Bis(perfluoroalkylsulfonyl)methanes and Related Disulfones[1]

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The improved synthesis and chemistry of the acidic bis(perfluoroalkylsulfonyl)methanes, $R_fSO_2CH_2SO_2R_f$, and related disulfones are described. New substituted β-disulfones, *e.g.*, olefins, alcohols, and halo disulfones, are provided by various organometallic reactions, alkylations, and halogenations of the methylene disulfones or derivatives. Free-radical reactions of the bromo disulfones, $CF_3SO_2CBrXSO_2CF_3$ (X = Br and H), are also reported.

Bis(perfluoroalkylsulfonyl)methanes, $R_fSO_2CH_2SO_2R_f$ ($R_f = CF_3$ and C_8F_{17}), have been prepared by reaction of methylmagnesium halides with perfluoroalkanesulfonyl fluorides using diethyl ether as solvent.[2,3] Since these disclosures, however, very little information relating to the preparation and chemistry of these novel, acidic methylene disulfones and related β-disulfones has been reported. This paper describes an improved and convenient method for preparing disulfones from sulfonyl fluorides and the preparation of a variety of substituted β-disulfones by organometallic reactions, alkylations, and halogenations of the methylene disulfones or derivatives.

Results and Discussion

Improved Synthesis.—The bis(perfluoroalkylsulfonyl)methanes **1–3** were obtained in moderate to high yields by reaction of methylmagnesium chloride (or bromide) with sulfonyl fluorides using tetrahydrofuran as solvent (eq 1). The yield of bis(trifluoromethylsulfonyl)methane (**1**) was 75%, whereas yields of **2** and **3** ranged from 50 to 60%. Under similar conditions, the ethylidene disulfones **4–6** were obtained

$$\underset{X\,=\,Br,\ Cl}{2R_fSO_2F + 2RCH_2MgX} \xrightarrow[25^\circ]{THF} \underset{1\text{–}7}{(R_fSO_2)_2CHR} \qquad (1)$$

1, R = H; $R_f = CF_3$
2, R = H; $R_f = C_4F_9$
3, R = H; $R_f = C_8F_{17}$
4, R = CH_3; $R_f = CF_3$
5, R = CH_3; $R_f = C_4F_9$
6, R = CH_3; $R_f = C_8F_{17}$
7, R = C_6H_5; $R_f = CF_3$

from ethylmagnesium halides, as exemplified by the synthesis of 1,1-bis(trifluoromethylsulfonyl)ethane (**4**) in 80% yield by reaction of ethylmagnesium chloride with CF_3SO_2F. Reaction of benzylmagnesium chloride with CF_3SO_2F gave **7** in a lower yield of 40%.

All of the reactions are conveniently carried out at room temperature under atmospheric pressure. In general, the use of tetrahydrofuran affords much higher yields of disulfones than aliphatic ethers such as diethyl ether. In previous work[2,3] reactions of sulfonyl fluorides with methylmagnesium iodide in diethyl ether gave the methylene disulfones **1** and **3** in yields of about 10%.

Synthesis of **1–7** involves a sequence of reactions in which the corresponding monosulfone is one of the intermediates. In the proposed scheme (eq 2–6;

$$R_fSO_2F \xrightarrow{RCH_2MgX} R_fSO_2CH_2R + MgFX \qquad (2)$$

$$R_fSO_2CH_2R \xrightarrow{RCH_2MgX} R_fSO_2CHRMgX + RCH_3 \qquad (3)$$

$$\begin{tikzcd} R_fSO_2CHRMgX \arrow[r, "R_fSO_2F"] & R_fSO_2CHRSO_2R_f + MgFX \quad (4) \arrow[d, shift left, "RCH_2MgX\ (5)"] \\ & R_fSO_2C(MgX)RSO_2R_f \arrow[u, shift left, "(6)\ H^+"] \end{tikzcd}$$

R = H, CH_3 or C_6H_5), the monosulfone is first formed by reaction of the sulfonyl fluoride with the Grignard reagent (eq 2). Transmetalation of the α hydrogen of the monosulfone with Grignard reagent occurs rapidly, giving $R_fSO_2CHRMgX$[4] (eq 3), which reacts with additional sulfonyl fluoride affording the disulfone, **1–7** (eq 4). Additional Grignard reagent is consumed in the process by the facile transmetalation of the α hydrogen of **1–7**, giving $R_fSO_2C(MgX)RSO_2R_f$ (eq 5) prior to the final hydrolysis step (eq 6). The higher yields of **1–7** were obtained by using 2–3 equiv of Grignard reagent. The properties of tetrahydrofuran apparently facilitate the transmetalation reactions and reaction 4 to afford higher yields of disulfones than obtained with aliphatic ethers such as diethyl and isopropyl ether. Tetrahydrofuran is known to be more basic than these ethers and more readily forms coordination complexes with organometallic compounds.[5,6]

The effect of the above solvents on the yield of disulfone and monosulfone is shown in Table I. In di-

TABLE I

SOLVENT EFFECTS

$$CF_3SO_2F + RCH_2MgCl \xrightarrow{solvent} CF_3SO_2CH_2R + (CF_3SO_2)_2CHR$$

R	Mole[a] ratio	Solvent	Yield, % Monosulfone	Disulfone
H	1.5	Et_2O	12	11
H	3.0	Et_2O	70	7
H	3.0	THF	5	75
CH_3	2.0	THF		80
CH_3	2.0	Et_2O	15	60
CH_3	2.0	*i*-Pr_2O	38	45

[a] Ratio of Grignard reagent to CF_3SO_2F; the sulfonyl fluoride was added to a 3 *M* solution of Grignard reagent at room temperature. All reactions are exothermic.

