1151. *Polar Influences in Radical Reactions. Part IV.* The Abstraction of Benzylic Hydrogen Atoms from Substituted Benzyl Methyl Ethers and Benzaldehyde Dimethyl Acetals by Atomic Bromine.*

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The abstraction of α-hydrogen atoms from benzyl methyl ether and benzaldehyde dimethyl acetal by atomic bromine at 80° obeys the Hammett relationship, giving a straight line with σ^+ values, and yields ρ-values of $-0{\cdot}35$ and $-0{\cdot}38$, respectively. The relative reactivity of the two systems has been shown to be 2·4 per molecule, in favour of the ether. On the basis of ρ-values and relative reactivities found for these and other systems, the relationship between ρ and the activation energy of the abstraction step is discussed.

Abstraction of α-hydrogen atoms by the trichloromethyl radical from the ether gives a ρ-value of $-0{\cdot}36$ at 80°.

Study of substituent effects on the reactivity of aromatic side-chains towards free radicals has provided the most fruitful approach for the assessment of polar influence in radical reactions. In the toluene system, abstraction of benzylic α-hydrogen atoms by a variety of radicals, including atomic bromine[1–3] and chlorine,[4,5] and free butoxyl,[6] peroxy-,[5,7] and trichloromethyl[8] radicals, has been shown to be correlated by the Hammett $\rho\sigma$ relationship. Other systems investigated include benzaldehyde[9] and cumene,[5,7] in attack by peroxy-radicals, and more recently this method has been extended to the reaction of allylbenzene with atomic bromine[10] and free trichloromethyl,[11] and to the reaction of dibenzyl ether with t-butoxy- and benzoyloxy-radicals,[12] and with atomic bromine.[13] We now report a similar study of hydrogen-abstraction by atomic bromine, generated from *N*-bromosuccinimide, from benzyl methyl ether and from benzaldehyde dimethyl acetal, as well as a measurement of the relative reactivity of the ether and acetal systems towards the same radical. Abstraction by the trichloromethyl radical in the former system has also been investigated.

It has been shown earlier[14,15] that dehydrogenation by bromine atoms (from *N*-bromosuccinimide) and by trichloromethyl radicals of both benzyl methyl ether and benzaldehyde dimethyl acetal occurs at the benzylic carbon atoms, to generate the radicals $\mathrm{Ph{\cdot}\dot{C}H{\cdot}OMe}$ and $\mathrm{Ph{\cdot}\dot{C}(OMe)_2}$, respectively, which then abstract bromine atoms to form the respective bromides $\mathrm{Ph{\cdot}CHBr{\cdot}OMe}$ and $\mathrm{Ph{\cdot}CHBr(OMe)_2}$. Of these, the former can be quantitatively converted into benzaldehyde (by pyrolysis and/or hydrolysis), whilst the latter breaks down into methyl benzoate and methyl bromide. In this work, the effect of nuclear substituents on hydrogen-abstraction by atomic bromine has been studied in both of these systems by intermolecular competitive reactions in which equimolecular quantities of two ethers, or acetals, are allowed to compete for an insufficient quantity of the reagent, *N*-bromosuccinimide. In the case of the ether, comparison of the rates of abstraction can be achieved by

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analysis of the mixture of benzaldehydes produced in each case, and this in turn can be conveniently carried out by chromatography, followed by spectrophotometric analysis, of the 2,4-dinitrophenylhydrazones. In the case of the acetal, inasmuch as its reaction with *N*-bromosuccinimide has been shown[14,15] to be quantitative, the rate at which the components react in the competitive reaction can be determined by estimation of the two acetals present before and after reaction with the bromo-imide. This can be done by converting the acetals into the benzaldehydes (which can be effected quantitatively), and estimating these as the 2,4-dinitrophenylhydrazones as before. Since the 2,4-dinitrophenylhydrazone of *p*-t-butylbenzaldehyde was found to be easily and effectively separated from those of other benzaldehydes by chromatography, *p*-t-butylbenzyl methyl ether and *p*-t-butylbenzaldehyde dimethyl acetal, respectively, were used as the reference standards in the two series of competitive reactions.

