The Competitive Rates of Reaction of a Series of Substituted Benzyl Methyl Ethers with N-Bromosuccinimide

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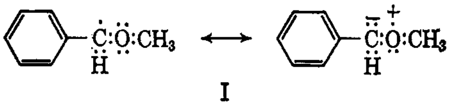
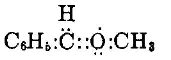
The relative rates of reaction of a series of nuclear-substituted benzyl methyl ethers ($XC_6H_4CH_2OCH_3$) with N-bromosuccinimide in carbon tetrachloride are not highly sensitive to the influence of ring substituents. The small variations in substituent effects observed for the reaction do not parallel those expected for a transition state involving development of negative charge on the benzylic carbon but rather favor a transition state involving positive polarization of the reaction center. On the basis of the substituent effects observed in the reaction of benzyl methyl ethers with N-bromosuccinimide and the results of a determination of the relative rates of reaction of *p*-nitro- and *p*-methoxyethylbenzene ($XC_6H_4CH_2CH_3$) and of *p*-methoxybenzyl cyanide (*p*-$CH_3OC_6H_4CH_2CN$) with N-bromosuccinimide, it has been concluded that the magnitude of the effect of a ring substituent X on the benzyl hydrogen abstraction process is controlled primarily by the ability of the group Y to contribute to the intrinsic stability of the radical ($XC_6H_4\dot{C}HY$) being formed in the activation process.

The reaction of benzyl methyl ether with N-bromosuccinimide proceeds much more rapidly than the corresponding reaction of the brominating agent with aralkyl hydrocarbons[1] and with other α-substituted toluenes.[2] The rate effect of the methoxyl substituent has been ascribed to its ability to donate electrons by resonance to stabilize the radical-like transition state (I) of the reaction step in which one of the benzylic hydrogen atoms is extracted. The alternate



I

nonpolar structure with more than an octet of electrons about oxygen is not considered to make a significant contribution to the resonance hybrid.



$$\mathrm{C_6H_5}{:}\overset{\mathrm{H}}{\ddot{\mathrm{C}}}{::}\underset{\cdot\cdot}{\dot{\mathrm{O}}}{:}\mathrm{CH_3}$$

Inasmuch as the transition state for the reaction of toluene with N-bromosuccinimide is not subject to stabilization through contribution of forms comparable to I, it has seemed of interest to determine whether there is an appreciable difference in the sensitivities of the benzyl methyl ether and toluene reactions to ring substituent effects. Accordingly, a number of substituted benzyl methyl ethers have been prepared and their relative rates of reaction with N-bromosuccinimide have been compared with those reported previously for bromination of the corresponding series of nuclear-substituted toluenes.[3]

Experimental

Materials.—Commercial samples of toluene, ethylbenzene, cumene, and benzyl methyl ether (Eastman Organic Chemicals), benzyl cyanide, diphenylmethane, 4-ethylnitrobenzene, and 4-methoxybenzyl cyanide (Aldrich Chemical Co., Inc.), N-bromosuccinimide (Arapahoe Chemical Inc.), and α-chlorotoluene (Matheson Coleman and Bell Chemicals) were used without further purification. Methyl phenylacetate, b.p. 218–219°, was prepared by the sulfuric acid catalyzed reaction of phenylacetic acid and methanol. *p*-Ethylanisole, b.p. 74–75° (10 mm.),[4] was obtained from the Wolff–Kishner reduction of *p*-methoxyacetophenone by methods described in detail elsewhere.[5]

All but two of the substituted benzyl methyl ethers were prepared through the reactions of the corresponding substituted toluenes with N-bromosuccinimide followed by treatment of the resulting crude benzyl bromides with sodium methoxide. *p*-Methoxybenzyl methyl ether and *m*-methoxybenzyl methyl ether were prepared starting from the corresponding benzyl alcohol rather than from the substituted toluene. The *m*- and *p*-methoxybenzyl alcohols were subjected to reaction with hydrogen bromide gas in benzene followed by treatment again

