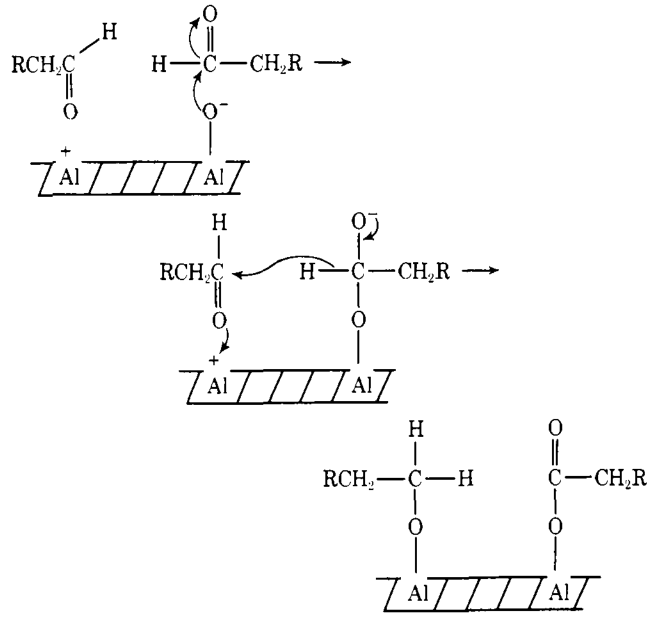
Scheme I



Experimental Section[14]

Melting points are uncorrected and were determined on a Mel-Temp melting point apparatus. The nuclear magnetic resonance (nmr) spectra were recorded on a Jeolco C-60HL spectrometer at 60 MHz using tetramethylsilane as an internal standard. Infrared spectra were determined in potassium bromide on a Perkin-Elmer Model 700 spectrophotometer.

Reaction of 1 with Alumina. 9-(*p*-Methoxyphenyl)-9-fluorenylacetaldehyde (1, 1.00 g) was dissolved in benzene-hexane (1:1) and placed on a column prepared with 100 g of activated alumina (Woelm neutral, activity grade I, pH 7.5). The column was eluted with benzene-hexane (1:1), benzene, benzene-chloroform (1:1), chloroform, chloroform-ether (9:1), chloroform-ether (3:1), ether, methanol, and 5% acetic acid in methanol. Unreacted aldehyde (0.474 g) was eluted in early chloroform fractions as determined by mixture melting point determination and infrared analysis. This was followed by elution of the alcohol 2 (0.254 g, 48%): mp 107.5-109° (tlc); ir 3330 cm^{-1} (OH); nmr ($CDCl_3$) δ 7.3 (m, 12, Ar), 3.7 (s, 3, CH_3O), 2.97 (t, 2, J = 6.0 Hz, -CH_2-), 2.87 (t, 2, J = 6.0 Hz, -CH_2O), and 1.27 (s, 1, OH). The band at δ 1.27 disappeared when the nmr spectrum was run in D_2O. The compound 3 was isolated from the column with 5% acetic acid-methanol elution.

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Registry No.—1, 31462-49-4; 2, 50515-86-1; 3, 50515-87-2; 4, 50515-88-3.

Supplementary Material Available. A supplementary experimental section will appear following these pages in the microfilm edition of this volume of the journal. Photocopies of the supplementary material from this paper only or microfiche (105 × 148 mm, 24× reduction, negatives) containing all of the supplementary material for the papers in this issue may be obtained from the Journals Department, American Chemical Society, 1155 16th St., N.W., Washington, D. C. 20036. Remit check or money order for $3.00 for photocopy or $2.00 for microfiche, referring to code number JOC-74-2796.

References and Notes

(1) To whom correspondence should be addressed.

(2) An acid-treated sample of the salt gave a positive aluminum lake test. No test was obtained prior to acid treatment.

(3) We have evidence, however, which suggests that there is a direct relationship between the amount of alumina used and the amount of reaction.

(4) Under more severe conditions (50% aqueous sodium hydroxide, 130°, 2.5 hr) a small amount of acid and alcohol formed, though the principal reaction was decarbonylation.

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(10) At this point the mechanism would be similar to that proposed for the base-catalyzed Cannizzaro reaction. See J. Hine, "Physical Organic Chemistry," McGraw-Hill, New York, N. Y., 1962, p 267, and references cited therein.

(11) A similar mechanism has recently been proposed by Kuiper, *et al.* (ref 8).

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(13) Preliminary studies indicate that aldehydes that are not substituted with large groups on the α carbon, such as hexanal or heptanal, undergo the aldol condensation on activated alumina.

(14) See paragraph at end of paper regarding supplementary material.

