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NUCLEOPHILIC DISPLACEMENT IN POLYHALOGENOAROMATIC COMPOUNDS. PART X. TRANSMISSION OF SUBSTITUENT EFFECTS IN POLYFLUOROBIPHENYL DERIVATIVES

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SUMMARY

The rate of methoxydefluorination (NaOMe-MeOH, 323.2 K) and the ^{19}F-NMR chemical shifts of some substituted penta- and nona-fluorobiphenyls have been measured. The observed substituent effects parallel those found in the corresponding pentafluorobenzenes and demonstrate the proportionate transmission of the total substituent electronic effect across the aromatic system.

INTRODUCTION

The transmission of electronic effects across aromatic systems remains a source of controversy. In attempts to separate components which are transmitted through σ-bond and π-bonds, substituent effects in polyannular systems have been compared with those found in the benzene system. Thus we have shown [1] that interannular substituent effects in polyfluoronaphthalenes parallel those found in the corresponding benzene system, although with some attenuation. A number of workers have used the biphenyl system, and the closely related fluorene system to study the phenomenon. Berliner and his co-workers [2] showed the effect of the 4'-nitro-substituent upon the rate of reaction of 4-bromo-3-nitrobiphenyl with piperidine, and compared this with the much larger effect found when the reactions of o-bromonitrobenzene and 2,4-dinitrobromobenzene were studied. Subsequently, Eaborn [3] reported substituent effects upon the rate of protiodetritiation of some 7-X-2-tritiofluorenes and of some 4'-X-4-tritiobiphenyls. These again were less than those in the corresponding tritiobenzene derivatives, in keeping with the smaller range of pK_a values found for the biphenylcarboxylic acids and -amines in contrast to their phenyl analogues [4], and suggest a considerable attenuation upon transmission across the second phenyl ring. Recently a similar attenuation has been measured in the transmission of substituent effects across the aromatic systems of α-(4-biphenylyl)benzyl chloride and its fluorene analogue as seen in their rates of solvolysis [5].

This kinetic and thermodynamic evidence is in agreement with the electric dipole moment studies of Everard and Sutton [6], who showed that the magnitude of a mesomeric interaction moment depends upon the length of the conjugated system across which it acts. Spectroscopic studies of biphenyl systems have also confirmed this behaviour; in particular, ^{19}F-NMR spectroscopy has been extensively applied in an attempt to determine the relative contributions of σ- and of π-bond transmission to the substituent chemical shift [S.C.S.]. Thus Taft [7] has related the S.C.S. in p-substituted fluorobenzenes to the reactivity parameters σ_I and σ_R, interpreting this relationship to show the dual dependence of p-substituent chemical shifts upon σ- and π-electron terms. More recently, Fukunaga and Taft [8] have suggested that in longer aromatic systems, e.g. substituted 4-fluorobenzophenones, the substituent polar effect on the ^{19}F-NMR shift is transmitted through the π-electron system. On the other hand, Dewar et.al [9] have argued that the polar effects of substituents are relayed via electric field effects. Analysis of ^{19}F-NMR chemical shifts in substituted fluorobenzenes and stilbenes led Ager and Phillips [10] to conclude that π-interactions were important in both m- and p-substituted fluorobenzenes.

Detailed kinetic studies of the transmission of substituent effects across biaryl systems have been limited to reactions in which the aromatic system itself becomes electron deficient. We have already shown [11] that methoxydefluorination is quite sensitive to substituent effects; methoxydefluorination of substituted polyfluorobiphenyls might therefore be a nucleophilic displacement reaction showing appreciable transmission of substituent effects across the two rings and therefore a suitable system to show the generality of this process. ^{19}F-NMR studies were also made to correlate the ground state and transition state behaviour of the systems.

DISCUSSION

Table 1 shows the rate constants of methoxydefluorination of seven derivatives of 2,3,4,5,6-pentafluorobiphenyl by methanolic sodium methoxide at 323.2 K. Because pentafluorotoluene [12], octafluorotoluene [13], 2,3,4,5,6-pentafluorobiphenyl [14] and decafluorobiphenyl [15] all lose fluorine predominantly (>95%) at the para-position (4-position of biphenyl), we have assumed that the substituted derivatives of pentafluorobiphenyl also undergo displacement almost entirely at the 4-position.

Table 1

Second-order rate constants for methoxydefluorination of $X.C_6H_4.C_6F_5$

X:	H	m-Me	p-Me	m-Cl	m-Br	m-NO_2	p-NO_2
10^4k_2:$^{(a)}$	1.23±0.07	1.10±0.07	0.72±0.02	7.5±0.5	5.3±0.6	25.6±1.4	32±2
k_X/k_H	1.0	0.89	0.59	6.1	4.3	20.8	26

(a) $l.mol^{-1}\ s^{-1}$ (NaOMe-MeOH; 323.2 K)

These figures can be compared with the substituent rate factors (f_X) derived from studies of the methoxydefluorination of pentafluorotoluene (f_{m-Me}, 2.1: f_{p-Me}, 0.6 [1]), and of polychloro- and polybromo-polyfluorobenzenes (f_{m-Cl}, 123 f_{m-Br}, 100 [11]). The rate constant for methoxydefluorination of nitropentafluorobenzene has been redetermined at 323.2 K (k_2, 9.5±1 $l.mol^{-1}\ s^{-1}$); earlier values [16] have relied upon the extrapolation of Arrhenius plots. As 92% attack occurs at the para-position [17], comparison with pentafluorobenzene (k_2, 1.01 x 10^{-4} $l\ mol^{-1}\ s^{-1}$) gives a substituent rate factor (f_{p-NO_2}) of 9.1 x 10^4.

