change process,[3] with both processes possibly proceeding via isocarbonyl intermediates or transition states ($M—C{\equiv}O\cdots Rh \rightarrow M\cdots C{\equiv}O—Rh \rightarrow M\cdots O{\equiv}C—Rh$).[16] That is, the unsaturated metal carbonyl intermediate containing a binding site for the CO-labilizing $R_3P{=}O$ ligand in this instance is provided by rhodium(I) withdrawal of carbon monoxide with concomitant formation of $Rh(C_8H_{14})(CO)Cl$. It has not escaped our attention that the linear bridging carbonyl (η^2(C,O) CO) illustrated above, in addition to providing the first step in the CO abstraction process, also represents a highly directional oxygen donor which might itself promote lability in either of the metal centers.[16]

Acknowledgments. The financial support of the National Science Foundation through Grant CHE 78-01758 and of Tulane University is greatly appreciated.

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(1) See, for example, Perutz, R.; Turner, J. J. *Inorg. Chem.* **1975**, *14*, 262.
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(5) The level of ^{13}CO enrichment was not extremely dependent on the quantity of excess $(n\text{-}Bu)_3P{=}O$ used, with phosphine oxide, metal ratios of 11:1 and 1.5:1 affording only slightly lower percentages of ^{13}CO in the $Cr(CO)_6$ products.
(6) Chandrasegaran, L.; Rodley, G. A. *Inorg. Chem.* **1965**, *4*, 1360.
(7) ^{13}C NMR spectra were determined at 15.03 MHz on samples of identical concentrations of natural-abundance and ^{13}CO-enriched $M(CO)_6$ species in acetone-d_6 solvent in 10-mm tubes employing a JEOL FX60 spectrometer. Spectra resulted from 1500–2500 transients with an acquisition time of 2.04, a pulse repetition rate of 5.0 s, and a flip angle of 30°. Quantitative intensity comparisons of the carbonyl resonances of acetone-d_6 at 205.1 ppm vs. that in the two samples were made to assess the level of ^{13}CO incorporation in the enriched sample. The agreement between ν(CO) infrared and ^{13}C NMR analyses was excellent.
(8) In a typical preparative-scale experiment, 0.47 g (1.00 mmol) of $py_3Mo(CO)_3$, 6.00 g (27.0 mmol) of $(n\text{-}Bu)_3P{=}O$, and 40 mL of dry hexane were placed in a 300-mL Schlenkware flask which was thoroughly degassed and refilled with 1.4 atm of ^{13}CO (~17.3 mmol). Heating at 70 °C with stirring for 16 h afforded upon workup $Mo(^{13}CO)_6$ in >50% purified yield. The workup procedure consisted of washing the hexane solution with two 80-mL portions of water to remove $(n\text{-}Bu)_3P{=}O$ and drying the hexane layer with $CaCl_2$, followed by vacuum distillation of the hexane solvent and sublimation of the hexacarbonyl product at 40 °C. Indications are that isolated yields may eventually be close to solution spectroscopic yields with improvements in techniques for separation of the volatiles, hexane and $Mo(^{13}CO)_6$.
(9) The level of ^{13}CO enrichment was observed to correspond to ^{13}CO replacement of the labile ligand (L) in the $L_nM(CO)_{6-n}$ starting materials, e.g., *c*-$Mo(CO)_4(pip)_2$ afforded $Mo(CO)_4(^{13}CO)_2$.
(10) Synthesis of $(py)Fe(CO)_4$ was accomplished using the procedure of Cotton and Troup.[11] The reaction of $(py)Fe(CO)_4$ with $(n\text{-}Bu)_3PO$ (1:2 molar ratio) was carried out in a ^{13}CO atmosphere at 50 °C in hexane solvent. After 4 h the level of ^{13}CO enrichment in the iron pentacarbonyl was ~70%.
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(13) CO_2 analysis was carried out on a Perkin-Elmer Sigma 2 gas chromatograph using a 6-ft, 0.025-in. stainless steel column packed with 80–100 mesh carbosphere (Alltech Associates) operated at 100 °C with helium as a carrier gas. The maximum level of CO_2 production would correspond to 0.003 mmol of CO_2/mmol of metal complex.
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(16) Indeed we have carried out preliminary experiments which indicate that $Rh(PPh_3)_2(CO)Cl$ activates CO displacement in reactions with $Cr(CO)_5(py)$, possibly resulting from initial $Rh—C{\equiv}O\cdots Cr(CO)_5$ interaction.

