Electron-Rich Aromatics. I. Solvolysis of 1-Arylethyl Acetates[1]

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Abstract: Solvolysis rates for a series of 1-arylethyl acetates have been determined in 30% ethanol. Rates for phenyl groups with *para* substituents (hydrogen, methyl, phenoxy, methoxy, N-methylanilino, and N,N-dimethylamino) correlate well with σ^+, $\rho = -5.70$. From rate constants for heteroaromatic compounds, the following σ^+ constants have been derived (based on the substituent constant for the entire aryl group): 2-thienyl, −0.84; 3-thienyl, −0.47; 5-methyl-2-thienyl, −1.17; 5-bromo-2-thienyl, −0.70; 2-benzothienyl, −0.43; 3-benzothienyl, −0.52; 2-furyl, −0.94; 3-furyl, −0.49; 5-methyl-3-furyl, −1.34; 2-benzofuryl, −0.47; 3-benzofuryl, −0.46; 1-methyl-2-pyrrolyl, −1.96; 1-methyl-2-indolyl, −1.16; 1-methyl-3-indolyl, −1.98; 9-ethyl-3-carbazolyl, −1.13; ferrocenyl, −1.55. Protodesilylation rates of Eaborn are found to correlate well with the present σ^+ values. Comparisons with other literature data are discussed.

By virtue of their chemical reactivity, certain organic compounds are appropriately grouped as "electron-rich aromatics." This classification implies a pronounced ability to stabilize an electron-deficient transition state or intermediate, as in electrophilic aromatic substitution and side-chain carbonium ion reactions.

The group of electron-rich aromatics includes suitably substituted benzenes, fused polycyclics, the five-membered heterocyclics, and iron-family metallocenes as prominent members. Although these aromatic systems as a group are the ones best suited for such "electron-deficient" reactions, there is a remarkable scarcity of quantitative comparisons of reactivity. Such a scarcity is unfortunate, in view of the widespread occurrence and importance of electron-rich aromatics in organic chemistry. Furthermore, our understanding of aromatic reactivity cannot be considered satisfactory unless it includes those systems which are best suited to this class of reactions.

In the series of substituted benzenes, the σ^+ correlation originally developed by Brown and coworkers[3] has proven quite successful in correlating a wide variety of electron-deficient rates and equilibria. Although it is reasonable that the balance of resonance and inductive effects should vary from one reaction to another, the blend of these effects represented by σ^+ constants appears to be a sufficiently good average to fit most cases. Our aim in this work is to define a set of σ^+ constants for a variety of electron-rich aromatics other than the substituted benzenes, and to examine their applicability to available data in the published literature. As in the original σ^+ correlation of Brown,[3] a solvolysis was chosen as the defining reaction on the basis of relative ease in studying a wide range of reactivities, and in defining the reaction site. (It should be noted that σ^+ constants as referred to in this report pertain to the entire aromatic group relative to a value of 0 for unsubstituted phenyl.) Because of the expected extremely high reactivity and instability of *t*-cumyl chloride analogs, less reactive substrates, 1-arylethyl acetates, were chosen. Solvolytic rates were compared in aqueous 30% ethanol.

Results

1-Arylethyl acetates were prepared in most instances by straightforward syntheses. Structures were confirmed by nmr and ir spectra. Some comment is warranted in a few cases in which it was not feasible to obtain analytically pure samples. In the cases where the aryl group was *p*-dimethylaminophenyl and *p*-(N-methylanilino)phenyl, some elimination occurred during distillation. The samples solvolyzed were shown to contain some of the corresponding styrene on the basis of nmr and ir spectra and refractive indices. Where the aryl group was 1-methyl-2-pyrrolyl or 1-methyl-3-indolyl, removal of solvent from the crude acetate led to polymerization after short standing at room temperature. The crude product, found by nmr to contain 30–50% of the alcohol, was again solvolyzed without further purification. In neither case is it at all likely for the impurity to introduce any errors in solvolysis results.

Solvolyses were carried out in 30% ethanol wherever reactivity permitted, and in some cases, in ethanol and other aqueous ethanol mixtures. Observed rate constants are listed in Table III, and rate constants extrapolated to 25° in 30% ethanol, along with the derived activation parameters, are summarized in Table I.

Solvolysis Mechanism. Before considering the solvolyses in Table I for a σ^+ correlation, it should first be established that the reactions occur by alkyl-oxygen fission with a carbonium ion intermediate, rather than through alternative mechanisms involving acyl-oxygen

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[3] (a) H. C. Brown and Y. Okamoto, *J. Am. Chem. Soc.*, **80**, 4979 (1958); (b) H. C. Brown and L. M. Stock, *ibid.*, **84**, 3298 (1962); (c) L. M. Stock and H. C. Brown in "Advances in Physical Organic Chemistry," Vol. 1, V. Gold, Ed., Academic Press, New York, N. Y., 1963, pp 35–154.

Table I. Solvolysis Rates, Activation Parameters, and Substituent Constants for 1-Arylethyl Acetates, 25°, 30% Ethanol[a]

Aryl group	k_{25}, sec^{-1}	$\Delta H^{\ddagger}$, kcal	$-\Delta S^{\ddagger}$, eu	σ^+
Phenyl	3.3×10^{-10} [b,c]	24.16 ± 1.28	20.9 ± 3.3	(0.000)
p-Methylphenyl	1.1×10^{-8} [b,d]	23.56 ± 1.91	15.9 ± 5.1	(−0.311)
p-Phenoxyphenyl	$(2.067 \pm 0.058) \times 10^{-7}$ [b]	21.65 ± 0.14	16.5 ± 0.4	(−0.500)
p-Methoxyphenyl	$(8.06 \pm 0.11) \times 10^{-6}$	19.94 ± 0.10	14.9 ± 0.3	(−0.778)
p-(N-Methylanilino)phenyl	$(1.10 \pm 0.11) \times 10^{-1}$ [b,e]	22.01 ± 0.76	10.9 ± 2.7	−1.55)
p-(N,N-Dimethylamino)phenyl	2.1[f,g]			(−1.7)
2-Thienyl	$(1.78 \pm 0.10) \times 10^{-5}$	19.83 ± 0.43	13.7 ± 1.3	−0.85
3-Thienyl	$(1.58 \pm 0.14) \times 10^{-7}$ [b]	22.40 ± 0.39	14.5 ± 0.1	−0.49
5-Methyl-2-thienyl	$(1.318 \pm 0.008) \times 10^{-3}$ [h]	15.47 ± 0.13	19.8 ± 0.4	−1.17
5-Bromo-2-thienyl	$(3.25 \pm 0.19) \times 10^{-6}$ [b]	19.71 ± 0.25	17.5 ± 0.7	−0.72
2-Furyl	$(7.09 \pm 0.19) \times 10^{-5}$	18.39 ± 0.46	15.9 ± 1.5	−0.95
3-Furyl	$(2.23 \pm 0.08) \times 10^{-7}$ [b]	20.51 ± 0.14	20.2 ± 0.4	−0.51
5-Methyl-2-furyl	$(1.166 \pm 0.009) \times 10^{-2}$ [i]	16.11 ± 0.13	13.3 ± 0.5	−1.34
1-Methyl-2-pyrrolyl	19[f,j]			−1.90
2-Benzothienyl	$(1.097 \pm 0.019) \times 10^{-7}$ [b]	22.21 ± 0.11	15.9 ± 0.3	−0.46
3-Benzothienyl	$(3.39 \pm 0.17) \times 10^{-7}$ [b]	21.64 ± 0.29	15.6 ± 0.9	−0.54
2-Benzofuryl	$(1.639 \pm 0.032) \times 10^{-7}$ [b]	22.22 ± 0.11	15.1 ± 0.3	−0.49
3-Benzofuryl	$(1.38 \pm 0.21) \times 10^{-7}$ [b]	22.40 ± 0.87	14.8 ± 2.6	−0.48
1-Methyl-2-indolyl	$(1.238 \pm 0.047) \times 10^{-3}$ [k]	15.02 ± 0.55	21.5 ± 1.8	−1.17
1-Methyl-3-indolyl	26[f,l]			−1.93
9-Ethyl-3-carbazolyl	$(8.100 \pm 0.092) \times 10^{-4}$ [m]	16.11 ± 0.25	18.7 ± 0.8	−1.14
Ferrocenyl	$(1.67 \pm 0.53) \times 10^{-1}$ [b,n]	14.3 ± 1.4	14.1 ± 5.3	−1.54

[a] Uncertainties in rate constants and activation parameters are 80% confidence limits from linear least squares analysis of plot of log k/T *vs.* $1/T$. Rate constants at 25° are interpolated or extrapolated from the plot. Values of σ^+ in parentheses are established values (ref 3); other values are chosen to fit the least-squares correlation line of log k *vs.* σ^+. [b] Extrapolated from temperatures outside the range 20–30°. [c] Standard deviation in log k_{25}, 0.23. [d] Standard deviation in log k_{25}, 0.18. [e] In 100% ethanol, $k_{25} = (9.03 \pm 0.25) \times 10^{-5}$; $\Delta H^{\ddagger} = 18.58 \pm 0.43$; $\Delta S^{\ddagger} = -14.7 \pm 1.4$. [f] Extrapolated from 100% ethanol. Uncertainties are dependent upon the (unknown) reliability of the solvent extrapolation. [g] In 100% ethanol, $k_{25} = (1.712 \pm 0.037) \times 10^{-3}$; $\Delta H^{\ddagger} = 18.33 \pm 0.22$; $\Delta S^{\ddagger} = -9.7 \pm 0.8$. [h] In 100% ethanol, $k_{25} = (7.78 \pm 1.25) \times 10^{-8}$; $\Delta H^{\ddagger} = 24.07 \pm 0.74$; $\Delta S^{\ddagger} -10.3 \pm 2.2$. [i] In 100% ethanol, $k_{25} = (1.776 \pm 0.036) \times 10^{-6}$; $\Delta H^{\ddagger} = 21.28 \pm 0.26$; $\Delta S^{\ddagger} = -13.5 \pm 0.8$. [j] In 100% ethanol $k_{25} = (1.73 \pm 0.18) \times 10^{-2}$; $\Delta H^{\ddagger} = 16.7 \pm 0.70$; $\Delta S^{\ddagger} = -10.5 \pm 2.0$. [k] In 100% ethanol, $k_{25} = (5.05 \pm 0.16) \times 10^{-7}$; $\Delta H^{\ddagger} = 21.56 \pm 0.18$; $\Delta S^{\ddagger} = -15.0 \pm 0.5$. [l] In 100% ethanol, $k_{25} = (2.47 \pm 0.81) \times 10^{-2}$; $\Delta H^{\ddagger} = 18.57 \pm 0.51$; $\Delta S^{\ddagger} = -3.6 \pm 1.8$. [m] In 100% ethanol, $k_{25} = (7.50 \pm 1.55) \times 10^{-7}$; $\Delta H^{\ddagger} = 20.15 \pm 0.98$; $\Delta S^{\ddagger} = -19.0 \pm 2.9$. [n] In 100% ethanol, $k_{25} = (9.10 \pm 0.17) \times 10^{-5}$; $\Delta H^{\ddagger} = 20.05 \pm 0.35$; $\Delta S^{\ddagger} = -9.8 \pm 1.1$.

