with ether, washed, dried, and hydrogenated over prereduced platinum oxide. Removal of ether (spinning-band column) and preparative gas chromatography (3 ft × 0.25 in., 20% diethylene glycol adipate column) gave 0.43 g of pure material having the retention time of 2- and 3-chloroheptane. Since these chloroheptanes were not separated on four different capillary columns, the mixture from pyrolysis and hydrogenation was analyzed by comparison of the nmr spectrum (neat) with spectra of quantitatively prepared mixtures of 2- and 3-chloroheptane. The spectrum was identical with that of a mixture prepared from 100 μl of 2-chloroheptane and 12 μl of 3-chloroheptane (corresponding to 10.7 mole % 3-chloroheptane). Assuming that our procedure did not result in selective product formation from the original mixture, or in chlorine migration, during pyrolysis (both assumptions seem to be reasonably good) the above-mentioned percentage is a measure of the chlorine shifted products in the cyclopropane ring-opening reaction.

Registry No.—**1a**, 930-57-4; **1b**, 15451-38-4; **1c**, 15451-39-5; **1d**, 15451-40-8; trifluoroacetic acid, 76-05-1.

Solvents of Low Nucleophilicity. XI. Modified Aromatic σ Values in the Addition of Trifluoroacetic Acid to Phenylbutenes[1]

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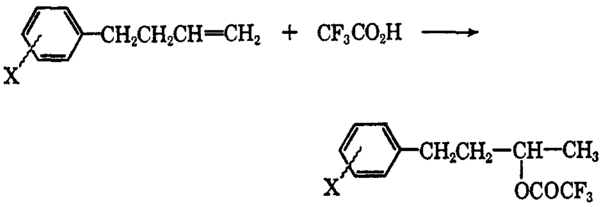
Rates of addition of trifluoroacetic acid to 4-phenyl-1-butenes substituted in the *meta* and *para* positions of the benzene ring were determined. Oxygen- and nitrogen-containing substituents were more electron attracting than expected from the σ^0 values of the substituents, owing to hydrogen bonding of the solvent to the substituents. The solvent modification of aliphatic and aromatic σ values is compared.

In connection with studies of enhanced inductive effects in trifluoroacetic acid attributable to hydrogen bonding between trifluoroacetic acid and oxygen- or nitrogen-containing groups,[2] we were prompted to examine the effect of such hydrogen bonding on aromatic substituent effects.

The reaction of substituted phenylbutenes with trifluoroacetic acid (eq 1) appeared to be ideally suited for such a study. The desirable absence of phenyl participation in this system may be inferred from the studies of Heck and Winstein.[3] Also, the potential cationic carbon in the carbonium ion intermediate which may be envisioned for the reaction of eq 1 is just far enough from the phenyl group to prevent rearrangement to a more stable benzyl cation by hydrogen shift in the rate-determining step.[4] Finally the large effects of distant substituents upon reaction rates for addition of trifluoroacetic acid to alkenes suggests that rate effects should be large compared to experimental errors, despite the relative remoteness of the substituents in the phenylbutenes. Actually there are only a few studies of aromatic substituent effects in cases where there is no possible conjugation between the substituent and the reaction site, and the discovery of additional reactions suitable for such studies is of interest itself.



(1)

Results

The phenylbutenes were obtained as a gift (for a reference, see the Acknowledgment), or synthesized as described in the Experimental Section. The rates of reaction with trifluoroacetic acid, measured at 60.0°, are given in Table I. Also listed are "effective σ_I" values to be discussed later. It is interesting that the rate constants vary over a range of 40-fold (for *p*-methyl and *p*-cyano) despite the distance of seven carbons between the substituent and the reaction site (counting the cationic carbon as 1). A Hammett plot of the data, using σ^n values[5] is shown in Figure 1. The correlation line is drawn through the points for nonhydrogen-bonding substituents. The substantially increased electron-attracting effect of oxygen- and nitrogen-containing substituents, ascribable to hydrogen bonding of the solvent to the substituent, is immediately apparent.

Table I

Rates of Addition of Trifluoroacetic Acid to 4-Phenyl-1-butenes at 60.0°

Substituent	10^6k, sec^{-1}	Effective σ_I[a]
p-CH_3	408	0.063
m-CH_3	353	0.080
H	257	0.1[b]
p-OCH_3	218	0.112
p-Cl	93.5	0.168
m-OCH_3	87.4	0.181
p-Br	84.5	0.176
m-Cl	71.7	0.206
p-CO_2CH_3	31.2	0.259
p-$COCH_3$	18.0	0.300
p-CN	10.5	0.341

[a] Values of σ_I for the substituted phenyl groups, calculated according to eq 11 (*cf.* discussion section). [b] From ref 12.

