in the second 0.870. In accordance with Student's criterion a probability of the coincidence of these mean values is below 0.01. Moreover in the correlations employing σ^ϕ, the reaction sets of different authors under equivalent or very like conditions lead to the same correlation parameters. For example, sets 2, 4, and 6, respectively, yield ρ 1.07, 1.09, and 1.05 and pK^0 = 0.87, 0.98, and 1.00. Sets 3 and 5 give ρ 1.90 and 1.66, and pK^0 = 5.93 and 6.17. Differences in these values do not exceed the mean deviations. The correlation with Charton's method gives substantially different parameters. The sets 2, 4, and 6 give h = 2.31, 0.23, and 3.02, α = −6.83, −4.78, and −3.78, β = −3.02, −4.05, and −0.62, respectively. The sets 3 and 5 give h = 7.99 and 7.26, α = −13.30 and −12.18, β = 0.44 and −4.80. There is obviously no physical sense in these differences. Thus the Charton correlations, although giving satisfactory results, may lead to serious errors when analyzing the substituent effects on the properties of organophosphorus compounds. This danger may be avoided by using the σ^ϕ constants.

The correlation of σ^ϕ with σ_I and σ_R using eq 7 gives approximately linear dependence with the deviations mentioned above. Such a dependence shows that for organophosphorus compounds the substituent electronic effects are transmitted to the reaction center through inductive and mesomeric mechanisms. It may be assumed that the inductive mechanisms at phosphorus and carbon are in principle the same. This is confirmed by a good linear correlation between σ^ϕ values of alkyl groups and the σ^* Taft constants. As for the resonance effects, there is only a rough similarity between them for purely carbon and phosphorus compounds. For the aryl group bonded to phosphorus a contribution of the resonance component in σ^ϕ coincides with that of the aryl groups at carbon. For the RO, RS, and R_2N groups these contributions are different. For example, for the R_nX groups where X is an atom of the second row (N, O, or F; n varies, respectively, from 2 to 0), the two-parameter correlation of the σ^ϕ constants with σ_I and σ_R leads to the following results: h = −0.46 ± 0.08, α = 2.69 ± 0.16, β = 1.28 ± 0.08, r_3 = 0.648,[26] R = 0.983. However, one should not pay too much attention to this good correlation, but it does indicate that a contribution of the resonance component in the effective constant σ_{eff} is equal to 0.48.

Thus, the contribution of the resonance component to the σ^ϕ constants is determined essentially by the nature of the group attached. The overlap of p and π orbitals of a bonded group with the phosphorus d orbitals obviously differs from that with the π orbitals of benzene ring or some other purely carbon π system. Its dependence on the distances and angles is other than that for the p–p or p–π overlap, and this explains the different contribution of the resonance components to the substituent constants. Thus Charton's dependence of σ^ϕ on σ_I and σ_R is confirmed. In spite of the low correlation coefficient this dependence indicates a common similarity of the substituent effects at phosphorus and carbon. Certainly it would be tempting to employ the σ_I and σ_R constants in the correlation analysis of the organophosphorus reactions, but a more detailed discussion reveals specific differences in the resonance effects of groups at phosphorus and carbon. Certainly one cannot take into account such differences in the correlation with σ_I and σ_R, but this can be done by using the σ^ϕ constants. Therefore in correlation of the reaction rate and equilibrium constants of the organophosphorus compounds the results are better with the σ^ϕ constants. Thus it is the σ^ϕ constants that one should use in solving the correlation problems in the organophosphorus chemistry.

(26) Pair correlation coefficient for σ_R and σ_I.