fission, or direct displacement by solvent. Earlier studies indicate the likelihood of a carbonium ion mechanism. For instance, the solvolysis of 1-ferrocenylethyl acetate in aqueous acetone has been conclusively demonstrated to occur *via* the carbonium ion,[4] and in a variety of cases, product and stereochemical studies strongly implicate similar intermediates.[5] In the present work, several additional pieces of evidence have been provided.

1. Solvolyses in aqueous and absolute alcohol yield the expected amount of acid. An acyl-oxygen mechanism should produce some ethyl acetate in place of the acetic acid. The solvolysis of 1-phenylethyl acetate was carried out under the most strenuous conditions (109–129° in 30% ethanol). Some formation of ethyl acetate at long reaction times was observed, presumably by spontaneous equilibration with the acetic acid and ethanol, but at low reaction times, the ratio of ethyl acetate to acetic acid was under 0.1, indicating that little, if any, of the reaction might have involved an acyl-oxygen fission mechanism.

2. The ρ value for substituted 1-phenylethyl acetates (*vide infra*) was found to be −5.70. This compares favorably with values for tertiary and secondary benzyl chlorides: −4.54 for *t*-cumyl chlorides;[3] about −6.5, derivable from data for 1-phenylethyl chlorides in 50% ethanol[6] (some of which required solvent extrapolations), and values ranging from −4.7 to −5.6 derivable from a more limited set of 1-phenylethyl chlorides in a variety of dioxane–water and dioxane–water–formic acid media.[7]

3. Azide trapping experiments were carried out with 1-(3-benzothienyl)ethyl acetate, one of the less reactive substrates, and 1-(*p*-dimethylaminophenyl)ethyl acetate, one of the more reactive ones. In the former case, it was found that the solvolysis rate in 30% ethanol was increased by a factor of 1.09 by 0.035 *M* sodium azide. Only 66% of the theoretical acid was formed, and the reaction products were found by nmr to consist of 39% of the alcohol, 30% of the ethyl ether, and 31% of the azide. A rate increase of 1.15 was produced by 0.035 *M* sodium perchlorate. The results correspond to a competition factor, $\alpha_{N_3^-}$,[8] for azide *vs.* solvent of about 13. The diversion of product without a corresponding rate increase provides convincing evidence that, at the very least, a large fraction of the reaction occurs through the carbonium ion.

With 1-(*p*-N,N-dimethylaminophenyl)ethyl acetate, the corresponding carbonium ion is much more stable and hence more selective. When the solvolysis in ethanol was performed in the presence of an excess of azide, trapping was so complete that too little acid was formed to determine a rate. When the solvolysis of 0.0066 *M* acetate was carried out in the presence of 0.0020 *M* sodium azide, virtually no acid was formed until azide ion was consumed, after which time the solvolysis proceeded with clean first-order kinetics at a

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[4] E. A. Hill and J. H. Richards, *J. Am. Chem. Soc.*, **83**, 3840 (1961).

[5] A. G. Davies and J. Kenyon, *Quart. Rev.* (London), **9**, 203 (1955).

[6] V. J. Shimer, Jr., W. E. Buddenbaum, B. L. Murr, and G. Lamaty, *J. Amer. Chem. Soc.*, **90**, 418 (1968).

[7] C. Mechelynek-David and P. J. C. Fierens, *Tetrahedron*, **6**, 232 (1959).

[8] The quantity α_x is the ratio of the second-order rate constant for reaction with nucleophile to the pseudo-first-order rate constant for reaction with solvent (J. Hine, "Physical Organic Chemistry," McGraw Hill Book Co., Inc., New York, N. Y., 1962, pp 131–136.

rate similar to that in the absence of added salt. The "inhibition period" before acid formation (16.5 min) was close to that predicted for 100% trapping (19 min) with no salt effect on the rate.

4. The common ion effect of acetate ion was observed for the solvolysis of 1-(*p*-N,N-dimethylaminophenyl)ethyl acetate ($\alpha_{\mathrm{OAc}^-} = 28.5$ for $[\mathrm{OAc}^-] = 0.121$ *M* in ethanol).

Solvent Effects and Extrapolation. Three of the acetates, *p*-N,N-dimethylaminophenyl, 1-methyl-2-pyrrolyl, and 1-methyl-3-indolyl, were too reactive to study in 30% ethanol, and so an extrapolation from absolute ethanol was needed. Several substrates were solvolyzed in both 30 and 100% ethanol, in the hope that a linear free energy correlation would be found between solvolysis rates in the two solvents. However, the scatter in this log–log plot was too great to allow much confidence in the extrapolation. *mY* plots[9] for several substrates pointed up the difficulty. Two substrates, 5-methyl-2-furyl and 5-methyl-2-thienyl, had substantially larger slopes (0.77 and 0.93) than three other substrates, *p*-(N-methylanilino)phenyl, 9-ethyl-3-carbazolyl, and ferrocenyl (0.53–0.60). It was concluded, somewhat arbitrarily, that the reactive substrates might more closely resemble the latter group, since they lack a ring oxygen or sulfur adjacent to the reacting center. Therefore, the extrapolation was based on a log k_{30} *vs.* log k_{100} plot for these three substrates, plus 1-methyl-2-indolyl. This plot had a slope close to unity, and an average deviation of experimental points of 0.14.

Some further comment on the solvent effects is in order. The *mY* plots for the second group of substrates showed some curvature on the high-water end beginning in the vicinity of 40% ethanol. Along with the variation in *m* values, the curvature suggests the possibility of mechanism changes, such as variation in the extent of nucleophilic solvent involvement, or perhaps a shift to rate-determining solvent attack on a carbonium–acetate ion pair. Plots of $\Delta S^{\ddagger}$ *vs.* $\Delta H^{\ddagger}$, log *k* *vs.* $\Delta H^{\ddagger}$, and log *k* *vs.* $\Delta S^{\ddagger}$ in 30 and 100% ethanol exhibited (1) a general dependence of rate upon activation enthalpy, (2) the absence of consistent relationship between rate and activation entropy, and (3) scatter in all plots that was apparently beyond experimental error. However, there was no consistent trend in these plots which might point to mechanistic change related in any obvious manner to structure or to reactivity. Nevertheless, regardless of its source, the variation of solvent effects places some limitations on the potential generality and accuracy of substituent constants derived from the solvolyses.

Some further investigations were made with 1-(9-ethyl-3-carbazolyl)ethyl acetate. In both 40 and 80% ethanol, a small common ion effect was found by comparing solvolysis rates in 0.10 *M* potassium acetate with 0.10 *M* potassium chloride. If anything, the common ion effect was larger in the 80% ethanol ($\alpha = 1.5$) than in 40% ethanol ($\alpha = 0.5$), whereas the opposite might be expected from a changing mechanism. α-Deuterium isotope effects in the two solvents were the same within experimental error (1.15 ± 0.04 and 1.14 ± 0.03). These values are somewhat lower than expected for a limiting S_N1 solvolysis of a C–O bond.[10] Recently, Noyce has reported a value of 1.20 for 1-(2-furyl)ethyl *p*-nitrobenzoate.[11] Though the precision of our determination is not high enough to indicate subtle changes, there is no strong trend which might suggest much different solvent involvement in the two media.

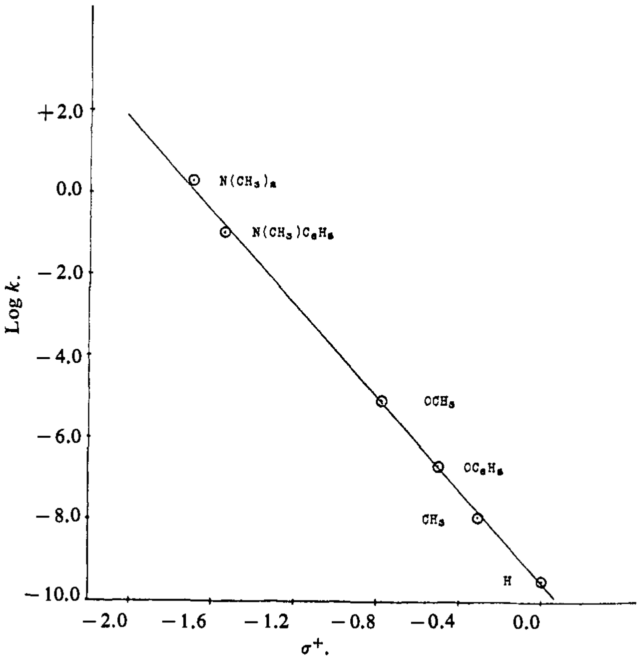

Figure 1. Plot of log *k* *vs.* σ^+ values for solvolyses of *para*-substituted 1-phenylethyl acetates in 30% aqueous ethanol at 25°.

