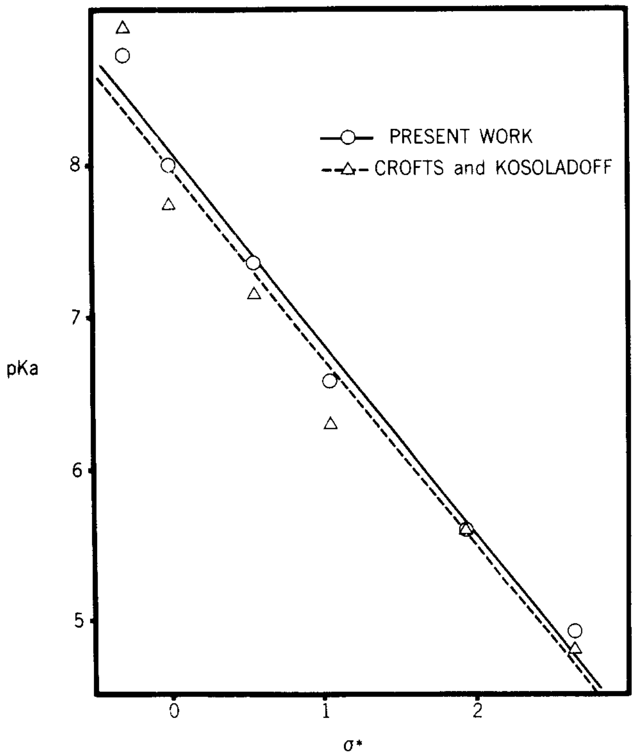

Figure 1. Equilibrium constants for the second ionization of alkylphosphonic acids correlated by the Taft equation.

$(pK_a)_{app}$, whose constituent quantities are all known, will be a linear function of ionic strength with the thermodynamic pK_a as its $I = 0$ intercept.

The data obtained here obey this relationship quite well. Least-squares analysis provides fits whose correlation coefficients are usually 0.98 or 0.99, and never less than 0.95, and whose slopes are generally 0.3 or 0.4; the latter is a reasonable magnitude for the difference $B^{2-} - B^{-}$.[10] These results are summarized in Table I. The average pK_a's listed there are simple unweighted means, and the error estimates given are standard deviations of these means. These probably do not take systematic errors adequately into account, and a more realistic estimate of the reliability of the present results may be 0.005–0.010 pK_a unit.

Thermodynamic pK_a's seem not to have been determined before for any of the acids studied here, but some apparent pK_a values are available. These are due principally to Crofts and Kosolapoff,[6a,b] who carried out potentiometric titrations and used the relationship $pK_a' = pH + \log [RPO_3H^-]/[RPO_3^{2-}]$ to calculate their results. Comparison of this expression with eq 4 shows that this method leaves out the quantity $3AI^{1/2}/(1 + I)^{1/2} - (B^{2-} - B^-)I$, whose evaluation requires knowledge of the ionic strength at which the measurements were made. Crofts and Kosolapoff do not specify this, but they do say that the mean concentration of phosphonic acids during their titrations was 0.005 M. From this, $I = 0.007$–0.013 M for 20–80% neutralization may be inferred, which leads to −0.12 to −0.14 for the difference $pK_a' - pK_a$. It is significant, therefore, that four of Croft and Kosolapoff's values are lower than the results obtained here: $pK_a' - pK_a = -0.26, -0.21, -0.29$, and -0.12 for $CH_3PO_3H^-$, $HOCH_2PO_3H^-$, $CH_2ClPO_3H^-$, and $CCl_3PO_3H^-$, respectively. For $CHCl_2PO_3H^-$, however, the difference is zero, and for $(CH_3)_3CPO_3H^-$ it is positive: $pK_a' - pK_a = +0.17$.

Additional apparent pK_a's of 5.58 and 4.71 are available for $CHCl_2PO_3H^-$ and $CCl_3PO_3H^-$.[4b] These are not inconsistent with the present results, but since neither the ionic strength nor the concentrations at which these values were obtained are specified, a more meaningful comparison is not possible.