The relative reactivity of the ether and acetal systems towards bromine atoms was measured by a similar competitive reaction between *p*-t-butylbenzyl methyl ether and *p*-chlorobenzaldehyde dimethyl acetal: the yield of *p*-t-butylbenzaldehyde obtained on hydrolysis of the reaction mixture gives an estimate of the extent to which the ether has reacted, while that of *p*-chlorobenzaldehyde affords a measure of the unreacted acetal. From the values so obtained the relative reactivity of the unsubstituted ether and acetal can be calculated.

EXPERIMENTAL

Materials.—Carbon tetrachloride, bromotrichloromethane, and *N*-bromosuccinimide were purified as previously described.[15] *p*-Methoxybenzyl chloride (prepared from anisyl alcohol[16]) and *p*-chlorobenzyl chloride (Eastman Kodak) were used without purification. *p*-t-Butylbenzyl bromide was obtained from bromination of *p*-t-butyltoluene with *N*-bromosuccinimide, and the *m*-chloro- and *p*-methyl-substituted homologues were prepared by photobromination of the corresponding toluenes.

Synthesis of Ethers.—The nuclear-substituted benzyl methyl ethers were prepared by methods A and/or B, and purified as previously[15] described. The method of preparation, percentage yield, and physical properties (b. p. and n_D^{25}) of the acetal and carbonyl-free ethers are as follows: 4-chloro: A (64%), B (89%), 114—114·5°/35 mm., 1·5179 (cf. ref. 17); 3-*chloro*: A (68), B (71), 114—115°/35 mm., 1·5186 (Found: C, 60·7; H, 5·8; Cl, 22·1. C_8H_9ClO requires C, 61·3; H, 5·8; Cl, 22·6%); 4-methyl: A (80), 100—101°/35 mm., 1·4986 (lit.,[18] 84°/20 mm., 1·4990); 4-*t-butyl*: A (86), 60—61°/0·1 mm., 1·4934 (Found: C, 80·7; H, 10·1. $C_{12}H_{18}O$ requires C, 80·8; H, 10·2%); 4-methoxy: B (68), 129—130°/35 mm., 1·5113 (lit.,[18] 125°/30 mm., 1·5107).

Synthesis of Dimethyl Acetals of Substituted Benzaldehydes.—*m*-Nitrobenzaldehyde dimethyl acetal was prepared as previously described.[19] *p*-t-Butyl and *m*-chloro-substituted acetals were obtained from the αα-dibromides of the corresponding toluenes by heating with methanolic potassium hydroxide (cf. method B for ether). The remaining acetals given below were synthesised by the method described elsewhere.[15] The percentage yields and physical constants (b. p. and n_D^{25}) of the carbonyl-free materials were: 4-methoxy: 84%, 96·5—97·0°/1 mm., 1·5032 (lit.,[20] 253°/760 mm.); 4-methyl: 83%, 113·5—114·0°/35 mm., 1·4912 (lit.,[21] 99—100°/15 mm.); 4-*t-butyl*: 77%, 135—135·5°/35 mm., 1·4898 (Found: C, 74·2; H, 9·7. $C_{12}H_{20}O_2$ requires C, 74·9; H, 9·7%); 4-chloro: 88%, 125·5—126°/35 mm., 1·5072 (lit.,[21] 114—115°/19 mm.); 3-*chloro*: 80%, 124—124·5°/35 mm., 1·5084 (Found: C, 57·4; H, 5·9. $C_9H_{11}ClO_2$ requires C, 57·9; H, 5·95%); 3-nitro: 74%, 121—121·5°/1 mm., 1·5223 (lit.,[19] 116—119°/1 mm.). The yields reported above were based on materials obtained after one fractionation through a 25 cm. Vigreux column. Carbonyl-free (by infrared) acetals were obtained by refractionation when necessary.