σ^+ Correlation. In Figure 1, values of log *k* for the solvolysis in 30% ethanol at 25° are plotted against σ^+ values tabulated by Brown and Okamoto.[3] The correlation has $\rho = -5.70 \pm 0.11$ and $r = 0.999$. The high quality of the correlation is somewhat deceptive, and probably partly fortuitous. Of the six substituents which define this line, only three (H, *p*-CH_3, *p*-OCH_3) have "primary" σ^+ values defined by Brown's solvolysis reaction. In our study, the first two of these were extrapolated from much higher temperatures, and the third required a solvent extrapolation in Brown's study because of its high reactivity.[12] Of the remaining substituents, σ^+ for *p*-phenoxy and *p*-dimethylamino are average "best" values selected from other reactions.[3] The value for *p*-N-methylanilino was estimated from the tabulated value for *p*-anilino (−1.4), and the relative values for *p*-amino, *p*-N-methylamino, and *p*-N,N-dimethylamino, none of which are "primary" values. Uncertainties as to the appropriate σ^+ values for the most electron-releasing substituents may lead to some error in the slope of the correlation line, and consequently in σ^+ values later assigned to new aryl groups. However, this error will not effect the order of aryl groups, and will have only minor effects on the *relative* σ^+ values of strongly electron-releasing substituents. Error in the solvent extrapolation for *p*-N,N-dimethylamino could also affect the slope. However, the over-all quality of the correlation suggests that errors introduced in σ^+ from this source are not serious.

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(9) E. Grunwald and S. Winstein, *J. Am. Chem. Soc.*, 70, 846 (1948); S. Winstein, E. Grunwald, and H. W. Jones, *ibid.*, 73, 2700 (1951); A. H. Fainberg and S. Winstein, *ibid.*, 78, 2770 (1956).

(10) V. J. Shiner, Jr., M. W. Rapp, E. A. Halevi, and M. Wolfsberg, *ibid.*, 90, 7171 (1968).

(11) D. S. Noyce and G. V. Kaiser, *J. Org. Chem.*, 34, 1008 (1969).

(12) Y. Okamoto and H. C. Brown, *ibid.*, 79, 1909 (1957).

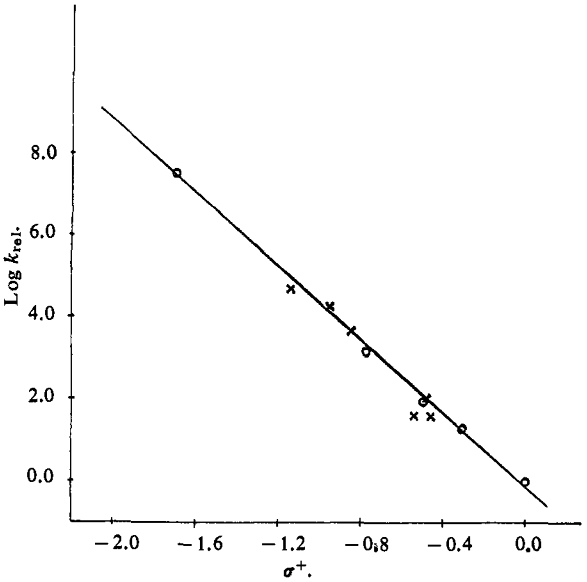

Figure 2. Plot of log k_{rel} *vs.* σ^+ values for protodesilylation of aryltrimethylsilanes in aqueous methanolic perchloric acid at 51° (ref 17); σ^+ values from Table I: O, substituted phenyl groups; ×, other aryl groups; ⊗, ferrocenyl.

From the correlation line for substituted phenyl groups, and rate constants for additional 1-arylethyl acetates, new σ^+ values were calculated for a variety of heteroaryl groups. These are listed also in Table I.

In a recent study,[13] Taylor has determined pyrolysis rates for 1-arylethyl acetates, and used these results to define σ^+ values for the 2 and 3 positions of thiophene and furan. The σ^+ values which they derived, −0.79, −0.38, −0.885, and −0.415, respectively, are in reasonable agreement with the present findings, and are reported to be consistent with reactivities in several reactions (protodesilylation, iododeboronation, protodetritiation, and molecular bromination) where there are sufficient data to define σ^+ values. Correlation with protodeboronation and protodemercuration was unsatisfactory.

Discussion

Although the σ^+ correlation is quite successful for substituted phenyl groups,[3] there is substantial evidence that the balance of inductive and resonance effects does vary from reaction to reaction, and treatments incorporating this variability have proven useful.[14] Some of the electron-rich aryl groups should provide a very critical testing of the usefulness of a single electrophilic substituent constant. For instance, a variety of evidence points to the conclusion that 2-furyl and 2-thienyl are substantially more electron withdrawing than phenyl in their inductive effect.[15] However, in electrophilic aromatic substitution, both compounds are generally more reactive than anisole, indicating an ability to release electrons by resonance. Certainly, if electron-deficient reactions vary much in their balance of resonance and inductive electron demand, this should show up in major deviations from σ^+ correlations.

Unfortunately, there is a rather meager supply of data available to test the applicability of $\sigma^+\rho$ correlations to electrophilic substitutions. The most extensive series of relative rates is in the protodesilylation reaction studied by Eaborn and coworkers.[17] Figure 2 shows a plot of log k for protodesilylation (in perchloric acid–methanol–water) *vs.* σ^+ values of this study. This plot results in $\rho = -4.48 \pm 0.18$ ($r = 0.993$). In their tabulation of reaction constants, Brown and Okamoto list a value of $\rho = -4.32$, $r = 0.972$,[3a] based, of course, only on substituted benzenes. From Figure 2, it may be seen that the heteroaromatic compounds scatter somewhat more than substituted benzenes about the correlation line. However, there is no systematic deviation of heteroaromatic compounds that suggests specific effects or influences.

Results of several less extensive studies are also available, but, unfortunately, none are as broad as would be desired. Several of these will be considered briefly.

Acylation of several heteroaromatic systems has been investigated. Relative rates for thiophene, 2-chlorothiophene, 2-methylthiophene, furan, and anisole with acetic anhydride and iodine or stannic chloride are reported.[18] Results from these two quite similar series give excessive scatter when plotted against σ^+ values of Table I,[19] with an average deviation of $10^{0.4}$ in rate, and ρ about −5.5. Uncatalyzed acylation by trifluoroacetic anhydride, studied competitively for thiophene, 2-methylthiophene, 2-methoxythiophene, furan, 2-methylfuran, and N-methylpyrrole, also gave considerable scatter.[20] However, an interesting pattern emerges. Rates for the two 2-furyl groups lie about $10^{1.1}$ to the fast side of a quite precise line defined by the other four ($\rho = -7.7$).

The apparent lack of success in correlating acylations with solvolysis-derived σ^+ values may have several causes. First acylation is generally a more selective reaction than either the protodesilylation or solvolysis. If it is, as a consequence, more sensitive to the resonance effect, the enhanced rates of 2-furyl compounds might be expected. Alternatively, the inductive and field portion of the substituent effect may be quite sensitive to the location of charge centers close to the heteroatom in the transition state. In the solvolysis, the leaving acetate ion partially counterbalances positive charge on the formally cationic carbon. Conceivable differences in charge type of the acylation reactions may be responsible for the correlation failure. Finally, there may be some mechanistic variations in the acylations, resulting from changes in rate-determning step. We are currently investigating the latter possibility through a study of deuterium isotope effects in a variety of acetylations.

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(13) R. Taylor, *J. Chem. Soc., B*, 1397 (1968).

(14) Y. Yukawa and Y. Tsuno, *Bull. Chem. Soc. Jap.*, 32, 971 (1959).

(15) pK values for benzoic, 2-furoic, and thiophene-2-carboxylic acid in water at 25° are 4.18, 3.16, and 3.53, respectively.[16a] These constants would lead to values of Hammett's σ for the 2-furyl and 2-thienyl groups of +*1.02* and +*0.65*. In another example, the rate of *ortho* nitration of 2-thienyl alcohol is about half that of benzyl alcohol.[16b]

(16) (a) A. Albert in "Physical Methods in Heterocyclic Chemistry," Vol. I, A. R. Katritzky, Ed., Academic Press, New York, N. Y., 1963, p 103; (b) B. Ostman, *Acta. Chem. Scand.*, 21, 1257 (1967).

(17) (a) F. B. Deans and C. Eaborn, *J. Chem. Soc.*, 2303 (1959); (b) C. Eaborn and J. A. Sperry, *ibid.*, 4921 (1961); (c) C. Eaborn, *ibid.*, 4858 (1956); (d) G. Marr and D. E. Webster [*J. Organometal. Chem.*, 2, 99 (1964)] determined the rate for the ferrocene derivative.

(18) P. Linda and G. Marino, *Tetrahedron*, 23, 1739 (1967).

(19) σ^+ for 5-chloro-2-thienyl was estimated from a relationship between σ^+ values for substituted phenyl and thienyl groups.

(20) S. Clementi, F. Genel, and G. Marino, *Chem. Commun.*, 498 (1967). A σ^+ value for 2-methoxythiophene was estimated from a relationship between σ^+ values of substituted phenyl and 2-thienyl groups. A relative rate for pyrrole is also available, but there is no σ^+ value.

Bromination rates of thiophene and the 2-carbomethoxy derivatives of thiophene, furan, and pyrrole in acetic acid have been reported.[21] With the assumption that relative rates of the parent heterocycles parallel those of their carbomethoxy derivatives, partial rate factors for the 2 position of the unsubstituted heterocycles were derived. Points for thiophene, α-bromothiophene, and furan fit the correlation line for substituted benzenes[3] as well as most other aryl groups do, although a more detailed examination suggests that 2-thienyl is slow relative to 2-furyl and 5-bromo-2-thienyl. However, pyrrole appears to be far too slow,[22] perhaps by more than 10^4, and the derived rate is somewhat smaller than for the *para* position of N,N-dimethylaniline. Partial rate factors for chlorination of thiophene and 2-chlorothiophene also fit reasonably well to the line for substituted benzenes.