Present Status of Solvent Modified σ Values.—Before proceeding to a closer examination of solvent-

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[1] Supported in part by National Science Foundation Grant GP 2917.

[2] P. E. Peterson, C. Casey, E. V. P. Tao, A. Agtarap, and G. Thompson, *J. Amer. Chem. Soc.*, **87**, 5163 (1965).

[3] R. Heck and S. Winstein, *ibid.*, **79**, 3105 (1957).

[4] Similar direct formation of a phenylethyl-type bridged cation cannot be ruled out *a priori*.

[5] The origin and applicability of σ^n values, which differ slightly from the Hammett σ values, is reviewed in the next section.

modified σ values observed in our study, it is appropriate to review briefly the somewhat complex picture which has evolved from recent studies of substituent effect correlations. The original Hammett σ values, based on substituted benzoic acid ionization constants, are now known to include some discernible effects of direct interactions between resonance–donor substituents such as p-CH_3O and the reaction site. By scrupulously excluding cases which might involve such interactions and using several reaction series, Bekkum, Verkade, and Wepster[6] obtained normal "σ^n" values presumably applicable to nonconjugating reaction sites of the type considered in the present paper. Using remote reaction sites (in phenylacetic acid ionizations) Taft[7] derived a similar set of values, designated σ^0. Some success was achieved in making a separation of σ^0 values into an inductive (polar) effect, σ_I, and a resonance effect $\sigma^0{}_R$, according to eq 2 and 3 which

$$\sigma_p{}^0 = \sigma_I + \sigma_R{}^0 \tag{2}$$

$$\sigma_m{}^0 = \sigma_I + 0.5\sigma_R{}^0 \tag{3}$$

are applicable to *para* and *meta* substituents, respectively, in reactions where there is no direct resonance between the substituent and the reaction site. For other reaction series correlated by the original Hammett σ values, a similar set of simultaneous equations (4 and 5) could be solved to yield approximately the

$$\sigma_p = \sigma_I + \sigma_R \tag{4}$$

$$\sigma_m = \sigma_I + {}^1/_3\sigma_R \tag{5}$$

same σ_I values, which are applicable also to *aliphatic* reactivity, but solution for σ_R values gave variable results for different reactions, suggesting that the correlation with Hammett σ values was itself a somewhat rough approximation in that slightly varying resonance effects were ignored.

The σ_I values "extracted" from aromatic σ values were found to be linearly related to "aliphatic" σ^* values, according to eq 6. Accordingly, values ob-

$$\sigma_I = 0.45\sigma^* \tag{6}$$

tained from either origin may be used interchangeably, although in practice the user must select a source of σ_I values if slightly differing values are available from aromatic and aliphatic reactivity, respectively. Attempts to further improve eq 2 and 3 by allowing variability of the parameters gave only inconclusively better results,[8] suggesting that 2 and 3 are adequate at present.

Finally, unexpected, but voluminously documented, correlations of σ_I and $\sigma_R{}^0$ with *meta*-substituted and *para*-substituted fluorobenzene fluorine nmr frequencies were reported, the *meta* frequencies surprisingly yielding *aliphatic* inductive constants directly according to eq 7.[9]

$$\int_{\mathrm{H}}^{m\text{-X}} = -7.10\,\sigma_I + 0.6\text{ ppm} \tag{7}$$

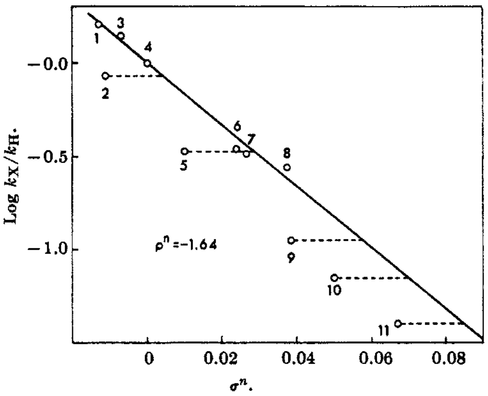

Figure 1.—Plot of log k_X/k_H *vs.* σ^n for Substituted Phenylbutenes. Identification: 1, p-CH_3; 2, p-CH_3O; 3, m-CH_3; 4, H; 5, m-CH_3O; 6, p-Cl; 7, p-Br; 8, m-Cl; 9, p-CO_2CH_3; 10, p-$COCH_3$; 11, p-CN.