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[1] Presented in part at the First Winter Fluorine Conference, St. Petersburg, Fla., Jan 23–28, 1972.

[2] H. A. Brown, 128th National Meeting of the American Chemical Society, Minneapolis, Minn., Sept 11–16, 1955.

[3] T. Gramstad and R. N. Haszeldine, *J. Chem. Soc.*, 4069 (1957).

[4] The transmetalation of $CF_3SO_2CH_3$ and some reactions of $CF_3SO_2CH_2MgBr$ are reported by L. M. Yagupolskii, A. G. Panteleimonov, and V. V. Orda, *J. Gen. Chem. USSR*, **34**, 3498 (1964).

[5] S. Patai, "The Chemistry of the Ether Linkage," Interscience, New York, N. Y., 1967.

[6] H. Normant, "Advances in Organic Chemistry: Methods and Results," Vol. II, Interscience, New York, N. Y., 1960, p 6.

ethyl ether, a 3-mol ratio of methylmagnesium chloride to CF_3SO_2F gave the monosulfone, $CF_3SO_2CH_3$, as the major product. Under comparable conditions, use of THF afforded the disulfone, $CF_3SO_2CH_2SO_2CF_3$, in 75% yield. Similar results were obtained with ethylmagnesium chloride, but the solvent effect was less pronounced. The highest yield of the ethylidene disulfone, $CF_3SO_2CH(CH_3)SO_2CF_3$, was obtained in THF and the order of effectiveness was THF > diethyl ether > isopropyl ether.

Acidity.—Bis(trifluoromethylsulfonyl)methane, $CF_3SO_2CH_2SO_2CF_3$ (**1**), appears to be the strongest known carbon acid of the methylene series. It is a stronger acid than $CF_3SO_2CH_2SO_2C_6H_5$ ($pK_a = 5.1$[7]) or dinitromethane ($pK_a = 3.6$[8]) and carboxylic acids, *e.g.*, benzoic acid and salicylic acid. Comparison of the acidity of **1** and trifluoroacetic acid ($pK_a = 0.23$[9] and -0.26[10]) was examined. Attempts to obtain the ionization constant of **1** by conductivity measurements in water were unsuccessful because of its relatively low solubility (maximum concentration, 1 *M*) and very high degree of ionization. Consequently, **1** could not be distinguished from trifluoroacetic acid or trichloroacetic acid in aqueous media. The acidity of **1** and comparison with trifluoroacetic acid were initially obtained in terms of the Hammett acidity function, H_0, using known procedures.[11] The H_0 values for trifluoroacetic acid, **1**, and HCl (1 *M* solutions) using *p*-nitroaniline as the base indicator and methyl isobutyl ketone as solvent were 1.7, 1.0, and -0.6, respectively. The data suggest that **1** is a stronger acid than trifluoroacetic acid and the estimated pK_a is about -1.

The high acidity of **1** is believed to be due primarily to the very strong electron-withdrawing effect of the two CF_3SO_2 groups. The trifluoromethylsulfonyl group has been reported as one of the strongest electron-withdrawing groups known.[12] In general, the methylene disulfones **1–3** form stable, usually nonhygroscopic, salts by neutralization with metal carbonates or organic bases. Stable salts are also readily prepared from the ethylidene disulfones **4–6** and various other substituted disulfones described in this paper.

Organometallic Reactions.—Transmetalation of the methylene disulfones was found to occur rapidly and quantitatively at room temperature with methylmagnesium chloride in THF (eq 7). The reaction is

$$\underset{\mathbf{1-3}}{(R_fSO_2)_2CH_2} \xrightarrow[\text{THF, 25°}]{CH_3MgCl} (R_fSO_2)_2CHMgCl + CH_4 \qquad (7)$$

$$\mathbf{8},\ R_f = CF_3 \quad \mathbf{9},\ R_f = C_4F_9 \quad \mathbf{10},\ R_f = C_8F_{17}$$

accompanied by evolution of an equivalent amount of methane. Under similar conditions, use of 2 equiv of methylmagnesium chloride resulted in transmetalation of both α hydrogens as indicated by the amount of methane produced.

Various substituted disulfones were obtained by reactions of the bis(perfluoroalkylsulfonyl)methylmagnesium chlorides **8–10** in THF with coreactants such as allyl halides, benzyl halides, chlorine, and bromine (Table II). The reported yields are based mainly on the use of 1 equiv of coreactant. A higher yield (80%) of the olefinic disulfone **11** was obtained by transmetalation of **1** with 2 equiv of methylmagnesium chloride and subsequent reaction with 2 equiv of allyl bromide.