Aromatic electrophilic hydrogen exchange rates have been measured for a wide variety of aromatics. Unfortunately, an almost equally wide variety of media and conditions have been used to study these reactions, so meaningful comparisons are very difficult to draw. In one study which is relevant to the present discussion, comparison of dedeuteration rates in varous methanol–water–sulfuric acid mixtures leads to partial rate factors which give an excellent correlation for phenyl and 2- and 3-thienyl ($\rho = -9.1$).[23] The rate for furan appears low by about 10 ft, and although the exchange rate for pyrrole was determined, there was no comparison in the same solvent with any of the other substrates. Relative protodetritiation reactivities quoted[13] for the 2 and 3 positions of thiophene in trifluoroacetic acid appear to be correlated satisfactorily. A more detailed discussion of isotopic hydrogen exchange is reserved for a subsequent report of experimental work currently in progress. Relative basicities of 1-methylindole and 1-methylpyrrole are qualitatively consistent with the solvolysis results.[24]

Studies of coupling with diazobenzenesulfonic acid[25] (including phenol, aniline, dimethylaniline, and pyrrole), acid-catalyzed rearrangement of 1-aryl-2-buten-1-ols[26] (including phenyl, *p*-anisyl, 2-furyl, and 2-thienyl), and infrared and basicity studies of chalcone analogs[27] (including phenyl, 2-furyl, 2-thienyl, and 2-pyrrolyl) fail to give any reasonable correlation. The latter study will be discussed in greater detail in a report of related studies from our laboratories.

Several more isolated pieces of data are available primarily for thiophene. pK_a values for a variety of di- and triarylcarbonium ions containing the 2-thienyl group, and for diphenyl(3-thienyl)carbonium ion, fit well to σ^+ correlations.[28] 2-Thienyl also fits well to a correlation of migrational aptitudes of substituted phenyl groups in tetraarylpinacols.[29] Rates of isotopic chloride exchange for benzyl, 2-thenyl, and 3-thenyl chloride in dimethylformamide have been reported.[30] Relative rates were 1.00, 2.95, and 0.84, and the results were discussed on the basis of molecular orbital calculations for a carbonium ionlike transition state, which was found to produce the same order of relative rates. Obviously, now that an authentic carbonium ion comparison is available, it may be concluded that the model used in the calculations was unrealistic, and that the displacement rates bear very little resemblance to carbonium ion stabilities.

Two rather puzzling partial rate factors, which may perhaps reflect mechanistic changes, have been reported for the 2 position of thiophene: 850 in nitration (acetic anhydride) and 97,000 in acetoxymercuration (acetic acid).[31] The ρ values for these two reactions, about -6 and -4.0, are inconsistent with the selectivities above, and would require σ^+ values of -0.5 and -1.25 for 2-thienyl. The high mercuration rate of thiophene has been confirmed,[32] and the effects of 5-substituents on mercuration of thiophene and selenophene have been found to be similar ($\rho \approx -5.8$). High relative rates of protodemercuration and protodeboronation[33] have previously been noted.[13] The low nitration rate could be a result of encounter-controlled reaction, as has been observed in aqueous sulfuric acid.[34] Curiously, rates of nitration of carbazole and diphenylamine in the same medium also appear slow in comparison with σ^+ values.[35]

Another type of reactivity comparison which may be made involves the internal competition between two positions in the same molecule. The present results agree with common generalizations concerning the greater reactivity of the 2 positions of furan and thiophene and the 3 position of indole. The greater electron release to the 3 position of benzothiophene is consistent with the bulk of electrophilic substitution data,[36] except for protodesilylation,[17] and benzoylation[36c] (benzoyl chloride, stannic chloride), which show equal reactivities in the two positions, and isopropylation,[36d] which shows greater reactivity in the 2 position. There appears to be no correlation between the isomer ratio and ρ for the reaction. Benzofuran has generally been found to give almost exclusive 2-orientation,[37] in contrast with the present solvolysis results which show little difference between the 2 and 3 positions. Although the 3 positions of benzofuran,

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(37) G. M. Badger, "The Chemistry of Heterocyclic Compounds," Academic Press, New York, N. Y., 1961, p 136 ff.

benzothiophene, and indole might be subject to the same steric restrictions as the 1 position of naphthalene, it is likely that the increased spread of exocyclic bond angles on the five-membered ring minimizes the potential steric effect in this reaction.

We have recently been informed by Professor D. S. Noyce[11,38] of solvolysis results for 1-arylethyl *p*-nitrobenzoates in 80% ethenol, including as aryl groups the 2 positions of furan, thiophene, and some derivatives, and the 2 and 3 positions of benzofuran and benzothiophene. Although a log–log plot for corresponding aryl groups shows deviations probably outside of experimental error, there is a reasonable correspondence of relative reactivities. Of particular note are the relative reactivities of the 1 and 3 positions of benzofuran and benzothiophene, which are in excellent agreement with the present work, and a rather precise correlation of the results for 2-thienyl and 2-furyl and their substituted derivatives. However, our study shows a greater reactivity difference between thiophene and anisole, and lower relative reactivity of the benzo derivatives.

Solvolysis rates which have been determined for several chloromethyl derivatives of furan, benzofuran, and dibenzofuran[39] are in reasonable accord with the present results and with very rough estimates for some substituted benzyl derivatives. A ρ value of about -6 may be estimated for the more reactive compounds, though it is likely that nucleophilic solvent participation becomes more important for the less reactive ones.

In the preceding discussion, little comment has been given on the ferrocenyl group, although a σ^+ value of -1.55 is listed in Table I, and in the correlation of protodesilylation reactivities in Figure 2, there is an obvious deviation of about 10^3. In other studies, a wide range of σ^+ values has been assigned to ferrocene, and their variation has been discussed.[40] We feel that this problem has mechanistic considerations which go beyond the concern of this paper, and prefer to discuss these results at a later time in connection with other work currently in progress in our laboratories.

We conclude tentatively that the solvolysis-derived substituent constants reported here for heteroaromatic systems probably provide a fair measure of electronic effects, when viewed on a broad scale of aromatic reactivity. However, significant deviation from σ^+ correlations are apparent, and the σ^+ values reported should be applied with some discretion in quantitative treatments of a narrow range of reactivities, where minor effects may obscure the broad trend of aromatic electron release. In particular, the solvent is clearly important in determining the exact relative reactivities in a given reaction. At the same time, the reactivity scale defined by the present set of σ^+ constants may help to point up mechanistic inconsistencies which warrant further investigation.

Experimental Section

All boiling points are uncorrected. Melting points were determined on a calibrated Fisher-Johns hot stage. Infrared spectra were obtained on Beckman IR-5 or IR-8, or a Unicam SP 500 spectrometer. Nuclear magnetic resonance spectra were determined on Varian Associates A-60 and HA-100 spectrometers with tetramethylsilane as internal standard. Microanalyses were performed at the University of Minnesota by Mrs. Olga Hamerston and Dr. T. S. Prokopov and their assistants, and by the Schwarzkopf Microanalytical Laboratory, Woodside, N. Y.

1-Arylethyl acetates were generally prepared from the corresponding alcohol and acetic anhydride in pyridine. The mixture was usually allowed to stand overnight at room temperature. Work-up was by one of two procedures.

A. (This procedure was followed unless otherwise specified.) The reaction solution was poured into excess ice-cold 6 *N* sulfuric acid, and extracted with ether. The ether solution was washed with an additional volume of ice-cold 6 *N* sulfuric acid, washed repeatedly with ice-cold 10% sodium carbonate until the aqueous phase remained basic, and finally with ice-cold water. The ethereal solution was quickly dried over anhydrous potassium carbonate, the ether was removed, and the product purified and characterized.

B. Pyridine, excess acetic anhydride, and acetic acid were removed at room temperature under less than 1 mm pressure, and the product was distilled or sublimed under vacuum. Frequently, acetate was prepared from crude alcohol.

1-Phenylethyl acetate was prepared from 1-phenylethanol (30 g, 0.246 mole) and acetic anhydride (24 g, 0.246 mole) in pyridine (30 ml) in 34% yield, bp 100–102° (15 mm) [lit.[41] bp 105–108° (15 mm)].

1-(*p*-Methylphenyl)ethyl Acetate. *p*-Methylacetophenone was reduced with lithium aluminum hydride to 1-(*p*-methylphenyl)-ethanol, bp 107° (20 mm). The acetate was prepared from the alcohol (29 g, 0.21 mole) and acetic anhydride (22 g, 0.22 mole) in pyridine (30 ml), bp 104–105° (12 mm) [lit.[41] bp 105–106° (21 mm)].

1-(*p*-Phenoxyphenyl)ethyl Acetate. *p*-Phenoxyacetophenone was reduced with lithium aluminum hydride to yield crude 1-(*p*-phenoxyphenyl)ethanol. Acetate was prepared from the crude alcohol (31 g, 0.121 mole) and acetic anhydride (16.3 g, 0.16 mole) in pyridine (16 ml) in 87% yield over-all: bp 135° (0.2 mm); n^{30}D 1.5474; ir (neat), 1640 (C=O), 1240 cm^{-1}; nmr (CCl$_4$) δ 1.47 (d, 3, J = 6.5 Hz, CH$_3$), 1.93 (s, 3, CH$_3$CO), 5.84 (q, 1, J = 6.5 Hz, C*H*OAC), 6.77–7.74 ppm (m, 9, aromatic).

Anal. Calcd for $C_{16}H_{16}O_3$: C, 74.98; H, 6.29. Found: C, 75.20; H, 6.51.

