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Exalted Resonance Demands in the Substituent Effects on the Acetolyses of 2-Arylethyl Trifluoromethanesulfonates Destabilized by CN and CF_3 Groups

Satoshi Usui,*[1,2] **Shoko Tsuboya,**[2] **Yukihiro Umezawa,**[2] **Ken Hazama,**[2] **and Mutsuo Okamura**[2]

[1]Department of Environmental Science, Faculty of Science, Niigata University, 8050 Ikarashi-2, Niigata 950-2181

[2]Graduate School of Science and Technology, Niigata University, 8050 Ikarashi-2, Niigata 950-2181

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Substituent effects on the acetolysis rates of 2-aryl-1-cyano-1-(trifluoromethyl)ethyl trifluoromethanesulfonates (α-OTf) and 2-aryl-2-cyano-2-(trifluoromethyl)ethyl trifluoromethanesulfonates (β-OTf) were investigated by using LArSR equation. The obtained ρ and r^+ values were $\rho = -3.28$, $r^+ = 0.98$ and $\rho = -3.48$, $r^+ = 0.93$ for the acetolysis of α-OTf and β-OTf, respectively. The obtained ρ values are comparable to those for typical aryl-assisted solvolyses, but the r^+ values are much larger. The large r^+ values suggest that the ester bond cleavages in the deactivated aryl-assisted solvolyses are assisted by the strong participation of the β-aryl group.

Solvolyses of substrates bearing a strong electron-withdrawing substituent at the reaction center have been attracting great amount of interest in the area of physical organic chemistry.[1] The investigations have mostly focused on the structure and reactivity of such a destabilized transition state or carbocation intermediate, which will provide fundamental insights into the carbocation chemistry. For this purpose, CF_3, CN, and carbonyl groups have been adopted for the electron-withdrawing groups.

A wide variety of 2-arylalkyl substrates are known to undergo aryl-assisted solvolyses[2,3] (k_Δ mechanism) in which the cleavage of the bond between the reaction center and the leaving group (C–L) is driven by the participation of neighboring aromatic π-electrons. Because of the direct interaction between the aryl π-electrons and the σ^*-orbital of the C–L bond, the structure and stability of the transition state are significantly affected by the substituent at the aromatic ring. Such perturbation of the substituent enables us to investigate the transition-state structure in terms of substituent effect on solvolysis rates.

The effects of aryl substituents on reaction rates have been examined extensively by using LArSR equation,[4]

$$\log k/k_\mathrm{H} = \rho(\sigma^\circ + r^+ \Delta\bar{\sigma}^+_\mathrm{R}) \tag{1}$$

where resonance demand, denoted as r^+, represents a measure of the delocalization of the positive charge in the transition state over the aromatic π-orbital. For the substituent effects on the rates of aryl-assisted solvolyses, moderate r^+ values of around 0.5, which systematically vary with substrate structure, have been obtained. The variation is interpreted as the change in the degree of phenyl participation in the transition state.[5,6]

Thus, the substituent effect on the solvolysis rates of 2-arylalkyl substrates would be a good criterion for evaluating the effect of the α-electron-withdrawing group on the transition-state structure. In this paper, 2-arylethyl solvolysis which is extremely destabilized by the two electron-withdrawing groups attached to the reaction center is of interest. From this perspective, the substituent effect on the acetolysis rates of 2-aryl-1-cyano-1-(trifluoromethyl)ethyl trifluoromethanesulfonates (abbreviated as α-OTf) was investigated by using LArSR equation, and the transition-state structure is discussed on the basis of its ρ and r^+ values.

Results and Discussion

When α-OTf was solvolyzed in acetic acid, ^{19}F NMR and ^{1}H NMR spectra of the sample solution exhibited changes according to substrate consumption and product formations, as shown in Figures 1 and 2 for the acetolysis of the p-Me-substituted derivative. In Figure 1, ^{19}F NMR signals at −75.3 and −77.7 ppm, which are assigned to two CF_3 groups in α-OTf, decayed via 1st-order kinetics, and signals at −65.2, −71.5, and −80.0 ppm were observed at the end of the acetolysis. The ^{19}F NMR signal at −80.0 ppm is reasonably ascribed to trifluoromethanesulfonic acid (abbreviated as TfOH) by comparison with that of the authentic sample. The solvolysis product exhibiting a ^{19}F NMR signal at −71.5 ppm was identified as 2-aryl-2-cyano-2-(trifluoromethyl)ethyl acetate (abbreviated as β-OAc) which exhibits an AB quartet ^{1}H NMR signal of the CH_2 group at 4.86 ppm as shown in Figure 2. The other product with a −65.2 ppm ^{19}F NMR signal exhibited a singlet ^{1}H NMR signal at 7.80 ppm and is ascribed to 3-aryl-2-(trifluoromethyl)acrylonitrile (abbreviated as Sty). In addition to these final products, an intermediate product, which exhibits ^{19}F NMR signals at −70.8 and −75.9 ppm, was accumulated and diminished with the progress of the acetolysis. This intermediate product exhibits an AB quartet ^{1}H NMR signal at 5.18 ppm and was identified as 2-aryl-2-cyano-2-(trifluoromethyl)ethyl trifluoromethanesulfonate (abbreviated as β-OTf).