TABLE II
ORGANOMETALLIC REACTIONS

$$(R_fSO_2)_2CHMgCl \xrightarrow[\text{THF}]{\text{coreactant}} \mathbf{11-17}$$

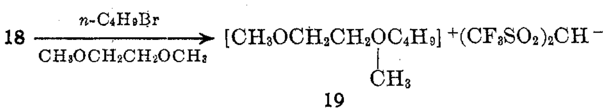
R_f	Coreactant	Product	Yield, %
CF_3	$CH_2{=}CHCH_2Br$	$(CF_3SO_2)_2CHCH_2CH{=}CH_2$ (**11**)	52
C_8F_{17}	$CH_2{=}CHCH_2Br$	$(C_8F_{17}SO_2)_2CHCH_2CH{=}CH_2$ (**12**)	40
CF_3	$C_6H_5CH_2Cl$	$(CF_3SO_2)_2CHCH_2C_6H_5$ (**13**)	35
CF_3	$\overline{CH_2CH_2O}$	$(CF_3SO_2)_2CHCH_2CH_2OH$ (**14**)	40
C_4F_9	$\overline{CH_2CH_2O}$	$(C_4F_9SO_2)_2CHCH_2CH_2OH$ (**15**)	50
CF_3	Br_2	$(CF_3SO_2)_2CHBr$ (**16**)	70
CF_3	Cl_2	$(CF_3SO_2)_2CHCl$ (**17**)	65

Alkylations.—Reactions of silver bis(trifluoromethylsulfonyl)methane[3] (**18**) with organic halides were studied as routes to substituted disulfones. Aprotic solvents such as acetonitrile, methylene chloride, *p*-dioxane, and 1,2-dimethoxyethane (glyme) were used. In general, high conversions of **18** and formation of silver halide occurred with most of the halides, including simple halides such as *n*-butyl bromide. Satisfactory yields (20–60%) of the substituted disulfones were obtained only in the case of the more active organic halides, *e.g.*, allyl bromide and benzyl chloride, which afford the more stable carbonium ions (eq 8). A prominent side reaction which occurred in solvents other than glyme is the formation of **1** presumed to be due to abstraction of proton from the reaction media by the disulfone, carbanion, $(CF_3SO_2)_2CH^-$.

$$\underset{\mathbf{18}}{(CF_3SO_2)_2CHAg} + \underset{\text{X = Br or Cl}}{RX} \xrightarrow{-AgX} (CF_3SO_2)_2CHR \qquad (8)$$

$$\mathbf{11},\ R = CH_2CH{=}CH_2 \quad \mathbf{13},\ R = CH_2C_6H_5$$

Alkylations in glyme afforded the ethylidene disulfone **4** instead of **1** as the major side product; similar results occurred using diglyme and tetraglyme. Reaction of *n*-butyl bromide with the silver salt **18** in glyme gave **4** in 75% yield accompanied by the formation of 1-butoxy-2-methoxyethane (**20**) (eq 9). The proposed intermediate in this reaction is the oxonium salt **19**, which can yield the products by dissociation and methylation of the disulfone carbanion.



$$\mathbf{18} \xrightarrow[CH_3OCH_2CH_2OCH_3]{n\text{-}C_4H_9Br} [CH_3O\underset{\displaystyle CH_3}{|}CH_2CH_2OC_4H_9]^+(CF_3SO_2)_2CH^-$$

19

$$\mathbf{19} \longrightarrow \underset{\mathbf{4}}{(CF_3SO_2)_2CHCH_3} + \underset{\mathbf{20}}{CH_3OCH_2CH_2OC_4H_9} \qquad (9)$$

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[7] L. M. Yagupolskii and N. V. Kondratenko, *Zh. Obshch. Khim.*, **33** (3), 920 (1963).

[8] "Methoden der Organischen Chemie, Metallorganishe Verbindungen" (Houben-Weyl), Vol 13 (1), Georg Thieme Verlag, Stuttgart, 1970, pp 35–64. A list of the acidities of about 115 carbon acids is given.

[9] W. Huber, "Titrations in Nonaqueous Solvents," Academic Press, New York, N. Y., 1967, pp 215 and 217.

[10] C. H. Rochester, "Acidity Functions," Academic Press, New York, N. Y., 1970, pp 39 and 65.

[11] M. A. Paul and F. A. Long, *Chem. Rev.*, **57**, 1 (1957).

[12] W. A. Sheppard, *J. Amer. Chem. Soc.*, **85**, 1314 (1963).

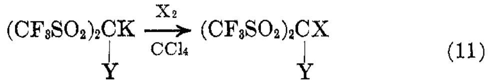
α-Halo Disulfones.—Chlorination or bromination of the potassium salt of **1** in carbon tetrachloride afforded the corresponding monohalo disulfone **16** or **17** in yields of 70–90% (eq 10). These disulfones

$$(CF_3SO_2)_2CHK + X_2 \xrightarrow[CCl_4,\ 25°]{-KX} (CF_3SO_2)_2CHX \qquad (10)$$

16, X = Br
17, X = Cl

are highly acidic and form thermally stable salts by neutralization with alkali metal carbonates. The dry silver and sodium salts of the bromo disulfone **16** were found to be stable up to 160 and 250°, respectively.