2,4-*Dinitrophenylhydrazine Reagent.*—The hydrazine (Merck, G. R. grade) was shaken with 2N-hydrochloric acid (from B.D.H. AnalaR concentrated hydrochloric acid) until a saturated solution was obtained. The approximate concentration was 5 mg./ml. at room temperature.

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Ultraviolet Spectra of 2,4-Dinitrophenylhydrazones of Substituted Benzaldehydes.—The 2,4-dinitrophenylhydrazones were prepared from the corresponding aldehydes by standard methods, and recrystallised at least three times from ethanol or chloroform. The ultraviolet absorption spectra in chloroform, determined on a Hilger Uvispek spectrophotometer, are as follows ($\lambda_{\text{max.}}$ in mμ and $\varepsilon \times 10^{-4}$ in parentheses): 4-methoxy: 393 (3·26) [lit.,[22] 390 (3·09)]; 4-methyl: 386 (2·99); 4-t-butyl: 385 (3·08); unsubstituted: 378 (3·05) [lit.,[23] 378 (3·03)]; 4-chloro: 378 (3·34) [lit.,[23] 375 (3·30)]; 3-chloro: 375 (3·22); 3-nitro: 370 (3·15) [lit.,[22] 370 (3·16)].

Competitive Reaction of Substituted Benzyl Methyl Ethers with N-*Bromosuccinimide.*—In a two-necked 100 ml. round-bottom flask, connected through a coiled water condenser to a U-tube containing potassium hydroxide pellets, was placed *N*-bromosuccinimide (4 mmoles) and 25 ml. of a solution in carbon tetrachloride of 10 mmoles each of *p*-t-butylbenzyl methyl ether and the other ether. The flask was flushed for 5 min. with dry nitrogen through the side-neck which was then stoppered. All ground joints were lightly greased with high-vacuum silicone grease to keep out moisture. The mixture was heated and magnetically stirred under reflux (80 ± 1°) on a pre-heated hot-plate. Refluxing commenced within 2 min., and the flask was illuminated at a distance of 9 cm. from the centre by a 150-w lamp. The reaction appeared complete in *ca.* 10 min. after an induction period (usually 2—3 min.), there being no bromo-imide remaining at the bottom of the flask. Refluxing and illumination was continued for 10 more minutes before the mixture was cooled to room temperature. Prolonged heating did not increase the final yield of the two aldehydes.

Two 5 ml. aliquots of the solution were pipetted through a cotton-wool plug and each shaken thoroughly with 80 ml. of the 2,4-dinitrophenylhydrazine reagent in a stoppered 250 ml. conical flask for 30 min. (longer shaking did not increase the yield of hydrazones). Carbon tetrachloride in each sample was removed under reduced pressure and the 2,4-dinitrophenylhydrazones collected on a weighed sintered glass crucible. The aqueous solution was decanted through the crucible, and the precipitate triturated with a small volume of ethanol, cooled in ice, transferred to the crucible, and washed with another small portion of ice-cold ethanol (the total volume used was kept below 5 ml.). The precipitate was thoroughly washed with 2N-hydrochloric acid, followed by water, dried *in vacuo* over concentrated sulphuric acid, and weighed.

For the analysis of the mixture of 2,4-dinitrophenylhydrazones, the mixture was milled in an agate vibration mill, a 5 mg. sample weighed, dissolved in a small volume of chloroform and chromatographed on 15—25 g. of bentonite–kieselguhr (4:1). The 2,4-dinitrophenylhydrazone of *p*-t-butylbenzaldehyde formed a well-defined band on the column and was easily eluted with chloroform; subsequent elution with chloroform–ethanol (10:1) then removed the other component. After suitable dilution with chloroform the concentration of the 2,4-dinitrophenylhydrazone was determined spectrophotometrically. No 2,4-Dinitrophenylhydrazine was detected on the column or in the chloroform solution by spectrophotometry (at 343 mμ).