The formation of β-OTf during the acetolysis is indicative of

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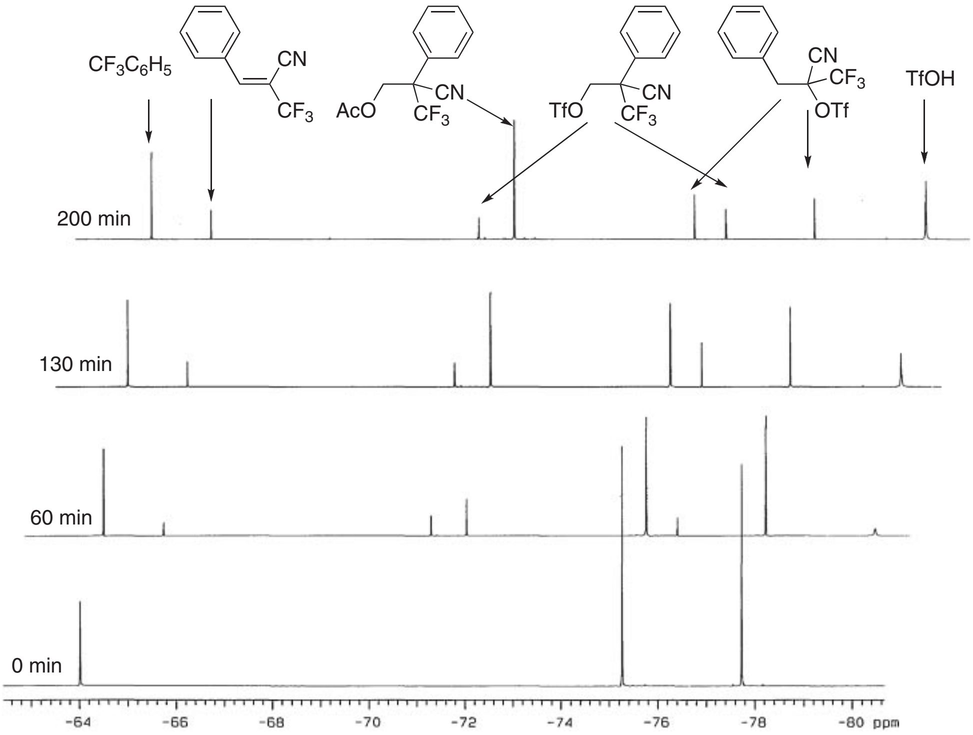


Figure 1. ^{19}F NMR spectra for the acetolysis of α-OTf at 130 °C.

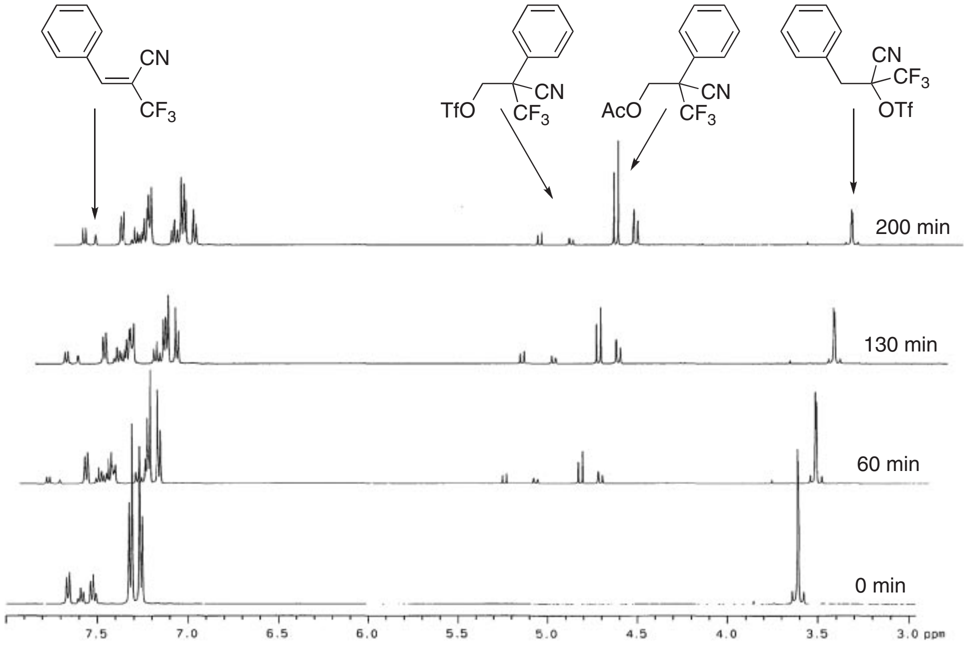


Figure 2. ^{1}H NMR spectra for the acetolysis of α-OTf at 130 °C.

