61064-12-8; DFP, 55-91-4; cyanide ion, 57-12-5; fluoride ion, 16984-48-8; *n*-butyllithium, 109-72-8; hexamethyldisilazane, 999-97-3; hexamethyldisilazallithium, 4039-32-1; ethyl acetate, 141-78-6; *n*-octanoyl chloride, 111-64-8; ethyl 3-oxodecanoate, 13195-66-9; 3-oxodecanoic acid, 13283-92-6; potassium 3-oxodecanoate, 61-64-11-7.

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(1) A. L. Green and B. Saville, *J. Chem. Soc.*, 3887 (1956). The phosphono- and phosphorofluoridates are extremely toxic; extreme care should be exercised in handling these compounds.

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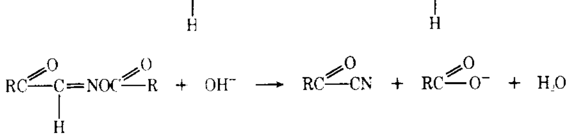
(5) E. V. Crabtree and E. J. Poziomek, *J. Org. Chem.*, **32**, 1231 (1967), were able to produce 8 × 10^{-3} mol of cyanide ion from a solution containing 2 × 10^{-4} mol of cyanide ion and 4 × 10^{-2} mol of II in 6 h, demonstrating the high effectiveness of cyanide ion in catalysis of decomposition of II. In the case reported in this paper, however, direct addition of cyanide ion failed to produce a catalytic effect in the time period of the reaction. Moreover, the observation that the production of cyanide followed first-order kinetics is not consistent with a postulation that cyanide ion is the reactive species. If cyanide were the cause of the decomposition, Figure 1 would have shown an increasing rate with time.

(6) The reaction of the acyl cyanide with oximate ion is considered to be composed of two consecutive reactions

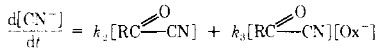


$$R\overset{O}{C}{-}CN + R\overset{O}{C}{-}\underset{H}{C}{=}NO^- \longrightarrow R\overset{O}{C}{-}\underset{H}{C}{=}NO\overset{O}{C}{-}R + CN^-$$

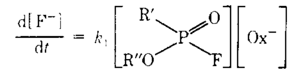
$$R\overset{O}{C}{-}\underset{H}{C}{=}NO\overset{O}{C}{-}R + OH^- \longrightarrow R\overset{O}{C}{-}CN + R\overset{O}{C}{-}O^- + H_2O$$

with the first step, i.e., the displacement of cyanide, rate controlling.

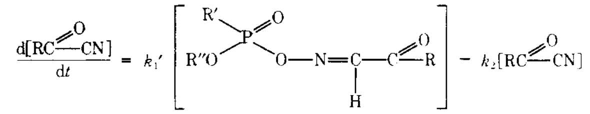
(7) The differential equations for the series of reactions at constant pH are



$$\frac{d[CN^-]}{dt} = k_2[R\overset{O}{C}{-}CN] + k_3[R\overset{O}{C}{-}CN][Ox^-]$$

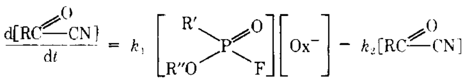


$$\frac{d[F^-]}{dt} = k_1\left[\mathrm{R'(R''O)P(=O)F}\right]\left[Ox^-\right]$$



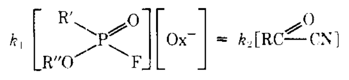
$$\frac{d[R\overset{O}{C}{-}CN]}{dt} = k_1'\left[\mathrm{R'(R''O)P(=O)}{-}O{-}N{=}\underset{H}{C}{-}\overset{O}{C}{-}R\right] - k_2[R\overset{O}{C}{-}CN]$$