The competitive experiments were performed in duplicate, and duplicate analyses carried out in each experiment. Table 1 reports the molar ratio of the 2,4-dinitrophenylhydrazones found, and the relative reactivity of the ethers towards *N*-bromosuccinimide.

Competitive Reaction of Substituted Benzyl Methyl Ethers with Bromotrichloromethane.—A solution (25 ml.) of bromotrichloromethane (20 mmoles), methyl *p*-t-butylbenzyl ether (10 mmoles), and the other ether (10 mmoles) in carbon tetrachloride reacted in a manner analogous to the *N*-bromosuccinimide system at 80° for 2½ hr. during which time 6—8% of the total ether had reacted. Under these conditions the solution remained colourless throughout the reaction and did not yield detectable quantities of aroyl bromides as shown by infrared spectroscopy (1800—1750 cm.$^{-1}$ region).

Two 5 ml. aliquots of the cooled solution were each shaken with 50 ml. of the 2,4-dinitrophenylhydrazine reagent for 30 min. and the mixture of 2,4-dinitrophenylhydrazones so obtained isolated and analysed. Results of the competitive experiments are reported in Table 4.

Competitive Reaction of Substituted Benzaldehyde Dimethyl Acetals with N-*Bromosuccinimide.*—Three mmoles each of two acetals (one being the *p*-t-butyl substituted acetal) were weighed into a 25 ml. volumetric flask, made up to the mark with anhydrous carbon tetrachloride, and mixed thoroughly. A 5 ml. aliquot of this solution was shaken for 1 hr. with 100 ml. of the 2,4-dinitrophenylhydrazine reagent and the mixture of hydrazones so obtained collected.

The remaining solution from the flask was treated at 80° with *N*-bromosuccinimide (2 mmoles)

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[23] L. A. Jones and C. K. Hancock, *J. Org. Chem.*, 1960, **25**, 226.

as described above. The infrared spectrum of the cooled solution showed slight hydrolysis of the acetals (aldehydes), but no detectable aroyl bromide (1800—1750 cm.$^{-1}$ region). A 5 ml. aliquot of this solution was shaken with 80 ml of the 2,4-dinitrophenylhydrazine reagent for 1 hr. The two lots of mixed 2,4-dinitrophenylhydrazones formed (before and after reaction with *N*-bromosuccinimide) were separately chromatographed and analysed as described above. Recovery of the individual acetals, as estimated from the yields of the respective 2,4-dinitrophenylhydrazones in the first lot, was found to be 99 ± 2% for all the acetals studied (duplicate experiments).

Treatment of Data for N-*Bromosuccinimide–Acetal System.*—The rate of hydrogen abstraction by atomic bromine from *p*-Bu^t·C_6H_4·$CH(OMe)_2$, relative to X·C_6H_4·$CH(OMe)_2$, was calculated from the expression (cf. Huyser[8])

$$\frac{K_B}{K_A} = \frac{\log (B_0/B_t)}{\log (A_0/A_t)}$$

where B_0 and A_0 are the initial amount, in mmoles, of *p*-Bu^t·C_6H_4·$CH(OMe)_2$ and X·C_6H_4·$CH(OMe)_2$ per 5 ml. solution, determined as their 2,4-dinitrophenylhydrazones, and B_t and A_t are the number of mmoles per 5 ml. solution remaining after reaction. The ratios B_0/B_t and A_0/A_t were determined from the weights of the mixed hydrazones isolated and the ratios of the two compounds before and after reaction. The percentage reaction based on *N*-bromosuccinimide used was calculated using the value $[(A_0+B_0)-(A_t+B_t)]$/(mmoles *N*-bromosuccinimide per 5 ml.). The results obtained are recorded in Table 2.

