Steric Hindrance in Aromatic Hydrogen Exchange

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Summary Acid-catalysed hydrogen exchange at the *ortho* position of tetraphenylmethane is sterically hindered, and is only the second known example of hindrance in the reaction.

Hydrogen exchange is the least sterically hindered of all electrophilic aromatic substitutions and until recently, no example of steric hindrance was known. Recent data for exchange in 1,3,5-triphenylbenzene,[1] taken along with those for monofluorobiphenyls,[2] showed conclusively that exchange at the *ortho* positions of the former molecule is hindered. We have, therefore, sought examples of hindrance in other crowded molecules and report here results for tetraphenylmethane.

From the partial rate factors for detritiation of toluene,[3] diphenylmethane,[4] triphenylmethane, and tetraphenylmethane in trifluoroacetic acid at 70°, we obtain the $\log f_o : \log f_p$ values shown in the Table. We stress that use of this parameter establishes the relative positional reactivities in linear energy terms (*i.e.* free of effects of selectivity differences between the aromatics). The ratio decreases slightly on going from toluene to diphenylmethane, which is consistent with the greater $-I$ effect of the substituent. Introduction of a second and third phenyl group into the substituent should produce a similar reduction leading to predicted ratios for triphenylmethane and tetraphenylmethane of 0·74 and 0·665, respectively. For triphenylmethane the ratio is slightly less than predicted and for tetraphenylmethane grossly so; exchange at the *ortho* position of tetraphenylmethane is, therefore, sterically hindered (and that of triphenylmethane may be slightly so). The hindrance in tetraphenylmethane is confirmed by the $\log f_o : \log f_m$ values which would be expected to be more constant than the $\log f_o : \log f_p$ values since variation in the inductive effect of the substituent would produce smaller relative changes in the positional reactivity; the ratio is dramatically smaller for tetraphenylmethane.

Table

Relative positional reactivities for protiodetritiation in CF_3CO_2H at 70°

	Aromatic			
	$PhCH_3$	$PhCH_2Ph$	$PhCHPh_2$	$PhCPh_3$
$\log f_o : \log f_p$ ..	0·885	0·810	0·66	0·354
$\log f_o : \log f_m$ ..	2·98	2·93	2·98	1·03

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[1] H. V. Ansell, R. B. Clegg, and R. Taylor, *J.C.S. Perkin II*, 1972, 760.
[2] R. Taylor, *J.C.S. Perkin II*, 1973, 253.
[3] R. Baker, C. Eaborn, and R. Taylor, *J. Chem. Soc.*, 1961, 4927.
[4] R. Baker, C. Eaborn, and J. A. Sperry, *J. Chem. Soc.*, 1962, 2382; K. C. C. Bancroft, R. W. Bott, and C. Eaborn, *ibid.*, 1964, 4806.