Frequencies of fluorobenzenes substituted in the *para* position with a group which is electron releasing by resonance were found to be correlated with the resonance parameters $\sigma_R{}^0$, especially when the relatively small "inductive" contribution, $\int_{\mathrm{H}}^{m\text{-X}}$, was subtracted (eq 8).[10] These relationships serve to de-

$$\int_{\mathrm{H}}^{p\text{-X}} - \int_{\mathrm{H}}^{m\text{-X}} = -29.5\,\sigma_R{}^0 \tag{8}$$

fine σ values in instances where reactivity data are not available. Furthermore they are subject to several discernible solvent effects, of which enhancements of σ_I and $\sigma_R{}^0$ values in trifluoroacetic acid are perhaps the most striking. But are the enhanced values applicable to *reactivity?* In the absence of experimental data, the authors[10] speculated that "the solvent effects on σ_R values obtained from eq 7 and 8 (this paper) may be taken to indicate the expected magnitudes of solvent effects on the reactivity effects of (hydrogen bonding) substituents, but the precise quantitative applicability of these substituent parameters is questionable."

Comparison of Nuclear Magnetic Resonance and Reactivity Data.—The rates of reaction of substituted phenylbutenes (Table I), along with early studies of substituted aliphatic alkenes, now provide a fairly comprehensive picture of the solvent modification of σ values as judged from reactivities in trifluoroacetic acid. In Table II values of $\Delta\sigma_I$ from nmr data for the change from normal solvents to trifluoroacetic acid are compared with $\Delta\sigma^n$ and $\Delta\sigma^0$ values based on deviations

TABLE II

SOLVENT MODIFICATION OF σ VALUES

Substituent	σ^n	σ^0	$\Delta\sigma^n$ [a]	$\Delta\sigma^0$ [b]	$\Delta\sigma_I$ (nmr)[c]
p-CH_3O	−0.111	−0.12	0.185	0.166	0.26
m-CH_3O	0.10	0.13	0.155	0.165	0.26
p-CO_2CH_3	0.385	0.46	0.173	0.119	0.24
p-$COCH_3$	0.502	0.46	0.201	0.270	0.28
p-CN	0.67	0.69	0.175	0.187	0.26
Average			0.178	0.181	

[a] Based on deviations from the "least squares" line through points for nonhydrogen-bonding substituents, log $k_H/k_X = -1.64\sigma^n - 0.004$. [b] Based on deviations from the "least squares" line log $k_H/k_X = -1.58\sigma^0 - 0.010$. [c] From ref 9.

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(6) H. Van Bekkum, P. E. Verkade, and B. M. Wepster, *Rec. Trav. Chem.*, **78**, 815 (1959).

(7) R. W. Taft, *J. Phys. Chem.*, **64**, 1805 (1960), and references cited therein.

(8) S. Ehrenson, *Progr. Phys. Org. Chem.*, **2**, 195 (1964).

(9) R. W. Taft, E. Price, I. R. Fox, I. C. Lewis, K. K. Anderson, and G. T. Davis, *J. Amer. Chem. Soc.*, **85**, 709 (1963).

(10) R. W. Taft, E. Price, I. R. Fox, I. C. Lewis, K. K. Anderson, and G. T. Davis, *ibid.*, **85**, 3146 (1963).

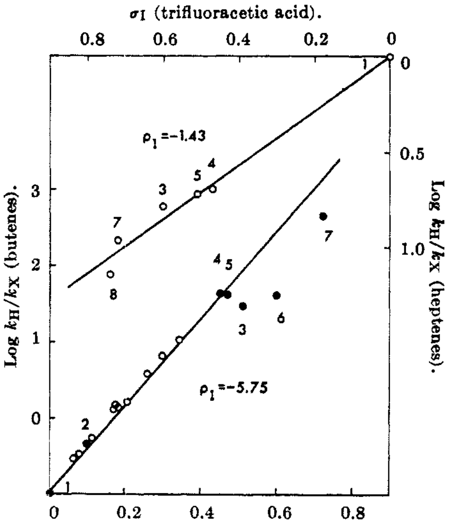
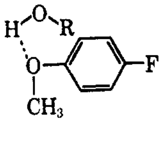


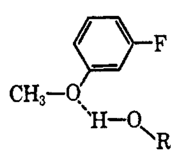
Figure 2.—Plot of log k_X/k_H vs. σ_I (trifluoroacetic acid) for the reaction of 4-substituted 1-butenes (lower plot) and 7-substituted 1-heptenes with trifluoroacetic acid. Note the reversed coordinate direction and changed scale in the heptene (upper) plot. Identification: 1, H; 2, C_6H_5; 3, OCH_3; 4, Br; 5, Cl; 6, $OCOCH_3$; 7, $OCOCF_3$; 8, C≡N. For the identification and description of our derived σ_I values for the substituted phenylbutenes (open circles, lower plot), see Table I and the discussion section.

