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STABILIZATION OF CARBANIONS BY POLYFLUOROARYL SUBSTITUTION. ENHANCED EQUILIBRIUM ACIDITIES OF CARBON ACIDS

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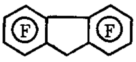
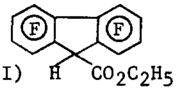
An impressive body of evidence has demonstrated the significant effect of polyfluoroaryl groups in stabilizing carbanions. Among these observations are the marked acceleration of rate of carbanionic rearrangements, anomalous reaction chemistry, and enhanced hydrocarbon acidities. In this study, the absolute equilibrium acidities of a wide range of polyfluorophenyl-substituted carbon acids have been determined spectrophotometrically in DMSO solution and compared with those of their phenyl analogues. The classes of compounds examined include acetonitriles, acetates, and hydrocarbons (diaryl- and triarylmethanes and the fluorenes I and II).


(I)


(II)

The C_6F_5-substituted compounds exhibit dramatic enhancements in acidity relative to their phenyl counterparts. In most cases, replacement of each C_6H_5 by C_6F_5 increases the acidity by 4-6 pKa units (Table). Both inductive and resonance effects are operative. In compounds such as II (pKa = 6.1) the resonance saturation effect causes diminution of the full influence of polyfluoroaryl substitution.

TABLE

COMPOUND	pKa	COMPOUND	pKa
$C_6H_5CH_2CN$	21.7	$C_6H_5CH(CO_2C_2H_5)CN$	8.0
$C_6F_5CH_2CN$	15.8	$C_6F_5CH(CO_2C_2H_5)CN$	5.1
$(C_6H_5)_2CHCN$	17.5	$(C_6H_5)_2CH_2$	33.2
$(C_6F_5)_2CHCN$	7.95	$(C_6F_5)_2CH_2$	22.0
$(C_6H_5)_2CHCO_2C_2H_5$	21.9	fluorene	22.6
$(C_6F_5)_2CHCO_2C_2H_5$	13.1	octafluorofluorene (I)	10.8