Competitive Reaction of Methyl p-*t-Butylbenzyl Ether and* p-*Chlorobenzaldehyde Dimethyl Acetal with* N-*Bromosuccinimide.*—A solution (25 ml.) of the acetal (0·743 g., 3·98 mmoles) and the ether (0·710 g.; 3·99 mmoles) in carbon tetrachloride was treated with *N*-bromosuccinimide (0·534 g., 3·00 mmoles) in the usual manner. A 5 ml. aliquot of the cooled solution was shaken for 1 hr. with 120 ml. of the 2,4-dinitrophenylhydrazine reagent, and the hydrazones formed isolated and weighed (0·355 g.). Chromatography and spectrophotometric estimation showed the ratio *p*-chlorobenzaldehyde : *p*-t-butylbenzaldehyde in the mixture to be 1·66. The amount of unreacted acetal found was 3·37 mmoles and that of *p*-t-butylbenzaldehyde formed 2·03 mmoles per 25 ml. of the solution. The reactivity of *p*-t-butylbenzyl methyl ether relative to that of *p*-chlorobenzaldehyde dimethyl acetal is thus 2·03 : (3·98—3·37) or 3·33 : 1. In a second experiment a ratio of 3·23 : 1 was obtained.

RESULTS AND DISCUSSION

The results of intermolecular competitive reactions of nuclear-substituted benzyl methyl ethers with *N*-bromosuccinimide, in carbon tetrachloride at 80°, using the *p*-t-butyl homologue as the reference standard, are given in Table 1. From these results the reactivities of the ethers, relative to the unsubstituted homologue (taken as unity), are calculated. These data, when correlated in terms of the Hammett equation by standard statistical methods,[24]

TABLE 1.

Competitive reactions of substituted benzyl methyl ethers with *N*-bromosuccinimide at 80°, ratios of 2,4-dinitrophenylhydrazones found.

Expt.	*p*-MeO : *p*-Bu^t	*p*-Me : *p*-Bu^t	*p*Bu^t : H	*p*-Bu^t : *p*-Cl	*p*-Bu^t : *m*-Cl
1	1·69; 1·67	1·085; 1·095	1·13; 1·14	1·19; 1·20	1·63; 1·60
2	1·65; 1·63	1·09; 1·10	1·16; 1·15	1·245; 1·245	1·57; 1·56
Mean	1·66	1·09	1·145	1·22	1·59
	Mole % of aldehydes isolated (based on bromo-imide used)				
1	74·0	68·3	74·0	72·0	73·8
2	73·7	77·0	73·7	72·0	75·2

Relative reactivity of ethers

Subst.	*p*-MeO	*p*-Me	*p*-Bu^t	H	*p*-Cl	*m*-Cl
k/k_0	1·90	1·25	1·145	1·00	0·94	0·72

$\log (k/k_0) = 0{\cdot}004 - 0{\cdot}35\ \sigma^+$; Standard deviation = $\pm 0{\cdot}017$; Correlation coefficient = 0·99.

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[24] H. H. Jaffe, *Chem. Rev.*, 1953, **53**, 191.

give a better fit with σ^+ values[25] than with σ values.[26] The ρ value is $-0·35$, which is expectedly of the same order as that for the dibenzyl ether system, obtained from intramolecular competitive reactions with the same radical at the same temperature ($\rho = -0·12$).[13] The results from the dimethyl acetals of substituted benzaldehydes, using also the *p*-t-butyl homologue as reference standard and under the same conditions, are listed in Table 2. These, when treated similarly as above, also give a better fit with the σ^+ constants in the Hammett plot, which yields $-0·38$ for ρ.

TABLE 2.

Relative rate constants of dimethyl acetals of substituted benzaldehydes towards *N*-bromosuccinimide at 80°.