Calculation of the pK_a Values of Alcohols from σ^* Constants and from the Carbonyl Frequencies of Their Esters

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As an alternative to direct measurement, the pK_a values of primary alcohols (RCH_2OH) may be calculated from σ^* constants by use of the equation pK_a (RCH_2OH) = $-1.316\sigma^*(R) + 15.74$ for alcohols in which C-2 is sp^3 or sp hybridized. For those alcohols in which C-2 is sp^2 hybridized, pK_a (RCH_2OH) = $-1.316\sigma^*(R) + 16.23$. Values of σ^* are based on pK_a data for the corresponding carboxylic acids (RCOOH) or on the carbonyl stretching frequencies of esters of RCH_2OH. Frequencies can be related to σ^* by bonding type: for C-2 (sp^3 or sp^2), $\sigma^*(R) = 0.08996\nu - 156.000$; for C-2 (sp), $\sigma^*(R) = 0.11757\nu - 203.991$; for C-2 ($sp^3$) but R = H or alkyl, $\sigma^*(R) = 0.10828\nu - 188.316$. For secondary alcohols, pK_a values can be calculated from $\Sigma\sigma^*$, the latter values being obtained by use of the additivity principle or from carbonyl frequencies of esters. Measurement of carbonyl frequency offers a novel and facile method for determination of σ^* values.

Aliphatic substituent constants (σ^* or σ_I) provide a measure of the relative effect of chain substituents on the electron density at a reactive atom or functional group. Originally, these constants were derived by Taft from ratios of the rates of acid and alkaline hydrolysis of esters and were shown, subsequently, to be applicable to a wide variety of reaction series, including the dissociation of carboxylic acids and alcohols.[2]

In connection with studies on alcohols as nucleophiles, reliable pK_a values were needed. The available

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(2) R. W. Taft, Jr., in "Steric Effects in Organic Chemistry," M. S. Newman, Ed., Wiley, New York, N. Y., 1956, Chapter 13.

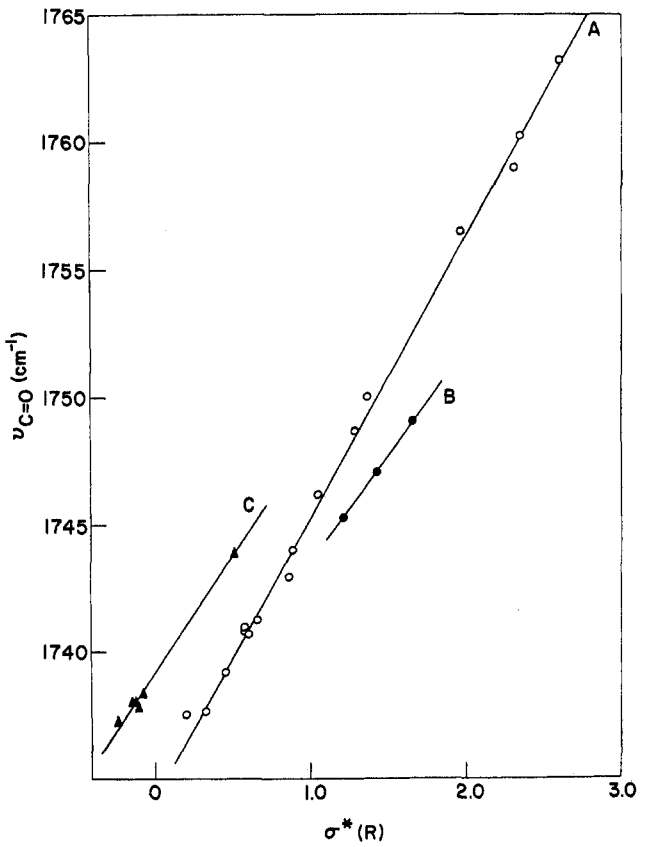

Figure 1.—Plots of σ^*(R) *vs.* $\nu_{C=O}$ ($RCH_2OCOCH_2CH_2Ph$). Line A includes esters of alcohols in which C-2 = sp^3 and carries an electronegative substituent, or C-2 = sp^2; line B for C-2 = sp; line C for C-2 = sp^3 and R = H or alkyl.

literature data[3-6] are scanty and sometimes inconsistent. In addition to the inaccuracies inherent in pH measurement in strongly alkaline media, the instabilities of some β-halogen-substituted alcohols in such media present special problems.[5] We, therefore, chose to calculate new pK_a values from substituent constants and an appropriate linear free energy relationship.[7] Correlations of σ^* with the pK_a values of some alcohols in water[5,6] and in isopropyl alcohol[2] have been demonstrated. We wished to enlarge the scope of the correlation with respect to the pK_a range as well as to secondary and tertiary alcohols. The validity of the calculated pK_a values might be examined by direct determination of pK_a or by correlation with rates of reaction.[8] An independent and particularly facile test was found, however, in our observation that the carbonyl stretching frequencies of esters can be correlated with the σ^* values of substituents in the alcohol moiety.