Halogenation of the potassium salts of **16** and **17** under similar conditions gave high yields of the *gem*-dihalo disulfones **21** and **22** (eq 11). Similarly, the α-haloethylidene disulfones **23** and **24** were obtained from the potassium salt of **4**. Bromination of the potassium salt of 4,4-bis(trifluoromethylsulfonyl)-butene-1 (**11**) also produced the olefinic bromo disulfone **25** in 62% yield. All of the halogenation reactions (eq 10 and 11) are rapid at room temperature and usually require only an equivalent amount of the halogenation agent.



$$\underset{\displaystyle Y}{(CF_3SO_2)_2CK} \xrightarrow[CCl_4]{X_2} \underset{\displaystyle Y}{(CF_3SO_2)_2CX} \qquad (11)$$

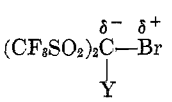
21, Y = X = Br
22, Y = X = Cl
23, Y = CH$_3$; X = Br
24, Y = CH$_3$; X = Cl
25, Y = CH$_2$CH=CH$_2$; X = Br

Bis(trifluoromethylsulfonyl)dibromomethane (**21**) was also obtained in 59% yield by reaction of **1** with alkaline sodium hypobromite solution (eq 12).

$$(CF_3SO_2)_2CH_2 \xrightarrow[NaOH]{NaOBr} (CF_3SO_2)_2CBr_2 \qquad (12)$$

21

Properties of the α-Bromo Disulfones.—The carbon-bromine bond of the α-bromo disulfones is indicated to be polarized so that the bromine is "positive" as in the case of N-halo compounds[13] and perfluoroalkyl iodides.[14] This property is due mainly to the very strong electron-withdrawing effect of the two CF$_3$SO$_2$ groups. Removal of the bromine as an anion is difficult and under forcing conditions replacement of bromine with hydrogen usually results. Homolytic dissociation of the carbon-bromine bond, however, occurs readily and is initiated by light or free-radical catalysts.



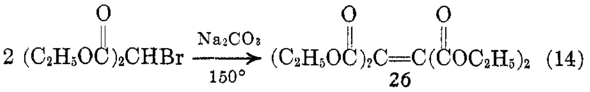
$$\underset{\displaystyle Y}{(CF_3SO_2)_2\overset{\delta^-}{C}}\text{—}\overset{\delta^+}{Br}$$

Y = H, CH$_3$, Br

The oxidizing property of the bromo disulfones is exemplified by the ease of reduction of the monobromo disulfone **16** with sodium iodide, yielding the sodium salt of **1**, iodine, and sodium bromide (eq 13).

$$\underset{\mathbf{16}}{(CF_3SO_2)_2CHBr} + 2NaI \xrightarrow[25°]{CH_3CN} (CF_3SO_2)_2CHNa + I_2 + NaBr \qquad (13)$$

A comparison of the reactivity of **16** with bromo derivatives of other methylene compounds was of interest. Reaction of monobromodiethyl malonate with anhydrous sodium carbonate at 150° is reported to give a 55–70% yield of the tetraethyl ester of ethylenetetracarboxylic acid[15] (**26**) (eq 14). Under similar conditions, **16** gave only its sodium salt in high yield (eq 15).



$$2\ (C_2H_5O\overset{O}{\overset{\|}{C}})_2CHBr \xrightarrow[150°]{Na_2CO_3} \underset{\mathbf{26}}{(C_2H_5O\overset{O}{\overset{\|}{C}})_2C{=}C(\overset{O}{\overset{\|}{C}}OC_2H_5)_2} \qquad (14)$$

$$\underset{\mathbf{16}}{(CF_3SO_2)_2CHBr} \xrightarrow[150°]{Na_2CO_3} (CF_3SO_2)_2CBrNa \qquad (15)$$

Pyrolysis of salts of **16** further demonstrates the "positive" nature of the bromine atom. Decomposition of anhydrous (CF$_3$SO$_2$)$_2$CBrK occurred exothermically at 240° to give CF$_3$Br, SO$_2$, and potassium fluoride as the major products.

Addition of the bromo disulfone **16** to terminally unsaturated olefins resulted when initiated by ultraviolet light or decomposing free-radical catalysts, *e.g.*, benzoyl peroxide or azobisisobutyronitrile (eq 16). The direction of addition, established by proton nmr, is the same as reported for perfluoroalkyl iodides.[16] In general, high conversions of **16** occurred to give 1:1 adducts and allylic bromination products, accompanied by the formation of **1**. With octene-1, the bromination side reaction occurred to the extent of about 40%, giving the methylene disulfone **1** and a mixture of bromooctene isomers (eq 17). The predominant bromooctene isomer was **30b** formed by rearrangement of **30a** during the process; the ratio of isomers was 3:1.

$$\underset{\mathbf{16}}{(CF_3SO_2)_2CHBr} + CH_2{=}CHR \longrightarrow (CF_3SO_2)_2CHCH_2CHBrR \qquad (16)$$

27, R = CH$_2$CH$_2$Cl; 70%
28, R = CH$_2$COOH; 50%
29, R = C$_6$H$_{13}$; 32%

$$\mathbf{16} + C_5H_{11}CH_2CH{=}CH_2 \longrightarrow (CF_3SO_2)_2CH_2 + \mathbf{30} \qquad (17)$$

$$\mathbf{30} = \underset{\mathbf{30a}}{C_5H_{11}CHBrCH{=}CH_2} + \underset{\mathbf{30b}}{C_5H_{11}CH{=}CHCH_2Br}$$

