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# The $\alpha$ -cyano group as a substituent in solvolysis reactions. An evaluation of inductive destabilization vs. mesomeric stabilization of cations by the cyano moiety [41]

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change process,<sup>3</sup> with both processes possibly proceeding via isocarbonyl intermediates or transition states ( $M-C\equiv O\cdots Rh \rightarrow M\cdots C\equiv O-Rh \rightarrow M\cdots O\equiv C-Rh$ ).<sup>16</sup> 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 ( $\eta^2(C,O) CO$ ) 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.<sup>16</sup>

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

## References and Notes

- (1) See, for example, Perutz, R.; Turner, J. J. *Inorg. Chem.* **1975**, *14*, 262.
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- (4) Daresbourg, D. J.; Salzer, A. *J. Am. Chem. Soc.* **1978**, *100*, 4119.
- (5) The level of  $^{13}CO$  enrichment was not extremely dependent on the quantity of excess  $(n-Bu)_3P=O$  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.
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- (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  $30^\circ$ . 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  $\nu(CO)$  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  $(n-Bu)_3P=O$ , 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  $^{13}CO$  ( $\sim 17.3$  mmol). Heating at  $70^\circ C$  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  $(n-Bu)_3P=O$  and drying the hexane layer with  $CaCl_2$ , followed by vacuum distillation of the hexane solvent and sublimation of the hexacarbonyl product at  $40^\circ C$ . 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  $Mo(^{13}CO)_4(^{13}CO)_2$ .
- (10) Synthesis of  $(py)Fe(CO)_4$  was accomplished using the procedure of Cotton and Troup.<sup>11</sup> The reaction of  $(py)Fe(CO)_4$  with  $(n-Bu)_3PO$  (1:2 molar ratio) was carried out in a  $^{13}CO$  atmosphere at  $50^\circ C$  in hexane solvent. After 4 h the level of  $^{13}CO$  enrichment in the iron pentacarbonyl was  $\sim 70\%$ .
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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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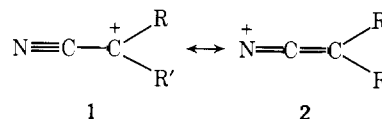
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## The $\alpha$ -Cyano Group as a Substituent in Solvolysis Reactions. An Evaluation of Inductive Destabilization vs. Mesomeric Stabilization of Cations by the Cyano Moiety

Sir:

Amazingly little is known about the effect of strong elec-

tron-withdrawing substituents on incipient carbonium-ion centers. Recently, interest in this area has been increasing.<sup>1</sup> We now report our preliminary results on the influence of the  $\alpha$ -cyano group on incipient carbonium-ion centers and to propose that  $\alpha$ -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**.



Interestingly, the resonance form **2** is a nitrenium ion, which should be much less stable than an analogous carbonium ion.<sup>2</sup> 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'.<sup>3</sup>

Recently, Koshy and Tidwell have found that an  $\alpha$ -trifluoromethyl group provides a rate retardation of  $10^6$  relative to hydrogen in the solvolysis of simple sulfonate esters.<sup>1j</sup> Similarly, Creary has found an H/ $\alpha$ -keto rate ratio of  $10^7$ .<sup>1k</sup> On the basis of the Taft polar substituent constants [ $\sigma^*(\text{NCCH}_2)$  (1.30),  $\sigma^*(\text{CF}_3\text{CH}_2)$  (0.92), and  $\sigma^*(\text{CH}_3\text{C}(=\text{O})\text{CH}_2)$  (0.60)],<sup>4</sup> it might be predicted that an  $\alpha$ -cyano moiety would have a greater rate retarding effect than either the  $\alpha$ -trifluoromethyl or  $\alpha$ -keto group. As shown in Table I, the influence of the  $\alpha$ -cyano group on the rate of solvolysis of 2-propyl sulfonates resulted in an H/ $\alpha$ -cyano ( $k_3/k_4$ ) rate ratio of only  $3.5 \times 10^3$ . 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  $\beta$ -cyano substitution.<sup>1l,5</sup>

A number of different explanations might be suggested for the relatively small rate effect resulting from the introduction of the  $\alpha$ -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.