Results

In his derivation of σ^* values, Taft depended primarily on rate data for acid and alkaline hydrolysis of esters, assuming that steric effects are equivalent in the transition states for the two reactions. The substantial, though not universal, validity of this assumption is borne out in the excellent correlations of σ^* with various other physical and chemical parameters. Charton[9a] has presented arguments, however, in favor of deriving new substituent constants (σ_I) from pK_a values of carboxylic acids, as Hammett had done originally for the aromatic series. The substituent constants used in this study are also based on pK_a values of carboxylic acids, the substituent being defined as R in RCOOH.[3,9b] Regression analysis of pK_a *vs.* σ^* for 40 aliphatic acids provided the line of eq 1 (n =

$$pK_a\,(RCOOH) = -1.700\sigma^*(R) + 4.644 \quad (1)$$

40, r = 0.9986, s = 0.0142).[10] Our result differs slightly from that obtained by Taft[2] (based on 16 acids) and by Barlin and Perrin.[7] The pK_a and σ^* values of some of the acids used to establish eq 1 are given in Table I, columns 2 and 3. Values of σ^* (calcd) were then obtained from eq 1 (Table I, column 4). Taft has noted the failure of eq 1 for α,β-unsaturated acids.[11] Analysis of pK_a/σ^* data for acids containing an sp^2 carbon at C-2 provides a regression line (eq 2; n = 5,

$$pK_a\,(RCOOH\text{-}sp^2) = -1.795\sigma^*(R) + 5.275 \quad (2)$$

r = 0.9999, s = 0.0106) of slope similar to that of eq 1. It is noteworthy that α,β-acetylenic acids follow eq 1 rather than eq 2.

Six primary alcohols, whose measured pK_a values were deemed reliable, were used to establish eq 3 (n =

$$pK_a\,(RCH_2OH) = -1.316\sigma^*(R) + 15.74 \quad (3)$$

6, r = 0.999, s = 0.0273) relating pK_a (RCH_2OH) with σ^* (calcd). This regression line differs slightly from that obtained by Ballinger and Long.[5] For alcohols in which C-2 is sp^2 hybridized, eq 4 is applicable.

$$pK_a\,(RCH_2OH\text{-}sp^2) = -1.316\sigma^*(R) + 16.23 \quad (4)$$

By use of these equations and σ^* (calcd), pK_a values for a large number of primary alcohols were calculated (Table I, column 6). For comparison, available literature values are given in Table I, column 8.

In connection with another investigation,[8c] 3-phenylpropionate esters of several moderately acidic alcohols had been prepared. It was noted that the carbonyl stretching frequencies of these esters showed a trend consistent with the acidities of the respective alcohol components. Careful measurement of the carbonyl frequencies, at high resolution and under standardized conditions (in CCl_4), of these and numerous other esters of the same acid, provided the values given in Table I, column 5. From a plot of the carbonyl frequency of $PhCH_2CH_2COOCH_2R$ *vs.* σ^*(R) (Figure 1), it became evident that the esters fell into three distinct groups, dependent on the nature of the bond between C-1 and C-2

(3) W. P. Jencks and J. Regenstein in "Handbook of Biochemistry," H. A. Sober, Ed., Chemical Rubber Publishing Co., Cleveland, Ohio, 1968, p J-159.

(4) E. M. Arnett, *Progr. Phys. Org. Chem.*, **1**, 353 (1963).

(5) P. Ballinger and F. A. Long, *J. Amer. Chem. Soc.*, **81**, 1050 (1959); **82**, 795 (1960).

(6) J. Murto, *Acta Chem. Scand.*, **18**, 1043 (1964).

(7) See also G. B. Barlin and D. D. Perrin, *Quart. Rev. (London)*, **20**, 75 (1966).