TABLE I

PHYSICAL CONSTANTS[a] OF SOME SUBSTITUTED BENZYL METHYL ETHERS ($XC_6H_4CH_2OCH_3$)

X	% yield[b]	B.p., °C. (mm.)	Lit. b.p., °C. (mm.)
p-CH_3O	55	74–75 (1.5)[c]	225 (760)[d]
m-CH_3O	51	77–79 (2)[e]	
p-NO_2	36	145–147 (15)	145 (15)[f]
m-NO_2	37	137–138 (11)	138–140 (11)[g]
p-CN	26	103–105 (4)	101 (4)[h]
m-CN	30	128–130 (14)	132 (14)[i]
p-$COOCH_3$	45	93–94.5 (1)[j]	
m-$COOCH_3$	20	94.5–95 (1.5)[k]	
p-Br	40	124–125 (30)	127 (30)[l]
m-Br	35	116–117.5 (21)	117–118 (21)[m]
p-Cl	32	59–61 (1)[n]	
m-Cl	39	58–60 (1.5)[o]	

[a] Commercial samples of *p*-chlorotoluene, *m*-chlorotoluene, *p*-bromotoluene, *m*-bromotoluene, methyl *p*-toluate, methyl *m*-toluate, *m*-tolunitrile, *p*-tolunitrile, *p*-nitrotoluene, *m*-nitrotoluene, and anisyl alcohol (Eastman Kodak Co.) and *m*-methoxybenzyl alcohol (Aldrich Chemical Co.) were used as starting materials in the synthesis of the substituted benzyl methyl ethers. [b] Yield based on initial toluene concentration. [c] *Anal.* Calcd. for $C_9H_{12}O_2$: C, 71.05; H, 7.90. Found: C, 71.18; H, 7.90. [d] Ref. 4, Vol. I, p. 180. [e] *Anal.* Calcd. for $C_9H_{12}O_2$: C, 71.05; H, 7.90. Found: C, 71.03; H, 8.09. [f] V. M. Zuborovski and G. P. Khodot, *Zh. Obshch. Khim.*, **30**, 1245 (1960). [g] F. G. Mann and F. H. C. Stewart, *J. Chem. Soc.*, 4127 (1954). [h] H. B. Hoss and M. L. Bender, *J. Am. Chem. Soc.*, **71**, 1767 (1949). [i] J. W. Baker, J. A. L. Brieux, and D. S. Saunders, *J. Chem. Soc.*, 404 (1956). [j] *Anal.* Calcd. for $C_{10}H_{12}O_3$: C, 66.66; H, 6.67. Found: C, 66.39; H, 6.52. [k] *Anal.* Calcd. for $C_{10}H_{12}O_3$: C, 66.66; H, 6.67. Found: C, 66.30; H, 6.57. [l] J. V. Spniewski and R. Adams, *J. Am. Chem. Soc.*, **48**, 507 (1926). [m] F. G. Mann and F. H. C. Stewart, *J. Chem. Soc.*, 2819 (1954). [n] *Anal.* Calcd. for C_8H_9ClO: C, 61.50; H, 5.77; Cl, 22.45. Found: C, 61.52; H, 5.95; Cl, 22.68. [o] *Anal.* Calcd. for C_8H_9ClO: C, 61.50; H, 5.77; Cl, 22.45. Found: C, 61.26; H, 5.99; Cl, 22.62.

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[1] R. E. Lovins, L. J. Andrews, and R. M. Keefer, *J. Org. Chem.*, **28**, 2846 (1963).

[2] R. E. Lovins, L. J. Andrews, and R. M. Keefer, *ibid.*, **29**, 1616 (1964).

[3] C. Walling, A. L. Rieger, and D. D. Tanner, *J. Am. Chem. Soc.*, **85**, 3129 (1963).

[4] I. Heilbron, "Dictionary of Organic Compounds," Vol. II, Oxford University Press, Fair Lawn, N. J., 1953, p. 518.

