of 7.6 g (0.055 mol) of 1,3-dimethoxybenzene in $EtNO_2$. After 1 hr the mixture was poured into 5% HCl-water, extracted with $CHCl_3$, and dried (Na_2SO_4), and the solvent was removed under vacuum. The crude product was crystallized from EtOH: mp 91–92°; yield 85%; nmr ($CDCl_3$) 2.10 (6), 2.26 (3), 3.68 (3), 3.76 (3), 6.46 (2), 6.80 (2), 7.55 (1).

Anal. Calcd for $C_{18}H_{20}O_3$: C, 76.02; H, 7.09; mol wt 284.34. Found: C, 75.88; H, 7.16; mol wt (dichloroethane 50°) 283.4.

Nmr. ^1H nmr spectra were obtained using a Varian A-60 spectrometer (60 MHz). Spectra of aromatic ketones examined consist of two types of signals corresponding to methyl and nuclear protons, respectively. Methyl peaks appear as sharp singlets. Aromatic protons have various appearances according to nuclear substitution patterns. However, nuclear protons in positions ortho to the carbonyl group resonate at lower field values with respect to those meta and para. This makes straightforward the assignment of ortho nuclear protons.

Dipole Moments. Purification of solvent, the apparatus used for the measurements of dielectric constants and refractive indices differences, and the Guggenheim procedure for the calculation of μ were described in a previous paper.[1] The dielectric constant data (Table III) were measured in benzene at 25 ± 0.01°.

Sulfonate Leaving Groups, Structure and Reactivity. 2,2,2-Trifluoroethanesulfonate

R. K. Crossland,*[1] W. E. Wells,[2] and V. J. Shiner, Jr.

Contribution from the Department of Chemistry, Indiana University, Bloomington, Indiana 47401. *Received July 25, 1970*

Abstract: An easily synthesized reactive new leaving group, 2,2,2-trifluoroethanesulfonate (tresylate), is described. Preparations of tresyl chloride and tresylate esters have been developed. Solvolysis rates of several tresylate esters have been determined and typically appear to be about 100 times *larger* than those of the corresponding *p*-toluenesulfonates (tosylates) and 400 times *smaller* than those of the corresponding trifluoromethanesulfonates (triflates). A linear free energy relationship is shown to correlate limiting solvolysis rates of $X{-}SO_3R$ esters and σ_m of X with a ρ of +10.3. Convenient solvolysis rates for a wide range of R groups and solvents are obtainable with these leaving groups.

Since the introduction of the Tipson procedure for the synthesis of tosylates,[3] synthetic and especially physical organic chemistry has been well served by arenesulfonate leaving groups.[4] The recent introduction of trifluoromethanesulfonates (triflates)[5,6] has increased the solvolytic reactivity spread between various sulfonate esters to about 80,000.[7,8] However, the reactivity spread is not gradual; the commonly used leaving groups (mesylate, tosylate, brosylate) differ in reactivity by only a factor of ten[9] while triflate is about 8000 times more reactive than brosylate, the most reactive of these groups. Thus, a considerable reactivity gap exists between triflate and other sulfonate esters.

Recently, the synthetic advantages of preparing sulfonate esters by the addition of alcohols to the appropriate sulfene[10] have been pointed out.[11] This method requires precursor sulfonyl halides possessing at least one hydrogen α to the sulfonyl group. As a part of a continuing investigation of leaving groups we have sought to develop new sulfonate esters of intermediate solvolytic reactivity which may be prepared using the sulfene mechanism. In this paper we report the synthesis and characterization of 2,2,2-trifluoroethanesulfonates (tresylates, -OTr) and present a new linear free energy correlation which approximately correlates the rates of solvolysis of sulfonate esters with the substituent on sulfur.

Based on a patent description[12] the first detailed synthesis of 2,2,2-trifluoroethanesulfonyl chloride (tresyl chloride) was published by Truce.[13] The low overall yield of this method (6.7%) clearly renders it unsuitable for preparative scale procedures. Our procedure differs from that of Truce in that the starting material was 2,2,2-trifluoroethyl mesylate instead of the corresponding tosylate and the displacement reaction with a sulfur nucleophile was carried out with thiocyanate instead of disulfide. The starting mesylate was readily available in high yield from trifluoroethanol.[11] Displacement of mesylate by thiocyanate was accomplished in dimethylformamide solution. The resulting alkyl thiocyanate was then oxidized to tresyl chloride with chlorine in wet trifluoroacetic acid to give an overall yield, based on 2,2,2-trifluoroethyl mesylate, of 41%. Tresylate esters may be prepared from alcohols by procedures analogous to those used to prepare mesylates.[11] However, in this case, the sulfene is more readily generated due to activation of the system toward dehydro-

$$CF_3CH_2OH \longrightarrow CF_3CH_2OMs \longrightarrow$$
$$CF_3CH_2SCN \longrightarrow CF_3CH_2SO_2Cl$$

---

(1) To whom correspondence should be addressed at the Shell Chemical Co., Torrance, Calif. 90509.