(8) (a) T. C. Bruice, T. H. Fife, J. T. Bruno, and N. E. Brandon, *Biochemistry*, **1**, 7 (1962); (b) J. R. Robinson and L. E. Matheson, *J. Org. Chem.*, **34**, 3630 (1969); (c) S. Takahashi and L. A. Cohen, *ibid.*, **35**, 1505 (1970).

(9) (a) M. Charton, *ibid.*, **29**, 1222 (1964); (b) K. Bowden, M. Hardy, and D. C. Perry, *Can. J. Chem.*, **46**, 2929 (1968).

(10) Regression lines were obtained by use of a General Electric 265 computer: n = number of compounds, r = correlation coefficient, and s = standard deviation of the slope.

(11) Reference 2, p 640.

TABLE I

ACIDITIES OF PRIMARY ALCOHOLS (RCH_2OH) AND CARBONYL FREQUENCIES OF THEIR ESTERS[a]

R	pK_a, RCOOH[b]	σ^* Lit.[c]	σ^* Calcd[d]	$\nu_{C=O}$, cm^{-1}	pK_a (RCH_2OH) Calcd[e]	pK_a (RCH_2OH) Lit.
F_3C	0.23	2.61[f]	2.60	1763.2	12.32	12.37[g,h]
F_2CH	1.24	2.05	2.00		13.11	~ 13.3[h]
FCH_2	2.66	1.10	1.17		14.20	
Cl_3C	0.65	2.65	2.35	1760.2	12.65	12.24[h]
Cl_2CH	1.30	1.94	1.97	1756.5	13.15	12.89[h]
$ClCH_2$	2.86	1.05	1.05	1746.2	14.36	14.31[g,h]
Br_3C	0.72	2.3[i]	2.31	1759.0	12.70	
Br_2CH	1.48	1.6[i]	1.86		13.29	
$BrCH_2$	2.90	1.02[i]	1.03		14.38	
ICH_2	3.12	0.88[i]	0.90	1744.0	14.56	
$NCCH_2$	2.43	1.30	1.30	1748.7	14.03	
CH_3OCH_2	3.53	0.66[i]	0.66	1741.3	14.87	14.82[g,h]
$C_2H_5OCH_2$	3.65		0.58	1741.0	14.98	15.12[k]
$PhOCH_2$	3.17	0.85	0.87	1743.0	14.60	15.1[l]
$PhCH_2$	4.31	0.22	0.20	1737.5	15.48	
$HOCH_2$	3.83	0.56	0.48		15.11	15.07[h]
H	3.77	0.49	0.51	1743.9	15.07	15.09,[g,m] 15.49[h]
CH_3	4.76	0	−0.068	1738.2	15.83	15.90,[g,h] 15.93[m]
C_2H_5	4.88	−0.10	−0.14	1738.0	15.92	16.10[l]
C_3H_7	4.82	−0.12	−0.10	1737.8	15.87	16.10[l]
i-C_3H_7	4.86	−0.19	−0.13	1738.0	15.91	16.10[l]
$(CH_3)_3C$	5.04	−0.30	−0.23	1737.3	16.04	
$HC\equiv C$	1.84[n]	1.7[o]	1.65	1749.1	13.57	13.55[g,h]
$CH_3C\equiv C$	2.60[n]		1.20	1745.3	14.16	
$PhC\equiv C$	2.23[n]	1.35	1.42	1747.1	13.87	
$CH_2=CH$	4.25	0.56[f]	0.57	1740.8	15.48	15.52[h]
$CH_3CH=CH$	4.69	0.36	0.33	1737.6	15.80	
$PhCH=CH$	4.44	0.41	0.46	1739.2	15.62	
Ph	4.20	0.60	0.60	1740.7	15.44	15.4[l]
3,5-Di-NO_2Ph	2.82[p]		1.37	1750.0	14.43	
OHC	3.32	1.1[i]	1.09		14.80	
CH_3CO	2.50	1.65	1.55		14.19	
PhCO	1.32[q]	2.2[f]	2.20		13.33	