[5] E. K. Weisburger and J. H. Weisburger, *J. Org. Chem.*, **20**, 1396 (1955).

TABLE II

COMPETITIVE RATES OF REACTION OF BENZYL METHYL ETHERS WITH N-BROMOSUCCINIMIDE[a]

Compd. A[b]	Compd. B[b]	$[A_0]$, mmoles	$[B_0]$, mmoles	$[A]$, mmoles	$[B]$, mmoles	$[NBS]_i$, mmoles	k_B/k_A
$C_6H_5CH(CH_3)_2$	p-$ClC_6H_4CH_2OCH_3$	45.8	29.6	35.7	14.0	25.2	2.9
$C_6H_5CH(CH_3)_2$	m-$ClC_6H_4CH_2OCH_3$	44.9	44.9	36.0	21.0	34.9	3.4
$C_6H_5CH(CH_3)_2$	p-$BrC_6H_4CH_2OCH_3$	44.4	36.6	34.4	13.6	30.2	3.9
$C_6H_5CH(CH_3)_2$	p-$BrC_6H_4CH_2OCH_3$	35.6	37.9	25.2	12.5	30.1	3.2
$C_6H_5CH(CH_3)_2$	m-$BrC_6H_4CH_2OCH_3$	47.6	33.0	36.3	15.3	30.4	2.9
$C_6H_5CH(CH_3)_2$	p-$CH_3OOCC_6H_4CH_2OCH_3$	48.8	29.5	38.8	12.8	27.0	3.6
$C_6H_5CH(CH_3)_2$	m-$CH_3OOCC_6H_4CH_2OCH_3$	47.7	24.6	38.5	11.5	22.0	3.5
$C_6H_5CH(CH_3)_2$	p-$NCC_6H_4CH_2OCH_3$	52.8	44.3	39.4	23.8	40.0	2.1
$C_6H_5CH(CH_3)_2$	m-$NCC_6H_4CH_2OCH_3$	44.0	44.9	33.1	27.5	35.0	1.7
$C_6H_5CH(CH_3)_2$	p-$O_2NC_6H_4CH_2OCH_3$	46.6	33.6	33.3	15.0	30.2	2.4
$C_6H_5CH(CH_3)_2$	m-$O_2NC_6H_4CH_2OCH_3$	47.5	25.6	34.9	13.5	22.6	2.1
$C_6H_5CH(CH_3)_2$	m-$O_2NC_6H_4CH_2OCH_3$	49.1	36.2	35.5	17.5	30.2	2.2
$C_6H_5CH(CH_3)_2$	$C_6H_5CH_2OCH_3$	57.5	48.4	47.7	24.0	39.0	3.6
$C_6H_5CH(CH_3)_2$	$C_6H_5CH_2OCH_3$	30.6	30.6	25.0	16.0	22.0	3.2
$C_6H_5CH(CH_3)_2$	p-$CH_3OC_6H_4CH_2OCH_3$	59.0	40.3	50.2	7.75	35.2	10
$C_6H_5CH(CH_3)_2$	p-$CH_3OC_6H_4CH_2OCH_3$	55.6	37.9	49.4	7.6	30.0	14
$C_6H_5CH(CH_3)_2$	p-$CH_3OC_6H_4CH_2OCH_3$	60.5	49.0	52.9	7.8	40.0	13
$C_6H_5CH(CH_3)_2$	m-$CH_3OC_6H_4CH_2OCH_3$	58.6	41.5	50.0	19.0	30.2	5.0
$C_6H_5C_2H_5$	p-$CH_3OC_6H_4CH_2OCH_3$	49.4	48.8	41.4	4.50	35.9	13
$C_6H_5C_2H_5$	m-$CH_3OC_6H_4CH_2OCH_3$	38.5	39.5	33.8	14.3	30.4	7.7
$C_6H_5C_2H_5$	m-$CH_3OOCC_6H_4CH_2OCH_3$	57.3	34.0	47.5	15.5	25.4	4.2
$C_6H_5C_2H_5$	m-$O_2NC_6H_4CH_2OCH_3$	52.1	50.5	39.0	23.3	39.8	2.7
$C_6H_5C_2H_5$	m-$BrC_6H_4CH_2OCH_3$	72.5	34.6	59.2	15.0	28.4	4.1
$C_6H_5C_2H_5$	$C_6H_5CH_2OCH_3$	41.5	41.0	33.5	17.9	30.0	3.8
$(C_6H_5)_2CH_2$	$C_6H_5CH_2OCH_3$	50.0	44.7	42.6	15.3	35.6	6.6
$(C_6H_5)_2CH_2$	m-$O_2NC_6H_4CH_2OCH_3$	46.3	46.9	36.0	17.8	38.1	3.9
$(C_6H_5)_2CH_2$	p-$ClC_6H_4CH_2OCH_3$	56.3	50.5	46.5	17.4	40.1	5.6