1-(*p*-Methoxyphenyl)ethyl Acetate. 1-(*p*-Methoxyphenyl)ethanol was prepared in 51% yield from the reaction of *p*-anisaldehyde with methylmagnesium iodide in ether: bp 115–120° (0.25 mm); n^{29}D 1.5414 [lit.[42] bp 140–141° (17 mm), n^{24}D 1.531]. The acetate was made from reaction of 15.2 g (0.10 mole) of the alcohol and 10.3 g (0.10 mole) of acetic anhydride in 12 ml of dry pyridine for 5 days at room temperature: bp 114–115° (3.5 mm); n^{26}D 1.5030 [lit.[41] bp 153–154° (27 mm); n^{25}D 1.5039]; ir (neat) 1730 (C=O) and 1245 cm^{-1}; nmr (CCl$_4$) δ 1.45 (d, 3, J = 6.5 Hz, CH$_3$), 1.94 (s, 3, acetate CH$_3$), 3.68 (s, 3, OCH$_3$), 5.81 (q, 1, J = 6.5 Hz, C*H*OAC), 6.99 ppm (m, 4, aromatic).

1-(*p*-N,N-Dimethylaminophenyl)ethyl Acetate. Reaction of methyllithium (0.10 mole) with *p*-N,N-dimethylaminobenzaldehyde (10.0 g, 0.067 mole) in ether (350 ml) yielded *p*-(N,N-dimethylaminophenyl)ethanol in 71–94% yield after recrystallization from petroleum ether (bp 60–70°), mp 59–60° [lit.[43] mp 59–60°]. The acetate was made from the alcohol (7.033 g, 0.047 mole) and acetic anhydride (6 g, 0.056 mole) in pyridine, and worked up by procedure B: bp 73–74° (0.01 mm); n^{25}D 1.5322. The ir spectrum showed bands at 1740 and 1250 cm^{-1} corresponding to the acetate, and additional bands at 1550, 1410, 1330, 925, and 890 cm^{-1} characteristic of *p*-N,N-dimethylaminostyrene. The nmr was appropriate for a mixture of the acetate [δ 1.43 (d, 3, J = 6.6 Hz, CH$_3$), 1.89 (s, 3, CH$_3$CO), 2.80 (s, 6, NCH$_3$), 5.72 (q, 1, J = 6.6 Hz, C*H*OAC), 6.85 ppm (m, 4, aromatic)] and the styrene [δ 2.83 (s, 6, NC*H*$_3$), 4.93, 5.42, and 6.73 (vinyl multiplet, J_{cis} = 11.0, J_{trans} = 17.2, J_{gem} = 1.5 Hz), 6.85 ppm (m, 4, aromatic)]. In the best prepara-

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Table II. Rate Constants for Solvolysis of 1-Arylethyl Acetates with Added Solutes

Aryl	Solvent (% ethanol)	*T*, °C	Solute	10^5k,[a] sec^{-1}
3-Benzothienyl	30	75.0		7.59 ± 0.15[b]
			0.035 *M* NaN_3	8.25 ± 0.29
			0.035 *M* $NaClO_4$	8.82 ± 0.20
p-(N,N-Dimethylamino)phenyl	95	0.0		37.1 ± 0.9[c]
			0.121 *M* $NaClO_4$	50.4 ± 1.5[b]
			0.121 *M* NaOAc	11.4 ± 1.0[b]
			0.0062 *M* NaOH	36.6 ± 3.0[b]
9-Ethyl-3-carbazolyl	40	25.0		26.7 ± 1.2[c]
			0.10 *M* KCl	26.5 ± 0.6
			0.10 *M* KOAc	25.6 ± 0.6
	80	25.0		1.08 ± 0.01[c]
			0.10 *M* KCl	1.06 ± 0.02
			0.10 *M* KOAc	0.92 ± 0.03
1-(9-Ethyl-3-carbazolyl)ethyl-acetate-*α*-*d*	40	25.0		23.5 ± 0.8[c]
	80	25.0		0.94 ± 0.02[c]

[a] Uncertainties are 80% confidence limits. [b] Average of two runs. [c] Average of four runs.

tions, up to 93% of acetate was present in the mixture. Attempted fractionation increased the amount of styrene present, so mixtures were used for kinetics.

1-(*p*-N-Methylanilinophenyl)ethyl Acetate. Acetylation of methyldiphenylamine (70 g, 0.38 mole) was carried out with acetic anhydride (27.6 g, 0.27 mole) and 85% phosphoric acid (1.75 ml). The mixture was stirred for 13 hr at 100° under nitrogen and poured into sodium bicarbonate solution. After extraction with ether, drying, and distillation, there was obtained 48.2 g (69%) of recovered methyldiphenylamine, bp 113–122° (0.5 mm), and *p*-N-methylanilinoacetophenone (15 g, 56% based on unrecovered starting material): bp 134–145° (0.05 mm); mp 86–87.5° (methanol, petroleum ether) [lit.[44] mp 87°]; ir (Nujol) 1670 cm^{-1}. Reduction with lithium aluminum hydride in ether yielded crude 1-(*p*-N-methylamilinophenyl)ethanol. Reaction of 5.10 g of the crude alcohol with acetic anhydride (4 g, 0.038 mole) in pyridine (8 ml) yielded the acetate: bp 150–159° (0.1–0.5 mm); $n^{25}\mathrm{D}$ 1.6114; ir (neat) 1728 (C=O), 1243 cm^{-1}; nmr (CCl_4) δ 1.43 (d, 3, J = 6.8 Hz, CH_3, 1.87 (s, 3, CH_3CO), 3.14 (s, 3, NCH_3), 5.82 (q, 1, J = 6.8 Hz, $CHCH_3$), 6.70–7.40 ppm (m, 9, aromatic). Absorption corresponding to the vinyl group of *p*-N-methylanilinostyrene was also observed at δ 5.07, 5.50, and 6.60 ppm, J_{cis} = 10.8, J_{trans} = 17.6, J_{gem} = 1.4 Hz. The mixture contained about 60% of the acetate. Attempted fractionation increased the proportion of styrene, so the mixture was used for solvolysis without further purification.

1-(2-Thienyl)ethyl acetate was prepared from 1-(2-thienyl)ethanol[45] (20 g, 0.156 mole) and acetic anhydride (18 g, 0.177 μmole) in pyridine (18.5 ml) in 81% yield: bp 93–95° (12 mm); $n^{21}\mathrm{D}$ 1.5048 [lit.[46] bp 78–81° (4 mm)]; ir (neat) 1740 (C=O) 1235 cm^{-1}; nmr (CCl_4) δ 1.57 (d, 3, J = 6.20 Hz, CH_3), 6.73–7.25 ppm (m, 3, aromatic).

Anal. Calcd for $C_8H_{10}O_2S$: C, 56.42; H, 5.92; S, 18.80. Found: C, 56.31; H, 6.20; S, 18.71.

1-(3-Thienyl)ethyl Acetate. Reaction of methyllithium (0.15 mole) with 3-thenaldehyde[47] (8.2 g, 0.073 mole) in ether (300 ml) yielded 1-(3-thienylethanol). The crude alcohol (4.0 g) was converted to the acetate by reaction with acetic anhydride (6 g, 0.056 mole) in pyridine (15 ml): bp 74° (2.6 mm); $n^{25}\mathrm{D}$ 1.5046; ir (neat) 1740 (C=O) 1245 cm^{-1}; nmr (CCl_4) δ 1.50 (d, 3, J = 6.9 Hz, CH_3), 1.95 (s, 3, CH_3CO), 5.93 (q, 1, J = 6.9 Hz, $CHCH_3$), 6.88–7.32 ppm (m, 3, aromatic).

Anal. Calcd for $C_8H_{10}O_2S$: C, 56.47; H, 5.92; S, 18.80. Found: C, 56.49; H, 5.90; S, 18.76.

1-(5-Methyl-2-thienyl)ethyl Acetate. 1-(5-Methyl-2-thienyl)ethanol was prepared by reduction of 5-methyl-2-acetylthiophene[48] with lithium aluminum hydride in ether. Crude alcohol (4.03 g) was converted to the acetate with acetic anhydride (5 g, 0.047 mole) in pyridine (10 ml), in 76% over-all yield from the ketone: bp 71° (0.20 mm); $n^{25}\mathrm{D}$ 1.4996; ir (neat) 1745 (C=O), 1234 cm^{-1}; nmr (CCl_4) δ 1.52 (d, 3, J = 7.0 Hz, $CHCH_3$), 1.93 (s, 3, CH_3CO), 2.38 (d, 3, J = 1.0 Hz, CH_3), 6.00 (q, 1, J = 7.0 Hz $CHCH_3$), 6.50 and 6.73 ppm (AB pattern, with additional coupling, J_{AB} = 3.4 Hz, aromatic).

Anal. Calcd for $C_9H_{12}O_2S$: C, 58.64; H, 6.57; S, 17.41 Found: C, 58.35; H, 6.75; S, 17.20.

1-(5-Bromo-2-thienyl)ethyl Acetate. Reduction of 5-bromo-2-acetylthiophene with lithium aluminum hydride yielded 1-(5-bromo-2-thienyl)ethanol. The acetate was prepared from the crude alcohol with acetic anhydride in pyridine and worked up by procedure B:[49] bp 138–140° (10 mm); nmr (CCl_4) δ 1.53 (d, 3, J = 6.6 Hz, CH_3), 1.94 (S, 3, CH_3CO), 5.97 (q, 1, J = 6.6 Hz, CHOAC), 6.08 ppm (m, 2, AB pattern with J_{AB} = 3.8 Hz, and further splitting of the high-field portion by 0.6 Hz, aromatic).

1-(2-Benzothienyl)ethyl Acetate. 1-(2-Benzothienyl)ethanol was prepared by reduction of 2-acetylbenzothiophene[50] with lithium aluminum hydride in ether, mp 62–63°. The acetate was made by reaction of the crude alcohol (1.67 g) with acetic anhydride (2.0 g 0.019 mole) in dry pyridine (5 ml) in 55% yield: bp 106° (0.06 mm); mp 30–31°; $n^{22}\mathrm{D}$ 1.5755; ir (neat) 1745 (C=O) 1235 cm^{-1}; (CCl_4) δ 1.62 (d, 3, J = 6.5 Hz, CH_3), 1.99 (s, 3, CH_3CO), 6.03 (q, 1, J = 6.5 Hz, CHOAC), 6.55–6.60 (m, 3, aromatic), and 7.63–7.95 ppm (m, 2, aromatic).