Calculation of Resonance Effect Reaction Parameters. I. Arylene, Vinylene, and Ethynylene Skeletal Groups

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Consider a set of compounds, XGY, in which X represents a substituent, Y a reaction site, and G the skeletal group to which X and Y are bonded. We have previously shown that the Hammett ρ values for various groups G may be calculated in the case of the ionization constants of carboxylic acids[1,2] and rates of alkaline hydrolysis of ethyl carboxylates.[2,3]

Taft[4] has proposed an expanded form of the Hammett equation. The ρ values calculated for groups G may be

$$Q_X = \alpha\sigma_{IX} + \beta\sigma_{RX} + h \tag{1}$$

identified with the α values of eq 1, as α represents the magnitude of the localized electrical effect, and these ρ values were calculated from an equation derived by combining the Hammett and Kirkwood-Westheimer equations. It seemed of interest to develop a method for calculating the β parameters of eq 1 as a function of G.

Dewar and Grisdale,[5] in calculating new σ constants for substituted naphthalene and biphenyl sets, have proposed that the delocalized effect is proportional to the formal negative charge q (at the carbon atom of G which bears the reaction site) in the ion $^-CH_2GH$. When G is derived from an alternant hydrocarbon, q may be simply and easily calculated[6] by the method developed by Dewar. We have examined the relation

$$\beta_G = mq_G + c \tag{2}$$

Equation 2 has been studied for the ionization of carboxylic acids in water at 25°, in 50% v/v $EtOH-H_2O$ at 25°, and in 80% v/v methyl cellosolve-H_2O at 25°. Also studied were the rates of alkaline hydrolysis of ethyl carboxylates in 85-88.7% $EtOH-H_2O$ at 30° and the rates of reaction of carboxylic acids with diphenyldiazomethane at 30° in EtOH.

We have also examined the applicability of eq 2 to the ionization of azaarenes. The q values for the corresponding arene, G, have been used in the correlation on the assumption that q_N, the charge on the nitrogen, will be directly proportional to the charge q on the corresponding carbon atom of G.

$$q_N = nq \qquad (3)$$

To determine the validity of eq 2, β values were correlated with q values by linear regression analysis. Many β values were determined for this purpose by correlation of the appropriate data with eq 1 by means of multiple linear regression analysis. The σ_I constants required were taken from our compilation.[7] The σ_R constants were obtained from eq 4. The σ_p constants were generally taken from the

$$\sigma_R = \sigma_p - \sigma_I \qquad (4)$$

collection of McDaniel and Brown.[8] For the data used and the results of the correlations with eq 1, see paragraph at end of paper regarding supplementary material. Values of β and of q are given in Tables I and II, respectively.

Results of the correlations with eq 2 are set forth in Table III. The results show that of the six sets studied, two gave excellent, three gave fair, and one gave poor correlation as determined by the F test. The "student t" test for the significance of m resulted in one excellent, one very good, three fair, and one poor result. The correlation for set 2 (2A in Table III) was improved by dropping the values for the *trans,trans-* and *cis,trans*-phenylbutadienylene groups (set 2B). The "student t" tests on sets 1, 2A, and 3–6 all show that the intercept c in eq 2 is not significant. In set 2B, however, c is significant at the 99.0% CL. It would seem that in most cases eq 5 would be sufficient.

$$\beta_G = mq_G \qquad (5)$$

The results obtained above indicate that eq 2 is generally obeyed at least approximately, and that eq 3 would be satisfactory in most cases. It seems likely that had more data been available, better correlations would have been obtained. It is interesting to note that excellent results were obtained in the case of the azaarenes (set 6), thus justifying eq 3.

We may therefore conclude that estimation of β is possible when m and c are known for the reaction being studied and q can be calculated. If eq 5 is really satisfactory, then it should be possible to combine data in a number of solvents at various temperatures by correlating γ_R values where

Table I
Values of β

1. Ionization Constants of Carboxylic Acids in H_2O at 25°

trans-CH=CH–, −2.09;[a] 4-$C_{10}H_6$-1-, −1.54; 4-C_6H_4-1-, −0.985;[b] *trans*-4-C_6H_4CH=CH–, −0.477; *cis*-4-C_6H_4-CH=CH–, −0.643[b]

2. Ionization Constants of Carboxylic Acids in 50% v/v EtOH–H_2O at 25°

trans-CH=CH–, −4.27;[a] 4-$C_{10}H_6$-1-, −1.85; 4-C_6H_4-1-, −1.38; 5-$C_{10}H_6$-1-, −0.569; 8-$C_{10}H_6$-2-, −0.548; 6-$C_{10}H_6$-2-, −0.633; 7-$C_{10}H_6$-1-, −0.568; *trans,trans*-4-C_6H_4CH=CHCH=CH–, −0.351; *cis,trans*-4-C_6H_4CH=CHCH=CH–, −0.337