The present results are correlated moderately well by the Taft equation.[11] Figure 1 shows the relationship obtained by least-squares analysis: $pK_a = (8.10 \pm 0.10) - (1.26 \pm 0.07)\sigma^*$. Although the correlation coefficient for this fit is good, $r = 0.994$, the average deviation from the line corresponds to a 30% difference in K_a or 0.13 pK unit; this is an order of magnitude greater than the estimated experimental uncertainty.

It is significant, however, that the apparent pK_a' values of Crofts and Kosolapoff give a considerably poorer correlation: $pK_a' = (7.98 \pm 0.21) - (1.24 \pm 0.15)\sigma^*$, $r = 0.973$, average deviation in K_a = 70% or 0.23 pK unit. It is interesting, on the other hand, that use of apparent pK_a's produces essentially no change in reaction constant; this is true even if the comparison is extended to a correlation based upon a much larger set of apparent pK_a's (22) which produced $\rho^* = 1.18$.[4b]

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Amplification of Cyanide Ion Production by the Micellar Reaction of Keto Oximes with Phosphono- and Phosphorofluoridates

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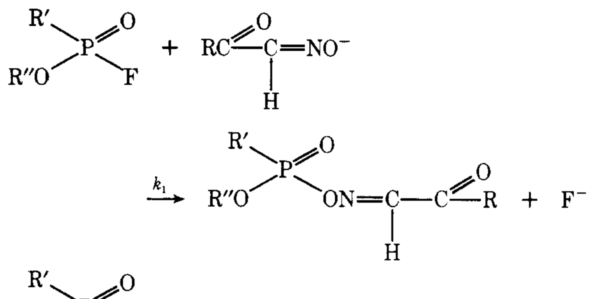
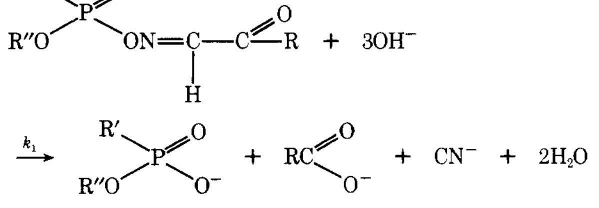
The reaction of keto oximes with phosphono- and phosphorofluoridates in alkaline aqueous solution proceeds according to the equations[1]


(1)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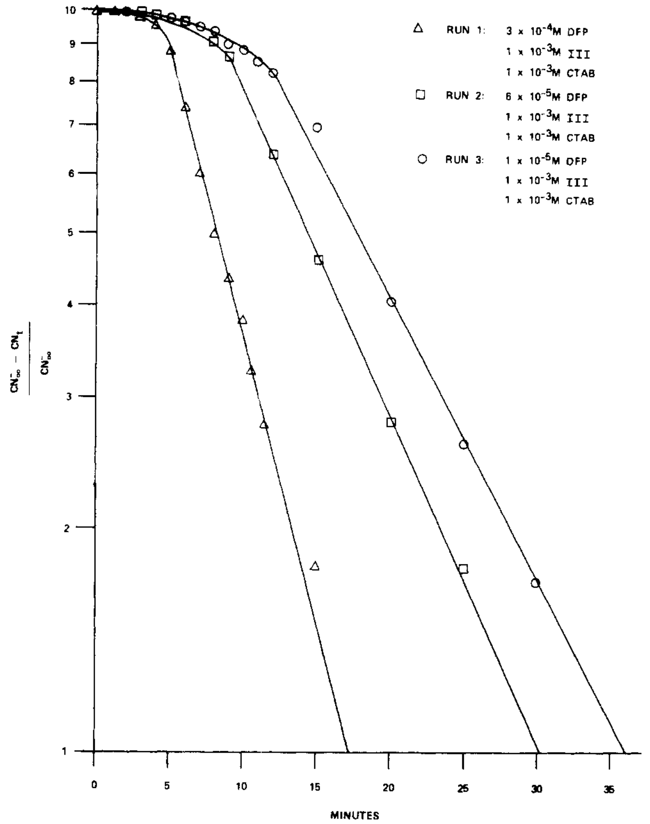


Figure 1. Rate of cyanide ion formation from DFP and III in presence of CTAB.