Since $k_1' \gg k_1$, then



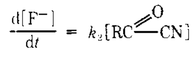
$$\frac{d[R\overset{O}{C}{-}CN]}{dt} = k_1\left[\mathrm{R'(R''O)P(=O)F}\right]\left[Ox^-\right] - k_2[R\overset{O}{C}{-}CN]$$

and at steady state conditions, i.e., d[RC(=O)CN]/d*t* = 0,



$$k_1\left[\mathrm{R'(R''O)P(=O)F}\right]\left[Ox^-\right] = k_2[R\overset{O}{C}{-}CN]$$

so that



$$\frac{d[F^-]}{dt} = k_2[R\overset{O}{C}{-}CN]$$

Then

$$\frac{d[CN^-]}{dt}\Big/\frac{d[F^-]}{dt} = 1 + \frac{k_3}{k_2}[Ox^-]$$

and at t_∞,

$$\frac{[CN^-]}{[F^-]} = 1 + \frac{k_3}{k_2}[Ox^-]$$

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π-Inductive Effects in Benzyl Compounds

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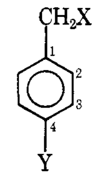
Received August 24, 1976

Considerable interest has been devoted to the nature of the transmission of substituent effects in α-substituted methyl aromatics.[1] The two mechanisms which have been generally proposed to explain the observed results involve hyperconjugative type interactions and π-inductive effects. As both of these mechanisms work in the same direction (for example, they decrease charge density at the para position) it is somewhat difficult to differentiate between them. ^{13}C NMR is well suited to such studies because it has been shown that the para carbon chemical shift is linearly related to the electron density at that position.[2] However, simple inspection of comparative shift data may result in an erroneous conclusion (vide infra). In order to assess the relative importance of hyperconjugative and π-inductive effects, it is instructive to use the dual substituent parameter (DSP) treatment.[3] Here, hyperconjugative interactions become apparent in the importance of the resonance term (**r**), while π-inductive effects appear in the inductive-field parameter (**f**).[3b]

Recently, Taft et al. have reported that for para-disubstituted benzenes, the π-inductive effect is manifest by a nonadditive behavior of the carbon-13 substituent effects.[4] Ab initio calculations have also indicated that π-inductive

Table I. ^{13}C NMR Chemical Shifts in Para-Substituted Benzyl Compounds[a]



Registry no.	X	Y	C_1	C_2	C_3	C_4	CH_2
106-42-3	H	CH_3	134.6	129.0	129.0	134.6	20.9
104-81-4	Br	CH_3	134.8	128.9	129.4	138.3	33.7
104-82-5	Cl	CH_3	134.6	128.5	129.3	138.1	46.1
589-18-4	OH	CH_3	138.0	127.1	129.1	137.6	64.8
106-38-7	H	Br	136.5	130.7	131.1	119.0	20.8
589-15-1	Br	Br	136.7	130.6	131.9	122.4	32.8
589-17-3	Cl	Br	136.4	130.1	131.9	122.4	45.3
873-75-6	OH	Br	139.8	128.5	131.5	121.3	64.3
104-93-8	H	OMe	129.7	129.9	113.8	157.7	20.4
2746-25-0	Br	OMe	130.3	129.9	114.7	159.7	33.9
824-94-2	Cl	OMe	130.0	129.7	114.0	159.6	46.3
105-13-5	OH	OMe	133.4	128.5	113.7	158.9	64.6
99-99-0	H	NO_2	146.2	129.9	123.4	146.2	21.5
100-11-8	Br	NO_2	144.9	129.9	123.9	147.7	30.9
100-14-1	Cl	NO_2	144.5	129.4	123.9	147.8	44.6
619-73-8	OH	NO_2	149.8	127.2	123.6	147.2	63.5
108-88-3	H	H	137.8	129.3	128.5	125.6	21.3
100-39-0	Br	H	137.8	129.0	128.6	129.0	33.4
100-44-7	Cl	H	137.5	128.6	128.5	128.3	46.2
100-51-6	OH	H	140.5	127.2	128.6	127.7	64.9

[a] In parts per million from Me_4Si.