Subst. in *A*	K_B/K_A Expt. 1	K_B/K_A Expt. 2	Mean	% Reaction Expt. 1	% Reaction Expt. 2
p-MeO	0·676	0·69	0·68	100·0	96·4
p-Me	1·08	1·06	1·07	98·7	99·8
None	1·23	1·24	1·235	101·5	102·0
p-Cl	1·52	1·42	1·47	95·3	95·7
m-Cl	1·86	1·78	1·82	99·5	97·4
m-NO$_2$	2·31	2·33	2·32	96·8	94·0

Relative reactivities

Subst.	*p*-MeO	*p*-Me	*p*-Bu^t	H	*p*-Cl	*m*-Cl	*m*-NO$_2$
k/k_0	1·81	1·32	1·235	1·00	0·84	0·68	0·53

$\log(k/k_0) = -0·02 - 0·38\,\sigma^+$; Standard deviation $= \pm 0·019$; Correlation coefficient $= 0·99$.

The competitive reaction between *p*-t-butylbenzyl methyl ether and *p*-chlorobenzaldehyde dimethyl acetal in carbon tetrachloride furnished a reactivity ratio, towards atomic bromine at 80°, of 3·3 per molecule, in favour of the ether. By using the appropriate values from Tables 1 and 2, the relative reactivity of the unsubstituted ether and acetal can therefore be calculated. This is found to be 2·4. Taking advantage of the results recently obtained on the reactivity of benzyl methyl ether, relative to toluene, ethylbenzene, and cumene[27] towards the same radical at approximately the same temperature, the relative reactivity of the acetal, relative to these hydrocarbons, can be computed. Together with the reported value for allylbenzene,[10] it is thus possible to arrange these substrates in a series of increasing reactivity as presented in Table 3, in which also are collected the relevant ρ values wherever available.

TABLE 3.

Relative reactivities and ρ values in abstraction by atomic bromine in carbon tetrachloride at 80°.

Substrate	Reactivity Per molecule	Reactivity Per α-hydrogen atom	ρ value
Toluene[a, b]	1·00[c]	1·00[c]	$-1·38$[d] $-1·39$[e]
Ethylbenzene[a]	8·7	13	—
Allylbenzene[b]	17·5	26	$-0·76$[b]
Cumene[a]	10·0	30	—
Benzaldehyde dimethyl acetal[f]	13·4	40	$-0·38$
Benzyl methyl ether[a, f]	32·2	48	$-0·35$
Dibenzyl ether	—	—	$-0·12$[g]

[a] Ref. 27 (at 77°). [b] Ref. 10 (at 69·5° in chlorobenzene). [c] Assumed. [d] Ref. 3. [e] Ref. 2 (in benzene). [f] This work. [g] Ref. 13.

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[25] H. C. Brown and Y. Okamoto, *J. Amer. Chem. Soc.*, 1958, **80**, 4979.
[26] D. H. McDaniel and H. C. Brown, *J. Org. Chem.*, 1958, **23**, 420.
[27] R. E. Lovins, L. J. Andrews, and R. M. Keefer, *J. Org. Chem.*, 1963, **28**, 2847.

An examination of the data in Table **3** reveals a consistent relationship between the relative reactivity of a system and its ρ value: the ascending order in magnitude of the reactivity of toluene, allylbenzene, benzaldehyde dimethyl acetal, and benzyl methyl ether is thus seen to be attended by a descending series in the value of ρ. This indicates that, in the attack by a radical under similar conditions (temperature, solvent, etc.), a system of a higher reactivity would exhibit less sensitivity towards the effects of nuclear substituents, and *vice versa*. Additional evidence of a qualitative nature is furnished by an earlier finding[5,7] on the peroxy-radical, which, in abstraction of hydrogen atoms from toluene and cumene, gave a lower ρ value for the more reactive system, cumene ($-0{\cdot}705$ at 90° and $-0{\cdot}375$ at 60°, respectively).