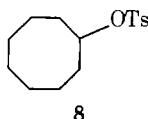
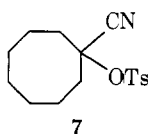
To evaluate the possibility of rate-limiting, concerted (E2) elimination, we measured the effect of  $\beta$ -deuterium substitution on the rate of solvolysis of 2-cyano-2-propyl trifluoromethanesulfonate. At  $25^\circ C$ , a  $\text{CH}_3/\text{CD}_3$  rate ratio<sup>6</sup> of 1.48 was observed. This value is very similar to the value of 1.46 found for 2-propyl *p*-bromobenzenesulfonate in trifluoroacetic acid.<sup>7</sup> More significantly, it is very close to the value of 1.54 obtained for the  $\text{CD}_3$  isotope effect observed in the solvolysis of 2-trifluoromethyl-2-propyl *p*-toluenesulfonate.<sup>1j</sup> These values are too small for a rate-limiting, concerted elimination.<sup>8,9</sup> The observation of an isotope effect similar to that found in the presence of an  $\alpha$ -trifluoromethyl group (which provides a  $10^6$  rate retardation) suggests that an  $\alpha$ -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.<sup>9</sup> To strengthen the basis for ruling out  $S_N2$  involvement by solvent,<sup>10</sup> 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

**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

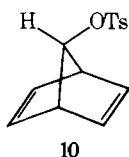
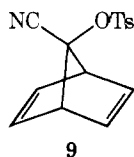
compd	temp, °C (+0.02 °C)	rate, s <sup>-1</sup>	$\Delta H^\ddagger$ , kcal/mol	$\Delta S^\ddagger$ , eu
N≡CC(CH <sub>3</sub> ) <sub>2</sub> OTs (3)	170.00	$(1.21 \pm 0.04) \times 10^{-3}$	27.5 ± 1.5	-10.5 ± 3.6
	155.00	$(5.19 \pm 0.01) \times 10^{-4}$		
	140.00	$(1.22 \pm 0.02) \times 10^{-4}$		
	25.0 <sup>a</sup>	$2.24 \times 10^{-10}$		
HC(CH <sub>3</sub> ) <sub>2</sub> OTs (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 <sup>a</sup>	$7.89 \times 10^{-7}$ <sup>b</sup>		
N≡CC(CH <sub>3</sub> ) <sub>2</sub> OTf (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 <sup>a</sup>	$3.86 \times 10^{-5}$		
N≡CC(CD <sub>3</sub> ) <sub>2</sub> OTf (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 <sup>a</sup>	$1.77 \times 10^{-5}$		

<sup>a</sup> Extrapolated from higher temperatures. <sup>b</sup> The rate of 2-propyl *p*-toluenesulfonate has previously been measured in 97% 2,2,2-trifluoroethanol:  $6.4 \times 10^{-7}$  s<sup>-1</sup>, Schadt, F. L.; Schleyer, P. v. R. *Tetrahedron Lett.* **1974**, 2335.  $6.66 \times 10^{-7}$  s<sup>-1</sup>, 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.



even in such solvent systems as aqueous ethanol.<sup>11</sup> As shown in Table II, comparison of **7**<sup>12</sup> with cyclooctyl *p*-toluenesulfonate (**8**) gave an H/CN rate ratio of  $1.87 \times 10^3$ . This value was almost identical with the H/CN rate ratio observed in the 2-propyl system.<sup>13</sup> 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  $\alpha$ -cyano group on an incipient carbonium-ion center is actually much smaller than predicted on the basis of  $\sigma^*$  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  $\sim 10^6$  when compared with literature values for **10**. While extrapolations are (of necessity) involved in this comparison,<sup>14</sup> 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.

In view of the data presented above, we believe that an  $\alpha$ -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 <sup>-1</sup>	$\Delta H^\ddagger$ , kcal/mol	$\Delta S^\ddagger$ , eu
<b>7</b>	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 <sup>a</sup>	$2.54 \times 10^{-6}$		
<b>8</b>	25.00	$(4.76 \pm 0.01) \times 10^{-3}$ <sup>b</sup>		
	0.00	$(3.31 \pm 0.02) \times 10^{-4}$		

<sup>a</sup> Extrapolated from higher temperatures. <sup>b</sup> A rate of  $5.16 \times 10^{-3}$  s<sup>-1</sup> has been reported for **8** at 25 °C in 97% 2,2,2-trifluoroethanol.<sup>11</sup>

**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.

## References and Notes

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- (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  $\beta$ -cyano effect, a rate retardation of well in excess of  $10^{10}$  should be observed for an  $\alpha$ -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/ $\alpha$ -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  $(k_8/k_9)^{1/2}$ .
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- (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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### Solvolytic Reactivity of $\alpha$ -Trifluoromethylcarbonyl Sulfonates. Correlation of Rate Retardation by Electron-Withdrawing Substituents and Solvent Participation in Tertiary Substrates<sup>1</sup>

Sir:

We report here that the trifluoromethyl group is enormously deactivating relative to hydrogen as an  $\alpha$  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  $\alpha$ -trifluoromethylcarbonyl sulfonates **1**<sup>2</sup> were measured in various solvents as summarized in Table I. The only product observed for **1a** was the alkene  $\text{CF}_3\text{CMe}=\text{CH}_2$ , whereas **1c** and **1d** led predominantly to the solvolysis product  $\text{CF}_3\text{CMePhOY}$  and lesser amounts of alkene.<sup>3</sup>