[a] With 3-phenylpropionic acid. [b] Taken from ref 3 and 9b except as noted. [c] Taken from ref 2 except as noted. [d] Calculated by use of eq 1 and 2. [e] Calculated by use of eq 3 and 4. [f] Reference 7. [g] Value used to establish eq 3. [h] Reference 5. [i] I. P. Biryukov and M. G. Voronkov, *Latv. PSR Zinat. Akad. Vestis*, 39 (1966); *Chem. Abstr.*, **68**, 44645 (1968). [j] P. R. Wells, "Linear Free Energy Relationships," Academic Press, New York, N. Y., 1968, p 38. [k] Estimated from Figure 1 of ref 6. [l] Reference 6. [m] Derived from kinetic data, ref 6. [n] G. H. Mansfield and M. C. Whiting, *J. Chem. Soc.*, 4761 (1956). [o] J. Hine and W. C. Bailey, Jr., *J. Amer. Chem. Soc.*, **81**, 2075 (1959). [p] J. F. J. Dippy, B. D. Hawkins, and B. V. Smith, *J. Chem. Soc.*, 154 (1964). [q] J. Böeseken, *Recl. Trav. Chim. Pays-Bas*, **40**, 568 (1921).

in the alcohol. The correlations are expressed by eq 5, for esters in which C-2 of the alcohol is sp^3 and carries an electronegative substituent, as well as for esters in which C-2 is sp^2 hybridized; eq 6 for esters in which C-2 is sp hybridized; and eq 7 for esters in which C-2

$$\sigma^*(R) = 0.08996\nu - 156.000 \quad (5)$$

$$\sigma^*(R) = 0.11757\nu - 203.991 \quad (6)$$

$$\sigma^*(R) = 0.10828\nu - 188.316 \quad (7)$$

is sp^3 but R = H or alkyl. The excellent correlations observed[12] demonstrate that the electronic influence of R in RCOOH is linearly related to its influence on the oxygen atom in RCH_2OH and on the carbonyl frequency in RCH_2OCOR'. Thus, new values of σ^*, or reevaluation of older values, may be obtained either from pK_a data on carboxylic acids or from carbonyl frequencies of esters of the corresponding primary alcohols. In turn, pK_a values of the alcohols may be calculated from such σ^*constants. For 22 primary alcohols, pK_a values calculated from σ^*(RCOOH ionization) and from σ^*(ester carbonyl frequency) agreed to within ±0.05 pK unit; three others (R = $PhCH_2$, $PhOCH_2$, and Br_3C) differed by 0.1 pK unit.

The validity of eq 3 and 4 for secondary and tertiary alcohols was also examined. Values of $\Sigma\sigma^*$ (Table II, column 5) were obtained by addition of the appropriate σ^* values (Table I, column 4), followed by subtraction of σ^*(H) for each hydrogen atom replaced in RCH_2OH. Values of $\Sigma\sigma^*$, calculated from carbonyl frequencies, are given in Table II, column 6. Although a critical test is limited by the scarcity of experimental pK_a values (Table II, column 8), the calculated pK_a values (Table II, column 7) are reasonably satisfactory, at least for secondary alcohols. The values of $\Sigma\sigma^*$ obtained for the two tertiary alcohols by the alternate methods differ significantly, those based on spectral data being considered the more reliable.

Discussion

The acidities of alcohols may be determined by direct measurement of ionic equilibria or, indirectly, from kinetic or spectral data. The difficulties inherent in

(12) Statistical data: (for eq 5) $n = 14$, $r = 0.999$, $s = 0.002$; (for eq 6) $n = 3$, $r = 0.9999$, $s = 0.002$; (for eq 7) $n = 6$, $r = 0.994$, $s = 0.005$.

TABLE II

ACIDITIES OF SECONDARY AND TERTIARY ALCOHOLS AND CARBONYL FREQUENCIES OF THEIR ESTERS

R	R′	R″	$\nu_{C=O}$, cm^{-1}	$\Sigma\sigma^{*a}$	$\Sigma\sigma^{*b}$	pK_a —(RR′R″COH)— Calcd[c]	Lit.
F_3C	F_3C	H	1785.8	4.69	4.65	9.62	9.3[d]
Cl_3C	Cl_3C	H	1780.0	4.19	4.13	10.30	
F_3C	CH_3	H	1765.5	2.02	2.02	13.08	11.8[e]
Ph	Ph	H	1741.7	0.69	0.68	15.34	15.63[f]
CH_3	CH_3	H	1733.3	−0.65	−0.63	16.57	17.1[g]
CH_3	CH_3	CH_3	1731.4	−1.23	−0.84	16.84	15.8,[h] 19.2[g]
F_3C	F_3C	F_3C	1820[i]	6.78	7.73	5.57	5.4[d]