[a] In carbon tetrachloride at 77°. [b] Total volume of A, B, and carbon tetrachloride was initially 50 ml. at room temperature.

with sodium methoxide to give the substituted ethers. The ethers were all purified by distillation at reduced pressure. Table I summarizes the results of the various syntheses. Eastman Organic Chemicals Spectrograde carbon tetrachloride was used as the medium in the bromination studies.

Relative Rates of Reaction of the Substituted Benzyl Methyl Ethers with N-Bromosuccinimide.—Procedures similar to those described previously[1,2] were used in determining the rate of reaction of each substituted benzyl methyl ether (relative to that of benzyl methyl ether) with N-bromosuccinimide. For each determination a carbon tetrachloride solution of known volume which contained weighed quantities of the substituted benzyl methyl ether and a reference compound (ethylbenzene, cumene, or diphenylmethane) was prepared. The solution was treated with a limited quantity of N-bromosuccinimide and a catalytic amount of benzoyl peroxide. The mixture was heated under reflux until all of the N-bromosuccinimide at the bottom of the reaction flask had disappeared (about 10 min.). The mixture was then analyzed by vapor phase chromatography for unreacted ether and reference compound. The chromatographic column was packed with Chromosorb W (45–60 mesh) impregnated with SE-30 silicone gum rubber and was operated at temperatures ranging from 150 to 220°. In Table II a list is given of some typical values of k_B/k_A [the ratio of rate constants for reaction of the substituted benzyl methyl ether (B) and the reference material (A) with N-bromosuccinimide] for the various compounds investigated. The ratios were calculated from the initial ($[A_0]$ and $[B_0]$) and final ($[A]$ and $[B]$) concentration of the reference compound A and the substituted benzyl methyl ether B using eq. 1. Values of r which are reported later in Table IV

$$k_B/k_A = \frac{\log [B_0]/[B]}{\log [A_0]/[A]} \tag{1}$$

are k_B/k_A values for the condition that A is benzyl methyl ether (that is r for benzyl methyl ether = 1). The values of r were calculated from the k_B/k_A and $k_A/k_{\text{benzyl methyl ether}}$ values which are recorded in Table II. Each r value is an average based on the results of at least two or more separate experiments with different initial concentrations, $[A_0]$ and $[B_0]$, of the substituted benzyl methyl ether and reference compound. In several cases the reactivity of the substituted ether was checked against two or three different reference compounds.