(2) Undergraduate Research Participant, 1970.

(3) R. S. Tipson, *J. Org. Chem.*, **9**, 235 (1944).

(4) For a survey of newer methods of preparing arenesulfonates, see R. M. Coates and J. P. Chen, *Tetrahedron Lett.*, 2705 (1969).

(5) T. Gramsted and R. N. Haszeldine, *J. Chem. Soc.*, 4069 (1957), and the references cited therein.

(6) R. L. Hansen, *J. Org. Chem.*, **30**, 4322 (1965).

(7) A. Streitwieser, Jr., C. L. Wilkins, and E. Kiehlman, *J. Amer. Chem. Soc.*, **90**, 1598 (1968).

(8) T. M. Su, W. F. Sliwinski, and P. v. R. Schleyer, *ibid.*, **91**, 5386 (1969).

(9) R. E. Robertson, *Progr. Phys. Org. Chem.*, **4**, 213 (1967).

(10) For a review of sulfenes as reaction intermediates, see G. Opitz, *Angew. Chem., Int. Ed. Engl.*, **6**, 107 (1967).

(11) R. K. Crossland and K. L. Servis, *J. Org. Chem.*, **35**, 3195 (1970).

(12) R. E. Oesterling, U. S. Patent 3,006,964 (Oct 31, 1961). Note: as pointed out by Truce (ref 13), the *Chemical Abstracts* reference [*Chem. Abstr.*, **56**, 9967c (1962)] is in error.

(13) W. E. Truce and J. R. Norell, *J. Amer. Chem. Soc.*, **85**, 3231 (1963).

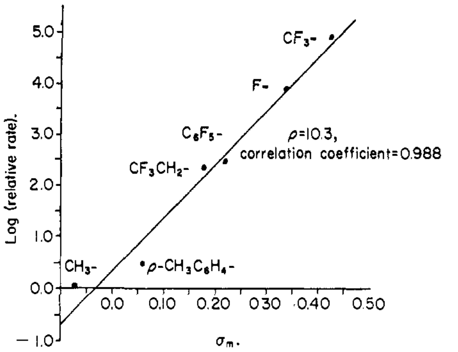

Figure 1. Hammett plot for the solvolytic alkyl oxygen cleavage of X-SO_3R. In general, σ_m constants were taken from C. D. Ritchie and W. F. Sager, *Progr. Phys. Org. Chem.*, **2**, 334 (1964): CH_3–, relative rate = 1; *p*-$CH_3C_6H_4$–, σ_m assumed to be the same as C_6H_5–, relative rate taken from ref 9; CF_3CH_2–, σ_m was taken from W. A. Sheppard and C. M. Shorts, "Organic Fluorine Chemistry," W. A. Benjamin, New York, N. Y., 1969, p 349; C_6F_5–, σ_m taken from M. G. Barlow, M. Green, R. W. Haszeldine, and H. G. Higson, *J. Chem. Soc. B*, 1025 (1966) (ref 18 suggests a slightly higher value of 0.26; relative rate measured by Mr. W. Dowd, Department of Chemistry, Indiana University, 1969); F–, relative rate taken from ref 8; CF_3–, relative rate taken from ref 7 and 8.

halogenation by the trifluoromethyl group. Hence, very mild reaction conditions may be used; usually esterification proceeds rapidly at −10 to −25° in chlorocarbon or hydrocarbon solvents.