from the correlation line of the Hammett plot of Figure 1 and the similar plot in which σ^0 values are used. In only one instance (p-CH_3O) does the available nmr data permit calculation of $\Delta\sigma_R{}^0$ from eq 8. Since the value of $\Delta\sigma_R{}^0$ thus derived is only 0.09, we may hopefully infer that the $\Delta\sigma_I$ values represent a large part of the solvent shift of $\sigma_m{}^0$ and $\sigma_p{}^0$ values derived from substituted fluorobenzene nmr data. This assumption certainly is subject to question, but some support is provided by the observation that $\Delta\sigma_I$ values from nmr data are larger than the over-all changes $\Delta\sigma$ based on phenylbutene reactivity. The nmr method seems to have overestimated the solvent shift of σ values, but it does reproduce the tendency for all $\Delta\sigma^n$ values to be essentially identical among the substituents studied. The somewhat different solvent shifts exhibited by $\Delta\sigma^0$ are attributable to the fact that our $\Delta\sigma$ values are only a few times larger than the expected errors in σ values. The largest discrepancy between σ^n and σ^0 values occurs for the p-CO_2R group (σ^n = 0.38, σ^0 = 0.46). The smaller σ^n value seems preferable in this instance because it seems likely that the carbethoxy group is less electron withdrawing than the p-$COCH_3$ group (σ^n = 0.50, σ^0 = 0.46), and also because it seems likely that the $\Delta\sigma$ values of these groups should be similar in magnitude, as found for $\Delta\sigma^n$ values.

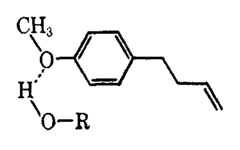
It is instructive to compare the hydrogen-bonded structures involved in the two types of measurement of substituent effect enhancement. This comparison is made below (structures **1a**, **1b**, and **2** for a typical substituent, OCH_3). Both **1a** and **1b** used for the nmr measurements, and **2**, used for the reactivity measurement, are comparable in structure in that an aromatic substituent is involved in each instance, although it could be argued that **1b** will contain an abnormally weak hydrogen bond, compared with **2**, as a consequence of the inductive effect of the *meta* fluorine. Such an effect would lead to smaller solvent modifications of σ values derived from nmr data, contrary to the observed trend. It is possible that the nmr data is influenced by differential hydrogen bonding to fluorine in fluorobenzene and substituted fluorobenzenes, an effect not present in phenylbutenes.[11] In conclusion, despite the similar structures of **1a**, **1b**, and **2**, nmr data seems to provide only a semiquantitative guide to solvent modifications of σ values, as originally anticipated.[10]



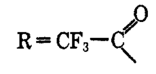
1a



1b

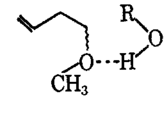


2

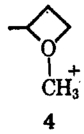


$R = CF_3-C(=O)-$

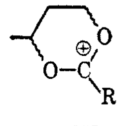
An even less favorable occasion for correlation arises in the comparison of **1b** with structures such as **3** (4-methoxy-1-butene) where the hydrogen-bonding capacity of the aromatic and aliphatic substituents might be expected possibly to be quite different. Nevertheless the previously discussed identification of *meta*-substituted fluorobenzene frequencies with *aliphatic* σ_I values (eq 6) seems to lead to a comparison of this type. A Hammett–Taft plot, in which σ_I values are used, offers a means of correlating the rates of reaction of 4-substituted 1-butenes, determined previously,[2] with those of phenylbutenes, reported in this paper. Since we have no other applicable values of σ_I available, we have nothing to lose from the inclusion of hydrogen-bonding substituents and enhanced σ_I values from nmr data in such a plot. We may, in any event, use nonhydrogen-bonding substituents and the corresponding solvent independent σ_I values from nmr data to establish the correlation line. Such a plot for 4-substituted 1-butene reactions is shown in Figure 2, with the correlation line passed through points for the nonhydrogen-bonding substituents chlorine and bromine. The incorporation of points for substituted phenylbutenes into the plot of Figure 2 is discussed in the next section. The hydrogen-bonding substituents for 4-substituted 1-butenes deviate from the line in a direction which could indicate that solvent augmented σ_I values have been over-estimated by the nmr method, or else that the rates of reaction of these substituents are faster than expected, owing perhaps to neighboring-group participation to give transition states of types **4** or **5**.



3



4



5, R = CH_3, CF_3

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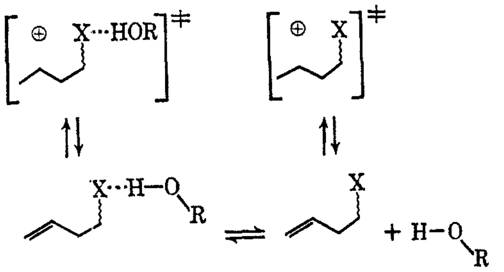
[11] For a study of the hydrogen-bonding properties of aliphatic fluoro compounds, see R. West, D. L. Powell, L. S. Whatley, M. K. T. Lee, and P. von R. Schleyer, *J. Amer. Chem. Soc.*, **84**, 3321 (1962).