The bromo disulfones were also found to be effective bromination agents for the side-chain bromination of aromatics. The most effective was bis(trifluoromethylsulfonyl)dibromomethane (**21**). Reaction of **21** with toluene in the presence of decomposing azobisisobutyronitrile yielded **1**, benzyl bromide, and benzal bromide (eq 18). A free-radical mechanism is suggested, since hydroquinone inhibits the reaction.

$$\underset{\mathbf{21}}{(CF_3SO_2)_2CBr_2} + PhCH_3 \xrightarrow[AIBN,\ 70°]{90\%} (CF_3SO_2)_2CH_2 + PhCH_2Br + PhCHBr_2 \qquad (18)$$

Experimental Section

General.—The perfluoroalkanesulfonyl fluorides were obtained by electrochemical fluorination.[17–19] Perfluorooctanesulfonyl

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[13] P. Kovacic, M. K. Lowery, and K. W. Field, *Chem. Rev.*, **70**, 639 (1970).

[14] R. E. Banks, "Fluorocarbons and Their Derivatives," Oldbourne Press, London, 1964, p 59.

[15] "Organic Syntheses," Collect. Vol. II, Wiley, New York, N. Y., 1943, p 273.

[16] G. Sosnovsky, "Free Radical Reactions in Preparative Organic Chemistry," Macmillan, New York, N. Y., 1965, p 36.

[17] T. J. Brice and P. W. Trott, U. S. Patent 2,732,398 (1956).

[18] J. Burdon, L. Farazmand, M. Stacey, and J. C. Tatlow, *J. Chem. Soc.*, 2574 (1957).

[19] T. Gramstad and R. N. Haszeldine, *J. Chem. Soc.*, 2640 (1957).

fluoride was purified by the method of Hansen.[20] Commercial Grignard reagents in THF or aliphatic ethers were generally used or were prepared by established methods.[21] All organometallic reactions were carried out under nitrogen. Reactions of trifluoromethanesulfonyl fluoride, bp −21°, were carried out under atmospheric pressure using a −78° condenser.

Infrared spectral data were obtained using a Perkin-Elmer 21 spectrophotometer. In most cases mineral oil mulls were used. A Varian Associates A-60 spectrometer was used for proton nmr with TMS as the internal standard and usually deuterated chloroform as solvent. All melting points were taken on a Thomas-Hoover melting point apparatus and are uncorrected.

Bis(trifluoromethylsulfonyl)methane (**1**).—Procedures for the preparation of **1**–**7** are exemplified as follows. In a 3-l. flask fitted with a stirrer, gas inlet tube, thermometer, and a −78° condenser was placed 1 l. of a 3 *M* solution of methylmagnesium chloride in THF. Trifluoromethanesulfonyl fluoride (154 g, 1.0 mol) was bubbled into the stirred solution over a 1.5-hr period (exothermic) keeping the temperature at 35–50° (ice–water bath). After heating at 50–60° for 2.5 hr, the mixture was cooled and hydrolyzed by the slow addition[22] of 500 ml of 3 *N* HCl. The organic phase was separated and distilled to remove THF and the residue was stirred with 500 ml of 1 *N* HCl. Extraction with diethyl ether followed by distillation of the dry ether solution ($MgSO_4$) gave 106 g (76%) of **1**, bp 99–101° (25 mm). Recrystallization (CCl_4) gave mp 35° [lit.[3] bp 90° (15 mm); mp 35°]; nmr ($CDCl_3$) τ 5.01 (s, CH_2).

Bis(nonafluorobutylsulfonyl)methane (**2**).—Nonafluorobutanesulfonyl fluoride (60 g, 0.2 mol) was added to 200 ml of 3 *M* methylmagnesium chloride in THF. After hydrolysis and distillation of THF from the organic phase, 41.5 g of crude product, soluble in diethyl ether, was obtained. Sublimation *in vacuo* afforded 34.4 g (60%) of **2**, mp 85–90°. Recrystallization (CCl_4) gave 24.2 g, mp 99–100°, nmr (acetone) τ 4.30 (s, CH_2). In a similar reaction, using diethyl ether instead of THF as solvent, a 10% yield of **2** was obtained.

Anal. Calcd for $C_9H_2F_{18}O_4S_2$: C, 18.6; H, 0.3; F, 59.0. Found: C, 18.5; H, 0.4; F, 58.9.

Bis(heptadecafluorooctylsulfonyl)methane (**3**).—Methylmagnesium bromide (550 ml of a 3 *M* solution in diethyl ether) was added to a stirred mixture of 310 g of heptadecafluorooctanesulfonyl fluoride and 900 ml of THF. After hydrolysis, the organic phase was distilled to remove solvent and the residue was stirred with 400 ml of 10 *N* HCl at 80° (2 hr). The mixture was diluted with water and filtered to give 250 g of crude product. The dry solid mixture was stirred twice with anhydrous acetone (300 ml). Filtration gave 125 g of **3**, mp 161–165°. Recrystallization (ethyl acetate) gave mp 166–167° (lit.[2] mp 166–167°). The filtrate was evaporated and the solid was recrystallized (CCl_4) to give 60 g of **3**, mp 75–80°, having linear and branched heptadecafluorooctyl groups.[23] The above reaction was also carried out using only diethyl ether as solvent. The yield of **3** was about 15% and the major product was $C_8F_{17}SO_2CH_3$[2] (65%), mp 104–105°.