Anal. Calcd for $C_{12}H_{12}O_2S$: C, 65.44; H, 5.49. Found: C, 65.71; H, 5.37.

1-(3-Benzothienyl)ethyl Acetate. 1-(3-Benzothienyl)ethanol was prepared by reduction of 3-acetylbenzothiophene[50] with lithium aluminum hydride in ether, mp 43–45°. The acetate was made from the crude alcohol (12.3 g) and acetic anhydride (10 g, 0.094 mole) in pyridine in 88% yield from ketone: bp 103° (0.05 mm); $n^{22}\mathrm{D}$ 1.5785; ir (neat) 1745 (C=O), 1240 cm^{-1}; nmr (CCl_4) δ 1.62 (d, 3, J = 6.5 Hz, CH_3), 1.95 (s, 3, CH_3CO), 6.38 (q, 1, J = 6.5 Hz), 7.14–7.44 and 7.58–7.91 ppm (m, 5, aromatic).

Anal. Calcd for $C_{12}H_{12}O_2S$: C, 65.44; H, 5.49. Found: C, 65.24; H, 5.76.

1-(2-Furyl)ethyl Acetate. 2-Acetylfuran (39.6 g, 0.36 mole) was reduced with lithium aluminum hydride in ether, and the crude alcohol was converted to acetate with acetic anhydride (35.6 g, 0.36 mole) in pyridine (40 ml): bp 61° (10 mm); $n^{25}\mathrm{D}$ 1.4556.[51]

1-(3-Furyl)ethyl Acetate. To a solution of 3-furoic acid[52] (7.0 g, 0.062 mole) in 100 ml of ether was added 0.2 mole of methyllithium in 200 ml of ether over a period of 20 min. The mixture was refluxed for 3.5 hr and hydrolized to yield recovered 3-furoic

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(48) We express appreciation to Drs. L. A. Hamilton and P. S. Landis of Socony Mobil Oil Co. for a gift of 5-methyl-2-acetylthiophene.

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Table III. Solvolysis Rates of 1-Arylethyl Acetates in Aqueous Ethanol

Aryl group	Solvent (% ethanol)	T, °C	Method[a]	10^5k, sec^{-1}
Phenyl	30	109.7	C	0.363 ± 0.018
		120.0	C	0.835 ± 0.015
		129.4	C	1.88 ± 0.15
p-Methylphenyl	30	89.9	C	1.724 ± 0.059
		95.3	C	2.31 ± 0.15
		99.9	C	4.44 ± 0.16
		109.5	C	9.71 ± 0.27
		109.7	C	9.10 ± 0.41
p-Phenoxyphenyl	30	50.0	B	0.3756 ± 0.0051
			B	0.3735 ± 0.0018
			B	0.3961 ± 0.0054
		60.0	B	1.096 ± 0.018
			B	1.090 ± 0.005
		75.0	B	4.42 ± 0.06
			B	4.56 ± 0.02
			B	4.74 ± 0.06
p-Methoxyphenyl	30	30.0	A	1.404 ± 0.020
			A	1.434 ± 0.022
		45.0	A	7.37 ± 0.12
			A	7.26 ± 0.15
			A	7.10 ± 0.11
		60.0	A	31.20 ± 0.44
			A	30.92 ± 0.44
			A	30.35 ± 0.39
p-(N-Methylanilino)phenyl	30	0.0	D	349 ± 3
			D	309 ± 2
			D	340 ± 4
			D	372 ± 4
		10.0	D	1541 ± 41
			D	1672 ± 23
		12.5.0	D	2215 ± 16
			D	1770 ± 48
				1801 ± 34
			D	2345 ± 97
		15.0	D	2427 ± 31
	50	25.0	D	949 ± 27
	60	25.0	D	427 ± 6
	70	25.0	D	246.6 ± 2.1
	80	25.0	A	104.0 ± 0.9
	95	25.0	A	26.10 ± 0.28
	100	25.0	A	9.40 ± 0.18
			A	9.32 ± 0.28
		35.0	A	25.55 ± 0.41
			A	25.34 ± 0.22
		45.0	A	70.3 ± 1.3
			A	73.4 ± 1.8
		70.0	A	642 ± 21
p-(N,N-Dimethylamino)-phenyl	95	0.0	A	35.42 ± 0.34
			A	37.44 ± 0.49
			A	36.98 ± 0.35
			A	38.51 ± 0.91
		12.5	A	150.4 ± 2.7
			A	163.3 ± 5.2
			A	144.4 ± 2.6
	100	0.0	A	9.29 ± 0.12
			A	9.58 ± 0.11
		12.5	A	40.84 ± 0.44
			A	41.02 ± 0.47
		25.0	A	178.3 ± 19.6
			A	180.8 ± 3.1
			A	173.1 ± 1.7
2-Thienyl	30	30.0	A	2.861 ± 0.08
			A	2.85 ± 0.17
		45.0	A	17.03 ± 0.37
			A	15.96 ± 0.18
			A	15.38 ± 0.28
		60.0	A	65.7 ± 1.5
			A	66.2 ± 1.4
			A	64.1 ± 1.2
3-Thienyl	30	60.0	B	0.937 ± 0.013
			B	0.950 ± 0.005
		70.0	B	2.335 ± 0.033
			B	2.483 ± 0.036
		85.0	A	11.02 ± 0.15
			A	10.90 ± 0.12

Table III (*Continued*)

Aryl group	Solvent (% ethanol)	T, °C	Method[a]	10^5k, sec^{-1}
5-Methyl-2-thienyl	30	15.0	A	47.7 ± 1.2
			A	46.1 ± 1.5
		25.0	D	130.7 ± 0.4
			D	132.2 ± 0.2
		35.0	D	327 ± 1
			D	318 ± 1
	40	25.0	A	43.63 ± 0.24
	50	25.0	A	13.29 ± 0.14
	60	25.0	A	4.62 ± 0.11
	100	57.5	A	0.493 ± 0.005
			A	0.505 ± 0.018
		62.5	A	0.794 ± 0.019
			A	0.795 ± 0.005
		70.0	A	1.862 ± 0.022
			A	1.872 ± 0.013
5-Bromo-2-thienyl	30	52.5	A	5.81 ± 0.08
			A	5.91 ± 0.11
		67.0	A	22.34 ± 0.44
		76.9	A	54.41 ± 0.76
			A	51.52 ± 0.82
			A	52.32 ± 1.00
2-Furyl	30	15.0	A	2.280 ± 0.077
		25.0	A	7.07 ± 0.05
			A	7.23 ± 0.12
		40.0	A	31.64 ± 0.30
			A	33.54 ± 0.23
3-Furyl	30	60.0	A	0.935 ± 0.025
			A	0.946 ± 0.024
		70.0	A	2.52 ± 0.11
			A	2.42 ± 0.08
		85.0	A	8.85 ± 0.17
			A	8.80 ± 0.20
5-Methyl-2-furyl	30	0.0	A	81.6 ± 2.1
			A	79.5 ± 3.7
		12.4	D	338 ± 2
			D	323 ± 4
			D	363 ± 7
			D	338 ± 1
		25.0	D	1160 ± 5
			D	1176 ± 10
			D	1165 ± 5
	60	25.0	A	51.8 ± 2.3
	95	35.0	A	3.28 ± 0.17
			A	3.17 ± 0.05
		50.0	A	14.45 ± 0.64
			A	15.87 ± 0.27
			A	14.97 ± 0.30
	100	35.0	A	0.5889 ± 0.0040
			A	0.5875 ± 0.0017
		50.0	A	3.197 ± 0.022
			A	3.063 ± 0.032
		70.0	A	20.42 ± 0.64
			A	19.49 ± 0.68
1-Methyl-2-pyrrolyl	100	−7.75		50.0 ± 1.2
		0.0	A	117 ± 3
			A	123 ± 3
			A	116 ± 2
			A	114 ± 2
		5.25	A	245 ± 7
			A	235 ± 5
			A	239 ± 6
		13.0	A	507 ± 18
			A	433 ± 20
			A	471 ± 17
2-Benzothienyl	30	50.0	B	0.2156 ± 0.0006
			B	0.2220 ± 0.0021
		60.0	B	0.6266 ± 0.0025
			B	0.6309 ± 0.0046
		75.0	B	2.794 ± 0.042
			B	2.819 ± 0.041
3-Benzothienyl	30	50.0	B	0.6195 ± 0.0074
			B	0.6232 ± 0.0058
		60.0	B	1.667 ± 0.021
			B	1.785 ± 0.013
			B	1.77 ± 0.020
		75.0	B	7.72 ± 0.17
			B	7.45 ± 0.12

Table III (*Continued*)

