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RELATIVE REACTIVITIES OF α-SUBSTITUTED BENZYL METHYL ETHERS TOWARDS ATOMIC BROMINE AND THE TRICHLOROMETHYL RADICAL

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Abstraction of benzylic hydrogen atoms by atomic bromine (from N-bromo succinimide) and by the trichloromethyl radical, from benzyl methyl ether (I, R = H) and benzaldehyde dimethyl acetal (I, R = OMe) has recently been shown[1] to proceed by the following mechanism:-

$$\underset{\text{(I)}}{\mathrm{Ph.CHR.(OMe)}} + \mathrm{Br}\cdot\ (\text{or}\ \cdot\mathrm{CCl_3}) \longrightarrow \mathrm{Ph.\dot{C}R.(OMe)} + \mathrm{HBr}\ \ (\text{or}\ \mathrm{CHCl_3})$$

$$\mathrm{Ph.\dot{C}R.(OMe)} + \mathrm{Br_2}\ (\text{or}\ \mathrm{BrCCl_3}) \longrightarrow \mathrm{Ph.CRBr.(OMe)} + \mathrm{Br}\cdot\ \ (\text{or}\ \cdot\mathrm{CCl_3})$$

$$\mathrm{Ph.CRBr.(OMe)} \longrightarrow \mathrm{Ph.CO.R} + \mathrm{MeBr}$$

We have now measured the relative rates of abstraction, by the above radicals, for a series of α-substituted benzyl methyl ethers (I, R = H, COOMe, Ph, and MeO), and of dibenzyl ether. The method adopted differs from that employed by other workers[2 - 4] for aromatic hydrocarbons in that (a) the results are based on analysis of the reaction products, rather than that of the unchanged starting materials, and (b) the reference standard used is ethylbenzene, which is comparable in reactivity with most of the substrates investigated. A comparison between ethylbenzene and toluene then relates the reactivity of the various systems to toluene, taken as unity. (See Table I and II). In the case of bromination with N-bromosuccinimide, the yield of products in every case amounted to at least 95%; in the case of bromotrichloromethane the reaction was terminated after 15 - 30% of the substrates had reacted.

Comparing with data already known for N-bromosuccinimide, the relative reactivity of 15.2 for ethylbenzene: toluene (Table I) is in good agreement with those of 15.8 and 14.2 recorded by Walling et. al.[2], and by Russell and Desmond[3], respectively. Similarly, the reactivity per molecule, relative to toluene, of 35 for benzyl methyl ether (Table II) accords with that of 39 reported by Lovins and coworkers.[5] Furthermore, the fact that atomic bromine and the trichloromethyl radical have much the same selectivity, as evidenced by the results now obtained, corroborates earlier findings.[6]

In a recent study,[1b] by application of the Hammett equation, of polar effects in hydrogen-abstraction from α-substituted toluenes, we have drawn attention to a consistent relationship between the ρ-values and the relative reactivities. Elaboration of this observation however, was hampered by the fact that the reactivity values available were limited in number and were often determined under different experimental conditions. The relative reactivity data now obtained, under identical conditions, allow a systematic study to be made of the relationship mentioned above. Work in this direction is in progress.

TABLE I

Competitive Reactions with N-Bromosuccinimide and Bromotrichloromethane at 80°

	Substrates		Relative Reactivity K_A/K_B	
	A	B	N-Bromosuccinimide	Bromotrichloromethane
1.	PhCHOMe	$PhCH_2CH_3$	2.38 ±0.10	2.23 ±0.06
2.	Ph_2CHOMe	$PhCH_2OCH_3$	1.03 ±0.01	1.03 ±0.06
3.	$PhCH(OMe)_2$	$PhCH_2CH_3$	1.11 ±0.01	1.04 ±0.01
4.	PhCH.(OMe).COOMe	$PhCH_2CH_3$	1.16 ±0.06	-
5.	$PhCH_2OCH_2Ph$	Ph_2CHOMe	1.43 ±0.04	1.44 ±0.01
6.	$PhCH_2CH_3$	$PhCH_3$	15.2 ±0.7	16.1 ±0.8

Note: All reactions were carried out as previously described,[1b] each in duplicate or triplicate, the deviations given being the average mean values. The products were analysed for carbonyl compounds and α-bromo-ethylbenzene by infrared spectroscopy, and for total α-bromo-aromatic compounds by titration with 0.05N sodium methoxide in methanol-benzene.

TABLE II

Relative Reactivity Scale at 80°

Substrates	N-Bromosuccinimide System		Bromotrichloromethane System	
	per molecule	per Hydrogen atom	per molecule	per Hydrogen atom
$PhCH_3$	1.00	1.00	1.00	1.00
$PhCH_2CH_3$	15.2	22.8	16.1	24.1
$PhCH(OMe)_2$	16.9	50.6	16.7	50.1
$PhCH_2OMe$	35.1	52.6	34.8	52.2
PhCH.(OMe).COOMe	17.6	52.9	-	-
$PhCH_2OCH_2Ph$	51.7	77.5[a]	51.7	77.5[a]
Ph_2CHOMe	36.2	109	35.9	108

Foot-note: (a) The relative reactivity of dibenzyl ether was calculated on the basis of there being two benzylic hydrogen atoms at the reacting centre.

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