the intervention of a non-classical phenonium (=spiro[2,5]-octadienylium) ion intermediate[7] which affords β-OTf and β-OAc by the nucleophilic addition of the trifluoromethanesulfonate anion and acetic acid, respectively. Hence, the acetolysis of α-OTf is suggested to proceed through rate-limiting phenonium ion formation followed by partitioning between the β-OAc and β-OTf formations as has been shown for the solvolysis of 2-phenylpropyl brosylate (=p-bromobenzenesulfonate).[2b] The rate of β-OTf formation is then expressed in terms of the rate of phenonium ion formation, $k_{\Delta\alpha}$, and the partitioning factor between the β-OAc and β-OTf formations, F. Acetolysis of β-OTf is supposed to afford β-OAc as a sole product, since β-OAc was the only nucleophilic substitution product throughout the acetolysis. This assumption is also supported by the fact that the formation of β-OAc, shown in Figure 3, did not obey 1st-order kinetics, but the sum of β-OAc and β-OTf did. As an analogy to the acetolysis of α-OTf, the acetolysis of β-OTf is also expected to proceeds through the

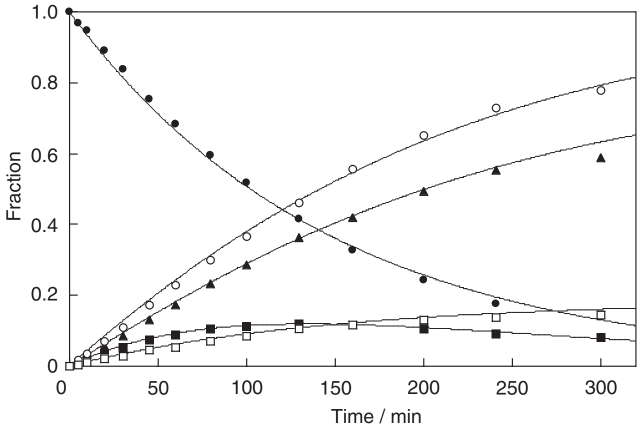
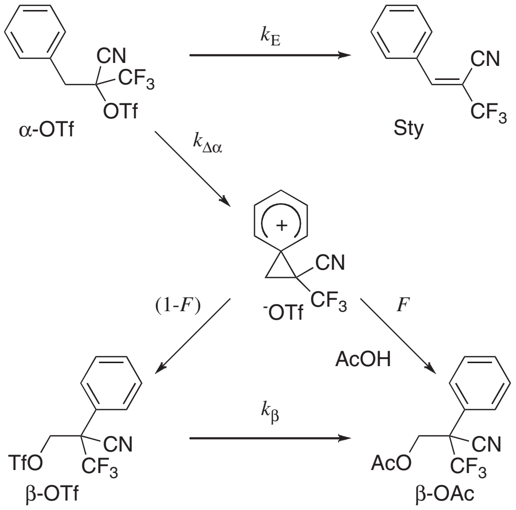


Figure 3. Time profiles of the substrate and product fractions for the acetolysis of α-OTf at 130 °C; closed circle, α-OTf; open circle, TfOH; closed triangle, β-OAc; closed square, β-OTf; open square, Sty.



Scheme 1.

phenonium ion, however, a solvent-assisted S_N2 displacement reaction (k_s mechanism) cannot be excluded from the acetolysis mechanism of β-OTf. The detailed mechanism will be discussed below based on the substituent effect on the acetolysis rates of β-OTf, k_β. As for the elimination product, time dependency of its formation obeyed 1st-order kinetics from the beginning to the end of the acetolysis, indicating that this product is directly obtained by the acetolysis of α-OTf. According to these observations, a summary of the acetolysis mechanism of α-OTf is depicted in Scheme 1.