Still further complications in the solvent modification of σ_I values might arise from the possibility of concurrent reaction through nonhydrogen-bonded transition states (Scheme I). In this connection the Hammett–Taft plot of rates of reaction of 7-substituted 1-heptenes is of some interest, since participation effects are probably negligible in the heptene reactions,[2] This plot, based on rate data published previously.[2] is also given in Figure 2. In this instance, the σ_I values based on nmr data account sufficiently well for the observed rates that postulation of a new set of aliphatic σ_I values based on aliphatic reactivity in trifluoroacetic acid seems unnecessary at present despite the insecure foundation of the nmr based values.

SCHEME I
REACTION THROUGH HYDROGEN-BONDED AND NONHYDROGEN-BONDED TRANSITION STATES



Attenuation of Substituent Effects. Role of the Aromatic Ring and of the Solvent.—Assuming that the Hammett equation and Hammett–Taft equation apply to the reactions of the phenylbutenes and the 4-substituted 1-butenes, respectively, it is possible to combine the two equations to give a single equation which represents both sets of reactivities, as shown previously.[12] The Hammett–Taft equation for the comparison of 4-phenyl-1-butene with 1-butene is given in eq 9 where the subscript Ph denotes 4-phenyl-1-butene and the subscript H denotes 1-butene. The Hammett equation for the comparison of *meta-* and *para*-substituted 4-phenyl-1-butenes with 4-phenyl-1-butene is shown in eq 10. The result of adding eq 9 and 10 is eq 11. An alternative form is given in eq 12.

$$\log (k_{Ph}/k_H) = \rho_I \sigma_{I_{Ph}} \qquad (9)$$

$$\log (k_{Ph_x}/k_{Ph}) = \rho\sigma \qquad (10)$$

$$\log (k_{Ph_x}/k_H) = \rho_I \sigma_{I_{Ph}} + \rho\sigma \qquad (11)$$

$$\log (k_{Ph_x}/k_H) = \rho_I[\sigma_{I_{Ph}} + (\rho/\rho_I)\sigma] \qquad (12)$$

In eq 10, 11, and 12, ρ and σ may be taken to be ρ^n and σ^n or ρ^0 and σ^0. The term in brackets (eq 12) is seen to be a substituent constant for substituted phenyl groups, applicable to aliphatic reactivity. In Figure 2 the points for substituted phenylbutenes (open circles) are those derived from eq 12, using σ^n values. The only reason for the inclusion of these points is to show the useful range of aliphatic σ values available from the inclusion of substituted phenyl groups as inductive substituents. No significance should be attached to the fit for these points since σ^n values for hydrogen-bonding substituents are defined as the values which give a fit in the Hammett plot (*i.e.*, they are our $\sigma^n + \Delta\sigma^n$ values). Phenylbutenes having nonhydrogen-bonding substituents fit the plot of Figure 2 to the extent that phenylbutene itself fits, and to the extent that the Hammett relationship is followed (Figure 1).

Applying the relationship $\sigma_p{}^0 = \sigma_I + \sigma_R{}^0$, eq 12 may be written as in eq 13 in which ρ and σ have been taken to be ρ^0 and σ^0.

$$\log (k_{Ph_x}/k_H) = \rho_I[\sigma_{I_{Ph}} + (\rho^0/\rho_I)\sigma_I + (\rho^0/\rho_I)\sigma_R{}^0] \qquad (13)$$

We note that the term ρ^0/ρ_I represents the factor by which the inductive portion of the aromatic substituent effect is attenuated, compared with the effect when the same substituent is attached to C-4 of 1-butene. From Table II, footnote *b*, and Figure 2, the value of ρ^0/ρ_I is 1.58/5.75 = 0.274. This attenuation factor is of interest in connection with studies of tosylate solvolyses in trifluoroacetic acid, where attenuation factors have been shown to be solvent dependent, the least attenuation with increasing distance between the substituent and the reaction site being found in trifluoroacetic acid.[13] Previously a value of ρ/ρ_I of 0.147 has been found[14] for the ionization of phenylacetic acids in water compared with ionization of acetic acids. As in purely aliphatic reactions the reactions of trifluoroacetic acid with phenylbutenes are seen to be characterized by remarkably little attenuation of inductive effects with increased distance between the substituent and the reaction site.