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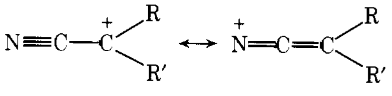
Received October 15, 1979

The α-Cyano Group as a Substituent in Solvolysis Reactions. An Evaluation of Inductive Destabilization vs. Mesomeric Stabilization of Cations by the Cyano Moiety

Sir:

Amazingly little is known about the effect of strong electron-withdrawing substituents on incipient carbonium-ion centers. Recently, interest in this area has been increasing.[1] We now report our preliminary results on the influence of the α-cyano group on incipient carbonium-ion centers and to propose that α-cyano groups are ambivalent in their relationships with attached carbonium-ion centers. Inductively, the cyano group is strongly destabilizing. However, much of this inductive effect can be balanced by a mesomeric (delocalization) effect involving resonance contributors **1** and **2**.



1 **2**

Interestingly, the resonance form **2** is a nitrenium ion, which should be much less stable than an analogous carbonium ion.[2] Thus, the extent to which **2** contributes to the structure of the intermediate cationic species will depend greatly on the nature of R and R'.[3]

Recently, Koshy and Tidwell have found that an α-trifluoromethyl group provides a rate retardation of 10^6 relative to hydrogen in the solvolysis of simple sulfonate esters.[1j] Similarly, Creary has found an H/α-keto rate ratio of 10^7.[1k] On the basis of the Taft polar substituent constants [$\sigma^*(NCCH_2)$ (1.30), $\sigma^*(CF_3CH_2)$ (0.92), and $\sigma^*(CH_3C({=}O)CH_2)$ (0.60)],[4] it might be predicted that an α-cyano moiety would have a greater rate retarding effect than either the α-trifluoromethyl or α-keto group. As shown in Table I, the influence of the α-cyano group on the rate of solvolysis of 2-propyl sulfonates resulted in an H/α-cyano (k_3/k_4) rate ratio of only 3.5×10^3. This is considerably smaller than the retardation factor expected on the basis of the Taft polar substituent constant and even less than the 10^4–10^7 rate retardation previously observed for β-cyano substitution.[11,5]

A number of different explanations might be suggested for the relatively small rate effect resulting from the introduction of the α-cyano group. Possibilities are (a) the reaction occurs by concerted elimination to give the only observed product methacrylonitrile; (b) the reaction occurs via solvent displacement followed by fast elimination of 2,2,2-trifluoroethanol; (c) the inductive destabilization of the cyano group is naturally less than calculated; or (d) the inductive destabilization of the cyano group is balanced by some other cation-stabilizing characteristic of the cyano group, namely mesomeric stabilization.

To evaluate the possibility of rate-limiting, concerted (E2) elimination, we measured the effect of β-deuterium substitution on the rate of solvolysis of 2-cyano-2-propyl trifluoromethanesulfonate. At 25 °C, a CH_3/CD_3 rate ratio[6] of 1.48 was observed. This value is very similar to the value of 1.46 found for 2-propyl *p*-bromobenzenesulfonate in trifluoroacetic acid.[7] More significantly, it is very close to the value of 1.54 obtained for the CD_3 isotope effect observed in the solvolysis of 2-trifluoromethyl-2-propyl *p*-toluenesulfonate.[1j] These values are too small for a rate-limiting, concerted elimination.[8,9] The observation of an isotope effect similar to that found in the presence of an α-trifluoromethyl group (which provides a 10^6 rate retardation) suggests that an α-cyano moiety should provide an even greater deceleration. However, this is not experimentally true.