The reaction rate constants and F value described in Scheme 1 were obtained by the following procedure. Based on Scheme 1, the rate equations for the substrate and products are as follows:

$$\frac{\mathrm{d}[\alpha\text{-OTf}]}{\mathrm{d}t} = -(k_{\Delta\alpha} + k_{\mathrm{E}})[\alpha\text{-OTf}] \tag{2}$$

$$\frac{\mathrm{d}[\beta\text{-OTf}]}{\mathrm{d}t} = (1 - F)k_{\Delta\alpha}[\alpha\text{-OTf}] - k_\beta[\beta\text{-OTf}] \tag{3}$$

$$\frac{\mathrm{d}[\mathrm{Sty}]}{\mathrm{d}t} = k_{\mathrm{E}}[\alpha\text{-OTf}] \tag{4}$$

Table 1. Reaction Rate Constants and Partitioning Factors for the Acetolyses of α-OTf at 130 °C

Substituent	$k_{\Delta\alpha}/10^{-5}\,\mathrm{s}^{-1}$	F	$k_{\mathrm{E}}/10^{-5}\,\mathrm{s}^{-1}$	$k_\beta/10^{-5}\,\mathrm{s}^{-1}$
p-MeO	251	0.67		293
p-MeS	114	0.69		79.5
p-MeO-m-Cl	22.7	0.66	1.82	44.0
3,4-Me_2	20.3	0.54	2.14	32.9
p-Me	9.23	0.57	2.08	13.5
3,5-Me_2	3.48	0.35	1.93	4.02
m-Me	1.65	0.37	1.75	1.62
H	0.668	0.32	1.94	0.783

$$\frac{\mathrm{d}[\beta\text{-OAc}]}{\mathrm{d}t} = Fk_{\Delta\alpha}[\alpha\text{-OTf}] + k_\beta[\beta\text{-OTf}] \tag{5}$$

By resolving these differential equations, the concentration of the substrate and the products are obtained as a function of time, as follows;

$$[\alpha\text{-OTf}] = [\alpha\text{-OTf}]_0 \exp(-(k_{\Delta\alpha} + k_{\mathrm{E}})t) \tag{6}$$

$$[\beta\text{-OTf}] = [\alpha\text{-OTf}]_0 \frac{(1 - F)k_{\Delta\alpha}}{k_\beta - k_{\Delta\alpha} - k_{\mathrm{E}}} \times \{\exp(-(k_{\Delta\alpha} + k_{\mathrm{E}})t) - \exp(-k_\beta t)\} \tag{7}$$

$$[\mathrm{Sty}] = [\alpha\text{-OTf}]_0 \frac{k_{\mathrm{E}}}{k_{\Delta\alpha} + k_{\mathrm{E}}} \exp(-(k_{\Delta\alpha} + k_{\mathrm{E}})t) \tag{8}$$

$$[\beta\text{-OAc}] = [\alpha\text{-OTf}]_0 - [\alpha\text{-OTf}] - [\beta\text{-OTf}] - [\mathrm{Sty}] \tag{9}$$

where $[\alpha\text{-OTf}]_0$ represents the concentration of α-OTf at $t = 0$. The reaction rate constants and F value were determined by the least-squares curve fitting[8] of the substrate and the product fractions obtained from the ^{19}F NMR signal integrals to eqs 6 to 9. The solid lines in Figure 3 indicate the substrate and product fractions calculated by the above equations with the thus-obtained $k_{\Delta\alpha}$, k_β, k_{E}, and F values for the acetolysis of α-OTf with the p-Me substituent.

Acetolyses of α-OTf with a series of aryl substituents exhibited similar solvolysis products and time dependencies of the substrate and products fractions, except for the p-MeO and p-MeS derivatives which gave no elimination products. Although competition of discrete k_Δ and k_s mechanisms and changes in their rate ratio with aryl substituents have been shown for many β-arylalkyl solvolyses,[3] no 2-aryl-1-cyano-1-(trifluoromethyl)ethyl acetate which would be obtained by k_s mechanism, was observed in the present acetolysis. This observation indicates that the acetolysis mechanism proposed in Scheme 1 is constant and the procedure for obtaining the reaction rate constants and F value described above is valid for all α-OTf derivatives studied here. The obtained reaction rate constants and F values are summarized in Table 1.

It is obvious from Table 1 that k_{E} are nearly constant, while $k_{\Delta\alpha}$ and k_β varied by a factor of about 400 with the change of substituent from H to p-MeO. The small substituent effect on k_{E} indicates that the elimination reaction proceeds by the E2 mechanism rather than by E1, since the E1 mechanism should involve a rate-determining phenonium ion formation so that it would result in a similar substituent effect as that for $k_{\Delta\alpha}$. Therefore, k_{E} values of around $2.0 \times 10^{-5}\,\mathrm{s}^{-1}$ are also expected for the acetolyses of p-MeO and p-MeS derivatives. Thus, the absence of Sty in the acetolyses of these electron-releasing

