

HYDROGEN ABSTRACTION FROM SUBSTITUTED BENZYL CHLORIDES BY THE TRICHLOROMETHYL RADICAL

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Abstract—A series of ring substituted benzylchlorides have been reacted under photolytic conditions with bromotrichloromethane at 70°. Competitive kinetics show the bromination reaction to be substantially dependent upon ring substituents. A rho value of -1.02 (correlating with σ^+) was obtained with a correlation coefficient of -0.996 . This is greater than has been observed for other α -substituted toluenes and is attributed to the slight radical destabilizing effect of the adjacent chlorine atom. A correlation between the ring substituent effects in various series of α -substituted toluenes and the electronic and steric requirements of the α -substituent has been developed.

The abstraction of benzylic H atoms by the trichloromethyl radical from substituted toluenes has been shown to be favored by electron donating groups in the aromatic ring.¹ Related systems have also been investigated in which various hydrocarbon,^{2,5} methoxy,^{4,6} or chloromethyl⁷ groups have been introduced for one or two of the benzylic H atoms. The presence of these groups, all of which may be regarded as radical stabilizing relative to hydrogen, is to decrease the dependence on ring substituents (rho value). A summary of these results is found in Table 1. At the time of the present

investigation no data for H abstraction from a deactivated benzyl position was available. A study of the electronic factors governing H abstraction from substituted benzyl chlorides by the trichloromethyl radical (sequence 1).

When the project was begun the possibility of a competing halogen abstraction reaction was examined. Carbon radicals such as trichloromethyl⁸ and chlorocarbonyl⁹ will readily abstract halogen atoms from 1-fluoro-, chloro- and bromoadamantanes. A corresponding reaction is not undergone by these systems with Br atom.¹⁰ As benzyl radicals might be

Table 1. Summary of H abstraction data from  by the trichloromethyl radical

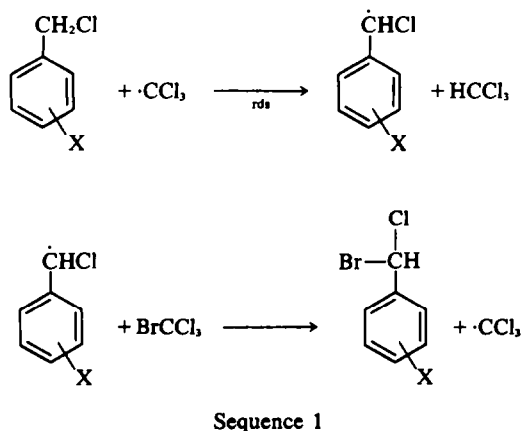
System	ρ^a	$\Sigma\sigma^{+b}$	ΣE_s^c	Ref
R = R' = H	-1.46 (50°)	$+0.000$	$+2.48$	1
	-1.24 (50°)			11
R = H, R' = Cl	-1.02 (70°)	$+0.114$	$+1.16^d$	present work
R = H, R' = $t\text{-C}_4\text{H}_9$	-0.94 (70°)	-0.256	-0.30	5
R = H, R' = CH_2Cl	-0.80 (80°)	-0.100	$+1.00$	7
R = R' = CH_3	-0.67 (70°)	-0.622	$+0.00$	3
R = H, R' = C_2H_5	-0.63 (70°)	—	—	2
R = H, R' = C_6H_5	-0.53 (80°)	-0.311	$+1.24^d$	4
R = H, R' = OCH_3	-0.36 (80°)	-0.778	$+1.19^d$	6
R = R' = OCH_3	-0.18 (80°)	-1.556	-0.10	4

^a For purposes of comparison all the above ρ values are those obtained with σ^+ parameters. In the case of R = H, R' = CH_2Cl a slightly better correlation was reported with σ .

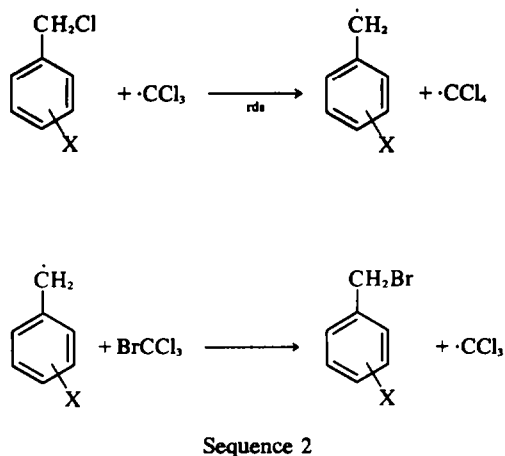
^b Obtained from J. E. Leffler and E. Grunwald, *Rates and Equilibria of Organic Reactions* p. 204. Wiley, New York (1963).

^c Obtained from Ref 14, p. 598.

