ₆ H ₅ CH ₂ CH ₃ ^d		7.04	5.03	4.31	1.54	2.10	(2.77)	4.99	0.328	8.21 ^c	
<i>p</i> -CN	C ₆ H ₅ CH ₃	A, 23450-31-9	7.02	2.18	5.35	3.71	4.79	1.60	6.62	3.30	4.95 ^f	
<i>p</i> -CN	C ₆ H ₅ CH ₃		7.71	2.24	5.15	3.57	5.49	(1.58)	7.41	3.38	5.07 ^f	
<i>m</i> -NO ₂	C ₆ H ₅ CH ₃	A, 5840-41-5	7.30	2.41	6.24	3.94	4.93	(2.30)	7.55	2.41	3.62 ^f	
<i>m</i> -NO ₂	C ₆ H ₅ CH ₃		7.35	2.41	5.66	3.61	4.90	(2.05)	7.30	2.47	3.71 ^f	

^a Initial N-bromosuccinimide. ^b Internal standard is ethylbenzene. ^c Internal standard is benzyl chloride. ^d $k_{\text{ethylbenzene}}/k_{\text{toluene}}$ per hydrogen is 25.2 (see ref 1a). ^e The competition reaction was conducted under irradiation with a 750-W projection lamp. ^f Internal standard is anisole. ^g Internal standard is diphenylmethane. ^h ABr is the quantity of *p*-methylbenzhydryl bromide produced. A small amount (0.48 mmol) of C₆H₅CH₂C₆H₄CH₂Br is also formed as a result of some bromination at the *p*-CH₃ substituent.

functionally incapable of serving as internal nucleophiles when located *ortho* to the reaction center. In this category are the diphenylmethanes with substituents such as Br, OCOC₆H₅,²⁷ and OCH₃, for which $k(\text{ortho})/k(\text{para})$ values vary from 0.37 to 0.56. That is, when participation cannot occur the *ortho* isomer is somewhat less reactive than the *para*. This is presumed to be a reflection of steric hindrance by the *ortho* substituent to the approach of a bromine atom in the abstraction of a hydrogen atom at the reaction center. Values of $k(\text{ortho})/k(\text{para})$ somewhat less than unity are also observed in those cases in which the substituents are

NO₂, COOC₆H₅, C₆H₅, OCSC₆H₅, and COSC₆H₅. The observation that in these cases the *ortho* isomers are not substantially more reactive than the *para* is taken as evidence that nucleophilic groups located *ortho* to the methylene group of a diphenylmethane do not, in fact, facilitate hydrogen abstraction.

A possible explanation for the lack of *o*-COOC₆H₅ involvement in this process is based on a consideration of the capacity of the carbonyl oxygen of that substituent to release electrons to the reaction center at the transition state. For purposes of simplification, it is assumed that an organic radical (I) is fully developed at this phase of the reaction and that the two rings of that radical lie perpendicular to each other;

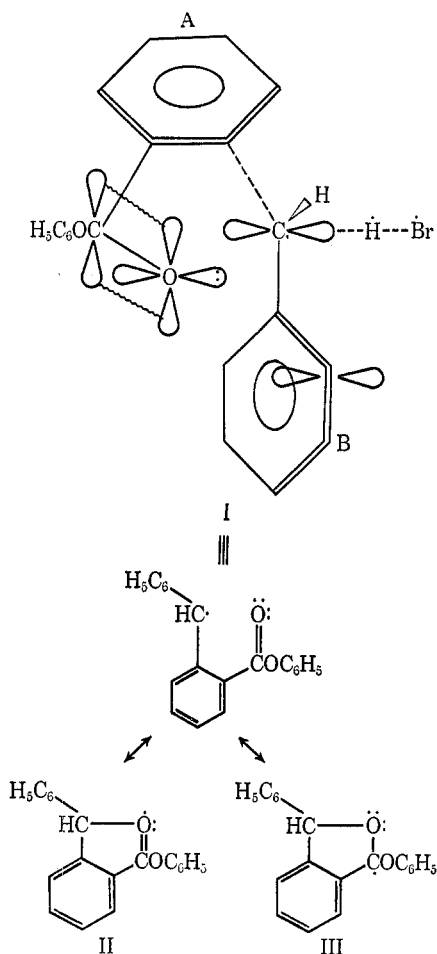
(27) Although this substituent is potentially nucleophilic in character, it does not so function in the solvolysis of *o*-benzoyloxybenzhydryl bromide.²