Aryl group	Solvent (% ethanol)	T, °C	Method[a]	10^5k, sec^{-1}
2-Benzofuryl	30	55.0	B	0.546 ± 0.005
			B	0.557 ± 0.002
		70.0	B	2.617 ± 0.026
			B	2.642 ± 0.055
			B	2.610 ± 0.024
		80.0	B	6.604 ± 0.072
			B	6.587 ± 0.095
3-Benzofuryl	30	55.0	A	0.491 ± 0.004
			A	0.459 ± 0.006
		60.0	A	0.838 ± 0.020
			A	0.850 ± 0.027
		70.0	A	2.28 ± 0.12
			A	2.21 ± 0.06
1-Methyl-2-indolyl	30	30.0	D	196.4 ± 1.3
			D	195.3 ± 1.1
		35.0	D	276.7 ± 1.6
			D	269.1 ± 1.7
		45.0	D	699 ± 12
			D	653 ± 4
			D	669 ± 7
	100	50.0	A	0.906 ± 0.019
			A	0.924 ± 0.013
		60.0	A	2.581 ± 0.007
			A	2.575 ± 0.047
		70.0	A	7.17 ± 0.26
			A	6.86 ± 0.21
1-Methyl-3-indolyl	100	5.3	A	238 ± 6
			A	253 ± 20
			A	260 ± 5
		11.5	A	536 ± 26
			A	553 ± 18
			A	491 ± 22
	100	0.0	A	123.8 ± 2.8
			A	129.9 ± 2.0
			A	131.7 ± 2.8
9-Ethyl-3-carbazolyl	30	25.0	D	81.74 ± 0.33
			D	82.13 ± 0.26
			D	79.47 ± 0.38
		35.0	D	200.0 ± 1.3
			D	192.2 ± 1.5
		45.0	D	518 ± 14
			D	485 ± 3
	40	25.0	A	25.3 ± 1.4
	50	25.0	A	11.23 ± 0.14
	60	25.0	A	5.192 ± 0.053
	70	25.0	A	2.407 ± 0.024
	80	25.0	A	1.126 ± 0.014
	90	25.0	A	0.381 ± 0.010
	100	50.0	A	1.089 ± 0.030
			A	1.049 ± 0.011
		62.5	A	3.95 ± 0.02
			A	3.84 ± 0.04
		70.0	A	7.29 ± 0.16
			A	6.97 ± 0.05
α-Naphthyl	30	85.0	C	0.268 ± 0.020
		112.4	C	4.28 ± 0.07
Ferrocenyl	30	−13.4	D	384 ± 3
	30	−10.1	D	522 ± 3
	30	−6.7	D	947 ± 36
	30	−4.95	D	1023 ± 3
	30	0.0	D	1562 ± 18
	30	0.0	D	1573 ± 9
	30	0.0	D	1483 ± 15
	50	25.0	D	1606 ± 10
	60	25.0	D	564 ± 8
	70	25.0	D	317.5 ± 1.4
	80	25.0	A	151.8 ± 1.1
	100	25.0	A	9.24 ± 0.09
			A	8.68 ± 0.10
		35.0	A	28.60 ± 0.20
			A	28.48 ± 0.30
		50.0	A	131.0 ± 4.0
			A	128.6 ± 2.6

[a] Kinetic methods: A, titration of aliquots; B, same, but using calculated infinity value; C, aliquots sealed in evacuated tubes; D, titration of acid by rapid intermittant addition of base to reacting solution.

acid (3.0 g, 43%) and 3-acetylfuran (1.78 g, 45% based on unrecovered starting material), and purified by sublimation at 27° (3 mm): mp 48-50° [lit.[53] mp 53-54°]; ir (Nujol) 1660 cm^{-1} (C=O).

3-Acetylfuran (1.77 g, 0.016 mole) was reduced with lithium aluminum hydride to 1-(3-furyl)ethanol, which was directly converted to the acetate with acetic anhydride (3.0 g, 0.029 mole) in pyridine (1.0 ml) in 73% over-all yield from ketone: bp 53-55° (3.25 mm); n^{25}D 1.4521; ir (neat) 1745 (C=O), 1250 cm^{-1}; nmr (CCl$_4$), δ 1.47 (d, 3, J = 6.6 Hz, CH$_3$), 1.93 (s, 1, CH$_3$CO); 5.92 (q, 1, J = 6.6 Hz, CHOAC), 6.43 (m, 1, aromatic), and 7.30-7.48 ppm (m, 2, aromatic).

Anal. Calcd for $C_8H_{10}O_3$: C, 62.32; H, 6.54. Found: C, 62.56; H, 6.68.

1-(5-Methyl-2-furyl)ethyl Acetate. 5-Methyl-2-acetylfuran[50] was reduced with lithium aluminum hydride in ether to yield 1-(5-methyl-2-furyl)ethanol. The crude alcohol (12.0 g) was converted to the acetate with acetic anhydride (17.7 g, 0.15 mole) in pyridine (12 moles): bp 34-36° (0.02-0.05 mm); n^{25}D 1.4602; ir (neat) 1740 (C=O), 1240 cm^{-1}; nmr (CCl) δ 1.52 (d, 3, J = 6.5 Hz, CHCH_3), 1.95 (s, 3, CH$_3$CO), 2.78 (d, 3, J = 0.8 Hz, ring CH$_3$), 5.73 (q, 1, J = 6.5 Hz, CHOAC), 5.73-6.22 ppm (AB pattern with additional coupling, 2, J_{AB} = 3.2 Hz, aromatic).

Anal. Calcd for $C_9H_{12}O_3$: C, 64.27; H, 7.19. Found: C, 63.75; H, 7.42.

1-(2-Benzofuryl)ethyl Acetate. 2-Acetylbenzofuran[54] was reduced with lithium aluminum hydride to 1-(2-benzofuryl)ethanol, mp 40° (ligroin) [lit.[54] mp 41°]. Reaction of the alcohol (21.0 g, 0.13 mol) with acetic anhydride (13.3 g, 0.13 mole) for 27 hr in dry pyridine (16 ml) yielded the acetate in 76% yield: bp 127-129° (0.9-1.25 mm); n^{24}D 1.5370; ir (neat) 1740 (C=O), 1235 cm^{-1}; nmr (CCl$_4$) δ 1.62 (d, 3, J = 6.5 Hz, CH$_3$), 1.99 (s, 3, CH$_3$CO), 6.03 (q, 1, J = 6.5 Hz, CHOAC), 6.57 (m, 1, aromatic), 7.63-7.95 (m, 4, aromatic).

Anal. Calcd for $C_{12}H_{12}O_3$: C, 70.57; H, 5.92. Found: C, 70.29; H, 5.98.

1-(3-Benzothienyl)ethyl Acetate. 3-Acetylbenzofuran[55] (2.25 g, 0.014 mole) was reduced with lithium aluminum hydride in ether, and the crude alcohol was directly converted to the acetate with acetic anhydride (3 g, 0.028 mole) in pyridine (5 ml), in 63% over-yield from the ketone. A second fractionation to remove small amounts of olefinic material yielded pure acetate: bp 83° (0.40 mm); n^{25}D 1.5330; nmr (CCl$_4$) δ 1.60 (d, 3, J = 6.6 Hz, CH$_3$), 1.97 (s, 3, CH_3CO), 6.13 (doubled quartet, 1, J = 6.6, 0.8 Hz, CHOAC), 7.34-7.70 ppm (m, 5, aromatic).

Anal. Calcd for $C_{12}H_{12}O_3$: C, 70.57; H, 5.92. Found: C, 70.85; H, 5.96.

1-(1-Methyl-2-pyrrolyl)ethyl Acetate. 1-(1-Methyl-2-pyrrolyl)-ethanol was prepared by addition of methyllithium (0.0245 mole) to 1-methylpyrrole-2-carboxaldehyde (3.14 g, 0.0196 mole) in ether. The crude alcohol was dissolved in freshly distilled triethylamine (20 ml), and the solution was cooled to −8° in an ice bath. An equivalent amount of acetyl chloride was added by syringe, and the resulting mixture was stirred for 5 min and allowed to warm to room temperature. Pentane (50 ml) was added, and the precipitated amine hydrochloride was filtered. The filtrate was stored in a freezer as a stock solution; solvent was removed under vacuum whenever the acetate was needed. The resulting product was unstable and polymerized within 1 hr at room temperature. Attempted syntheses by the standard procedure (acetic anhydride-pyridine) or by reaction of the methyllithium aldehyde reaction product with acetic anhydride were unsuccessful. The product was shown to be a mixture of 1-(1-methyl-2-pyrrolyl)ethanol [ir (neat) 3330 (OH); nmr (CCl$_4$) δ 1.42 (d, 3, J = 6 Hz, CHCH_3), 3.50 (s, 3, NCH_3), 3.98 (s, 1, OH), 4.63 ppm (q, 1, J = 6 Hz, CHOH)] and 1-(1-methyl-2-pyrrolyl)ethyl acetate [ir 1730 (C=O), 1240 cm^{-1}; nmr δ 1.50 (d, 3, J = 6 Hz, CHCH_3), 1.85 (s, 3, CH_3CO), 3.42 (s, 3, N-CH$_3$), and a multiplet at 5.68-6.17 ppm, including CHOAC and aromatic protons of both compounds]. Integration of the nmr spectrum showed that the mixture was 45% acetate.

1-(1-Methyl-2-indolyl)ethyl acetate was received as a gift from Dr. W. E. Noland, and was purified by sublimation at 85° (0.01 mm): mp 90-91°; ir (Nujol) 1730 (C=O), 1245 cm^{-1}.

1-(1-Methyl-3-indolyl)ethyl Acetate. 1-Methyl-3-acetylindole[56] (2.0 g, 0.0116 mole) was reduced with lithium aluminum hydride in ether at 0°. The crude alcohol was dissolved in freshly distilled triethylamine (20 ml), and freshly distilled acetyl chloride (0.81 ml, 0.0113 mole) was added dropwise to the stirred solution maintained at 0°. The resulting mixture was allowed to warm to room temperature and pentane (50 ml) was added. The precipitated amine hydrochloride was filtered, and the filtrate concentrated in a vacuum (maintained below room temperature) to give a light brown oil (2.0 g), which polymerized on standing at room temperature. The product was shown to be a mixture of 1-(1-methyl-3-indolyl)-ethanol [ir (neat) 3330 cm^{-1}(OH); nmr (CCl$_4$) δ 1.53 (d, 3, J = 6.5 Hz, CHCH_3), 3.33 (s, 3, NCH_3), 4.98 (s, 1, OH), 5.02 ppm (q, 1, J = 6.5 Hz, CHOH)] and 1-(1-methyl-3-indolyl)ethyl acetate [ir 1725 (C=O), 1245 cm^{-1}; nmr δ 1.60 (d, 3, J = 7 Hz, CHCH_3), 1.83 (s, 3, COCH_3), 3.33 (s, 3, NCH_3), 6.20 (q, 1, J = 7 Hz, CHOAC), and multiplets at 1.67-7.20 and 7.52-7.78 ppm (aromatic protons of both compounds)]. Integration of the nmr spectrum showed that the mixture contained 70% of the acetate.