Solvent participation in a S_N2 manner could be considered. 2,2,2-Trifluoroethanol is a relatively nonnucleophilic solvent which has been used widely for the study of solvolytic reactions because of this property. In addition, the isotope effect of 1.48 argues against such involvement.[9] To strengthen the basis for ruling out S_N2 involvement by solvent,[10] we solvolyzed the highly hindered 1-cyano-1-cyclooctyl tosylate (**7**) in 100% 2,2,2-trifluoroethanol. Cyclooctyl *p*-toluenesulfonate has been reported to solvolyze without nucleophilic solvent assistance

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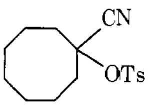
Table I. Rates of Solvolysis of 2-Propyl Sulfonate and 2-Cyano-2-propyl Sulfonates in 100% 2,2,2-Trifluoroethanol Buffered with 2,6-Lutidine

compd	temp, °C (+0.02 °C)	rate, s^{-1}	$\Delta H^{\ddagger}$, kcal/mol	$\Delta S^{\ddagger}$, eu
$N{\equiv}CC(CH_3)_2OTs$ (**3**)	170.00	$(1.21 \pm 0.04) \times 10^{-3}$	27.5 ± 1.5	−10.5 ± 3.6
	155.00	$(5.19 \pm 0.01) \times 10^{-4}$		
	140.00	$(1.22 \pm 0.02) \times 10^{-4}$		
	25.0[a]	2.24×10^{-10}		
$HC(CH_3)_2OTs$ (**4**)	110.00	$(1.32 \pm 0.02) \times 10^{-3}$	19.1 ± 0.2	−22.3 ± 0.5
	95.00	$(4.57 \pm 0.10) \times 10^{-4}$		
	80.00	$(1.45 \pm 0.03) \times 10^{-4}$		
	25.0[a]	7.89×10^{-7}[b]		
$N{\equiv}CC(CH_3)_2OTf$ (**5**)	65.00	$(2.81 \pm 0.01) \times 10^{-3}$	21.4 ± 0.5	−8.9 ± 1.6
	50.00	$(6.61 \pm 0.10) \times 10^{-4}$		
	35.00	$(1.26 \pm 0.13) \times 10^{-4}$		
	25.0[a]	3.86×10^{-5}		
$N{\equiv}CC(CD_3)_2OTf$ (**6**)	65.00	$(1.17 \pm 0.03) \times 10^{-3}$	20.3 ± 0.2	−12.0 ± 0.7
	50.00	$(2.88 \pm 0.01) \times 10^{-4}$		
	35.00	$(5.60 \pm 0.01) \times 10^{-5}$		
	25.0[a]	1.77×10^{-5}		

[a] Extrapolated from higher temperatures. [b] The rate of 2-propyl *p*-toluenesulfonate has previously been measured in 97% 2,2,2-trifluoroethanol: 6.4×10^{-7} s^{-1}, Schadt, F. L.; Schleyer, P. v. R. *Tetrahedron Lett.* **1974**, 2335. 6.66×10^{-7} s^{-1}, Schadt, F. L.; Bentley, T. W.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1976**, *98*, 7667. See also Shiner, V. J., Jr.; Fisher, R. D.; Dowd, W. *Ibid.* **1969**, *91*, 7748.



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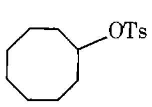

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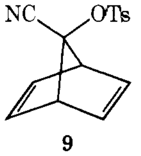
even in such solvent systems as aqueous ethanol.[11] As shown in Table II, comparison of **7**[12] with cylooctyl *p*-toluenesulfonate (**8**) gave an H/CN rate ratio of 1.87×10^3. This value was almost identical with the H/CN rate ratio observed in the 2-propyl system.[13] This supports the contention that nucleophilic solvent participation is not the source of the relatively small H/CN rate ratio.