A plot of $\log_{10}(k_X/k_H)$ from Table 1 against $\log_{10}f_X$, using the appropriate substituent factor, is a line of slope 0.32±0.03. This may be compared with the value (0.44) found by similar treatment of the rate constants for methoxydefluorination of decafluorobiphenyl (k_2, 8.4±0.2 x 10^{-2} $l\ mol^{-1}\ s^{-1}$), 4H-nonafluorobiphenyl (k_2, 4.4±0.2 x 10^{-2} $l\ mol^{-1}\ s^{-1}$) and 4-methoxynonafluorobiphenyl (k_2, 1.34±0.03 x 10^{-2} $l\ mol^{-1}\ s^{-1}$), with the factor (0.26) associated with the solvolysis of the substituted α-(4-biphenylyl)-benzyl chloride [5], with the value obtained (0.2-0.4) from comparing the dissociation constants of the aroic acids [4], and the saponification of substituted ethyl aroates (0.24) [18]. A value of 0.22 may also be derived from Berliner's study of piperidinodebromination [2]. In each case, the existence of such a proportionality factor suggests that the substituent effect seen in the benzene derivative is transmitted, although attenuated, across the second ring in the biphenyl derivative without consideration of the source of the electronic effect transmitted -- that is, regardless of whether the major part of the substituent effect is inductive or mesomeric in origin.

Table 2 shows the chemical shifts of fluorine atoms in the 3- and 4-positions of some substituted 2,3,4,5,6-pentafluorobiphenyls (^{19}F-NMR).

Table 2

^{19}F-NMR Chemical shifts (δ; p.p.m. upfield of $CFCl_3$) and substituent chemical shifts (Δδ; p.p.m.) of $X.C_6H_4.C_6F_5$

X	Hammett σ	$Log_{10}k_2$ $^{(a)}$	3-F		4-F	
			δ	Δδ	δ	Δδ
H	0.00	-3.91	163.2	0.0	156.8	0.0
3'-Me	-0.07	-3.96	163.0	-0.2	156.7	-0.1
4'-Me	-0.17	-4.14	163.0	-0.2	156.8	0.0
3'-Cl	0.37	-3.22	162.2	0.8	155.0	1.8
3'-Br	0.39	-3.28	161.8	1.4	154.6	2.2
$3'-NO_2$	0.71	-2.59	161.2	2.0	153.3	3.5
$4'-NO_2$	0.78	-2.49	161.1	2.1	153.1	3.7

(a) Rate constant of methoxydefluorination at 323.2 K; 1 mol^{-1} s^{-1}

A linear relationship exists between the Hammett substituent constant (σ) and the substituent chemical shifts at either the 3- or the 4-positions, as well as between σ and $\log_{10}k_2$. The linear relationship between $\log_{10}k_2$ and Δδ(4-F) implies similar (or at least proportional) electronic effects operating in both ground state and transition state.

It seems that the electronic effect of the substituent is transmitted, although to different extents, to both these positions in the second ring. Again, the origin of the electronic effect (inductive or mesomeric effect) does not affect its transmission in our series of compounds. The distance through which this relay occurs (seven carbon-carbon bonds) suggests that π-bond transmission is the major route. This is in agreement with the results of Everard and Sutton [6], who explained the dipole moments of some derivatives of biphenyl, stilbene and 1,4-diphenyl-1,3-butadiene in terms of a long-range inductive contribution transmitted by the π-bond system. Such a contribution accounts for the observation of Ager and Phillips [10] that the halogen substituents appear to be π-electron withdrawing in their effect upon ^{19}F-NMR substituent chemical shifts.

EXPERIMENTAL

Decafluorobiphenyl (m.p. 68.5 - 69.5°), and hexafluorobenzene were commercial samples (Imperial Smelting Co., Avonmouth); nitropentafluorobenzene was obtained from Bristol Organics. 2,3,4,5,6-Pentafluorobiphenyl (m.p. 112 - 112.5°), and its 3'-chloro- (m.p. 62.3 - 63.0°; 30%), 3'-bromo- (m.p. 66 - 67°; 30%). 3'-nitro- (m.p. 111 - 2°; 10%), 4'-nitro- (m.p. 89 - 90° 5%), 3'-methyl- (m.p. 43 - 4°; 40%), and 4'-methyl- (m.p. 119 - 120°; 40%) derivatives were obtained by the thermal decomposition of the appropriate aroyl peroxide in hexafluorobenzene, and showed physical constants in agreement with literature values [19].

The course of the methoxydefluorination of these biaryls was followed using a fluorine-ion selective electrode [20].

4H-nonafluorobiphenyl (m.p. 77°; lit., [21] 77°) was obtained from 4-hydrazinononafluorobiphenyl [15]; 4-methoxynonafluorobiphenyl (m.p. 50 - 51° was isolated from the reaction of equimolar amounts of decafluorobiphenyl and sodium methoxide in methanol. The rates of methoxydefluorination of these compounds, and of decafluorobiphenyl, were followed by acid-base titration; measurement of the rate of formation of fluoride ion in the reaction of decafluorobiphenyl gave the same rate constant and demonstrated the stoichiometry of the slow stage.

Standard solutions of methanolic sodium methoxide were prepared by reported methods [11]; in each case the polyfluoroarenes showed good second-order rate constants over a considerable range of initial concentrations and extents of reaction.

^{19}F-NMR spectroscopy was carried out using dilute solutions in fluorotrichloromethane (internal standard; Perkin-Elmer R12B; 56.4 MHz).

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