Since *meta*-substituted benzenes contain three more carbon atoms between the substituent and the reaction site than the parent compounds, it is interesting to calculate the attenuation factor per carbon atom in the two cases cited above. The results are $0.274 = (0.65)^3$ and $0.147 = (0.528).^3$ These attenuation factors per carbon atom are very similar to the attenuation factors per methylene group (ϵ values) which characterize the addition of trifluoroacetic acid to ω-substituted 1-alkenes (ϵ 0.065) and the ionization constants of aliphatic acids in water (ϵ 0.41, 0.47, 0.49 and 0.39, for the substituents Cl, Br, I, and CN in acetic and propionic acids).[15] Clearly the benzene ring is not especially effective, compared to an aliphatic chain, in transmitting the inductive effect of *meta* substituents. The slower attenuation observed for the reaction of butenes in trifluoroacetic acid is expected, based on the previously published hypothesis[13] that the charge on a carbonium ion is delocalized to some extent by overlap with neighboring bonds (hyperconjugative interaction). According to this view, moving the substituent farther from the reaction site allows increased delocalization of the carbonium ion charge, so that in effect the carbonium ion charge follows the substituent down the chain as the substituent is placed farther from the reaction site. Since our hypothesis concerning the role of charge delocalization in aliphatic carbonium ions[13] is speculative, its continuing success in predicting trends in attenuation of substituent effects is of interest as added evidence for the hypothesis.

Implications of Variable σ Values for Aromatic Reactivity.—The solvent variability of aromatic σ^n or σ^0 values, demonstrated in our study, implies that σ and σ^+ values will show similar effects. So far the

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[12] C. D. Ritchie and W. F. Sager, *Progr. Phys. Org. Chem.*, **2**, 332 (1964).

[13] P. E. Peterson, R. J. Bopp, D. M. Chevli, E. L. Curran, D. E. Dillard, and R. J. Kamat, *J. Amer. Chem. Soc.*, **89**, 5902 (1967).

[14] *Cf.* ref 12. The value 0.147 is obtained from the values ρ = 0.56 and $\rho_I = \rho^*/0.45 = 3.82$.

[15] Calculated from data given by G. Kortum, W. Vogel, and K. Andrussow in "Dissociation Constants of Organic Acids in Aqueous Solution," Butterworth and Co. Ltd., London, 1961.

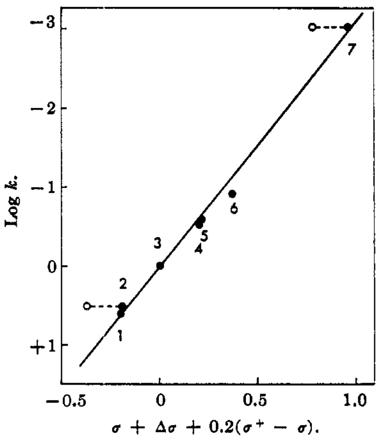

Figure 3.—Plot of log k_X/k_H for the ditritiation of 4′-substituted [4-^{3}H]biphenyls (from ref 17) *vs.* an expression using modified σ values (closed circles) and unmodified σ values (open circles). Identification: 1, CH_3; 2, OCH_3; 3, H; 4, Cl; 5, Br; 6, 3Cl; 7, NO_2.

implication based upon inspection of plots relating rates of aromatic substitution reactions to σ^+ reactivities[16] and also upon inspection of the nmr data of ref 9 and 10 is that acetic and formic acid will show much smaller, possibly negligible, substituent modifications arising from hydrogen bonding between the solvent and various substituents. However, in one reported instance of electrophilic aromatic substitution in trifluoroacetic acid (detritiation of 4′-substituted 4-tritiated biphenyls) solvent modified effects of nitro and methoxy substituents closely similar to those reported here for hydrogen-bonding substituents were found.[17] The origin of the effects was not completely clear, however. They were ascribed to " 'incipient protonation,' which may be hydrogen bonding."[18] It was of interest to determine whether correction terms, Δσ, having the approximate magnitude observed in our study, would lead to a linear free-energy relationship in the case of the detritiation data. Accordingly we corrected the σ values in the equation previously found[17] to correlate the rates of disilylation of 4′-X-4-trimethylsilylbiphenyls in *acetic* acid containing sulfuric acid, using as correction terms our $\Delta\sigma^n$ value for CH_3O and the estimated Δσ value 0.18 for NO_2, to obtain the result shown in Figure 3. The reasonably good results suggest that Δσ values of the type found in our study may be applicable also to σ^+ and σ reactivities. In view of possible complications arising from equilibria of the type shown in Scheme I, however, it would not be surprising if even special sets of σ constants will fail to give linear free-energy relationships for various types of reactions in trifluoroacetic acid. On the other hand, the use of modified σ constants is especially attractive for *remote* substituents, since complications arising from the equilibria of Scheme I should be absent (because substituents are assured of being hydrogen bonded in the transition state as well as in the ground state). It is precisely such cases which are of great interest in testing theoretical predictions of reactivity, as Dewar and Grisdale have pointed out.[19] Since reactions in trifluoroacetic acid seem especially well suited for such studies, owing to the large magnitude of ρ values so far encountered, and to the relatively high solubility of nonpolar and polar reactants, it may well be worthwhile to further define the nature of substituent effect modifications induced by trifluoroacetic acid.