In all of the compounds studied, with the exception of p-methoxybenzyl methyl ether, the total amount of hydrocarbon consumed was in close agreement with the quantity of N-bromosuccinimide used (see Tables II and IV). The r value reported for p-methoxybenzyl methyl ether is considered to be only semiquantitative in nature because of the poor product balance obtained in the reaction of the ether with the reference hydrocarbon (the product balance being defined as $[A_0 + B_0] - [A + B] = [NBS]_i$). The amount of ether and reference hydrocarbon consumed was always significantly more than the amount of N-bromosuccinimide used (15–20% in excess of [NBS]). A study of the products of the reaction revealed that, in addition to the formation of succinimide (100% based on initial NBS concentration) and anisaldehyde (40–50% based on amount of ether consumed), small amounts (2% based on amount of ether consumed) of anisic acid, identified by its infrared spectrum, were being formed. The lack of agreement between the initial N-bromosuccinimide concentration and the amount of p-methoxybenzyl methyl ether and reference hydrocarbon consumed is probably due to loss of ether by processes other than reaction with N-bromosuccinimide. After reaction of 8.35 mmoles of cumene, the reference hydrocarbon, and 3.44 mmoles of N-bromosuccinimide there remained 4.80 mmoles of unreacted cumene. The fact that a good product balance was observed in this reaction suggests that any discrepancies are due to side reactions involving the ether and not the reference hydrocarbon. The side reactions responsible for excessive consumption of p-methoxybenzyl methyl ether have not been established. Two such possibilities may be the dimerization of the initial hydrocarbon radical or the destruction of the ether by hydrogen bromide. Neither of these possibilities has been rigorously investigated. Although a complete study of the products formed in the reaction of benzyl methyl ether with N-bromosuccinimide has not been made, the major product is the corresponding benzaldehyde.[6] For example, after treatment of a solution of benzyl methyl ether (0.046 mole) in carbon tetrachloride with 0.02 mole of N-bromosuccinimide, 0.021 mole of unreacted benzyl methyl ether remained and 0.015 mole of benzaldehyde was formed.

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(6) M. Okawara, H. Sato, and E. Imoto, *J. Chem. Soc. Japan, Ind. Chem. Sect.*, **58**, 924 (1955).

TABLE III

COMPETITIVE RATES OF REACTION OF SOME SUBSTITUTED ETHYLBENZENES, SUBSTITUTED BENZYL CYANIDES, AND α-SUBSTITUTED TOLUENES WITH N-BROMOSUCCINIMIDE[a]

Compd. A[b]	Compd. B[b]	$[A_0]$, mmoles	$[B_0]$, mmoles	[A], mmoles	[B], mmoles	[NBS], mmoles	k_B/k_A
$C_6H_5C_2H_5$	p-$O_2NC_6H_4C_2H_5$	39.5	54.5	16.3	46.0	30.1	0.19
$C_6H_5C_2H_5$	p-$CH_3OC_6H_4C_2H_5$	70.1	51.3	56.0	25.3	40.2	3.1
$C_6H_5CH(CH_3)_2$	p-$O_2NC_6H_4C_2H_5$	45.8	60.1	19.0	51.6	40.3	0.17
$C_6H_5CH_2CN$	p-$CH_3OC_6H_4CH_2CN$	80.1	49.4	72.3	18.6	39.5	9.7
$C_6H_5C_2H_5$	p-$CH_3OC_6H_4CH_2CN$	41.6	58.2	12.3	50.3	35.3	0.11
$C_6H_5CH_3$	p-$CH_3OC_6H_4CH_2CN$	70.9	52.4	46.8	35.0	44.9	0.99
$C_6H_5C_2H_5$	$(C_6H_5)_2CH_2$	48.4	39.3	27.1	26.2	35.0	0.71
$C_6H_5CH(CH_3)_2$	$(C_6H_5)_2CH_2$	40.9	53.7	23.4	37.7	34.8	0.63
$C_6H_5CH_3$	$C_6H_5CH_2COOCH_3$	65.0	45.7	30.5	38.8	40.3	0.22
$C_6H_5CH_3$	$C_6H_5CH_2COOCH_3$	51.0	51.0	19.3	40.5	40.0	0.24
$C_6H_5CH_3$	$C_6H_5CH_2Cl$	62.9	37.2	38.6	31.2	30.1	0.36
$C_6H_5CH_3$	$C_6H_5CH_2Cl$	39.0	63.7	19.8	51.1	30.1	0.33
$(C_6H_5)_2CH_2$	$C_6H_5CH_2Cl$	44.2	45.2	11.0	43.2	35.7	0.035
$(C_6H_5)_2CH_2$	p-$O_2NC_6H_4C_2H_5$	46.0	59.7	17.6	48.0	40.6	0.22
$(C_6H_5)_2CH_2$	p-$CH_3OC_6H_4C_2H_5$	52.7	50.9	41.8	21.0	45.0	3.9
$(C_6H_5)_2CH_2$	p-$CH_3OC_6H_4CH_2CN$	42.6	66.5	17.1	58.8	35.9	0.14
$C_6H_5CH_3$	$C_6H_5CH_2CN$	69.9	66.0	10.6	58.5	60.0	0.07
$C_6H_5CH_3$	$C_6H_5CH_2CN$	47.2	61.6	16.1	58.0	40.0	0.06