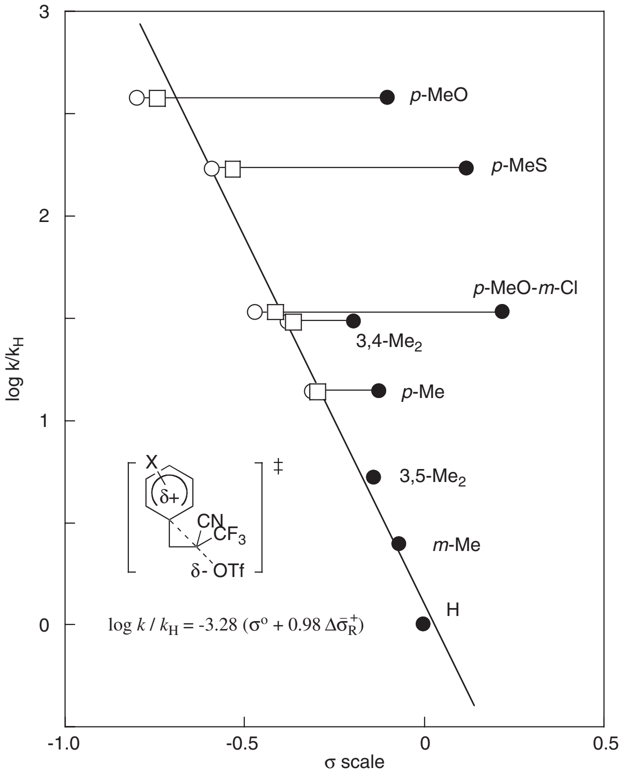


Figure 4. LArSR plot for the acetolysis of α-OTf at 130 °C: closed circle, σ^o; open circle, σ^+; open square, $\sigma_{app.}$ ($r^+ = 0.98$).

substituents is explained by the large $k_{\Delta\alpha}/k_E$ rate ratios of over 50 to afford a negligible amount of Sty.

As shown in Figure 4, the substituent effect on $k_{\Delta\alpha}$ was successfully analyzed by using LArSR equation to result in $\rho = -3.28$ and $r^+ = 0.98$ with a good precision of $R = 0.990$. The obtained ρ value of -3.28 is comparable to $\rho = -3.83$ observed for the acetolysis rates of neophyl (=2,2-dimethyl-2-arylethyl) brosylates at 75 °C[5b] or $\rho = -3.87$ for the k_Δ acetolysis rates of 2-arylethyl tosylates (*p*-toluenesulfonates) at 115 °C[5a] and is consistent with the proposed k_Δ mechanism. On the other hand, the r^+ value is much larger than $r^+ = 0.57$ for the acetolysis rates of neophyl brosylates or $r^+ = 0.63$ for the k_Δ acetolysis rates of 2-arylethyl tosylates and is rather comparable to $r^+ = 1.00$ for the benzylic S_N1 solvolysis rates of *t*-cumyl (=1-methyl-1-arylethyl) chlorides.[9]

In general, the variation in r^+ is interpreted as arising from the following origins. One is a change in the transition-state structure, which governs the overlap of the vacant orbital at the reaction center and the aromatic π-orbital. Therefore, *t*-cumyl solvolysis with full overlap between the two orbitals results in r^+ of unity, while sterically distorted benzylic S_N1 solvolyses afford small r^+ values.[10] Moderate r^+ values obtained for the aryl-assisted solvolyses are thus ascribed to the partial overlap between the aromatic π-orbital and the σ^*-orbital of the C–L bond.[5,6] Another origin is the change in the stability of the positive charge in the transition state, which affects the magnitude of the positive charge to be delocalized over the aromatic π-orbital. By this origin, the r^+ value increases with the destabilization of the positive charge, which otherwise ought to be stabilized by the delocalization over the aromatic π-orbital. This variation in r^+ values is shown for benzylic S_N1 solvolyses with a series of electron-withdrawing substituents at the reaction center,[11] where an increase of the r^+ value by a factor of 1.4 has been observed by the substitution of the α-Me group with a CF_3 group in the *t*-cumyl solvolysis.

In the acetolysis of α-OTf, it may be plausible that the two electron-withdrawing CN and CF_3 groups strongly destabilize the positive charge in the aryl-assisted transition state, forcing a large positive charge to be delocalized over the aromatic π-orbital. However, the acetolysis of α-OTf exhibited essentially the same ρ value as those for the aryl-assisted 2-arylalkyl acetolyses without an electron-withdrawing substituent, and no increase of the ρ value was observed as was shown for the destabilized benzylic S_N1 solvolyses.[11f] This result suggests that the magnitude of the positive charge delocalized over the aromatic π-orbital is same as those for typical aryl-assisted solvolyses. Therefore, the enlargement of r^+ in the present solvolysis should be responsible for the increase in the overlap between the aryl π-orbital and the σ^*-orbital of the C–L bond that is caused by the decrease in the bond length between the aryl carbon and the reaction center in the transition state. This change in the transition-state structure implies a strong aryl π-electron participation, which assists the C–L bond cleavage in the deactivated intramolecular nucleophilic substitution reaction.