TABLE II
RATES RELATIVE TO TOLUENE FOR THE REACTIONS OF SUBSTITUTED DIPHENYLMETHANES WITH N-BROMOSUCCINIMIDE

$C_6H_5CH_2C_6H_4X$, X	k_X/k_{toluene} (per H), CCl_4 , 77°	$k(\text{ortho})/k(\text{para})$	$C_6H_5CH_2C_6H_4X$, X	k_X/k_{toluene} (per H), CCl_4 , 77°	$k(\text{ortho})/k(\text{para})$
<i>o</i> -OCH ₃	22.9	0.56	<i>o</i> -Br	4.61	0.37
<i>p</i> -OCH ₃	40.9		<i>p</i> -Br	12.4	
<i>o</i> -C ₆ H ₅	14.4	0.56	<i>o</i> -COOC ₆ H ₅	5.50	0.70
<i>p</i> -C ₆ H ₅	25.6		<i>p</i> -COOC ₆ H ₅	7.82	
<i>o</i> -OCOC ₆ H ₅	6.40	0.41	<i>o</i> -COSC ₆ H ₅	2.35	0.33
<i>p</i> -OCOC ₆ H ₅	15.7		<i>p</i> -COSC ₆ H ₅	7.18	
<i>o</i> -OCSC ₆ H ₅	9.45	0.70	<i>o</i> -NO ₂	1.56	0.39
<i>p</i> -OCSC ₆ H ₅	13.9		<i>p</i> -NO ₂	4.05	
<i>p</i> -CH ₃	28.1		<i>p</i> -Cl	13.2	
H	17.6 ^a		<i>p</i> -COOCH ₃	8.19	
<i>m</i> -OCH ₃	17.4		<i>p</i> -CN	5.01	
<i>p</i> -F	16.0		<i>m</i> -NO ₂	3.67	

^a Reference 1a.

the reasons for the latter assumption are much the same as those presented in the earlier discussion of *o*-carbophenoxy participation in the formation of a diphenylmethyl cation.² It is highly unlikely that the nonbonding electrons of carbonyl oxygen are involved in stabilization of the radical. This would lead to an energetically unfavorable electronic arrangement (II), since oxygen does not have low-en-

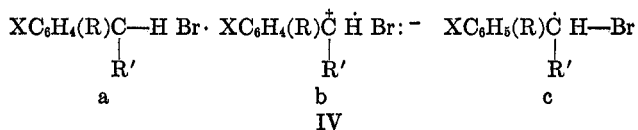


ergy d orbitals to provide for accommodation of nine electrons in its valence shell. Participation by ether oxygen of the carbophenoxy group can be ruled out on the same grounds. For effective involvement of

the π electrons of the carbonyl group (III), the π orbital must be rotated through an angle of *ca.* 90° (so that it overlaps the partially filled orbital at the reaction center). This also may be energetically unlikely, since it is accomplished with the sacrifice of conjugation of the carbonyl group with ring A. Much the same argument can be advanced in accounting for the lack of evidence for acceleration by the ring substituent in the radical bromination of *o*-nitrodiphenylmethane.

The thionbenzoyloxydiphenylmethanes ($C_6H_5CH_2C_6H_4OCSC_6H_5$) and thiolcarbophenoxydiphenylmethanes ($C_6H_5CH_2C_6H_4COSC_6H_5$) have been included in this study on the premise that, unlike oxygen, sulfur can readily expand its valence shell to accommodate more than eight electrons and that the reactions of the *ortho* isomers might, therefore, be subject to intramolecular catalysis. Although the outcome is negative in both instances, it should be noted that neighboring-group participation in which the sulfur of the *o*-phenylthio group is involved has been reported to occur in the free-radical decomposition of *t*-butyl *o*-(phenylthio)perbenzoate.⁶

Application of the Hammett ρ - σ Correlation.—The structure at the transition state (IV) for bromine atom abstraction of benzylic hydrogen is considered to receive contribution from a, b, and c.²³ In situations in which b makes a significant contribution to structure,



separation of a hydrogen atom at the reaction center must have proceeded to a considerable degree.²⁹ Under such circumstances ρ values obtained in a Hammett correlation of relative substrate reactivities with substituent constants (σ or σ^+) for groups X should be substantially negative. The ρ value of -1.38 reported for the reactions of ring-substituted toluenes²⁶

(28) See ref 1a for a discussion and pertinent references.

(29) G. A. Russell and R. C. Williamson, Jr., *J. Amer. Chem. Soc.*, **86**, 2357 (1964).