[a] Calculated from the values in Table I, column 4. [b] Calculated by use of eq 5–7. [c] Calculated by use of eq 3 and 4, and the values of $\Sigma\sigma^*$ in column 6. [d] B. L. Dyatkin, E. P. Mochalina, and I. L. Knunyants, *Tetrahedron*, **21**, 2991 (1965). [e] A. L. Henne and R. L. Pelley, *J. Amer. Chem. Soc.*, **74**, 1426 (1952); the validtiy of this value is doubtful (see ref 5). [f] Estimated from Figure 1 of ref 6. [g] Derived from kinetic data, ref 6. [h] M. Martin, *J. Chim. Phys.*, **59**, 736 (1962). [i] Reference 16, as the acetate ester.

Although carbonyl frequencies have been measured for a large number of esters, variation in the nature of the alcohol component has been limited, largely, to the simplest alkyl cases. It is, therefore, not surprising that little range in carbonyl frequency has been observed for esters of a single acid. Infrared data for the acetates of a number of polyfluoro alcohols have been reported, together with qualitative evidence for a dependence of the band position on the pK_a of the alcohol involved.[16] By measuring the carbonyl frequencies of a large number of esters whose alcohol components cover a range of 8 pK units in their acidities, we have been able to demonstrate the existence of linear correlations between frequency and σ^*, and, indirectly, with alcohol pK_a. Accurate measurement of the carbonyl frequencies of esters of other alcohols should permit the calculation and prediction of their acidities, as well. A few random measurements indicated that the carboxylic acid component of the ester should not vary in order to obtain linear correlations.

TABLE III

ESTERS OF 3-PHENYLPROPIONIC ACID[a]

Ester	Registry no.	Mp or bp (mm), °C	Ester	Registry no.	Mp or bp (mm), °C
Ethyl	2021-28-5	83–84 (1)	Benzhydryl (A)[b]	28049-02-7	53–54
Propyl	13326-06-2	75 (0.3)	Chloroethyl	28049-03-8	118–119 (0.8)
Isopropyl	22767-95-9	89 (0.9)	Dichloroethyl	28049-04-9	134 (1.5)
Butyl	20627-49-0	91 (0.3)	Tribromoethyl	28049-05-0	159 (0.4)
Isobutyl	28048-94-4	99 (0.6)	Hexachloroisopropyl (B)	28049-06-1	36–37
tert-Butyl[c]	16537-10-3	84–85 (0.5)	1,1,1-Trifluoro-2-propyl	28049-07-2	84 (1.4)
Neopentyl	28048-96-6	82 (0.3)	Methoxyethyl	28049-08-3	113–115 (0.6)
Allyl	15814-45-6	97–98 (0.8)	Ethoxyethyl	22524-30-7	116 (0.4)
Cinnamyl	28048-98-8	162–163 (0.3)	Phenoxyethyl	28049-09-4	143 (0.1)
2-Butynyl	28048-99-9	108 (0.3)	Phenethyl	28049-10-7	142 (0.2)
Phenylpropargyl	28049-00-5	163 (0.3)	Iodoethyl	28049-11-8	115 (0.1)
Benzyl	22767-96-0	165 (2)	Cyanoethyl	28049-12-9	121 (0.2)

[a] All compounds provided acceptable elemental analyses. The methyl, propargyl, trichloroethyl, trifluoroethyl, hexafluoroisopropyl, and 3,5-dinitrobenzyl esters have been reported previously (ref 8c). [b] Solvents for recrystallization: A, cyclohexane; B, petroleum ether. [c] Prepared by an alternative method, bp 86–88° (1.5 mm): W. v. E. Doering and R. M. Haines, *J. Amer. Chem. Soc.*, **76**, 482 (1954).

direct measurement have already been noted.[5] Kinetic methods may involve the use of alcohols or their anions as nucleophiles[6] or may be based on the relative reactivities of their esters toward various nucleophilic species.[8] Although several impressive correlations of alcohol acidity with rate data have been obtained, the complications which may result from variable steric interactions[13] and solvation requirements cannot be ignored. We were, therefore, led to consider the advantages of acquiring such data by use of spectral characteristics of esters, for which concentration, solvent, and steric effects should be minimal.