	Me	R	R'
<b>1a</b>	$\text{CH}_3$	$\text{CH}_3$	<i>p</i> -Tol
<b>1b</b>	$\text{CH}_3$	$\text{CH}_3$	$\text{CH}_3$
<b>1c</b>	$\text{CH}_3$	Ph	<i>p</i> -Tol
<b>1d</b>	$\text{CD}_3$	Ph	<i>p</i> -Tol

The reactivities of the  $\text{CF}_3$ -substituted sulfonates **1** are greatly depressed compared with those of the corresponding hydrogen substituted compounds. Thus, rate ratios for  $\alpha$  substituents,  $k_{\text{H}}/k_{\text{CF}_3}$ , are  $1.1 \times 10^5$  to  $2.3 \times 10^6$  from comparisons with rates for  $\text{Me}_2\text{CHOTs}$ <sup>4,5</sup> and derived rates for  $\text{PhCHMeOTs}$ <sup>6</sup> in various solvents. These ratios approach that of  $10^7$  which we have measured<sup>7</sup> for the rates of protonation of the styrenes  $\text{PhCR}=\text{CH}_2$  in aqueous acid.

Recently substituent parameters have been derived for the influence of  $\alpha$  substituents R in solvolysis reactions (eq 1).<sup>8</sup>

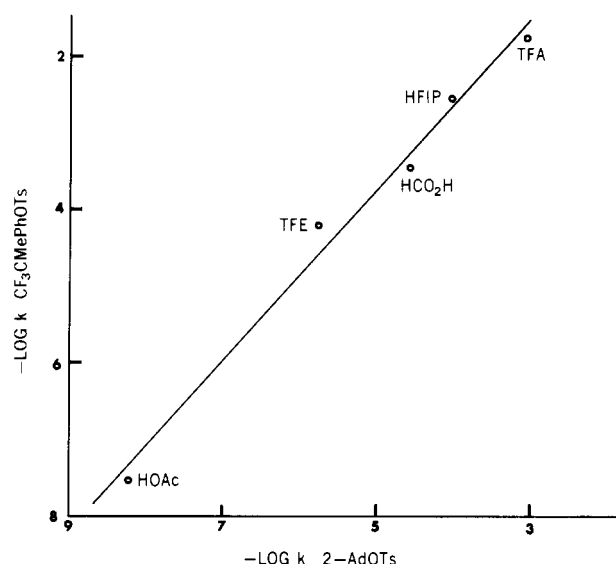
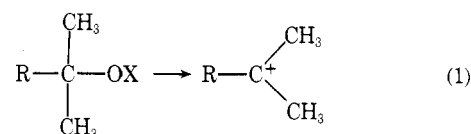


Figure 1. Comparison of the effect of solvent variation on the reactivity of  $\text{CF}_3\text{CMePhOTs}$  (**1c**) and 2-adamantyl tosylate at 25 °C.



This approach was originally discussed by Traylor and Ware<sup>8a</sup> and has been extended by Peters<sup>8b</sup> and by Harris and McManus,<sup>8c</sup> and the designation of  $\gamma^+$  for these parameters seems destined for general acceptance. Application of their treatment leads to a  $\gamma^+$  parameter of 3.0 for  $\text{CF}_3$ ,<sup>9</sup> establishing this as the most deactivating group examined by this method. For comparison,  $\gamma^+$  parameters for H, Me, and Ph are 2.56, 0.63, and 0.0, respectively.

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

In the case of  $\text{CF}_3\text{CMePhOTs}$  (**1c**) a linear free-energy relationship (Figure 1) exists for rates in various solvents compared with those for 2-adamantyl tosylate<sup>5a</sup> with a slope corresponding to an  $m_{\text{OTs}}$  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  $m_{\text{OTs}}$  indicates a great demand for solvation induced by the electron-withdrawing  $\text{CF}_3$  group. The isotope effect  $k(\text{CH}_3)/k(\text{CD}_3) = 1.54$  for **1c** is also characteristic<sup>11</sup> of a  $k_c$  process (cf.  $k(\text{CH}_3)/k(\text{CD}_3) = 1.48$  for 2-methyl-2-adamantyl chloride).<sup>11b</sup>

For **1a** and **1b**, reactivities in the more nucleophilic solvents  $\text{H}_2\text{O}$  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,<sup>10a</sup> namely the ratio  $[k(\text{ROT})]/k(2\text{-AdOTs})]_{\text{solvent}}/[k(\text{ROT})]/k(2\text{-AdOTs})]_{\text{TFA}}$ , gives values for **1a** of 200 in  $\text{H}_2\text{O}$  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<sup>10</sup> ion-pair mechanism of solvolysis:



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.<sup>10a,e</sup>