3. Ionization Constants of Carboxylic Acids in 80% MCS–H_2O at 25°

trans-CH=CH–, −3.34; [a] 4-C_6H_4-1-, −1.68; *trans*-4-C_6H_4CH=CPh–, −0.838; *cis*-4-C_6H_4CH=CPh–, −0.517

4. Rate Constants for the Alkaline Hydrolysis of Ethyl Carboxylates in 85–88.7% w/w EtOH–H_2O

4-$C_{10}H_6$-1-, 2.23; 4-C_6H_4-1-, 2.34; *cis*-4-C_6H_4CH=CH–, 1.12; *trans*-4-C_6H_4CH=CH–, 1.15; 4-$C_6H_4C_6H_4$-4-, 0.633

5. Rate Constants for the Reaction of Carboxylic Acids with Diazodiphenylmethane in EtOH at 30°

trans-CH=CH–, 1.60;[a] 4-C_6H_4-1-, 0.861; *trans*-4-C_6H_4-CHCH–, 0.357; 4-$C_6H_4C_6H_4$-4-, 0.224[b]

6. Ionization Constants of Azaarenes in H_2O at 20°

4-C_9H_6N-1-, −6.29; 4-C_6H_4N, −5.11; 5-C_9H_6N-1-, −1.49;[c] 7-C_9H_6N-1-, −2.73;[c] 4-C_6H_4CH=CHC_5H_4N-4-, −0.768

[a] From M. Charton, *Progr. Phys. Org. Chem.*, **10,** 81 (1973). [b] Calculated from the ρ value obtained from correlation with the Hammett equation. [c] From M. Charton, *J. Org. Chem.*, **30,** 3341 (1965).

Table II
Values of q Calculated by the Method of Dewar

G	q	G	q
trans-CH=CH–	0.500	6-$C_{10}H_6$-2-	0.0588
4-$C_{10}H_6$-1-	0.200	7-$C_{10}H_6$-1-	0.0588
4-C_6H_4-1-	0.143	5-$C_{10}H_6$-1-	0.050
trans-4-C_6H_4CH=CH–	0.125	8-$C_{10}H_6$-2-	0.050
cis-4-C_6H_4CH=CH–	0.125	4-$C_6H_4C_6H_4$-4-	0.0323
trans-4-C_6H_4CH=CPh–	0.0909	4-C_6H_4CH=CHC_6H_4-4-	0.0286
cis-4-C_6H_4CH=CPh–	0.0909	*trans,trans*-4-C_6H_4CH=CHCH=CH–	0.111
		cis,trans-4-C_6H_4CH=CHCH=CH–	0.111

Table III
Results of Correlations with Equation 2

Set	m	c	r^a	F^b	$s_{est}{}^c$	s_m	$s_c{}^c$	n^d
1	−3.70	−0.338	0.891	11.52[j]	0.349	1.09[j]	0.285[n]	5
2A	−8.57	0.0544	0.968	104.6[e]	0.340	0.838[e]	0.165[o]	9
2B	−8.30	−0.146	0.9996	5908[e]	0.0434	0.108[e]	0.0232[g]	7
3	−6.15	−0.326	0.961	24.12[j]	0.428	1.25[j]	0.335[n]	4
4	10.3	0.203	0.829	6.608[k]	0.485	4.02[k]	0.547[o]	5
5	2.88	0.183	0.952	19.45[j]	0.233	0.654[j]	0.175[m]	4
6	−31.9	−0.217	0.981	75.98[f]	0.530	3.65[g]	0.434[o]	5

[a] Confidence levels of F and of "Student t" tests of s_m and s_c are indicated by superscripts.[e–p] r = correlation coefficient. [b] F tests for significance of regression. [c] Standard errors of estimate, m, and c. [d] Number of points in the set. [e] 99.9% confidence level (CL). [f] 99.5% CL. [g] 99.9% CL. [h] 98.0% CL. [i] 97.5% CL. [j] 95.0% CL. [k] 90.0% CL. [l] <90.0% CL. [m] 80.0% CL. [n] 50.0% CL. [o] 20.0% CL. [p] 20.0% CL.

$$\gamma_{\mathrm{R,G}} = \frac{\beta_{\mathrm{G}}}{\beta_{\mathrm{G}^\circ}} = \frac{mq_{\mathrm{G}}}{mq_{\mathrm{G}^\circ}} \qquad (6)$$

The β values were obtained under the same reaction conditions. Choosing the p-phenylene group as G°

$$\gamma_{\mathrm{R,G}} = q_{\mathrm{G}}/0.143 = 7q_{\mathrm{G}} \qquad (7)$$

For a comparison of values of γ_{R} calculated from eq 7 with observed values of γ_{R} see paragraph at end of paper. The results obtained show that eq 7 is only a crude approximation; calculation of β values is best accomplished by eq 2.