[a] In carbon tetrachloride at 77°. [b] Total volume of A, B, and carbon tetrachloride was initially 50 ml. at room temperature.

Relative Rates of Reaction of Some Substituted Ethylbenzenes, Benzyl Cyanides, and α-Substituted Toluenes with N-Bromosuccinimide.—The procedure outlined for the determination of the rates of reaction of the substituted ethers was employed in the determination of the relative rates of reaction of the substituted ethylbenzenes and benzyl cyanides with N-bromosuccinimide. The reference compounds used were ethylbenzene, cumene, benzyl cyanide, toluene, and diphenylmethane. Again the analyses of the reaction mixtures for unreacted substrates and reference hydrocarbons were carried out using the vapor phase chromatography equipment described earlier. Table III contains typical values of k_B/k_A which are based on the results of these experiments. Because of a discrepancy between the r value reported earlier[2] for benzyl chloride using ethylbenzene and cumene as reference hydrocarbons and the value obtained using toluene and diphenylmethane as reference hydrocarbons (see Table III), an investigation of the products of the reactions was made. From the reaction of ethylbenzene with N-bromosuccinimide, styrene, the dehydrohalogenation product of α-bromoethylbenzene, was identified as one of the products by gas chromatographic analysis. Similarly, α-methylstyrene, again identified by a comparison of its retention time with that of a pure sample, was found to be a major product of the reaction of cumene with N-bromosuccinimide. Because of the possibility that the discrepancy between the two sets of data resulted from the reaction of hydrogen bromide with benzyl chloride, dry hydrogen bromide was bubbled slowly through a refluxing solution containing 49.4 mmoles of benzyl chloride in 50 ml. of carbon tetrachloride for 15 min. After refluxing the solution for an additional 15 min., it was established by vapor phase chromatographic analysis that 45.0 mmoles of starting benzyl chloride was left unreacted.

No study was made of the products from the reaction of benzyl cyanides with N-bromosuccinimide. Robb and Schultz[7] report the preparation of α-bromobenzyl cyanide from the slow addition of bromine to benzyl cyanide at elevated temperatures (presumably by radical processes). The reaction is reported to be accompanied by the evolution of hydrogen bromide and the α-bromobenzyl cyanide formed in 60% yield was stable over a period of 2 days.

Results

The relative rates of autoxidation of certain (benzyl ring) substituted benzyl phenyl ethers and benzyl alkyl ethers, induced by peroxy radicals, have been reported. The rates appear to be insensitive to the influence of the aromatic ring substituents[8] ($\rho = 0$). It has been suggested that this insensitivity is related to the capacity of the ether oxygen to act as a powerful electron-supplying group. Presumably the electronic influence of ether oxygen is sufficiently pronounced so that it overshadows the polar effects of ring substituents in controlling the rate of abstraction of the exocyclic benzyl hydrogen.[8]

Table IV contains the values of r for the various substituted benzyl methyl ethers which have been studied in the present investigation. The reaction of these ethers with N-bromosuccinimide also shows a low sensitivity to ring-substituent effects in contrast to the corresponding reaction of ring-substituted toluenes. The correlation of log r for the toluene system with σ^+ shows an appreciable polar substituent effect ($\rho = -1.38$).[3] Attempts to correlate the minor substituent effects, observed in the reaction of benzyl methyl ethers with N-bromosuccinimide, with substituent parameters have been unsuccessful. The variations in log r (Table IV) do not closely parallel the electron releasing capacities