The production of fluoride (step 1) is rate controlling and 1 mol of cyanide ion is produced per mole of organophosphorus compound reacting. Ford and Watts[2] showed that the reaction between isopropyl methylphosphonofluoridate (I) and 1-phenylbutane-1,2,3-trione 2-oxime (II) produced, depending upon the pH, between 1 and 2 mol of cyanide ion per mole of I reacting. At high pH levels, the reaction was postulated to go through the formation of an acyl cyanide with subsequent hydrolysis to produce 1 mol of cyanide ion per mole of I; at lower pH levels, a reaction between the phosphonylated intermediate and the excess oxime was thought to produce 2 mol of cyanide ion per mole of I reacting. The bimolecular rate constant for the reaction of I and II (k_1 in eq 1) was 72 M^{-1} min^{-1}.

Tabushi et al.[3] reported that the reactivity of the anion of *N*-methyl-*N*-lauroylhydroxamic acid as an ester hydrolysis catalyst was greatly enhanced when used in a cetyltrimethylammonium bromide (CTAB) micelle. In our search for more reactive nucleophiles which would produce cyanide in their reaction with organophosphorus esters, we investigated the reaction of 1-oximino-2-ketononane (III) with I and diisopropyl phosphorofluoridate (DFP) in the presence and absence of micelle-forming compounds.

In the reaction of III with DFP or I in aqueous solution buffered at pH 9.3 with sodium tetraborate–sodium hydroxide buffer, we found that the equations given above adequately explained our observations. The first-order rate constant of the reaction of DFP with 10^{-3} M III, measured by the rate of fluoride ion (fluoride ion electrode) or cyanide ion (cyanide ion electrode) production, was 0.017 min^{-1}, and that of I with III under the same conditions, 0.10 min^{-1}. The reaction of DFP with II under similar conditions gave a first-order rate constant of 0.01 min^{-1} and, from the data of Ford and Watts, II at 10^{-3} M, pH 9.3, might be expected to give a first-order constant of 0.072 min^{-1} with I. Thus III behaves as a normal keto oxime, the small difference in rates between the two oximes being attributable to their pK_a's[4], pK_a (III) = 8.2, pK_a (II) = 7.1.

Table I. Ratio of $[CN^-]/[F^-]$ in Reactions of DFP and I with III (10^{-3} M) at pH 9.3 in Presence of CTAB (10^{-3} M)

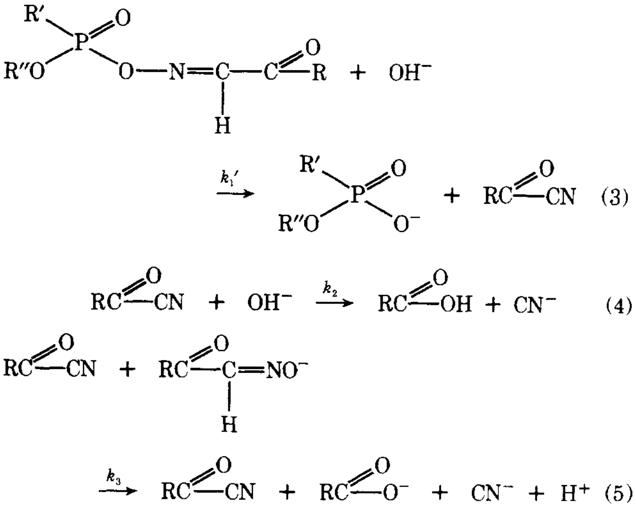
[DFP] mol/l.	[I],[a] mol/l.	$[CN^-]/[F^-]$
3×10^{-4}		3
6×10^{-5}		9.0
1×10^{-5}		13.4
	6.2×10^{-5}	4.7
	6.2×10^{-5} [b]	8.5
	6.2×10^{-5} [c]	4.2
	5.3×10^{-4}	10.9
	0.57×10^{-5}	10.2
	0.057×10^{-5}	19.3

[a] Corrected for hydrolysis. [b] 1% ethylene glycol added to reaction mixture. [c] 1% 1-butanol added to reaction mixture.

In the presence of CTAB, the rate of fluoride ion production was only marginally accelerated (a factor of 2) in the reaction between DFP and III, and not at all in the reaction of I and II. However, in both reactions, many times the 1 to 2 mol of cyanide per mole of organophosphorus compound were produced.