On the basis of the data provided, it might be proposed that the inductive effect of an α-cyano group on an incipient carbonium-ion center is actually much smaller than predicted on the basis of σ^* values. In an approach to evaluating this possibility, we decided to study a system where major delocalization of the developing positive charge would occur through neighboring-group participation. If neighboring-group participation resulted in an H/CN rate ratio significantly greater than those observed for the 2-propyl and cyclooctyl systems, it could be concluded that the natural inductive destabilization by the cyano group is greater than those indicated by the data in Tables I and II. Solvolysis of **9** in 2,2,2-trifluoroethanol buffered with 2,6-lutidine resulted in an H/CN rate ratio of ~10^6 when compared with literature values for **10**. While extrapolations are (of necessity) involved in this comparison,[14] we feel that there is little doubt but that the H/CN rate ratio for this pair (**9** and **10**) is considerably larger than those listed in Tables I and II. Thus, this represents a *minimal* inductive effect. This indicates that, in situations where charge delocalization is extensive, the mesomeric effect of the cyano moiety is significantly decreased while the inductive effect remains impressively strong.



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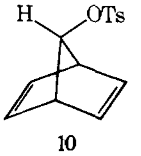

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In view of the data presented above, we believe that an α-cyano group can be at the same time inductively destabilizing and mesomerically stabilizing on an incipient carbonium-ion center. We are continuing to investigate the generation and reactions of electron-deficient cationic centers.

Table II. Rates of Solvolysis of Cyclooctyl *p*-Toluenesulfonate and 1-Cyanocyclooctyl *p*-Toluenesulfonate in 100% 2,2,2-Trifluoroethanol Buffered with 2,6-Lutidine

compd	temp °C (+0.02 °C)	rate, s^{-1}	$\Delta H^{\ddagger}$ kcal/mol	$\Delta S^{\ddagger}$, eu
7	95.00	$(3.79 \pm 0.03) \times 10^{-3}$	22.1 ± 0.1	−10.0 ± 0.4
	80.00	$(1.02 \pm 0.01) \times 10^{-3}$		
	65.00	$(2.40 \pm 0.04) \times 10^{-4}$		
	25.0[a]	2.54×10^{-6}		
8	25.00	$(4.76 \pm 0.01) \times 10^{-3}$[b]		
	0.00	$(3.31 \pm 0.02) \times 10^{-4}$		

[a] Extrapolated from higher temperatures. [b] A rate of 5.16×10^{-3} s^{-1} has been reported for **8** at 25 °C in 97% 2,2,2-trifluoroethanol.[11]

Acknowledgments. We are indebted to the National Science Foundation for Grant CHE78-10231 which supported this investigation. We thank Professor T. T. Tidwell for informing us of his results prior to publication.

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(2) For a leading reference see Gassman, P. G. *Acc. Chem. Res.* **1970**, *3*, 26.

(3) *If the nature of* R *or* R′ is such *that* extensive *stabilization is provided* to *the* carbonium-ion center (for instance, through major neighboring-group participation), the contribution from **2** may be minimal. Gassman, P. G.; Talley, J. J., submitted for publication.

(4) Taft, R. W. In "Steric Effects in Organic Chemistry", Newman, M. S., Ed.; Wiley, New York, 1956; Chapter 13.

(5) On the basis of the β-cyano effect, a rate retardation of well in excess of 10^{10} should be observed for an α-cyano effect. This is derived from the 2.8 factor for the decrease in inductive effect on addition of an insulating methylene group. An H/α-cyano ratio of $\sim 10^{11}$–10^{18} would be predicted on the basis of an inductive retardation as the only effect of the cyano function.

(6) This ratio comes from $(k_5/k_6)^{1/2}$.

(7) Streitwieser, A., Jr.; Dafforn, G. A. *Tetrahedron Lett.* **1969**, 1263.