TABLE IV

RELATIVE REACTIVITIES, r,[a] OF SUBSTITUTED BENZYL METHYL ETHERS ($XC_6H_4CH_2OCH_3$) IN THEIR REACTIONS WITH N-BROMOSUCCINIMIDE

X	r
H	1.00
p-Cl	0.87 ± 0.03[b]
m-Cl	0.97 ± 0.02
p-Br	1.1 ± 0.1
m-Br	0.90 ± 0.06
p-$COOCH_3$	1.00 ± 0.06
m-$COOCH_3$	0.95 ± 0.08
p-CN	0.64 ± 0.02
m-CN	0.50 ± 0.02
p-NO_2	0.71 ± 0.03
m-NO_2	0.63 ± 0.03
p-CH_3O	3.4 ± 0.5
m-CH_3O	1.8 ± 0.2

[a] The term r is defined by eq. 1 with benzyl methyl ether as the reference compound A. All values apply to reaction in carbon tetrachloride at 77°. [b] The uncertainties in r are average deviations from the mean of four or more determinations.

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[7] C. M. Robb and E. M. Schultz, *Org. Syn.*, **28**, 55 (1948).

[8] G. A. Russell and R. C. Williamson, Jr., *J. Am. Chem. Soc.*, **86**, 2357 (1964).

TABLE V

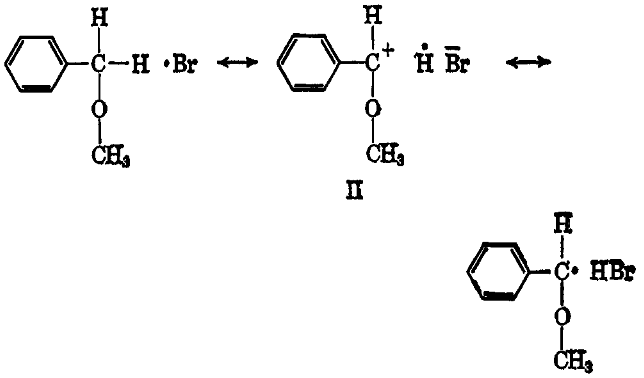
RELATIVE REACTIVITIES, *r*, OF SUBSTITUTED BENZYL METHYL ETHERS, ETHYLBENZENES, TOLUENES, AND BENZYL CYANIDES IN THEIR REACTIONS WITH N-BROMOSUCCINIMIDE[a]

Compd.	*r*	Compd.	*r*[b]	Compd.	*r*	Compd.	*r*
$C_6H_5CH_2OCH_3$	1.00	$C_6H_5CH_3$	1.00	$C_6H_5C_2H_5$	1.00	$C_6H_5CH_2CN$	1.00
p-$O_2NC_6H_4CH_2OCH_3$	0.71	*p*-$O_2N_2C_6H_4CH_3$	0.05	*p*-$O_2N_2C_6H_4C_2H_5$	0.20	*p*-$O_2NC_6H_4CH_2CN$[c]	...
p-$CH_3OC_6H_4CH_2OCH_3$	3.4	*p*-$CH_3OC_6H_4CH_3$	11.7	*p*-$CH_3OC_6H_4C_2H_5$	3.0	*p*-$CH_3OC_6H_4CH_2CN$	10.0

[a] In refluxing carbon tetrachloride. [b] Values taken from C. Walling, A. L. Rieger, and D. D. Tanner, *J. Am. Chem. Soc.*, **85**, 3129 (1963). [c] *p*-$O_2NC_6H_4CH_2CN$ is not appreciably soluble in carbon tetrachloride. An *r* value could not, therefore, be determined for this compound.

of the ring substituents as measured by σ, σ^+, σ^n, or σ_1[9] values.