^d Interpolated value based on $E_s(\text{Cl}) = -0.08$ and $E_s(\text{OCH}_3) = -0.05$.



expected to be more stable than their α -chloro counterparts, halogen abstraction from benzyl chlorides (sequence 2) could be a competing process.



It could be experimentally shown, however, that under the present conditions neither carbon tetrachloride nor benzyl bromides were formed from the compounds utilized. The disappearance of the benzyl chlorides could, therefore, be equated solely with an H abstraction reaction.

Table 2 shows the results of the present study. Relative rates of H abstraction were directly obtained usually using gas-liquid chromatography as the analytical device. In the case of *p*-methoxybenzyl chloride, however, excessive tailing of starting material and products was observed due to decomposition. The kinetic data for this compound was obtained relative to toluene using NMR spectroscopy to analyze samples. The two methods of analysis were found to be equivalent for several compounds, however, GLC was prefer-

Table 2. Relative rates of benzylic H abstraction from substituted benzyl chlorides at 70°

Substituent	σ^+	$\frac{k_X}{k_H}$	number of runs
<i>p</i> -CH ₃ O ^a	-0.778	7.14 ± 0.40	7
<i>p</i> -CH ₃ ^b	-0.311	2.56 ± 0.16	6
<i>p</i> -t-C ₄ H ₉	-0.256	2.22 ± 0.13	5
H	0.0	1.00	—
<i>p</i> -Cl	+0.114	0.95 ± 0.01	5
<i>m</i> -F ^c	+0.352	0.48 ± 0.02	5
<i>m</i> -Cl	+0.399	0.50 ± 0.03	5

^a Obtain relative to toluene using NMR spectroscopy as the analytical tool.

^b Corrected for reaction at the methyl position.

^c Run relative to the *p*-methyl compound.

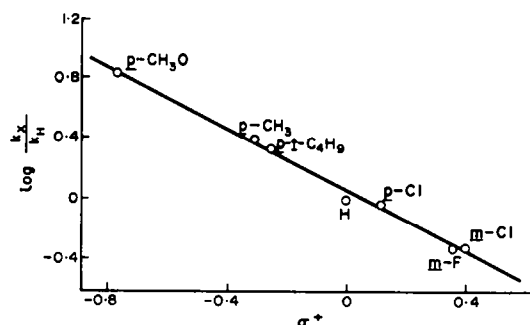


Fig 1. Linear free-energy relationship between logs of relative rates of abstraction from benzyl chlorides by trichloromethyl radicals and σ^+ .

red because of its greater precision. The results are graphically given in Fig 1.

A rho value of -1.02 ± 0.02 was found for the reaction series correlating with σ^+ parameters. The correlation coefficient was -0.996 . When σ parameters were utilized a rho value of -1.41 ± 0.13 was found. Correlation was much poorer having a coefficient of only -0.908 . This seems to be a general occurrence. All the examples cited in Table 1, with the exception of the β -chloroethylbenzenes, show somewhat better correlation with σ^+ parameters.

The rho value of -1.02 indicates a greater substituent dependence than has been noted for other α -substituted toluenes. As the α -chlorine atom should be slightly radical destabilizing this agrees with expectation. Hydrogen abstraction from the parent toluenes appears, however, to be more selective. This might be incorrect. The toluenes were studied at a lower temperature than the other series. Also, upon reinvestigation a smaller rho value of -1.24 has been recently found for this system even at the lower temperature.¹¹

The relationship between benzylic substitution and the observed rho values is of interest. Friedrich *et al.* have shown that the relative rates of α -substituted toluenes undergoing H abstraction by Br atom will be a function of the α -substituent.¹² Optimum correlation was obtained by using the σ_p^+ substituent rather than some aliphatic substituent constant. This has been treated as indicating direct mesomeric and hyperconjugative interaction between the incipient radical and the substituent in the transition state of the abstraction step. Similar results have been for H abstraction from α -alkyl- and α,α -dialkyl toluenes by the trichloromethyl radical.¹³ In this latter study, however, it was necessary to use a modified form of the expanded Taft equation to correlate data.¹⁴ This is a

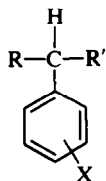
$$\log \frac{k_x}{k_0} = -5.78 (\Sigma \sigma^+) + 0.85 (\Sigma E_s) - 3.75$$

consequence of the greater size of this latter abstracting agent. This is strongly suggestive that the rho values in Table 1 might be correlated by a similar equation. Of the nine systems given in that table seven were used to define the relationship. Insufficient data was available for the allylbenzenes while the toluenes were studied at a temperature appreciably different from that at which the other compounds were examined. The equation obtained was

$$\rho = -0.606 \Sigma \sigma^+ + 0.195 \Sigma E_s - 1.063$$

where both the steric and electronic substituent constants refer to groups attached to the benzylic carbon. The calculated rho values are shown in Table 3. The average difference between experimental and calculated values is 0.04 rho units. Fig-