Semilog plots of the fraction of the total cyanide ion formed with time (Figure 1) revealed that after an initial slow release of cyanide, the production rate increased to a point and then followed first-order kinetics, with the time required to reach the portion of the curve showing first-order kinetics increasing with decreasing DFP concentration. The above observations, viz., greater than theoretical production of CN^-, first-order kinetics, and delay time to first-order kinetics, suggested that (a) a second reaction involving the destruction of the oximate ion (Ox^-) with simultaneous formation of cyanide ion was occurring, (b) the compound reacting with oximate was maintaining a constant concentration during the time the formation of cyanide showed first-order kinetics, and hence (c) there is a buildup of the compound to a steady state concentration.

The high yield of cyanide ion was shown not to be due to fluoride or cyanide ions[5] or to the phosphorus or carbon acids resulting from the overall reaction. On the other hand, octanoyl cyanide or octanoyl fluoride did produce the amplification reaction. It was hypothesized, therefore, that, in the micellar medium, octanoyl cyanide is an intermediate and that it reacted simultaneously along two paths, viz., hydrolysis and with the unused oximate anion,[6] and that the equations representing the reactions of III and DFP or I in micellar medium are



$$R'R''OP(=O)-O-N=C(H)-C(=O)R + OH^- \xrightarrow{k_1'} R'R''OP(=O)O^- + RC(=O)CN \quad (3)$$

$$RC(=O)CN + OH^- \xrightarrow{k_2} RC(=O)OH + CN^- \quad (4)$$

$$RC(=O)CN + RC(=O)-C(H)=NO^- \xrightarrow{k_3} RC(=O)CN + RC(=O)O^- + CN^- + H^+ \quad (5)$$

where k_1, k_2, and k_3 are rate constants and $k_1 \ll k_1'$.

Under steady state conditions (the concentration of the acyl cyanide remains constant) the ratio of $[CN^-]$ to $[F^-]$ is[7]

$$\frac{[CN^-]}{[F^-]} = 1 + \frac{k_3}{k_2}[Ox^-] \qquad (6)$$

The hydrolysis rate constant (k_2) of octanoyl cyanide at pH 9.3 in presence of 10^{-3} M CTAB was 0.25 min^{-1}; k_3, estimated from the data in Figure 1, was found to be $(4.6 \pm 0.7) \times 10^3$ M^{-1} min^{-1}. Thus, the expected ratio of $[CN^-]/[F^-]$ at constant $[Ox^-] = 10^{-3}$ M is 20.8.

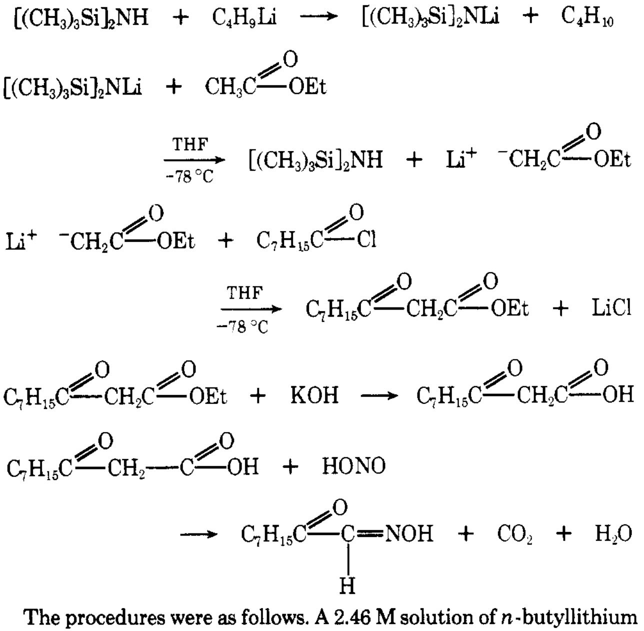
The cyanide to fluoride ratios found for DFP and I in their reaction with III in the presence of CTAB are shown in Table I. The ratio of $[CN^-]$ to $[F^-]$ approaches the calculated value of 21 as the difference in concentrations between III and I or DFP widens.

The reactions of DFP and I with the same oxime were also studied in the presence of the cetyl dimethylglycine (CDG). No acceleration of F^- release was found for either DFP or I in the presence of CDG; the ratios of $[CN^-]/[F^-]$ were ca. 10 for DFP and 7 for I. In all respects CDG and CTAB promoted the same reaction profile leading to cyanide amplification.

