Enhancement of Equilibrium Acidities of Hydrocarbons by Polyfluoroaryl Substitution†

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WE have prepared a number of pentafluoro- and tetrafluoro-phenyl-substituted hydrocarbons and have evaluated the influence of these fluorophenyl groups on the equilibrium acidities of these compounds.

Friedel–Crafts alkylation of pentafluorobenzene by CH_2Cl_2 or $CHCl_3$ gives $(C_6F_5)_2CH_2$ (I) and $(C_6F_5)_3CH$ (II), respectively.[1] Similarly, $(p\text{-}MeC_6F_4)_3CH$ (III) and $(p\text{-}MeOC_6F_4)_3CH$ (IV) are readily prepared from the corresponding tetrafluorobenzene. Compound (II) can also be prepared in 70% yield by reaction of tris(pentafluorophenyl)methanol and phosphorus tribromide.[2] The formation of bromine after a 1 hr. induction period, suggests that reaction proceeds *via* the bromide, which is not isolated (equation 1).

$$(C_6F_5)_3COH + PBr_3 \rightarrow [(C_6F_5)_3\overset{\delta-}{C}\text{-}\overset{\delta+}{Br}] \xrightarrow{HBr} \underset{(II)}{(C_6F_5)_3CH} + Br_2 + HBr + POBr \quad (1)$$

The polarization of the C–Br bond to give some "positive" bromine character is likely, as three pentafluorophenyl groups are electron-attracting, and finds experimental support in the unusual stability of the tris(pentafluorophenyl)carbanion, $(C_6F_5)_3C^-$.

When $(C_6F_5)_2CHBr$ is treated with n-butyllithium at −70°, *sym*-tetrakis(pentafluorophenyl)-ethane (V) is obtained in 35—40% yield (equation 2).

$$\begin{array}{rcl} (C_6F_5)_2CHBr + n\text{-}BuLi & \xrightarrow{-70^\circ} & (C_6F_5)_2CH^- \\ & & + \\ Br + \underset{(V)}{(C_6F_5)_2CH\text{-}CH(C_6F_5)_2} & \leftarrow & (C_6F_5)_2CHBr \quad (2) \end{array}$$

The equilibrium acidities of compounds (I)—(V) were determined spectrophotometrically using Streitwieser's technique[3] [lithium cyclohexylamide (LiCHA) in cyclohexylamine]. It was not possible to use 9-phenylfluorene as the reference hydrocarbon, since its anion absorbs strongly in the same region (*ca.* 420 mμ) as the carbanions (lithium carbanide ion pairs) of the polyfluoroaryl hydrocarbons. However, fluorene (pK_a 22·83)[3] proved to be a very satisfactory reference acid.

The average values (four or five runs) of the equilibrium constants between pairs of compounds competing for a limited amount of base are shown in Table 1. From these data an acidity order for compounds (I)—(V) toward LiCHA can be derived (Table 2). The acidities of all five compounds lie in the p*K* range 15·8—22·7.

TABLE 1

Average values of equilibrium constants in reaction with LiCHA

HA	HB	*K*	Log *K*
(I)	Fluorene	38 ± 5·5	1·58±0·06
(V)	Fluorene	1·46± 0·02	0·16±0·006
(I)	(V)	33·5 ± 4·9	1·53±0·06
(II)	(III)	109 ±19·5	2·04±0·10
(IV)	(I)	99·8 ± 2·3	1·99±0·01
(III)	(IV)	25·4 ± 2·5	1·40±0·04

TABLE 2

Acidity order of fluorohydrocarbons toward LiCHA

Compound	Relative log *K*	p*K*
Fluorene	0	(22·83)
$(C_6F_5)_2CHCH(C_6F_5)_2$	0·16±0·006	$22{\cdot}6_7$
$(C_6F_5)_2CH_2$	1·58±0·06	$21{\cdot}2_5$
$(p\text{-}MeOC_6F_4)_3CH$	3·57±0·07	$19{\cdot}2_6$
$(p\text{-}MeC_6F_4)_3CH$	4·97±0·11	$17{\cdot}8_6$
$(C_6F_5)_3CH$	7·01±0·21	$15{\cdot}8_2$

Comparison with the equilibrium pK_a's of triphenylmethane (31·48) and diphenylmethane (33·1)[3] shows that substitution of each phenyl group by a pentafluorophenyl group results in an enhancement of the acidity by 5—6 p*K* units. Electron-releasing substituents in (III) (*p*-Me: inductive) and (IV) (*p*-OMe: mesomeric) destabilize the carbanion and cause a diminution of acidity relative to (II).

Streitwieser has concluded from kinetic acidity studies[4] that more than half of the enhanced acidity of triphenylmethane over that of saturated hydrocarbons is due to the inductive effect of the benzene

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rings. Less than half can be attributed to resonance-stabilization of the carbanion, owing to steric restraints imposed by three aromatic rings, which cause significant departure from coplanarity. There is relatively little difference (Δ pK = 1·62) between triphenylmethane and diphenylmethane, since in the latter, resonance-stabilization of the carbanion makes a more important contribution.

In $(C_6F_5)_3C^-$, steric restraints should be even more demanding than in $(C_6H_5)_3C^-$. Moreover, relief of C–F dipole–dipole repulsions should cause a further departure from coplanarity.

Therefore, we ascribe the remarkable enhancement of acidity in polyfluoroaryl hydrocarbons primarily to the strong inductive influence of the C_6F_5 and p-RC_6F_4 groups. The large difference in acidity between (I) and (II) (ΔpK = 5·4) is indicative of this effect.

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