1-(9-Ethyl-3-carbazolyl)ethyl Acetate. 3-Acetyl-9-ethylcarbazole[57] (13.1 g, 0.055 mole) was reduced with lithium aluminum hydride in ether. The crude alcohol was converted to the acetate with acetic anhydride (10 g, 0.094 mole) in dry pyridine (20 ml) for 45 hr: mp 52-54° (petroleum ether, bp 60-70°); ir (Nujol) 1730 (C=O), 1235 cm^{-1}; nmr (CCl$_4$) δ 1.30 (t, 3, J = 7.0 Hz, CH$_2$CH_3), 1,60 (d, 3, J = 6.5 Hz, CHCH$_3$), 1.97 (s, 3, CH_3CO), 4.17 (q, 2, J = 7.0 Hz, NCH_2), 6.03 (q, 1, J = 6.5 Hz, CHOAC), 6.90-7.53 (m, 5, aromatic), 7.87-8.17 ppm (m, 2, aromatic).

Anal. Calcd for $C_{18}H_{19}NO_2$: C, 76.84; H, 6.81; N, 5.25. Found: C, 77.11; H, 6.61; N, 5.24.

Acetate deuterated in the position α to the ring was made in analogous fashion, using lithium aluminum deuteride. The nmr spectrum was consistent with essentially complete deuteration.

1-Ferrocenylethyl acetate[58] was prepared as reported previously, and purified by sublimation at 70° (0.2 mm): mp 67.5-69° [lit. mp 67-68°, 70.2-71°]; ir (Nujol) 1730 (C=O), 1240 cm^{-1}.

Solvolysis products were isolated in several instances. In the solvolysis of 1-(p-N,N-dimethylamino)ethyl acetate in ethanol, water was added and the product was extracted with ether, dried, and the solvent was removed, yielding an oil whose nmr spectrum was consistent with the ethyl ether: δ 1.08 (t, 3, J = 7.0 Hz, CHCH_3), 2.87 (s, 6, NCH_3), 3.23 (q, 2, J = 7.0 Hz, OCH_2), 4.18 (q, 1, J = 6.0 Hz, OCH), 6.50-7.17 ppm (m, 4, aromatic). 1-(p-N,N-Dimethylaminophenyl)ethyl azide was isolated in 65% yield by solvolysis of the acetate (1.20 g, 0.006 mole) in 200 ml of 0.05 M sodium azide in 95% ethanol. The solvent was stripped under vacuum, and the residue taken up in ether, washed with water, dried, and distilled: bp 88-90° (0.10 mm); n^{25}D 1.5601; ir (neat) 2100 cm^{-1} (N=N).

1-(3-Benzothienyl)ethyl acetate (0.3484 g) was solvolyzed for 8.5 half-lives at 75° in 100 ml of 30% ethanol which was 0.035 M in sodium azide. The reaction solution was cooled and poured into ice water, and extracted with ether to yield, after drying and evaporation, an oil: ir (neat) 2100 (N=N), 3300 cm^{-1} (OH). In the nmr spectrum, the presence of the alcohol (39%) was determined by the coincidence of peaks with an authentic sample, the ethyl ether (30%) by the presence of typical ethoxy absorption at δ 1.03 and 3.25 ppm, and the azide (31%) by difference in the regions for the CHCH$_3$ absorptions.

Kinetics

The aqueous ethanol solvents were prepared by mixing the nominal volumes of ethanol and water, both solvents measured at 25°. Boiled deionized water and absolute alcohol were used. 100% ethanol solvent was used from freshly opened pint bottles.

Most solvolyses were carried out in 100-ml volumetric flasks. Liquid substrates or solutions of a solid substrate in 0.5 ml of acetone were injected by syringe. Aliquots were removed at appropriate intervals, and quenched by an equal volume of solvent (95% ethanol

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(53) P. Grunanger and A. Mantogani, *Gazz. Chim. Ital.*, **89**, 913 (1959).

(54) E. D. Elliott, *J. Am. Chem. Soc.*, **73**, 754 (1951); attempts to prepare 2-acetylbenzofuran from coumarilic acid and methyllithium in ether or tetrahydrofuran were unsuccessful.

(55) M. Martynoff, *Bull. Soc. Chim. Fr.*, 1056 (1952).

(56) Received as a gift from Dr. W. E. Noland.

(57) N. G. Ph. Buu-Hoi and R. Royer, Jr., *J. Org. Chem.*, **15**, 123 (1950).

(58) F. S. Arimoto and A. C. Haven, Jr., *J. Am. Chem. Soc.*, **77**, 6295 (1955); E. A. Hill and J. H. Richards, *ibid.*, **83**, 3840 (1961).

or acetone) at a temperature appropriate to the rapidity of the reaction. The solvent had previously been purged with nitrogen, and was agitated during titration by further bubbling. Acetic acid formed in the solvolysis was titrated with 0.01–0.02 *M* sodium hydroxide, using a micrometer microburet, to a cresol red, phenol red, or *m*-cresol purple end point. In a few instances, titrations were made with an automatic titrator (Radiometer) to the predetermined end point pH. In most cases, the reaction was followed through at least 2 half-lives, with at least eight to ten points taken and an infinity titer was taken in duplicate after 10 half-lives. In a few instances where reactions were quite slow, so that solvent evaporation might introduce errors, a calculated value was used. In all runs over 50°, the pipet was preequilibrated to the bath temperature.

For a few reactions, variations in the procedure described above were necessary. (1) For the slowest substrates (phenyl, *p*-methylphenyl, and 1-naphthyl), 5-ml aliquots were sealed under vacuum in glass tubes, heated appropriate periods of time, and analyzed as before. In the case of the two first-mentioned substrates, it was found that infinity titers were smaller than expected, and decreased further with time beyond 10 half-lives. Examination of the solvolysis solutions by gas chromatography (FFAP) showed that significant amounts of ethyl acetate had been formed. It was necessary to correct the infinity titer, and in most cases, points beyond the first half-life, for the amount of acetic acid converted to ethyl acetate, as determined by gas chromatography. In the case of 1-naphthyl, the reaction was followed through less than 1 half-life, and the calculated infinity value was used, so correction was not needed. (2) For reactions studied at lower temperature, runs were carried out in a flask equipped with a nitrogen inlet, which enabled sweeping of the mouth of the flask to prevent moisture condensation. The pipet for removal of aliquots was cooled to the bath temperature. (3) Reactions with half-lives of less than 10 min were conveniently followed by "rapid intermittant titration" of the acid as formed in the reaction solution.[59] Titrations were made with sodium hydroxide or ethoxide in the appropriate solvent, to the visual color change of a phenol red indicator. The absence of base catalysis under these conditions was demonstrated by the identity of rates obtained in duplicate determinations in which the pH was maintained predominantly on the acidic and basic sides of the indicator end point, and the consistency of results obtained by rapid intermittant titration with those from the aliquot technique. Generally 15–20 points were taken although the number was smaller for the most rapid reactions. In reactions studied in 95 or 100% ethanol, peculiar behavior was encountered. The basic indicator color was observed after the first addition of base, and it changed after a short time to the yellow acidic color, but subsequent additions of base produced no color change. After the expected infinity time for the reaction, normal indicator behavior was again observed. Solvolyses by the aliquot technique, by rapid intermittent titration using a pH meter as indicator, and single kinetics points derived from the first addition of base showed that the peculiarities did not lie in the solvolysis reaction itself. It is concluded that for the most reactive substrates, the highly stabilized carbonium ion reacts selectively with the basic form of the indicator, producing a "trapping product" with visible spectrum similar to that of the acid form. With extended reaction times, this product solvolyzes, freeing the indicator for normal behavior.

Several solvolyses were performed in the presence of added solutes: sodium hydroxide, sodium perchlorate, sodium azide, and sodium acetate. Results are listed in Table II. With sodium hydroxide, aliquots were added to a quenching solution containing enough acetic acid to neutralize the base, and then back-titrated in the normal manner with sodium hydroxide. In reactions with sodium hydroxide, acetate, and azide, precision was reduced somewhat by the buffering action of the salt on the titration. In the solvolysis of 1-(*p*-N,N-dimethylaminophenyl)ethyl acetate, no acid formation was noted in the presence 0.05 *M* sodium azide. With 2.0×10^{-3} *M* sodium azide, no acid formation was observed for 16.5 min, after which time acid formation followed first-order kinetics. The solvolysis rate of the azide was determined for use in correcting infinity values for the acetate solvolyzed in the presence of sodium azide.

Rate constants were calculated by a weighted least squares procedure that has been described previously.[60] The rate constants of individual runs are listed in Table III. Individual uncertainties are 80% confidence limits. In a few instances, in which differences between runs were substantially greater than the confidence limits, it is probable that a systematic experimental error within a run is present, such as evaporation of solvent on slow reactions, or insufficient temperature control at low temperatures. Activation parameters and extrapolated or interpolated best rates at 25° were also evaluated by a least-squares analysis, in which each run was weighted according to the inverse of the variance in its rate constant. These results are in Table I. Uncertainties are again 80% confidence limits. The least squares slope was determined for σ^+–ρ correlations, and new σ^+ values were derived from the correlation line. As an indication of the sensitivity of the substituent constants to experimental errors, it may be noted that with the derived ρ value of -5.70, rate constants in error by factors of 1.25 and 2.00 would lead to errors in σ^+ values of 0.017 and 0.052 units, respectively.

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[60] E. A. Hill and J. H. Richards, *J. Am. Chem. Soc.*, **83**, 3840 (1961); F. S. Acton, "Analysis of Straight-Line Data," John Wiley and Sons, Inc., New York, N. Y., 1959, pp 23–24. We gratefully acknowledge the contribution of computer time by the UWM Computer Center.