It might seem that the strong π-electron participation contradicts the little increase in the magnitude of positive charge delocalized over aryl π-orbital. This phenomenon is probably due to the intramolecular S_N2 characteristic of the transition state of aryl-assisted solvolysis. The transition state of S_N2 reaction, having partial bonds between the reaction center and the incoming nucleophile as well as the leaving group, exhibits less sensitivity of a developed positive charge to an electronic perturbation compared to that of non-assisted (k_c) solvolysis since the two partial bonds can be affected to compensate for the perturbation. Such a characteristic is shown in the theoretical calculations of the acid-catalyzed phenonium ion formation from 2-arylethyl alcohols, where the positive charge delocalized over the aryl π-orbital is less affected by the change of the aryl substituent in the transition state than in the phenonium ion.[12] Furthermore, the deactivation of the acetolysis by the α-CN and CF_3 groups would make the C–L bond in the transition state hard to dissociate. The S_N2 transition state involving high bond orders for both the incoming nucleophile and the leaving group is often expressed as a "tight" transition state, which exhibits development of a small positive charge.

By the extreme destabilization of 2-arylethyl solvolysis, its transition state is considered to resemble the phenonium ion intermediate, since the strongest π-electron participation in the aryl-assisted solvolysis is expected in the structure of the phenonium ion intermediate. Here, the r^+ value for the stability of the destabilized phenonium ions is of interest. The stabilities of the phenonium ions having no electron-withdrawing substituent have experimentally been obtained by bromide ion transfer reaction in the gas phase or by theoretical calculation, and the LArSR analyses afforded $r^+ = 0.62$[13] or $r^+ = 0.65$,[12] respectively. Mishima et al. concluded that the agreement of these r^+ values with $r^+ = 0.63$ obtained for the

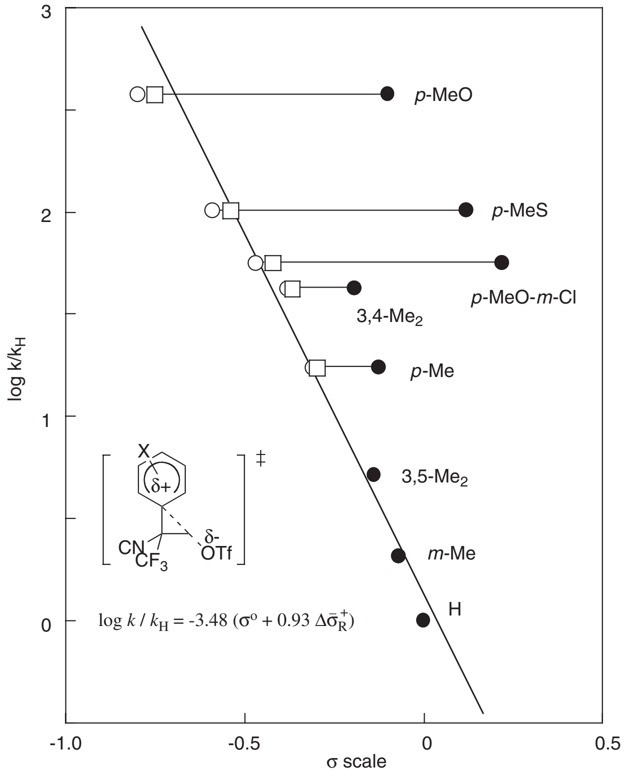


Figure 5. LArSR plot for the acetolysis of β-OTf at 130 °C: closed circle, σ^o; open circle, σ^+; open square, $\sigma_{app.}$ ($r^+ = 0.93$).

k_Δ acetolysis rates of 2-arylethyl tosylates implies that the r^+ values for the S_N1 solvolyses are essentially identical to those for the stabilities of the corresponding carbocation intermediates.[12,13] Thus, the present result might suggest that the stability of the phenonium ions destabilized by the CN and CF_3 groups affords a large r^+ value that is close to unity. The r^+ value for the stability of destabilized phenonium ions can be evaluated by a comparison with those obtained for Friedel–Crafts reactions, since the spiro structure of the phenonium ion intermediate resembles those of the σ-complex intermediates in the Friedel–Crafts reactions. In fact, the r^+ value of 0.98 for the present acetolysis is in the range of 0.78 to 1.4, which is shown for the Friedel–Crafts reactions.[14]