Solvolysis of α-methyl-3,5-ditrifluoromethylbenzyl mesylate and tresylate in 80% ethanol at 25.0° showed the tresylate ester to be about 175 times more reactive than the mesylate.[14] For the 2-adamantyl system the tresylate/tosylate rate ratio is 107 at 25° in 50% ethanol.[15] We have found tresylates to be especially useful in mechanistic studies using structures and solvent systems which give inconvenient rates with other leaving groups. We have observed that the rate of solvolysis of sulfonate esters by a limiting (without covalent attachment of solvent at the transition state[16]) or SN1-like[17] process correlates approximately (least squares fit) with σ_m of the substituent on sulfur (Figure 1) and a ρ value of + 10.3. We feel the fit to be more than adequate (correlation coefficient = 0.988), because of the variety of solvents and structures from which the relative rates were derived and the large reactivity span covered by the correlation. A comparison of tresylate to pentafluorobenzenesulfonate is pertinent. Recently Sheppard has suggested[18] that the inductive effects of the 2,2,2-trifluoroethyl and pentafluorophenyl groups should be similar, with the latter one being slightly larger. Our relative rate data indicate that this is the case.

The correlation, though approximate, allows the prediction of the gross effects of various sulfonyl substituents on solvolytic reaction rates. It is evident from the magnitude of the ρ value that substantial negative charge develops on sulfur at the transition state in the limiting or SN1 case. However, when the transition state for solvolysis is less than limiting, charge development and hence the ρ value should reflect the nucleophilic character (N,[16] SN2[17]) of the transition state.[19] More simply the rate ratio between various leaving groups should be a measure of this character. For some time the tosylate/bromide rate ratio has been used as this type of mechanistic probe.[19,20] We suggest that the tresylate/mesylate rate ratio may be both a more reliable indicator and more precise than the tosylate/bromide rate ratio because large differences in leaving group hydrogen bonding ability, size,[21] and symmetry are absent.[22] In addition, to the degree that leaving group ability depends on conjugate acid strengths, the correlation may be useful in assessing the relative strengths of various sulfonic acids. We are continuing work to expand and refine further the predictive ability of the linear free energy correlation and hopefully develop other new useful leaving groups.

Experimental Section

General. Boiling points are uncorrected. The ^1H nmr spectra were recorded on a Varian A-60 spectrometer using internal tetramethylsilane as a reference. The ^{19}F nmr spectra were recorded on a Varian HA-100 spectrometer; chemical shifts are reported downfield from internal trifluoroacetic acid. Infrared spectra were recorded on a Perkin-Elmer Model 137 spectrometer. The 2,2,2-trifluoroethanol was purchased from Halocarbon Corp. and distilled before use.

2,2,2-Trifluoroethyl mesylate was prepared as previously outlined.[11] From 100 g (1.00 *M*) of 2,2,2-trifluoroethanol, 115 g (1.14 *M*) of triethylamine, and 126 g (1.10 *M*) of methanesulfonyl chloride was obtained 154 g (86.8%) of product, bp 97–99° (35 mm). The ^1H nmr spectrum (neat) showed a singlet at 3.13 ppm (3 H) and a quartet at 4.62 ppm (2 H, $J_{H,F}$ = 8.0 Hz).

2,2,2-Trifluoroethyl Thiocyanate. A solution of 97.2 g (1.2 *M*) of sodium thiocyanate in 200 ml of dimethylformamide (DMF) was brought to reflux and distilled until the head temperature reached 153° (about 40 ml of DMF collected). To the cooled solution was added 53.4 g (0.30 *M*) of the preceding mesylate. The reaction mixture was slowly distilled and the fraction with bp 140–152° (about 100 ml) was collected over a period of 1–1.5 hr. The distillate was taken up in 200 ml of methylene chloride, extracted five times with 100-ml aliquots of water and once with brine, and dried over magnesium sulfate. Solvent was removed and the residue vacuum distilled; the fraction with bp 53–72° (30 mm) was collected. The ^1H nmr spectrum of the distillate (CCl_4) showed about 2% DMF, about 90% product thiocyanate (quartet at 3.45 ppm, $J_{H,F}$ = 9.7 Hz), and from 5 to 12% of an unidentified contaminant (quartet at 3.53 ppm, $J_{H,F}$ = 8.6 Hz), possibly the corresponding isothiocyanate. Traces of other impurities were also evident. The ^{19}F nmr spectrum of the product showed a triplet at 8.01 ppm. The ir spectrum (CCl_4) showed a weak absorption at 2150 cm^{-1} (-SCN). The yield of product, corrected for impurities, was 24.6 g (58.0%).