It has been suggested that, under the same conditions, a reaction series with a lower activation energy is associated with a lower ρ value,[5,11] and *vice versa*. The results now at hand would appear to support this suggestion, if the assumption is made that the relative reactivity of the substrate gives an indication (in the reverse sense) of the said activation energy. There appears to be considerable evidence to substantiate this assumption. Thus, in the abstraction of hydrogen atoms from aliphatic hydrocarbons by atomic bromine, the relative reactivities of the primary, secondary, and tertiary hydrogen atoms (the ratio being 1:82:1640 at 146°)[28] can be seen to be correlated with the activation energies reported for the abstraction step, namely 13·4, 10·2, and 7·5 kcal. mole^{-1}, respectively.[29] Similarly, the ratio of the reactivity, per α-hydrogen atom, of toluene, ethylbenzene, and cumene[5] towards abstraction by the same radical at 80°, namely 1:23·6:50, is again consistent with the kinetic isotopic effects K_H/K_D of the three substrates towards the same radical at 77°, which are 4·86, 2·67, and 1·81, respectively.[30] Hence, in the substrates listed in Table 3, the effect of the α-substituents (*e.g.*, the vinyl group in allylbenzene and methoxy- or benzyloxy-group in the ethers) would appear to be that of lowering the activation energy of the abstraction step, probably through stabilisation of the transition state.

The trichloromethyl radical has been shown to exhibit high selectivity, comparable to that of atomic bromine, in abstraction of hydrogen atoms from aliphatic hydrocarbons[31] and from benzylic carbon atoms.[32] The results from competitive photobromination of substituted benzyl methyl ethers by bromotrichloromethane at 80°, using the *p*-t-butyl homologue as reference standard, are presented in Table 4. These give a better correlation with σ^+ than with σ constants in the Hammett treatment, and yield $-0{\cdot}36$ for ρ. For the same reaction, the ρ-value previously found for toluene[8] is $-1{\cdot}46$ at 50° and for allylbenzene,[11] $-0{\cdot}39$ at 70°. Although the magnitude of ρ shows a relationship with the reactivity of the substrate

TABLE 4.

Competitive reactions of substituted benzyl methyl ethers with bromotrichloromethane at 80°. Ratios of 2,4-dinitrophenylhydrazones.

Expt.	*p*-MeO:*p*-Bu^t	*p*-Me:*p*-Bu^t	*p*-Bu^t:H	*p*-Bu^t:*p*-Cl	*p*-Bu^t:*m*-Cl
1	1·69; 1·68	1·08; 1·075	1·20; 1·19	1·30; 1·31	1·63; 1·63
2	1·63; 1·64	1·07; 1·06	1·17; 1·16	1·29; 1·30	1·57; 1·58
Mean	1·66	1·07	1·18	1·30	1·60

Relative reactivities of ethers

Subst.	*p*-MeO	*p*-Me	*p*-Bu	H	*p*-Cl	*m*-Cl
k/k_0	1·96	1·26	1·18	1·00	0·91	0·74

$\log(k/k_0) = 0{\cdot}00 - 0{\cdot}36\,\sigma^+$; Standard deviation $= \pm 0{\cdot}014$; Correlation coefficient $= 0{\cdot}99$.

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[28] P. C. Anson, P. S. Fredricks, and J. M. Tedder, *J.*, 1959, 918.

[29] G. C. Fettis, J. H. Knox, and A. F. Trotman-Dickenson, *J.*, 1960, 4177.

[30] K. B. Wiberg and L. H. Slaugh, *J. Amer. Chem. Soc.*, 1958, **80**, 3033.

[31] B. P. McGrath and J. M. Tedder, *Bull Soc. chim. belges.*, 1962, **71**, 772.

[32] G. A. Russell and C. DeBoer, *J. Amer. Chem. Soc.*, 1963, **85**, 3136.

similar to that in the reaction of atomic bromine, it should be pointed out that the ρ-value for the allylbenzene system is probably open to question, since no less than 80—95% of the trichloromethyl radicals added to the olefinic double bond, and the correlation with the Hammett equation was therefore based on what, in effect, was a minor reaction.

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