Experimental Section

Synthetic Procedures.—All compounds prepared in our study exhibited the expected infrared and nmr spectra. Distillations were performed on spinning-band columns.

4-(*p*-Bromophenyl)-1-butene.—A published procedure was followed.[20] *p*-Bromobenzyl bromide (37 g, 0.15 mole) in 50 ml of anhydrous ether was added over a period of 1 hr to a stirred mixture of 3.6 g (0.15 g-atom) of magnesium turnings, 1.00 ml of ether, and a small crystal of iodine. After an additional 10 min, 15.3 g (0.2 mole) of allyl bromide in 50 ml of anhydrous ether was added during an interval of 10 min. After 0.5 hr the ether was replaced with benzene, and the mixture was refluxed 1 hr and poured into 250 ml of 2 *N* HCl. Distillation of an ether extract gave 9.9 g (32%) of 4-(*p*-bromophenyl)-1-butene, bp 65–67° (0.6 mm).

Anal. Calcd for $C_{10}H_{11}Br$: C, 56.89; H, 5.25. Found: C, 56.45; H, 5.37.

4-(*p*-Cyanophenyl)-1-butene.—Our procedure was based on one previously described.[21] 4-(*p*-Bromophenyl)-1-butene (21 g, 0.1 mole), cuprous cyanide (20.6 g, 0.115 mole), and dimethyl formamide (100 ml) were allowed to reflux for 6 hr. The brown mixture was poured into a solution of ferric chloride hydrate (40 g) and concentrated hydrochloric acid (10 ml) in water (50 ml) and heated at 60–70° for 20 min. The dark-colored layers were separated with some difficulty, and the hot aqueous layer was extracted with toluene. The organic extracts were washed (dilute hydrochloric acid, water, 10% sodium hydroxide), filtered, dried, and distilled to give 10.5 g (67%) of 4-(*p*-cyanophenyl)-1-butene, bp 101–105° (1.2 mm).

Anal. Calcd for $C_{11}H_{11}N$: C, 84.04; H, 7.05. Found: C, 83.67; H, 7.26.

4-(*p*-Carboxyphenyl)-1-butene and 4-(*p*-Carbomethoxyphenyl)-1-butene.—4-(*p*-Cyanophenyl)-1-butene (4.71 g, 0.030 mole), was dissolved in 95% ethanol (20 ml). A solution of sodium hydroxide in aqueous ethanol (1:1, 10 ml) was added, and the solution was refluxed overnight. Most of the alcohol was then removed by distillation, and the ice-cooled residue was acidified with 10% hydrochloric acid solution. The white precipitate was separated by filtration, washed twice with water, and recrystallized from aqueous ethanol to give 4.65 g (90%) of 4-(*p*-carboxyphenyl)-1-butene, mp 120–121°.

Anal. Calcd for $C_{11}H_{12}O_2$: C, 74.98; H, 6.86. Found: C, 74.68; H, 6.75.

The ethereal solution of diazomethane, prepared from N,N′-dimethyl-N,N′-dinitrosoterephthalimide (70% in mineral oil, from Aldrich Chemical Co., Inc.) and potassium hydroxide (16.8 g) in water (50 ml) and ethoxy ethylene glycol (35 ml), was added to 4-(*p*-carboxylphenyl)-1-butene (prepared as above) until the solution retained a yellow color. After the solution was kept for 30 min at room temperature, ether was removed by distillation, and the ester was distilled to yield 4.0 g (93%), bp 89–93° (0.7 mm).

Anal. Calcd for $C_{12}H_{14}O_2$: C, 75.76; H, 7.41. Found: C, 75.73; H, 7.41.

4-(*p*-Acetylphenyl)-1-butene.—The procedure was that used previously to prepare 9-acetylphenanthrene.[22] Methylmagnesium iodide was prepared from magnesium turnings (2.88 g, 0.12 g-atom) and methyl iodide (17.04 g, 0.12 mole) in anhydrous ether (50 ml) under nitrogen atmosphere. Ether was then replaced with benzene. 4-(*p*-cyanophenyl)-1-butene (9.42 g, 0.12 mole) was added quickly to the above solution and stirred

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under reflux for 3 hr. It was then cooled in an ice bath to 0°, 6 *N* hydrochloric acid (30 ml) was added with stirring and the mixture was refluxed for 6 to 8 hr.

After cooling the layers were separated, and the organic layer was washed with dilute sodium carbonate solution and water. The solvent was removed by distillation and the product was distilled under reduced pressure to yield 5.1 g (49%), bp 81-83° (0.45 mm).

Anal. Calcd for $C_{12}H_{14}O$: C, 82.72; H, 8.10. Found: C, 83.10; H, 7.87.