The substituent effect on the solvolysis rates of β-OTf was also successfully analyzed by using LArSR equation to result in $\rho = -3.48$ and $r^+ = 0.93$ with a correlation coefficient of $R = 0.988$, as shown in Figure 5. Because ρ values of less than -1 and an r^+ value of zero have been shown in the substituent effects on k_s solvolyses of 2-arylalkyl substrates,[3c,5] the similarity of the substituent effects between for $k_{\Delta\alpha}$ and for k_β suggests that the acetolysis of β-OTf also proceeds by the k_Δ mechanism. The obtained r^+ value of 0.93 is somewhat smaller than that for $k_{\Delta\alpha}$ but is obviously larger than those for the typical aryl-assisted solvolyses and indicates the significance of the aryl π-electrons in the transition state of the acetolysis of β-OTf. It is interesting that enlargement of r^+ is observed even though the electron-withdrawing groups are attached to the β-position but not to the α-position of the reaction center. The enlargement of r^+ by the electron-withdrawing group at the β-position has been shown for the solvolysis of 2-aryl-2-(trifluoromethyl)ethyl nosylate (=m-nitrobenzenesulfonates)[15] and is interpreted as being caused by the destabilization of the transition state by the β-CF_3 group. It should be noted that the r^+ value for the acetolysis of β-OTf is even larger than the value of 0.77 for the acetolysis of 2-aryl-2-(trifluoromethyl)ethyl nosylates and is rather comparable to that for α-OTf. This result suggests that the transition state of the acetolysis of β-OTf is as strongly aryl-assisted as is the acetolysis of α-OTf.

Conclusion

The acetolysis of α-OTf afforded Sty by the E2 mechanism and phenyl-rearranged β-OAc and β-OTf through aryl-assisted phenonium ion formation. The obtained β-OTf underwent further aryl-assisted acetolysis to afford β-OAc as a sole product. Kinetic analysis of these acetolysis successfully afforded reaction rate constants $k_{\Delta\alpha}$, k_β, and k_E as well as the partitioning factor F in Scheme 1. The substituent effects on $k_{\Delta\alpha}$ and k_β, were analyzed by using LArSR equation, resulting $\rho = -3.28$, $r^+ = 0.98$ and $\rho = -3.48$, $r^+ = 0.93$, respectively. The obtained ρ values were comparable to those for the typical aryl-assisted solvolyses but r^+ values were much larger than were those for the solvolyses. The enlargement of the r^+ values without an increase in the ρ value suggests the changes in the transition-state structures so that the overlap of the aryl π-electrons and the σ^*-orbital of the C–L bond is more significant. This change in the transition-state structure is interpreted as that the C–L bond cleavage in the deactivated intramolecular nucleophilic substitution reaction of 2-arylethyl solvolyses is assisted by the strong participation of the β-aryl group.

Experimental

Synthesis. A series of arylacetic acids were obtained by Willgerodt reaction from corresponding acetophenones.[16] Chlorination of arylacetic acids with $SOCl_2$ gave arylacetyl chlorides[17] which were reacted with anhydrous trifluoroacetic acid and pyridine to afford 1-aryl-3,3,3-trifluoro-2-propanones.[18] Cyanation of the ketones with sodium cyanide followed by the addition of aqueous hydrochloric acid afforded 2-aryl-1-cyano-1-(trifluoromethyl)ethyl alcohol.[19] The obtained cyanohydrins were reacted with trfluoromethanesulfonic anhydride in the presence of pyridine to give α-OTf.[20] Typical synthetic procedures for p-Me derivatives are described below.

Synthesis of *p*-Methylphenyl Acetic Acid. A mixture of p-methylacetophenone (0.199 mol), sulfur (9.58 g), and morpholine (0.299 mol) was heated at 130 °C for 2 days. The reaction mixture was poured into 50 mL of hot ethanol, and the precipitates were collected and washed with cold ethanol. The obtained morpholide was hydrolyzed with 100 mL of 10% aq NaOH solution at 130 °C for one day. Crude p-methylphenylacetic acid was obtained by the acidification of the reaction mixture with hydrochloric acid and was purified by recrystallization from benzene/n-hexane solution.

Synthesis of *p*-Methylphenylacetyl Chloride. Thionyl chloride (0.32 mol) was added to p-methylphenylacetic acid (0.16 mol) and the mixture was refluxed for 1 h. The excess $SOCl_2$ was removed by distillation under reduced pressure, followed by the addition of 15 mL of dry benzene and drying under vacuo.