Efforts to correlate the stretching frequencies of alcohols with the electronic nature of substituents have been unsuccessful, due to complications such as association, internal hydrogen bonding, conformational effects, and a low sensitivity of the frequency to acidity changes.[14] On the other hand, the intensities of the same absorption bands have been related to σ^* for a moderate number of compounds.[15]

As may be seen from Figure 1, separate plots are required to correlate alcohols containing electron-withdrawing and electron-releasing substituents, as well as those with α,β-acetylenic linkages. Since the physical basis of any correlation of infrared frequency with electronic effects is poorly understood, the existence of these separate categories is, for the present, best left in the realm of empirical observation.

The results also indicate that the transmission coefficient, for induction through a lone pair atom, need not vary with the electronegativity of the substituent. Although the constancy of such a coefficient is often taken for granted, few studies have been available which permit a clarification of the question.

Experimental Section[17]

Alcohols.—The alcohols employed were of the highest purity commercial materials available. Hexachloro-2-propanol, mp 86–87°, was prepared by reduction of hexachloroacetone with sodium borohydride in tetrahydrofuran.[18] Similarly, phenyl-

(13) R. W. A. Jones and J. D. R. Thomas, *J. Chem. Soc. B*, 661 (1966).
(14) L. J. Bellamy, "Advances in Infrared Group Frequencies," Methuen & Co., London, England, 1968, Chapter 4.
(15) T. L. Brown, *J. Amer. Chem. Soc.*, **80**, 6489 (1958); *Chem. Rev.*, **58**, 581 (1958).
(16) R. Filler and R. M. Schure, *J. Org. Chem.*, **32**, 1217 (1967).
(17) Melting points and boiling points are uncorrected. Microanalyses were performed by the Microanalytical Services Section of this laboratory, under the direction of Dr. W. C. Alford.
(18) M. Geiger, E. Usteri, and C. Gränacher, *Helv. Chim. Acta*, **34**, 1335 (1951).

propargyl alcohol, bp 112° (1 mm), was prepared by borohydride reduction of phenylpropargyl aldehyde.[19] 3,5-Dinitrobenzyl alcohol was obtained by reduction of 3,5-dinitrobenzoic acid with diborane in tetrahydrofuran. The crude product was chromatographed on silica gel (chloroform–methanol, 95:5) and recrystallized from chloroform, mp 78–81°.

Anal. Calcd for $C_7H_6N_2O_5$: C, 42.42; H, 3.05; N, 14.14. Found: C, 42.60; H, 3.25; N, 14.19.

Esters.—All esters of 3-phenylpropionic acid were prepared by a modification of the trifluoroacetic anhydride method previously described.[8c] A mixture of trifluoroacetic anhydride (210 g, 1 mol) and 3-phenylpropionic acid (150 g, 1 mol) was stored at 40° for 2 hr. Following removal of trifluoroacetic acid under reduced pressure, a residual oil (220 g) was obtained, consisting mainly of the mixed anhydride. Although the latter could be purified by distillation [bp 67° (0.3 mm)], the crude material was used for further work. To 12.5 g of the mixed anhydride, at 0°, was added 0.05 mol of alcohol, and the mixture stored at ambient temperature overnight. The reaction mixture was poured into 3% sodium bicarbonate and the ester separated by filtration or ether extraction. The esters were purified by distillation under reduced pressure or recrystallization (Table III). Yields varied from 60 to 90%. In the case of *tert*-butyl alcohol, the components were mixed at −20° and stored at 0° for 2 days.