1,1-Bis(trifluoromethylsulfonyl)ethane (**4**).—Ethylmagnesium bromide was prepared by reaction of 286 g (2.6 mol) of ethyl bromide and 58 g (2.4 g-atoms) of magnesium in 950 ml of dry tetrahydrofuran. To the solution was added 243 g (1.6 mol) of trifluoromethanesulfonyl fluoride using procedures described for **1**. After hydrolysis and removal of THF from the organic phase, the crude product was dissolved in methylene chloride and the dry solution ($MgSO_4$) was distilled to give 185 g (79%) of **4**: bp 98–99° (20 mm); nmr ($CDCl_3$) τ 4.93 (m, 1, CH), 7.95 (d, 3, CH_3). Under similar conditions, reaction of the sulfonyl fluoride with ethylmagnesium chloride in THF gave **4** in 77% yield.

Anal. Calcd for $C_4H_4F_6O_4S_2$: C, 16.3; H, 1.4; F, 38.8. Found: C, 16.3; H, 1.3; F, 39.2.

The triethylamine salt of **4** was prepared by neutralization of **4** with triethylamine in diethyl ether. The insoluble product was heated at 70° *in vacuo* to afford the salt as a viscous liquid.

Anal. Calcd for $C_{10}H_{19}F_6NO_4S_2$: C, 30.4; H, 4.8; F, 28.8. Found: C, 30.3; H, 4.7; F, 28.8.

1,1-Bis(nonafluorobutylsulfonyl)ethane (**5**).—Nonafluorobutanesulfonyl fluoride (271 g, 0.9 mol) was added to ethylmagnesium bromide (1.2 mol) in 500 ml of THF. After hydrolysis, the organic phase was diluted with water. Filtration followed by recrystallization (CCl_4) gave 147 g of **5**, mp 83–84°.

Anal. Calcd for $C_{10}H_4F_{18}O_4S_2$: C, 20.2; H, 0.7; F, 57.6. Found: C, 20.2; H, 0.7; F, 57.6.

1,1-Bis(heptadecafluorooctylsulfonyl)ethane (**6**).—Ethylmagnesium bromide (0.5 mol) in 200 ml of diethyl ether was added to a stirred mixture of 150 g (0.3 mol) of $C_8F_{17}SO_2F$ and 200 ml of diethyl ether. After hydrolysis, the ether phase was filtered, giving 105 g of **6**, mp 152–157°. Recrystallization (FC-75[24]) gave mp 160–161°.

Anal. Calcd for $C_{18}H_4F_{34}O_4S_2$: C, 21.7; H, 0.4; F, 65.0. Found: C, 21.7; H, 0.4; F, 64.4.

Bis(trifluoromethylsulfonyl)phenylmethane (**7**).—Trifluoromethanesulfonyl fluoride (185 g, 1.3 mol) was bubbled into benzylmagnesium chloride (2.5 mol) in 900 ml of THF and 250 ml of diethyl ether. After hydrolysis, the organic phase was evaporated. The solid residue was stirred with water (2.5 l.) and neutralized with sodium hydroxide. The mixture was filtered, and the filtrate was acidified with HCl and then extracted with diethyl ether. Evaporation of the ether gave 92 g of crude **7**. Sublimation *in vacuo* gave 69 g of **7**, mp 100–102°. Recrystallization (hexane) afforded a high-purity sample melting at 101–101.5°.

Anal. Calcd for $C_9H_6F_6O_4S_2$: C, 30.4; H, 1.7; F, 32.0. Found: C, 30.5; H, 1.7; F, 31.8.

4,4-Bis(trifluoromethylsulfonyl)butene-1 (**11**).—To a stirred solution of 25 g (0.09 mol) of the methylene disulfone **1** in 125 ml of THF was added 83 ml of a 3.0 *M* solution of methylmagnesium chloride (0.25 mol) in THF (exothermic and methane evolved). To the solution was added 30.9 g (0.25 mol) of allyl bromide and the mixture was stirred under reflux for 1.5 hr. After cooling and hydrolysis (60 ml of 3 *N* HCl), the organic phase was separated and the major portion of solvent was removed by distillation. The residue was stirred with water and extracted with diethyl ether. Distillation of the dry etherate ($MgSO_4$) gave 22.4 g (79%) of **11**: bp 102–104° (24 mm); nmr ($CDCl_3$) τ 5.08 (t, 1, CH), 6.77 (t, 2, $CH_2CH{=}CH_2$), 4.1 (m, 1, $CH{=}CH_2$), 4.6 (m, 2, $CH{=}CH_2$); ir 6.05 μ (C=C).

Anal. Calcd for $C_6H_6F_6O_4S_2$: C, 22.5; H, 1.9; F, 35.6. Found: C, 21.7; H, 1.7; F, 36.1.