Rate Determinations.—The iodine monobromide titrimetric method used to follow the disappearance of alkenes has been described previously.[23] A quantitative hydrogenation procedure was used in the case of 4-(*m*-methoxyphenyl)-1-butene and 4-(*p*-methoxyphenyl)-1-butene, since the aromatic ring was brominated by the titrimetric reagent in these instances. Aliquots (2 or 3 ml) were withdrawn from the reacting solutions and injected through a serum cap into the reaction vessel of an atmospheric pressure hydrogenation apparatus, which contained 25 mg of 10% palladium on carbon (presaturated with hydrogen) and 5 ml of acetic acid to quench the reaction of trifluoroacetic acid with the alkene. The reaction vessel and the 10-ml hydrogen buret were jacketed and maintained at 25.0° by water circulated from a constant-temperature bath. Both a "course" (mercury) and "fine" (butyl tartrate) manometer were used to achieve volume readings of high precision. The rate constant for the reaction of 4-phenyl-1-butene with trifluoroacetic acid was measured both by the titrimetric method ($10^5k = 25.7$ sec^{-1}) and by hydrogenation ($10^5k = 25.1$ sec^{-1}).

Registry No.—4-(*p*-Bromophenyl)-1-butene, 15451-32-8; 4-(*p*-cyanophenyl)-1-butene, 15451-33-9; 4-(*p*-carbomethoxyphenyl)-1-butene, 15451-34-0; 4-(*p*-carboxyphenyl)-1-butene, 15451-35-1; 4-(*p*-acetylphenyl)-1-butene, 15451-36-2; trifluoroacetic acid, 76-05-1.

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Intermediates in Nucleophilic Aromatic Substitutions. III.[1] Meisenheimer Complexes of 1-Alkoxy-2,4-dinitronaphthalenes

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The rate constants for the formation and decomposition of the Meisenheimer complex (1) formed by the attack of methoxide ion on 1-methoxy-2,4-dinitronaphthalene (4) in methanolic solution have been determined at 8.10, 25.00, and 35.00°, allowing a determination of K, k_1, k_2, and energies and entropies of activation for the process. These data indicate **1** to be approximately 250 times more stable than the corresponding complex formed from 1-methoxy-2,4-dinitrobenzene but significantly less stable than the corresponding picryl complex. The rate of decomposition of crystalline **1** in methanol and in aqueous buffers has been examined over the pH range 4.97–10.85 at 25.00°; the decomposition is strongly catalyzed by acids. In addition to **1**, the stable crystalline Meisenheimer complexes (**2** and **3**) resulting from the attack of ethoxide ion on **4** and on 1-ethoxy-2,4-dinitronaphthalene (**5**) have been isolated; complex **2** was also prepared by reaction of methoxide ion with **5**. Infrared and proton magnetic resonance spectral studies establish complexes **1–3** to be 1,1-dialkoxy-2,4-dinitro-5,6-benzocyclohexadienylides.

Meisenheimer complexes are brightly colored adducts formed by the attack of a nucleophile at an electron-deficient position of an aromatic ring. The structures and stabilities of these complexes and their role in nucleophilic aromatic substitutions has received considerable attention in recent years.[3] Proton magnetic resonance (pmr) spectra of the 1-alkoxy-2,4,6-trinitrobenzene Meisenheimer complexes showed the two alkoxyl groups to be covalently linked to the same carbon atom.[4] In the preceding paper of this series,[5] we reported the isolation of complexes formed by the attack of alkoxide ions on 2,4-dinitroanisole and 2,4-dinitrophenetole and showed them to be 1,1-dialkoxy-2,4-dinitrocyclohexadienylides by pmr and infrared studies. The equilibrium constant for the formation of the potassium methoxide complex of 2,4-dinitroanisole in methanolic dioxane[5] was found to be several 1000-fold smaller than that for the ethoxyl complex of 2,4,6-trinitroanisole in ethanol.[6]

Dewar has calculated[7] that the formation of cyclohexadienyl intermediates from substituted benzenes requires a 10 kcal mol^{-1} loss inre sonance energy, whereas the resonance energy difference between naphthalene and the 1,1-disubstituted naphthalene intermediate is only 2 kcal mol^{-1}. One would expect, therefore, a smaller activation energy for nucleophilic substitution at a naphthalenoid than at a benzenoid carbon atom. This expectation has been verified by Elias and Parker[8] who found that the energy of activation for the nucleophilic substitutions of 1-chloro-2,4-dinitronaphthalene is approximately 3 kcal mol^{-1} less than that for 1-chloro-2,4-dinitrobenzene. Similarly, one would expect the formation of more stable Meisenheimer complexes with 1-substituted naphthalenes than with the corresponding benzene compounds. Although the formation of the methoxyl complex of 1-methoxyl-2,4-dinitronaphthalene in methanolic so-

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