Infrared Spectra.—Spectra were measured on solutions of esters in carbon tetrachloride (0.012–0.025 *M*) using a Perkin-Elmer Model 521 spectrophotometer, whose monochromator and source compartments were flushed continuously with dry nitrogen. The carbonyl region was scanned slowly (15 sec/cm^{-1}) and spectra were recorded in duplicate, at a chart speed of 5 cm^{-1}/cm. Intervals were marked with frequency counter-synchronized pips, whose positions were calibrated against standard water vapor lines, recorded under the same conditions. The transmittance minima given in Tables I and II are the averages of six readings (on duplicate runs) and have been corrected by calibration against water vapor. In general, readings agreed to better than ±0.2 cm^{-1}.

(19) H. H. Guest, *J. Amer. Chem. Soc.*, **47**, 860 (1925).

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Substituent Effects in the Reaction Rates of 2-Arylhexafluoroisopropyl Glycidyl Ethers with Dibutylamine

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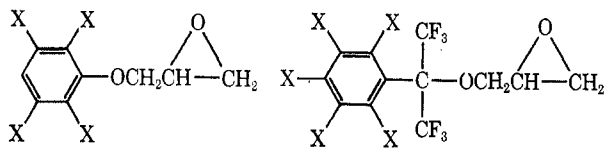
The effects of ring fluorine substituents upon the reactivity of compounds of structure $ArC(CF_3)_2OCH_2\overline{CHCH_2}O$ (**2**) with dibutylamine in alcohol have been studied. It was found that *o*-fluorine atoms exert a pronounced activating influence upon the rate of epoxide ring opening, whereas *m*- and *p*-fluorines exert a deactivating influence. These effects are not generally additive, however, in compounds containing several ring fluorine atoms. In addition, an *o*-bromine atom was found to accelerate the amine–epoxide reaction, while *o*-methyl groups had an opposite effect. Second-order rate constants are presented for each of the reactions studied, and a mechanism consistent with the observed substituent effects is proposed.

In a recent study[1] we observed that tetrafluorophenyl glycidyl ether[2] (**1b**) reacts more slowly with dibutylamine in alcohol than does phenyl glycidyl ether (**1a**), whereas the glycidyl ether of 2-pentafluorophenylhexafluoropropanol-2 (**2b**) under identical conditions reacts nearly twice as fast as does its non-ring-fluorinated analog **2a**. Furthermore, it was found that meta CF_3 groups deactivate both parent compounds by comparable amounts.



1a, X = H
b, X = F

2a, X = H
b, X = F

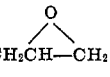
Since both F and CF_3 substituents deactivate the epoxide ring of **1a**, and meta CF_3 groups also deactivate **2a**, the activation of compound **2b** over **2a** seemed quite unusual. In order to determine the factors responsible for this behavior, it was desirable to study the rates of reaction of amines with compounds similar to **2b**. We therefore undertook an investigation of the amine reactivity of molecules of structure **2** containing various patterns of fluorine substitution on the aromatic ring. In addition, two compounds containing ring substituents other than fluorine were synthesized and studied.

Results and Discussion

Synthesis of the Glycidyl Ethers.—Table I presents structures and physical properties of the compounds, all of which are new to the literature, used for kinetic studies. Syntheses were achieved *via* the addition of Grignard or aryllithium reagents to hexafluoroacetone, followed by reaction of the tertiary alcohols with epichlorohydrin and base (*e.g.*, Scheme I). Table I lists nmr data for the compounds.

Several aspects of the synthetic work appear to be noteworthy. The reaction of 1,2,4,5-tetrafluorobenzene with stoichiometric amounts of butyllithium and hexafluoroacetone in tetrahydrofuran produced a 1:1 mixture of mono- and disubstituted products, rather than favoring monoaddition as expected.[3] However, by using diethyl ether as the solvent the ratio of mono- to disubstitution could be increased to 100:1 (Scheme II). This pronounced solvent shift is presumably due to the weaker solvating ability of the diethyl ether for the dilithio derivative.[3,4]

(1) S. A. Reines, J. R. Griffith, and J. G. O'Rear, *J. Org. Chem.*, **35**, 2772 (1970).

(2) The term "glycidyl" is used to denote the structure 

(3) R. J. Harper, E. J. Soloski, and C. Tamborski, *J. Org. Chem.*, **29**, 2385 (1964).

(4) R. J. Harper and C. Tamborski, *Chem. Ind. (London)*, 1824 (1962).