The observed substituent effects (Table IV), though qualitative in nature, do not parallel those expected if structures of the type represented by I were to make a significant contribution to transition state of the reaction. Rather the trend observed ($CN < NO_2 < H < OCH_3$) is more closely representative of what would be expected if there were positive polarization of the reaction center such as shown in II.



II

A further investigation has been made of the magnitude of polar effects of groups X with changes in Y in controlling the rate of benzyl hydrogen abstraction in systems of the type $XC_6H_4CH_2Y$. In particular the relative reactivities (with respect to attack by N-bromosuccinimide) of the *p*-NO_2 and *p*-CH_3O derivatives of benzyl methyl ether, ethylbenzene, toluene, and benzyl cyanide[10] have been compared with those of the unsubstituted compounds. The results are summarized in Table V. Martin and Gleicher[11] report that the ρ-value for the reaction of ring-substituted allylbenzenes with bromine atoms is about one-half or one-third as great as the ρ-value for the corresponding reaction of ring-substituted toluenes with bromine atoms. The results of Table V indicate that the *p*-NO_2 group and *p*-CH_3O group have pronounced effects on the rates of reactions of toluene and benzyl cyanide[10] with N-bromosuccinimide but have a much smaller influence on the reactions of benzyl methyl ether and ethylbenzene with N-bromosuccinimide.

In the light of the cited results of earlier investigators and those summarized in Tables IV and V it is tentatively concluded that a major factor in the control of the magnitude of the effect of a ring substituent X on a hydrogen abstraction process is the intrinsic stability of the benzyl radical $C_6H_5\dot{C}HY$ being formed in the activation process. That is, the rate effect of ring substituents is more significant in the formation of the less stable $C_6H_5\dot{C}H_2$ and $C_6H_5\dot{C}HCN$ radicals than in the formation of the more stable $C_6H_5\dot{C}HOCH_3$ and $C_6H_5\dot{C}HCH_3$ radicals.

During the course of this investigation it became necessary to check certain results reported in a previous publication.[2] It was discovered that an arithmetical error had been made earlier in calculating the value of *r* for the reaction of diphenylmethane and N-bromosuccinimide in carbon tetrachloride at 77°. A revised value of $r = 6.7 \pm 0.06$, relative to $r = 1$ for toluene, is now reported.[12] A reinvestigation of the relative reactivities of methyl phenylacetate and benzyl cyanide has resulted in a revision of *r* values for these compounds. The new values based on four or more determinations using toluene as the reference compound ($r = 1$) are for $C_6H_5CH_2CN$, $r = 0.09 \pm 0.01$, and for $C_6H_5CH_2COOCH_3$, $r = 0.23 \pm 0.02$. It has been observed that when ethylbenzene or cumene is used as the competing hydrocarbon in the determination of the relative reactivity of benzyl chloride, values of *r* like those reported previously[2] (2.8) are obtained. However, when diphenylmethane or toluene is used as the competing hydrocarbon the value of *r* for benzyl chloride is 0.31 (relative to $r = 1.00$ for toluene). Since hydrogen bromide reacts slowly with benzyl chloride under the conditions used (see Experimental section) and since extensive dehydrohalogenation of the brominated ethylbenzene and cumene[13] occurs during the reaction, the value of $r = 0.31 \pm 0.05$ obtained using toluene and diphenylmethane as competing hydrocarbons in the competition reaction with N-bromosuccinimide is considered to be more reliable than the value of 2.8 obtained using ethylbenzene and cumene.

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(9) P. R. Wells, *Chem. Rev.*, **63**, 171 (1963).

(10) The relative rate of reaction of *p*-nitrobenzyl cyanide with N-bromosuccinimide could not be determined because of experimental difficulty.

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

(12) G. A. Russell and K. M. Desmond [*J. Am. Chem. Soc.*, **85**, 3139 (1963)] obtained a value of *r* for the reaction of diphenylmethane with N-bromosuccinimide of 6.5 ± 1 relative to toluene ($r = 1$).

(13) The isolation of styrene and α-methylstyrene as reaction products is taken as evidence for dehydrohalogenation of the brominated reference hydrocarbons.