Table 3. Correlation of rho values for H abstraction from by the trichloromethyl radical



System	rho	
	experimental	calculated*
R = H, R' = Cl	-1.02	-0.92
R = H, R' = t-C ₄ H ₉	-0.94	-0.97
R = H, R' = CH ₂ Cl	-0.80	-0.81
R = R' = CH ₃	-0.67	-0.69
R = H, R' = CH ₃	-0.53	-0.62
R = H, R' = OCH ₃	-0.36	-0.36
R = R' = OCH ₃	-0.18	-0.14

* Based upon the relationship $\rho = -0.606 \Sigma \sigma^+ + 0.195 \Sigma E_s - 1.063$.

ure 2 illustrates a plot between calculated and experimental values. The slope of the line is nearly unity (0.97), as would be expected, with a reasonable correlation coefficient of 0.981. The agreement is encouraging, particularly in view of the temperature differences among the data. It will be interesting to see if further systems will conform to this relationship, although small variation in the variable parameters must be expected.

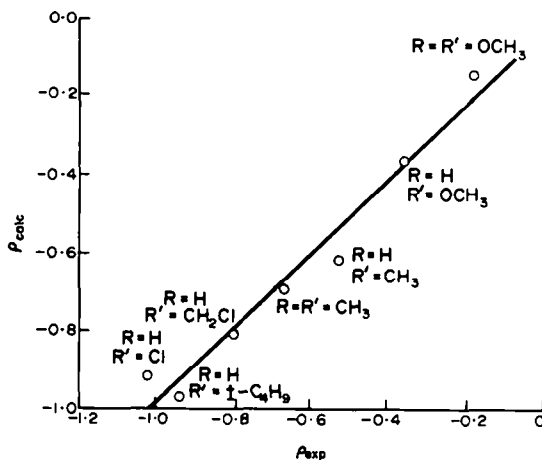


Fig 2. Experimental vs. calculated rho values.

EXPERIMENTAL

Materials. Bromotrichloromethane, chlorobenzene, di-*t*-butylbenzene, toluene, benzyl chloride, and *p*-methyl-, *p*-chloro-, *m*-fluoro and *m*-chlorobenzyl-chloride were obtained commercially. All were purified before use. Purities in excess of 99% were found by GLC. Physical properties conformed to those in the literature. *p*-Methoxy- and *p*-*t*-butylbenzyl chloride were prepared from the corresponding benzyl alcohols by treatment with thionyl chloride. Purity equal to the other compounds was found.

Product study. In several cases reactions were monitored by GLC and NMR spectroscopy. Through one half-life of starting benzyl chloride an apparent material balance between product and chloroform was observed. No benzyl bromide could be detected by either approach and no carbon tetrachloride could be found by GLC. A detailed product study was also run. A mixture of 5.103 g (40.340 mmoles) of benzylchloride and 30.773 g (155.028 mmoles) of bromotrichloromethane were reacted for 48 h. At the end of this time unreacted bromotrichloromethane was removed and the mixture treated with 15 g AgNO₃ in 50 ml water and allowed to stand overnight at ca 50°. The silver halides were removed by filtration and the organic materials extracted from the aqueous mixture with ether. Upon work-up 22.431 mmoles of benzyl alcohol and 15.118 mmoles of benzaldehyde (characterized as its DNPH derivative) were obtained. Material balance was 93.1%.

Kinetic studies. Solutions of two benzyl chlorides, bromotrichloromethane and chlorobenzene were prepared in the approximate molar ratio of 1:1.6:0.5. Ap-

proximately 0.75 ml of the soln was placed in each of the several ampoules. The ampoules were cooled to dry ice-isopropyl alcohol temp until the solns solidified. The ampoules were evacuated at 2.0–3.0 mm. and flushed with N₂ several times with three intermediate thawings. The ampoules were sealed under vacuum and one was reserved for the analysis of the unreacted starting materials. The remainder were placed horizontally just below the surface of a mineral oil constant temp bath maintained at 70.0 ± 0.5°. The soln was irradiated with UV light provided by a Sylvania 275-W sun lamp placed 20 cm. above the surface of the oil. Reaction times varied from 14 to 19 h, by which time 20 to 70% of the total benzyl chlorides had reacted. The ampoules were then cooled and opened. Analysis of the mixtures, both before and after the reaction was carried out via GLC on a 5% S.E. 30 on chromosorb W column.

Those runs depending upon NMR analysis were treated in the following way. Solns of toluene, benzyl chloride, bromotrichloromethane and *p*-di-*t*-butylbenzene were prepared in the ratio 1:1:6:0.1. Identical reaction conditions were employed as before. After the ampoules had been cooled and opened small portions of TMS were added to each. Changes in the integrated areas of the Me group in toluene and the methylene group in the benzyl chloride (both relative to the invariant aliphatic proton signal of the *p*-di-*t*-butylbenzene) were used to define the extent of reaction.

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