(8) In general, E2 eliminations exhibit CH_3/CD_3 isotope effects of 2–8. Saunders, W. H., Jr.; Cockerill, A. F. "Mechanisms of Elimination Reactions"; Wiley: New York, 1973; pp 79–84. See also Shiner, V. J., Jr. In "Isotope Effects in Chemical Reactions", Collins, C. J., Bowman, N. S., Ed.; Van Nostrand-Reinhold: Princeton, N.J., 1970; Chapter 2, pp 142–145.

(9) Deuterium isotope effects on reactions with major S_N2 components are thought to be smaller than we have observed. For a detailed discussion and leading reference see Fisher, R. D.; Seib, R. C.; Shiner, V. J., Jr.; Szele, I.; Tomic, M.; Sunko, D. E. *J. Am. Chem. Soc.* **1975**, *97*, 2408.

(10) For a leading discussion of S_N2 solvent participation in solvolysis see Bentley, T. W.; Bowen, C. T.; Parker, W.; Watt, C. I. F. *J. Am. Chem. Soc.* **1979**, *101*, 2486. We believe that the data provided in this reference is consistent with the absence of nucleophilic solvent assistance in the solvolysis of **7**.

(11) Harris, J. M.; Mount, D. L.; Smith, M. R.; McManus, S. P. *J. Am. Chem. Soc.* **1977**, *99*, 1283. Harris, J. M.; Mount, D. L.; Smith, M. R.; Neal, W. C., Jr.; Dukes, M. D.; Raber, D. J. *Ibid.* **1978**, *100*, 8147.

(12) Compound **7** was prepared from cyclooctanone according to our published method: Gassman, P. G.; Talley, J. J. *Tetrahedron Lett.* **1978**, 3773.

(13) It is interesting to note that **7** yields 92% 1-cyanocyclooctene as the only identifiable product from this solvolysis.

(14) The details of this comparison and of the synthesis, solvolysis, and product studies related to **9** will be forthcoming: P. G. Gassman and J. J. Talley, submitted for publication.

(15) Proctor and Gamble Fellow, 1977–1978; University of Minnesota Dissertation Fellow, 1978–1979.

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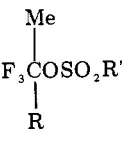
Received August 6, 1979

Solvolytic Reactivity of α-Trifluoromethylcarbinyl Sulfonates. Correlation of Rate Retardation by Electron-Withdrawing Substituents and Solvent Participation in Tertiary Substrates[1]

Sir:

We report here that the trifluoromethyl group is enormously deactivating relative to hydrogen as an α substituent in solvolysis reactions and that a tertiary sulfonate ester bearing this group shows evidence for strong nucleophilic solvent participation.

The rates of reaction of α-trifluoromethylcarbinyl sulfonates **1**[2] were measured in various solvents as summarized in Table I. The only product observed for **1a** was the alkene $CF_3CMe{=}CH_2$, whereas **1c** and **1d** led predominantly to the solvolysis product $CF_3CMePhOY$ and lesser amounts of alkene.[3]



$$CF_3C(Me)(R)OSO_2R'$$

	Me	R	R′
1a	CH_3	CH_3	*p*-Tol
1b	CH_3	CH_3	CH_3
1c	CH_3	Ph	*p*-Tol
1d	CD_3	Ph	*p*-Tol

The reactivities of the CF_3-substituted sulfonates **1** are greatly depressed compared with those of the corresponding hydrogen substituted compounds. Thus, rate ratios for α substituents, k_H/k_{CF_3}, are 1.1×10^5 to 2.3×10^6 from comparisons with rates for Me_2CHOTs[4,5] and derived rates for $PhCHMeOTs$[6] in various solvents. These ratios approach that of 10^7 which we have measured[7] for the rates of protonation of the styrenes $PhCR{=}CH_2$ in aqueous acid.