In the calculation of q by the method of Dewar, the carbon atoms in the species -GCH$_2$:- are divided into two sets of $n + 1$ and n atoms. The value of q at the atoms of the n set is zero. Examples are m-phenylene, and 6-substituted 1-naphthylene groups. Sets such as these do show significant values of q, however. We have previously attempted[9] to predict β values for such sets from the equation

$$\beta = m'\sum q_{\mathrm{adj}} + c \qquad (8)$$

where $\sum q_{\mathrm{adj}}$ is the sum of the q's on the carbon atoms adjacent to that carbon atom which bears the reaction site. To determine the validity of eq 8, values of β_{G} for the ionization of carboxylic acids in 50% v/v EtOH-H$_2$O and the ionization of azaarenes in H$_2$O at 20° were correlated with it. The correlations obtained were not significant. We may reject eq 8 as a means of predicting β values.

We propose that q values for groups such as m-phenylene and 6-substituted 1-naphthylene may be calculated from some reference series for which good values of m and c are available. Values of q for other types of groups for which calculation by the method of Dewar is not possible may also be obtained from eq 2 when β, m, and c are known. Such groups are those which contain triple bonds, and those in which a saturated side chain intervenes between reaction site and ring. For values of q calculated in this manner, see paragraph at end of paper.

It is interesting to note that for the -C≡C-, 4-C$_6$H$_4$C≡C-, and 4-C$_6$H$_4$C≡CC$_6$H$_4$-4- groups a linear relationship exists between their q values and the q values of the corresponding groups with double bonds in place of the triple bonds. Thus

$$q_{\mathrm{C{\equiv}C-}} = nq_{\mathrm{C{=}C}} + d \qquad (9)$$

For a comparison of β values calculated from the q values obtained from eq 2 with observed β values see paragraph at end of paper.

Supplementary Material Available. Data used in correlations with eq 1, results of these correlations, values of γ_{R}, q values calculated from eq 2, and values calculated from these q values will appear following these pages in the microfilm edition of this volume of the journal. Photocopies of the supplementary material from this paper only or microfiche (105 × 148 mm, 24× reduction, negatives) containing all of the supplementary material for the papers in this issue may be obtained from the Journals Department, American Chemical Society, 1155 16th St., N.W., Washington, D. C. 20036. Remit check or money order for $4.00 for photocopy or $2.00 for microfiche, referring to code number JOC-74 -2797.

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Oxidative Decyanation of Arylacetonitriles. A Synthesis of Ligusticumic Acid

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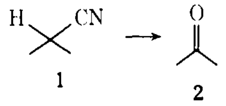
Little methodology exists for effecting the oxidative decyanation of secondary nitriles 1 to ketones 2.[1] As primary nitriles can be monoalkylated to afford secondary nitriles,[2] a procedure capable of effecting this transformation (1 → 2) would render nitriles a member of the class of synthetic intermediates called acyl carbanion equivalents.[3] We now wish to report a convenient synthesis of aryl alkyl ketones and diaryl ketones from substituted arylacetonitriles.



Anions derived from the reaction of secondary arylacetonitriles 3 underwent regioselective N-silylation with *tert*-butyldimethylchlorosilane[4] to provide *N*-*tert*-butyldimethylsilyl ketenimines 4 in good yield (see Table I) and C-silylation with trimethylchlorosilane to provide α-trimethylsilyl nitriles 5.[5] On bromination or iodination of **4**,

Table I
Silylation and Oxidative Decyanation of Arylacetonitriles ArCHRCN

ArCHRCN registry no.	Ar	R	Yield[a] of ketenimine **4**, %	Yield of ketone **7**, %
1823-91-2	Ph	Me	89	71[b]
51965-61-8	p-FPh	Me	72	79[b]
2184-88-5	p-ClPh	Me	71	61[b]
769-68-6	Ph	Et	73	81[b]
5558-29-2	Ph	i-Pr	78	82[c]
15601-30-6	Ph	n-Oc	76	77[c]
86-29-3	Ph	Ph	90	63[c]
24168-42-1	α-Np	Me	71	63[b]

[a] Isolated by distillation at reduced pressure. [b] Isolated using Girard T reagent. [c] Isolated by thick layer chromatography on Merck silica gel F254.