There is little (factor of 2) or no enhancement of the nucleophilicity of the keto oximate by a micelle environment. This may be due to poor portioning of the organophosphorus compounds into the micelle. III gives a slight enhancement with DFP, the more lipophilic of the two compounds. The acyl cyanide probably forms in the aqueous phase and then diffuses into the micelle environment where subsequent reaction with III takes place. This could account for the "induction" periods shown in Figure 1. In micellar environment the reaction between III and acyl cyanide is preferred over hydrolysis for two reasons: first, the hydrolysis rate of the acyl cyanide is less in the less polar environment of the micelle than in water, thus making it more available for reaction with III; and secondly, the concentration of III in the micellar phase is relatively high.

Experimental Section

1-Oximino-2-ketononane was prepared as shown in the following equations.[8a]



$$[(CH_3)_3Si]_2NH + C_4H_9Li \longrightarrow [(CH_3)_3Si]_2NLi + C_4H_{10}$$

$$[(CH_3)_3Si]_2NLi + CH_3\overset{O}{\overset{\|}{C}}{-}OEt \xrightarrow[-78\,^{\circ}C]{THF} [(CH_3)_3Si]_2NH + Li^+\ {}^-CH_2\overset{O}{\overset{\|}{C}}{-}OEt$$

$$Li^+\ {}^-CH_2\overset{O}{\overset{\|}{C}}{-}OEt + C_7H_{15}\overset{O}{\overset{\|}{C}}{-}Cl \xrightarrow[-78\,^{\circ}C]{THF} C_7H_{15}\overset{O}{\overset{\|}{C}}{-}CH_2\overset{O}{\overset{\|}{C}}{-}OEt + LiCl$$

$$C_7H_{15}\overset{O}{\overset{\|}{C}}{-}CH_2\overset{O}{\overset{\|}{C}}{-}OEt + KOH \longrightarrow C_7H_{15}\overset{O}{\overset{\|}{C}}{-}CH_2\overset{O}{\overset{\|}{C}}{-}OH$$

$$C_7H_{15}\overset{O}{\overset{\|}{C}}{-}CH_2{-}\overset{O}{\overset{\|}{C}}{-}OH + HONO \longrightarrow C_7H_{15}\overset{O}{\overset{\|}{C}}{-}\underset{H}{\underset{|}{C}}{=}NOH + CO_2 + H_2O$$

The procedures were as follows. A 2.46 M solution of *n*-butyllithium in hexane (122 ml) was added to 66 ml (0.32 mol) of hexamethyldisilazane in 100 ml of dry ether at a rate to maintain a gentle reflux. After addition of the *n*-butyllithium was complete, the mixture was heated to reflux temperature for an additional 30 min. Removal of the solvents by distillation at atmospheric pressure, followed by vacuum distillation of the residue, gave 40.0 g (240 mmol) of hexamethyldisilizallithium, bp 95 °C (0.3 Torr), lit. 80–84 °C (0.01 Torr),[8b] yield 79.8%.

A THF solution of hexamethyldisilizallithium (50 ml, 1.02 N = 50 mmol) was cooled to −78 °C in a dry ice/acetone cooling bath. Ethyl acetate (2.2 g, 25.0 mmol) was added over 5 min. The solution was allowed to stir at −78 °C for an additional 15 min. *n*-Octanoyl chloride (4.1 g, 25.0 mmol) was added maintaining the temperature ≤ 65 °C, and the solution was allowed to stir for 30 min following addition. The reaction was quenched at −78 °C with 15 ml of 20% w/w aqueous HCl and warmed to room temperature. The organic layer was separated and the aqueous layer extracted with two 50-ml portions of ether. The combined organic layers were extracted with saturated $NaHCO_3$, dried ($MgSO_4$), and concentrated to give 5.1 g of a clear oil. The oil was distilled to give 4.81 g (22.4 mmol) of the desired ethyl 3-oxodecanoate: bp 87–88 °C (0.3 Torr); yield 89.6% based on *n*-octanoyl chloride; IR (film) 3.44 (s, CH), 5.74 (s, ester C=O), 5.87 (s, ketone C=O), 6.12 (w, enol C=C), 6.84, and 7.12 μ; NMR ($CDCl_3$) δ 0.88 [t, J = 5 Hz, $C\mathbf{H}_3(CH_2)_5$, 3], 1.26 [broad peak, $-(C\mathbf{H}_2)_5-$ and $C\mathbf{H}_3CH_2O$, 13], 2.55 (t, J = 7 Hz, CH_2CO, 2), 3.45 (s, $COCH_2CO_2$, 2), and 4.34 (q, J = 8 Hz, CH_2O, 2).