Recently substituent parameters have been derived for the influence of α substituents R in solvolysis reactions (eq 1).[8]

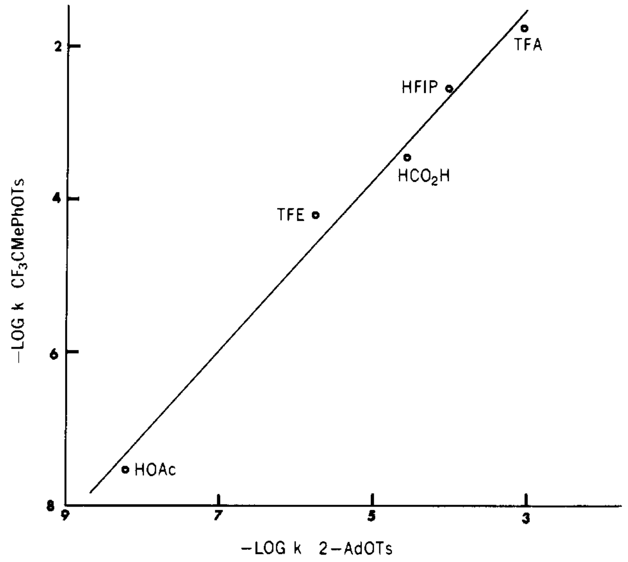
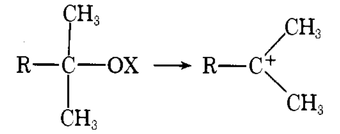


Figure 1. Comparison of the effect of solvent variation on the reactivity of $CF_3CMePhOTs$ (**1c**) and 2-adamantyl tosylate at 25 °C.

 (1)

$$R{-}C(CH_3)_2{-}OX \longrightarrow R{-}C^+(CH_3)_2 \qquad (1)$$

This approach was originally discussed by Traylor and Ware[8a] and has been extended by Peters[8b] and by Harris and McManus,[8c] and the designation of γ^+ for these parameters seems destined for general acceptance. Application of their treatment leads to a γ^+ parameter of 3.0 for CF_3,[9] establishing this as the most deactivating group examined by this method. For comparison, γ^+ parameters for H, Me, and Ph are 2.56, 0.63, and 0.0, respectively.

Recent studies[5a,10] of the effect of solvent on solvolytic reactivity have established that nucleophilic solvent participation is involved in some but not all secondary sulfonates[5a,10,11a,c] and may even occur in *tert*-butyl halides.[10e]

In the case of $CF_3CMePhOTs$ (**1c**) a linear free-energy relationship (Figure 1) exists for rates in various solvents compared with those for 2-adamantyl tosylate[5a] with a slope corresponding to an m_{OTs} value for **1c** of 1.11. This result indicates that **1c** reacts by rate-determining formation of a carbonium ion (k_c process) and the magnitude of m_{OTs} indicates a great demand for solvation induced by the electron-withdrawing CF_3 group. The isotope effect $k(CH_3)/k(CD_3) = 1.54$ for **1c** is also characteristic[11] of a k_c process (cf. $k(CH_3)/k(CD_3) = 1.48$ for 2-methyl-2-adamantyl chloride).[11b]

For **1a** and **1b**, reactivities in the more nucleophilic solvents H_2O and acetic acid are enhanced relative to trifluoroacetic acid suggesting significant nucleophilic solvent participation in the former. A quantitative measure of the degree of solvent participation,[10a] namely the ratio $[k(ROTs)/k(2\text{-}AdOTs)]_{solvent}/[k(ROTs)/k(2\text{-}AdOTs)]_{TFA}$, gives values for **1a** of 200 in H_2O and 4200 in acetic acid. These values are even higher than those for 2-propyl tosylate and indicate major solvent assistance in **1a**.

The reactivities of **1a–d** are interpretable in terms of the generally accepted[10] ion-pair mechanism of solvolysis:

$$CF_3CMeROTs \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} CF_3CMeR^+OTs^- \xrightarrow[k_2]{YOH} \text{products} \qquad (2)$$

For **1c** k_1 is rate determining, but for **1a** k_2, involving solvent assisted elimination, is evidently the slow step. Similar behavior has been suggested for *tert*-butyl halides.[10a,e]

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