4,4-Bis(heptadecafluorooctylsulfonyl)butene-1 (**12**).—Allyl bromide (5.1 g, 0.04 mol) was added to a solution of **10** prepared by reaction of methylmagnesium chloride (0.04 mol) in tetrahydrofuran with a stirred suspension of 25 g (0.03 mol) of the methylene disulfone **3** in 125 ml of tetrahydrofuran. The resultant solution was stirred at 60° for 1 hr and hydrolyzed with 25 ml of 3 *N* HCl, and 250 ml of H_2O was added. The organic phase was separated and diluted with 250 ml of H_2O. Filtration gave 25 g of solid. Recrystallization ($CHCl_3$) gave 13 g of impure **12**, mp 85–104°. Extraction with $CF_2ClCFCl_2$ followed by evaporation of the solvent gave 8.7 g: mp 85–86.5°; nmr ($CF_2ClCFCl_2$) τ 5.05 (t, 1, CH), 6.76 (t, 2, $CH_2CH{=}CH_2$), 3.5–4.9 (m, 3, $-CH{=}CH_2$).

Anal. Calcd for $C_{20}H_6F_{34}O_4S_2$: C, 23.5; H, 0.6; F, 63.3. Found: C, 23.4; H, 0.8; F, 62.6.

1,1-Bis(trifluoromethylsulfonyl)-2-phenylethane (**13**).—Methylmagnesium chloride (0.15 mol) in 50 ml of THF was added to 25 g (0.09 mol) of **1** in 125 ml of THF. To the solution was added 19 g (0.15 mol) of distilled benzyl chloride and the mixture was stirred at 60° for 1 hr. Procedures for the isolation of **13** were the same as described for **11**. Distillation gave 9.5 g of **13**: bp 71–72° (0.05 mm); mp 38–39°; nmr ($CDCl_3$) τ 4.90 (t, 1, CH), 6.20 (d, 2, CH_2), 2.65 (m, 5, aromatic).

Anal. Calcd for $C_{10}H_8F_6O_4S_2$: C, 32.4; H, 2.2; F, 30.8. Found: C, 32.2; H, 2.3; F, 30.9.

3,3-Bis(trifluoromethylsulfonyl)propan-1-ol (**14**).—The procedures described for **11** were used. Ethylene oxide (4.8 g, 0.11 mol) was added to a cooled solution (5°) of **8** prepared by reaction of methylmagnesium bromide (0.05 mol) in diethyl ether with 10 g (0.04 mol) of **1** in 100 ml of THF (−78° condenser). The mixture was allowed to warm to 25° and stirred for 1.5 hr. After hydrolysis and extraction with diethyl ether, distillation gave 6.4 g of **1** and 1.6 g of **14**: bp 112° (5 mm); nmr ($CDCl_3$) τ

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(20) R. L. Hansen, U. S. Patent 3,346,612 (1967).

(21) M. S. Kharasch and O. Reinmuth, "Grignard Reactions of Nonmetallic Substances," Prentice-Hall, Englewood Cliffs, N. J., 1954.

(22) Addition of the first 5-ml portion of 3 *N* HCl should be carried out with caution, since the initial reaction is vigorous and methane is evolved from unreacted methyl Grignard.

(23) The starting sulfonyl fluoride contained about 80% linear and 20% branched perfluorooctyl groups.

(24) FC-75 is a commercial inert fluorochemical available from the 3M Co.

4.50 (t, 1, CH), 7.30 (m, 2, $\mathbf{CH_2}CH_2OH$), 6.08 (m, 2, $CH_2\mathbf{CH_2}OH$), and 7.60 (s, 1, OH).

3,3-Bis(nonafluorobutylsulfonyl)propan-1-ol (**15**).—Ethylene oxide (7.4 g, 0.17 mol) was added to a cooled solution (5°) of **9**, prepared by reaction of methylmagnesium chloride (0.06 mol) in tetrahydrofuran and 21.5 g (0.04 mol) of the disulfone **2** in 125 ml of tetrahydrofuran. The mixture was stirred at 60° for 1 hr. After hydrolysis and extraction with diethyl ether, evaporation of the organic phase gave 24 g of a semisolid. The solid was washed with water and dissolved in hot butyl chloride. Cooling to 0° and filtration gave 5 g of **2**, and evaporation of the filtrate gave 10 g of **15**. Recrystallization (CCl_4) gave mp 58–60°; nmr ($CF_2ClCFCl_2$) τ 4.31 (t, 1, CH), 7.26 (t, 2, $\mathbf{CH_2}CH_2OH$), 6.09 (m, 2, $CH_2\mathbf{CH_2}OH$), 8.06 (s, 1, OH).

Anal. Calcd for $C_{11}H_6F_{18}O_5S_2$: C, 21.2; H, 1.0; F, 54.8. Found: C, 21.0; H, 1.0; F, 55.0.

Preparation of Salts.—The general procedure for preparation of the potassium and silver salts of the various acidic disulfones involved neutralization of the acid with the corresponding carbonate in methanol followed by filtration, evaporation of the filtrate, and drying of the salt at 70–100° *in vacuo*. The syntheses of the sodium and silver salts of **1** in aqueous media were reported previously.[3]

Organic salts were also prepared from **1** and other acidic disulfones by neutralization in diethyl ether or methanol. As an example, neutralization of 50 g of **1** in diethyl ether with 15.8 g of morpholine gave 54.6 g of the insoluble salt, which was purified by washing with diethyl ether and drying *in vacuo*, mp 99.5–101.5°.