Synthesis of 1-(*p*-Methylphenyl)-3,3,3-trifluoro-2-propanone. To a 20 mL of CH_2Cl_2 solution of trifluoroacetic anhydride

(0.033 mL), *p*-methylphenylacetyl chloride (0.011 mol) dissolved into 5 mL of CH_2Cl_2 was added at −60 °C. Dry pyridine (0.022 mol) was added dropwise to the solution and stirred for 3 h at −60 °C. After the addition of 60 mL of H_2O, the reaction mixture was extracted with CH_2Cl_2. The crude product was distilled under reduced pressure.

Synthesis of 2-Cyano-1-(*p*-methylphenyl)-3,3,3-trifluoro-2-propanol. 1-(*p*-Methylphenyl)-3,3,3-trifluoro-2-propanone (0.00532 mol) was dissolved into 30 mL of diethyl ether followed by the addition of a 22 mL of NaCN (0.00681 mol) aq solution. After 1 h of vigorous stirring, the reaction mixture was cooled by ice bath and a 2.2 mL of 6 mol dm^{-3} aqueous hydrochloric acid solution was added to the reaction mixture. Crude cyanohydrine was obtained by extraction with diethyl ether and was purified with the aid of conventional silica gel column chromatography.

Synthesis of 1-Cyano-2-(*p*-methylphenyl)-1-(trifluoromethyl)ethyl Triflate. A mixture of 2-cyano-1-(*p*-methylphenyl)-3,3,3-trifluoro-2-propanol (0.00487 mol) and dry pyridine (0.00633 mol) in 3 mL of CH_2Cl_2 was cooled with an ice bath under a nitrogen atmosphere. Trifluoromethanesulfonic anhydride (0.00584 mol) and was added to the solution and was kept below 0 °C for 24 h. The trifluoromethanesulfonate ester was purified by successive silica gel column chromatographies of the reaction mixture.

Acetolysis. About 15 mg of α-OTf was dissolved into 1 mL of commercially available acetic acid-d_4 and ampouled into a ^{1}H NMR tube under an Ar atmosphere. The sample tube was immersed into a thermostated oil bath at 130 °C, and ^{1}H and ^{19}F NMR spectra were recorded at 20 °C by using a Varian Unity Plus 500. The products were identified by NMR spectra, and fractions of substrate and products at each reaction time were determined from their signal integrals in ^{19}F NMR spectra. NMR signals of the solvent and trifluoromethylbenzene were used as internal references for ^{1}H and ^{19}F NMR spectroscopies, respectively. Typical spectral data of the substrate and solvolysis products for the acetolysis of *p*-Me derivative are shown below.

Spectral Data of 1-Cyano-2-(*p*-methylphenyl)-1-(trifluoromethyl)ethyl Trifluoromethanesulfonate. ^{1}H NMR (500 MHz, CD_3COOD): δ 7.32 (2H, d, $J = 8.06$ Hz, ArH), 7.26 (2H, d, $J = 8.06$ Hz, ArH), 3.61 (2H, ABq, $J = 14.7$ Hz, $\Delta\delta = 0.0049$, CH_2), 2.36 (3H, s, CH_3); ^{19}F NMR (470 MHz, CD_3COOD): δ −75.3 (3F, s, CCF_3), −77.7 (3F, s, OSO_2CF_3).

Spectral Data of 2-Cyano-2-(*p*-methylphenyl)-2-(trifluoromethyl)ethyl Acetate. ^{1}H NMR (500 MHz, CD_3COOD): δ 7.20–7.60 (4H, m, ArH), 4.86 (2H, ABq, $J = 11.6$ Hz, $\Delta\delta = 0.0869$, CH_2), 2.37 (3H, s, CH_3); ^{19}F NMR (470 MHz, CD_3COOD): δ −71.5 (3F, s, CCF_3).

Spectral Data of 2-Cyano-2-(*p*-methylphenyl)-2-(trifluoromethyl)ethyl Trifluoromethanesulfonate. ^{1}H NMR (500 MHz, CD_3COOD): δ 7.20–7.60 (4H, m, ArH), 5.18 (2H, ABq, $J = 11.0$ Hz, $\Delta\delta = 0.153$, CH_2), 2.42 (3H, s, CH_3); ^{19}F NMR (470 MHz, CD_3COOD): δ −75.9 (3F, s, OSO_2CF_3), −70.8 (3F, s, CCF_3).

Spectral Data of 1-(*p*-Methylphenyl)-2-(trifluoromethyl)-acrylonitrile. ^{1}H NMR (500 MHz, CD_3COOD): δ 7.87 (2H, d, $J = 8.0$ Hz, ArH), 7.80 (1H, s, ArCH), 7.58 (2H, d, $J = 8.0$ Hz, ArH), 2.39 (3H, s, CH_3); ^{19}F NMR (470 MHz, CD_3COOD): δ −65.2 (3F, s, CCF_3).

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