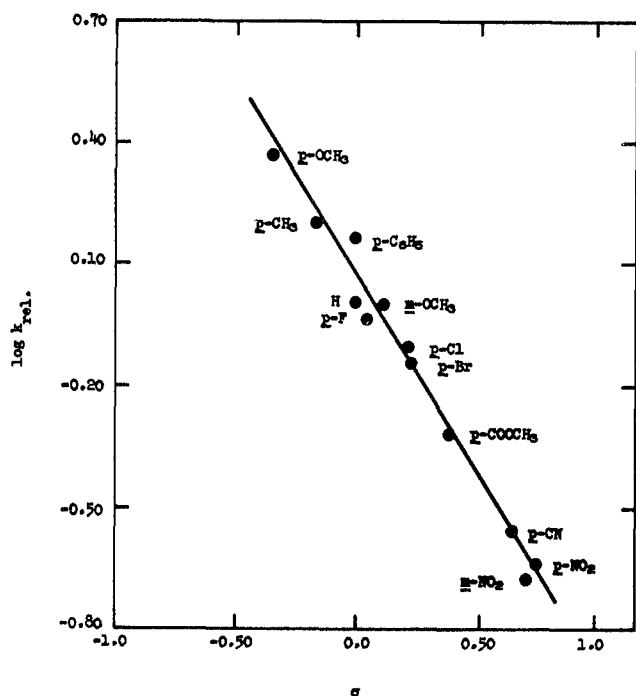


Figure 1.—Logarithms of rates, relative to that for diphenylmethane, for the reactions of $C_6H_5CH_2C_6H_4X$ with N-bromosuccinimide (CCl_4 , 77°) vs. σ values for the substituents X.

with bromine atoms has been explained in these terms.²⁹ Presumably there is relatively little C-H rupture at the transition state for benzylic bromination of the more reactive cumenes³⁰ ($k_{C_6H_5CH(CH_3)_2}/k_{C_6H_5CH_3} = 57.5$)^{1a} and the highly reactive benzyl methyl ethers³¹ ($k_{C_6H_5CH_2OCH_3}/k_{C_6H_5CH_3} = 159$).^{1a} For these processes the ρ values are small (-0.38 and -0.35 , respectively). Ethylbenzenes ($k_{C_6H_5CH_2CH_3}/k_{C_6H_5CH_3} = 25.2$)^{1a} and allylbenzenes ($k_{C_6H_5CH_2CH=CH_2}/k_{C_6H_5CH_3} = 26.2$)³² which are of intermediate reactivity exhibit ρ values of intermediate magnitude (-0.69 ³³ and -0.76 ,³² respectively).³⁴

(30) G. J. Gleicher, *J. Org. Chem.*, **33**, 332 (1968).

(31) R. L. Huang and K. H. Lee, *J. Chem. Soc.*, 5963 (1964).

(32) M. M. Martin and G. J. Gleicher, *J. Org. Chem.*, **28**, 3266 (1963).

(33) R. L. Huang and K. H. Lee, *J. Chem. Soc., C*, 935 (1966).

A plot of average values (Table II) of $\log k_{C_6H_5CH_2C_6H_4X}/k_{diphenylmethane}$ ($\log k_{rel}$) vs. σ is presented in Figure 1.³⁵ In this case the observed ρ value is -0.97 (correlation coefficient $r = 0.990$ and standard deviation $s = 0.044$). The corresponding plot when σ^+ values are used has a slope (ρ) of -0.72 ($r = 0.973$ and $s = 0.054$). This ρ value (-0.97) for the reaction of diphenylmethanes lies between those for the reactions of substituted toluenes and ethylbenzenes with bromine atoms. Correspondingly, diphenylmethane lies between toluene and ethylbenzene in reactivity ($k_{C_6H_5CH_2C_6H_5}/k_{C_6H_5CH_3} = 17.6$).^{1a}

For benzhydryl chloride alcoholysis, in which the degree of polarization at the transition state is unquestionably high, ρ is of the order of -4 (as based on correlation with σ^+).³⁶ Compared with benzhydryl halide solvolysis, the reaction of substituted diphenylmethanes toward bromine atoms is accompanied by a relatively low degree of polarization during activation. Conceivably extensive polarization is an essential feature of processes in which nucleophilic *ortho* substituents have a noticeably favorable effect on reactivity. In this connection it should be recalled that there is strong evidence that at the transition state for the *o*-phenylthio-assisted thermal decomposition of *t*-butyl (*o*-phenylthio)perbenzoate significantly polar structural character has developed.³⁷

Registry No.—N-Bromosuccinimide, 128-08-5.

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(34) For earlier discussion of the relationships between the relative reactivities of various benzyl systems, their Hammett reaction constants, and the degree of bond breaking at the transition state in processes involving bromine atoms, see ref 30 and 33.

(35) All values of σ except that for *p*-COOCH₃ are taken from H. C. Brown and Y. Okamoto, *J. Amer. Chem. Soc.*, **80**, 4979 (1958). The σ value for *p*-COOCH₃ is from J. Hine, "Physical Organic Chemistry," 2nd ed, McGraw-Hill Book Co., Inc., New York, N. Y., 1962, p 87.

(36) S. Nishida, *J. Org. Chem.*, **32**, 2692 (1967).

(37) D. L. Tuleen, W. G. Bentrude, and J. C. Martin, *J. Amer. Chem. Soc.*, **85**, 1938 (1963).