Ethyl 3-oxodecanoate was saponified with excess 0.5 N KOH for 24 h at room temperature. The resultant solution was extracted with ether; the acidified water phase gave a white solid, mp 83–84 °C. Titration gave an equivalent weight of 184 (theory 186), $pK_a = 5.22$.

Anal. Calcd for $C_{10}H_{18}O_3$: C, 64.49; H, 9.46. Found: C, 64.43; H, 9.46.

Spectra: IR (KBr) 2.94 (w, OH), 3.44 (m, CH), 5.85 (s, C=O), 5.92 (s, C=O), 7.04 and 7.24 μ (m, CH); NMR ($CDCl_3$) δ 0.90 [t, J = 5 Hz, $C\mathbf{H}_3(CH_2)_5-$, 3], 1.32 [broad peak, $-(CH_2)_5-$, 10], 2.12 [t, J = 7 Hz, $-(CH_2)_5C\mathbf{H}_2CO$, 2], 3.55 (s, $COCH_2CO_2$, 2), 8.08 (broad peak, CO_2H, 1).

Potassium 3-oxodecanoate (1.63 g) was dissolved in 25 ml of distilled water, and 8.53 mmol (0.6 g) of sodium nitrite was added. The resultant clear solution had a pH of 13.0. The solution was treated with 20% w/w aqueous sulfuric acid in the following manner. Acid was added dropwise and precipitate formed and redissolved; this procedure was followed until a pH of 6.0 was obtained. Additional acid was then added to maintain the pH between 4.8 and 5.3. Reaction is complete when the clear (pH 5.3) solution can be taken to pH 4 with no further precipitation (~90 min). The acidic solution was adjusted to pH 12.5 and extracted with ether to remove any 2-decanone formed. The solution was then adjusted to pH 7, extracted with ether, and dried ($MgSO_4$), and the ether concentrated in vacuo to give 0.75 g of the desired keto oxime. The product was recrystallized from petroleum ether to give a white solid: mp 26 °C; IR ($CHCl_3$) 2.82 (s, bonded OH), 3.03 (b, nonbonded OH), 3.44 (s, CH), 5.95 (s, C=O), 6.02 (s, C=N), 6.35 (m, N–O), 6.85 and 7.15 (m, CH), and 10.2 μ (s, C–O); NMR ($CDCl_3$) δ 0.88 (t, J = 5 Hz, $C\mathbf{H}_3CH_2$, 3), 1.3 [broad peak, $-(CH_2)_5-$, 10], 2.75 (t, J = 7 Hz, CH_2CO, 2), 7.57 [s, $C(=NOH)\mathbf{H}$, 1], 8.33 (s, OH, 1).

Anal. Calcd for $C_9H_{17}NO_2$: C, 63.16; H, 10.01; N, 8.18. Found: C, 62.77; H, 10.47; N, 8.07.

The keto oxime was further characterized by preparation of the semicarbazone derivative: mp 142–143 °C; IR ($CHCl_3$ solution) 2.89 (s, NH), 3.03 (s, OH), 3.44 (s, CH), 6.03 (s, C=N), 6.42 (s, C=O), 6.89 (s, CH), and 10.2 μ (s, C–O).

Anal. Calcd for $C_{10}H_{20}N_4O_2$: C, 52.61; H, 8.83; N, 24.54. Found: C, 52.87; H, 8.83; N, 24.32.

NMR spectra were run on a Varian EM360 spectrometer; IR spectra were run on a Perkin-Elmer 247 grating spectrophotometer; and titrations were run using a Metrohm E-436 potentiograph. Reported melting points are uncorrected and were determined on a Fisher-Johns or Mel-Temp melting point apparatus. All elemental analyses were performed by Stanford University.