2,2,2-Trifluoroethanesulfonyl chloride (tresyl chloride) was prepared by bubbling excess chlorine over a period of 1.5 hr into a solution of 21.2 g (0.15 mol) of 2,2,2-trifluoroethyl thiocyanate (appropriate amount of preceding distillate used) in 20 ml of trifluoroacetic acid and 7.70 ml (0.30 mol of water) of concentrated hydrochloric acid at 25–30°. The reaction mixture was vacuum transferred at 15 mm and the distillate collected in a trap cooled in ice.[23] The distillate was then vacuum distilled to give 19.2 g

---

(14) Rates were determined conductometrically. For example, see V. J. Shiner, Jr., W. E. Buddenbaum, B. L. Murr, and G. Lamaty, *J. Amer. Chem. Soc.*, **90**, 418 (1968), and the references cited therein.

(15) Data for the tresylate were from V. J. Shiner, Jr., and R. D. Fisher,, *ibid.*, **93**, 2553 (1971). Data for the tosylate were taken from P. v. R. Schleyer, J. L. Fry, L. K. M. Lam, and C. J. Lancelot, *ibid.*, **92**, 2542 (1970).

(16) S. Winstein, E. Grunwald, and H. W. Jones, *J. Amer. Chem. Soc.*, **73**, 2700 (1951).

(17) C. K. Ingold, "Structure and Mechanism in Organic Chemistry," Cornell University Press, Ithaca, N. Y., 2nd ed, 1969, Chapter VII, p 418 ff.

(18) W. A. Sheppard, *J. Amer. Chem. Soc.*, **92**, 5419 (1970).

(19) H. M. R. Hoffman, *J. Chem. Soc.*, 6753 (1965).

(20) J. L. Fry, C. J. Lancelot, L. K. M. Lam, J. M. Harris, R. C. Bingham, D. J. Raber, R. E. Hall, and P. v. R. Schleyer, *J. Amer. Chem. Soc.*, **92**, 2538 (1970).

(21) For example the conductivity parameters, Λ_0 and S_0, are nearly identical for methanesulfonic acid and 2,2,2-trifluoroethanesulfonic acid in a variety of solvents.

(22) For a discussion of these factors as applied to the tosylate/bromide rate ratio, see H. M. R. Hoffman, *J. Chem. Soc.*, 6762 (1965).

(70.0%) of colorless product, bp 64–67° (45 mm) (lit. bp 65° (45 mm),[10] 65.5–66° (50 mm[11])).[24] The ^{1}H nmr spectrum of the product (CCl_4) showed a quartet at 4.47 ppm ($J_{\text{H,F}} = 8.3$ Hz); the ^{19}F spectrum showed a triplet at 12.88 ppm. The ir spectrum (cap film) showed strong absorptions at 1380 and 1180 cm^{-1} ($-SO_2-$).

Preparation of Tresylates. To an approximately 0.2 *M* solution of the alcohol in methylene chloride[25] solution containing a 15% molar excess of triethylamine at −15 to −25° (ice–salt or ice–methanol bath) was added a 10% excess of tresyl chloride over a period of 15–30 min.[26] Stirring for an additional 10–15 min completed the reaction. The reaction mixture was transferred to a separatory funnel, and washed with ice water, cold 10% hydrochloric acid, saturated sodium bicarbonate solution, and brine. Drying the methylene chloride solution over magnesium sulfate followed by solvent removal gave the tresylate, usually as a colorless oil.[27] ^{1}H nmr spectra of tresylate esters show a quartet at about 3.9 ppm ($J_{\text{H,F}} = 8.8$ Hz).

Acknowledgment. This research was supported in part by Grant AT(11-1)-1008 from the U. S. Atomic Energy Commission (Document No. COO-1008-14).

---

(23) Excess chlorine, hydrogen chloride, cyanogen chloride, and most of the trifluoroacetic acid pass through the 0° trap. An efficient liquid nitrogen trap following the 0° trap is recommended. Do not distill to dryness; although we have had no difficulty, a possibility of peroxide formation during the chlorination exists.

(24) If too little water is present in the reaction mixture a considerable fraction, bp 45–50° (45 mm), is obtained. The ^{1}H nmr spectrum of this fraction (CCl_4) shows a quartet at 4.24 ppm ($J_{\text{H,F}} = 9.5$ Hz). This material is believed to be the corresponding sulfinyl chloride and may be obtained in good yield if only 1 mole of water/mole of thiocyanate is used.

(25) Depending on the solubility of the alcohol and product, tresylate, pentane, or hexane may also be used as solvent.

(26) Triethylamine was distilled from phthalic anhydride, dried over potassium hydroxide pellets, and redistilled. Methylene chloride was taken from a freshly opened bottle. Anhydrous reaction conditions were maintained.