Table II. ^{13}C NMR Substituent Shifts for C_1 and C_4 in Para-Substituted Benzyl Compounds

	Y				
X	CH_3	Br	OMe	NO_2	H
			C_1		
Br	0.2	0.2	0.6	−1.3	0.0
Cl	0.0	−0.1	0.3	−1.7	−0.3
OH	3.4	3.1	3.1	3.6	2.7
			C_4		
Br	3.7	3.4	2.0	1.5	3.4
Cl	3.5	3.4	1.9	1.6	2.7
OH	3.0	2.3	1.2	1.0	2.1

Table III. DSP Analysis of the C_1 and C_4 Carbon Chemical Shifts[a]

	f	**r**	a^b	b^b	i	$\bar{r}$	Av dev	Range
				C_1				
CH_2OH	5.16	19.55	0.694	0.909	140.5	0.994	0.63	16.4
CH_2Cl	3.63	18.33	0.579	0.944	137.4	0.999	0.20	14.5
CH_2Br	3.74	18.39	0.585	0.942	137.7	0.998	0.24	14.6
CH_2H	4.39	20.57	0.595	0.935	137.8	0.996	0.34	16.5
				C_4				
H	4.33	0.24	0.988	0.065	125.6	0.990	0.15	3.4
CH_3	4.85	−0.99	0.988	−0.449	134.6	1.000	0.01	3.7
Br	4.81	0.07	0.999	−0.297	119.0	0.999	0.05	3.4
OMe	2.82	0.27	0.997	−0.235	157.7	1.000	0.00	2.0
NO_2	2.21	0.13	0.994	−0.263	146.2	0.995	0.05	1.6

[a] $\delta = \mathbf{f}F + \mathbf{r}R + \delta_0$. [b] Correlation coefficient of $\delta = \mathbf{f}F + \delta_0$ (a) or $\delta = \mathbf{r}R + \delta_0$ (b).

Table IV. One-Bond Coupling Constants for the Methylene Carbon

Y	X	J, Hz
H	Br	152.5
Br	Br	152.6
OMe	Br	153.2
NO_2	Br	153.2
Br	OH	142.8
OMe	OH	141.5
H	OH	140.0
H	H	126.0
Br	H	126.7
OMe	H	126.0
NO_2	H	127.1

effects are important in the benzene series.[5] In this light, it was decided to investigate the substituent effects for some para-substituted benzyl compounds,[6] using the DSP treatment.

All of the chemical shift values and the substituent shifts at C_1 and C_4 are given in Tables I and II, respectively. Assignments were made by consideration of substituent effects based on simple benzyl derivatives,[7] para-substituted toluene data, and on the "fingerprint" pattern of the proton coupled spectrum.[8] For instance, each half of the coupled spectrum for C_3 appears as a doublet ($J \approx 3.5$–8.0 Hz, depending on the para substituent), while the C_2 resonance appears as a quintet or a sextet depending on the size of the long-range coupling constants. Full analysis of the spectral patterns was not attempted owing to some second-order effects.

The DSP analysis of the substituent effect observed at C_1, obtained by varying the para substituent, is given in Table III. The result is quite unexceptional indicating that resonance effects are dominant. The relative importance of the **f** and **r** values is seen to vary slightly, suggesting that there may be a small difference in the π-inductive effect of CH_3, CH_2OH, CH_2Br, and CH_2Cl.[4]

The DSP analysis for the C_4 chemical shifts was performed by varying the α-methyl substituent. It is immediately obvious that the para substituent markedly influences the magnitude of the inductive **f** term. The resonance interactions, in comparison, are unimportant and the values given for **r** may be an artifact of the regression analysis. The data strongly suggest that hyperconjugative interactions at the para position are at best a minor contributor to the observed substituent effect in benzyl systems. This observation is consistent with the data based on ^{19}F NMR obtained for p-fluoro-α-substituted toluenes.[9] The influence of the para substituent on the **f** value is seen to be substantial and the trend observed is similar to that found for the para-substituted benzene systems.

The above conclusion is further supported by the one-bond carbon–hydrogen coupling constants for the methylene carbon (Table IV). If hyperconjugative interactions are important, then rehybridization of the methylene carbon from $sp^3 \rightarrow sp^2$-like should occur to some extent. This should result in an increase of this coupling constant value.[10] The values obtained, however, are quite normal and thus inconsistent with the hyperconjugative notion.

Acknowledgment. The financial support of this work by the Robert A. Welch Foundation is gratefully acknowledged.

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