Organometallic reactions were carried out in glassware that had been dried at 120 °C for 12 h followed by flame drying under nitrogen immediately before use. A nitrogen atmosphere was maintained until reactions were quenched.

All kinetic runs were performed as pseudo-first-order reactions, with the concentration of III being in most cases at least ten times greater than that of DFP or I; reactions were run in borate buffer (pH ~9.3) at 30 °C in a constant temperature bath. Cyanide and fluoride ion productions were monitored with Orion specific ion electrodes using suitable millivoltmeters and recorders.

Acknowledgment. The authors wish to thank Drs. D. Denson and G. Manser for their synthesis of 1-oximino-2-ketononane and Mr. R. Moll for technical assistance.

Registry No.—I, 107-44-8; III, 58040-72-5; III semicarbazone, 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.

References and Notes

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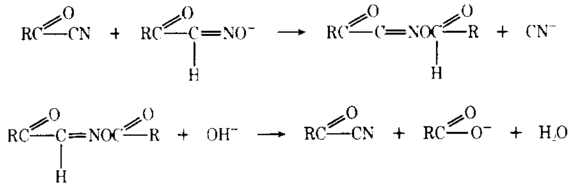
(5) E. V. Crabtree and E. J. Poziomek, *J. Org. Chem.*, **32**, 1231 (1967), were able to produce 8 × 10^{-3} mol of cyanide ion from a solution containing 2 × 10^{-4} mol of cyanide ion and 4 × 10^{-2} mol of II in 6 h, demonstrating the high effectiveness of cyanide ion in catalysis of decomposition 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

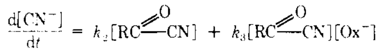


$$RC(=O)CN + RC(=O)C(H)=NO^- \longrightarrow RC(=O)C(H)=NOC(=O)R + CN^-$$

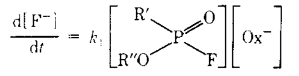
$$RC(=O)C(H)=NOC(=O)R + OH^- \longrightarrow RC(=O)CN + RC(=O)O^- + H_2O$$

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

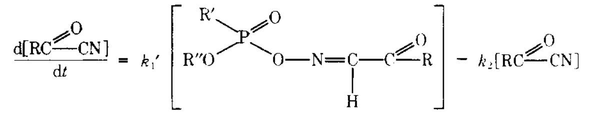
(7) The differential equations for the series of reactions at constant pH are



$$\frac{d[CN^-]}{dt} = k_2[RC(=O)CN] + k_3[RC(=O)CN][Ox^-]$$

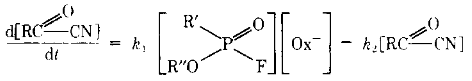


$$\frac{d[F^-]}{dt} = k_1\left[R'R''OP(=O)F\right]\left[Ox^-\right]$$



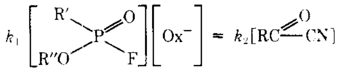
$$\frac{d[RC(=O)CN]}{dt} = k_1'\left[R'R''OP(=O)ON=C(H)C(=O)R\right] - k_2[RC(=O)CN]$$

Since $k_1' \gg k_1$, then



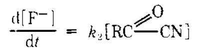
$$\frac{d[RC(=O)CN]}{dt} = k_1\left[R'R''OP(=O)F\right]\left[Ox^-\right] - k_2[RC(=O)CN]$$

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



$$k_1\left[R'R''OP(=O)F\right]\left[Ox^-\right] = k_2[RC(=O)CN]$$

so that



$$\frac{d[F^-]}{dt} = k_2[RC(=O)CN]$$

Then

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

and at t_∞,

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

(8) (a) M. W. Rathke and J. Deitch, *Tetrahedron Lett.*, 2953 (1971), and references cited therein; (b) E. H. Amonoo-Neizer, R. A. Shaw, D. D. Skovlin, and B. C. Smith, *J. Chem. Soc.*, 2997 (1965).

π-Inductive Effects in Benzyl Compounds

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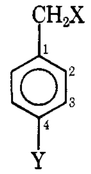
Table I. ^{13}C NMR Chemical Shifts in Para-Substituted Benzyl Compounds[a]



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

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