(27) The more reactive the product tresylate, the more slowly the tresyl chloride was added and the lower the temperature. For very reactive systems the glassware used in the work-up was prechilled and the temperature of the tresylate was never allowed to exceed 0°. Occasionally, it is necessary to omit the bicarbonate washes. In this case the product must be used at once as decomposition on storage is rapid

---

Stable Carbocations. CXIX.[1] Carbon-13 Nuclear Magnetic Resonance Spectroscopy Study of the Structure of Allyl Cations

George A. Olah,* Paul R. Clifford,[2a] Yuval Halpern,[2b] and Robert G. Johanson[2b]

Contribution from the Department of Chemistry,
Case Western Reserve University, Cleveland, Ohio 44106.

Received November 30, 1970

Abstract: The structure of a series of substituted allyl cations was studied by ^{13}C nmr spectroscopy. The results indicate little 1,3-interaction in most allyl cations. However, the 4-chloro-1,2,3,4-tetramethylcyclobutenyl cation does show significant 1,3-interaction. A novel reaction, the generation of an allyl cation by hydride abstraction from an olefin, is also reported.

The structure of the allyl cation and its substituted derivatives has been the subject of extensive studies.[3] Theoretical calculations give conflicting answers as to whether structure **1** (little or no 1,3-interaction) or structure **2** (substantial 1,3-interaction) is to be preferred.[4,5] While proton magnetic resonance (pmr) and uv data have been interpreted in terms of structure **2**,[6] chemical evidence has been inconclusive. For example, a recent study of the solvolysis of secondary allylic chlorides indicates that the transition state in the solvolysis resembles **1** rather than **2**,[7] while a solvolysis study in the cyclobutyl ring system (where, as Katz[6a] has pointed out, steric constants should lead to abnormally large 1,3-interaction) indicates that the transition state resembles **2**.[8] In view of the disparate results and the known sensitivity of ^{13}C nmr chemical shifts to charge density, we felt that a ^{13}C magnetic resonance (cmr) study would help elucidate the structure of the allyl cations. In the course of this work we have also found a new method for the generation of allyl cations, *i.e.*, hydride abstraction from an olefin.

1

2

Results

Generation of Allyl Cations and Their Nmr Studies. The allyl cations studied were generally prepared from the appropriate cyclopropyl alcohols *via* ionization in SbF_5–SO_2 or SO_2ClF solution or by ionization of allylic halides or alcohols. All had pmr spectra identical with those previously reported.[6a,9,10]

Addition of 1,2,5-trimethylcyclopentan-2-ol (**4**) to a solution of SbF_5 in SO_2 at −78° yielded ion **3g** with pmr

---

(1) Part CXVIII: G. A. Olah, *J. Amer. Chem. Soc.*, in press. Note change in title of series of publication to "Stable Carbocations," instead of previously used "Stable Carbonium Ions." Carbonium ions, as outlined in part CXVIII, are pentacoordinated ions as contrasted with trivalent carbenium ions; the generic naming of carbocations (in accordance with the naming of carbanions) seems to be appropriate.

(2) (a) National Institutes of Health Postdoctoral Research Fellow; (b) Postdoctoral Research Associates.

(3) For a review, see N. C. Deno in "Carbonium Ions," G. A. Olah and P. v. R. Schleyer, Ed., Vol. II, Interscience, New York, N. Y., 1967, pp 783–785.

(4) I. M. Simonetta and E. Heilbronner, *Theor. Chim. Acta*, **2**, 228 (1967).

(5) D. T. Clark and D. R. Armstrong, *ibid.*, 13, 365 (1969).

(6) (a) T. J. Katz and E. H. Gold, *J. Amer. Chem. Soc.*, **86**, 1600 (1964); (b) G. A. Olah and M. B. Comisarow, *ibid.*, **86**, 5682 (1964).

(7) R. H. Griffin and J. G. Jewett, *ibid.*, **92**, 1104 (1970).

(8) E. F. Kiefer and J. D. Roberts, *ibid.*, **84**, 784 (1962).

(9) (a) N. C. Deno, H. G. Richey, Jr., N. Friedman, J. D. Hodge, J. J. Houser, and C. U. Pittman, Jr., *ibid.*, **85**, 2995 (1965); (b) G. A. Olah and M. Calin, *ibid.*, **90**, 4672 (1968).

(10) G. A. Olah and J. M. Bollinger, *ibid.*, **90**, 6082 (1968).