Anal. Calcd for $C_7H_{11}F_6NO_5S_2$: C, 22.9; N, 3.8; H, 3.0. Found: C, 22.9; N, 3.9; H, 2.9; H_2O, 0.08.

Other organic salts of **1** were prepared from diethylamine (mp 101–102.5°), *N*-methylaniline (mp 105–107°), piperidine (mp 68–70°), and guanidine (mp 112–114°).

Alkylations.—The reaction of silver bis(trifluoromethylsulfonyl)methane (**18**) with allyl bromide in *p*-dioxane exemplifies the procedures used. Allyl bromide (12.1 g, 0.1 mol) was added slowly to a stirred solution of 38.7 g (0.1 mol) of dry **18** in 50 ml of spectrograde *p*-dioxane (exothermic). The mixture was stirred in the dark at 25° for 1 hr and under reflux for 4 hr. Filtration and distillation of the filtrate gave 24.1 g, bp 65–67° (4 mm). Glc[25] indicated a 2.6:1 mixture of 4,4-bis(trifluoromethylsulfonyl)butene-1 (**11**) and **1** (yield of **11**, 52%). Yields of **11** using other solvents are as follows: glyme (30%), methylene chloride (40%), and acetonitrile (20%).

Bis(trifluoromethylsulfonyl)bromomethane (**16**).—To a suspension of 54 g (0.17 mol) of the neutral and dry potassium salt of **1** in 225 ml of carbon tetrachloride was added 27.6 g (0.17 mol) of bromine in 30 ml of carbon tetrachloride. The mixture was stirred at 25° until the bromine color disappeared. Filtration followed by distillation of the filtrate gave 56.5 g (91%) of **16**, bp 93–94.5° (9 mm), nmr ($CDCl_3$) τ 3.77 (s, CH).

Anal. Calcd for $C_3HBrF_6O_4S_2$: C, 10.0; Br, 22.3; F, 31.7. Found: C, 9.9; Br, 22.4; F, 31.5.

In experiments using the potassium salt of **1**, containing small amounts of K_2CO_3, **16** contaminated with the dibromide **21** was obtained. Purification was carried out by neutralization of the mixture with K_2CO_3 (methanol), washing the dry salt with CCl_4 to remove **21**, followed by acidification of the salt and redistillation.

The sodium salt of **16** was prepared by neutralization of the acid with Na_2CO_3 (methanol). The salt was azeotropically dried with benzene and then *in vacuo* at 80°, mp 254–256° dec.

Anal. Calcd for $C_3BrF_6O_4S_2Na$: C, 9.5; Br, 21.0; F, 29.9; Na, 6.0. Found: C, 9.7; Br, 20.9; F, 29.8; Na, 5.8.

Bis(trifluoromethylsulfonyl)chloromethane (**17**).—To a suspension of 25 g (0.08 mol) of the potassium salt of **1** in 250 ml of CCl_4 was added 5.5 g (0.08 mol) of chlorine (exothermic). The mixture was stirred at 25° for 2 hr. Filtration followed by distillation of the filtrate gave 19.2 g of **17**, bp 84–86° (18 mm), nmr ($CDCl_3$) τ 3.83 (s, CH), containing a small amount of **22**.

Anal. Calcd for $C_3HClF_6O_4S_2$: C, 11.5; Cl, 11.3; H, 0.3. Found: C, 11.2; Cl, 13.2; H, 0.2.

Bis(trifluoromethylsulfonyl)dibromomethane (**21**).—Bromine (5.8 g) was added to a solution of 4.3 g of sodium hydroxide in 50 ml of H_2O, cooled to 0°. A solution, prepared from 5.0 g (0.02 mol) of the methylene disulfone **1**, 2.5 g of sodium hydroxide, and 25 ml of H_2O, was added to the stirred sodium hypobromite solution. The mixture was stirred at 25° for 63 hr and filtered and the filtrate was acidified with 3 *N* HCl. The mixture was extracted with methylene chloride, and the extract was shaken with 5% Na_2CO_3, dried ($MgSO_4$), and distilled, giving 3.7 g of **21**, bp 107–108° (17 mm).

Anal. Calcd for $C_3Br_2F_6O_4S_2$: C, 8.2; Br, 36.5; F, 26.0; mol wt, 438. Found: C, 8.6; Br, 37.1; F, 26.5; mol wt ($CHCl_3$), 432.

The compound was also prepared in 79% yield by bromination of the potassium salt of the monobromo disulfone **16** in CCl_4.

Bis(trifluoromethylsulfonyl)dichloromethane (**22**).—The compound was obtained in 80% yield by chlorination of the potassium salt of the monochloro disulfone **17** using procedures described for **17**. **22** had bp 95.0–95.5° (40 mm).

Anal. Calcd for $C_3Cl_2F_6O_4S_2$: C, 10.3; Cl, 20.3. Found: C, 10.4; Cl, 19.7.

1,1-Bis(trifluoromethylsulfonyl)-1-bromoethane (**23**).—Bromination of the potassium salt of the ethylidene disulfone **4** in CCl_4 gave **23** (83%), bp 89–90° (10 mm).

Anal. Calcd for $C_4H_3BrF_6O_4S_2$: C, 12.9; Br, 21.4; F, 30.6. Found: C, 12.9; Br, 21.2; F, 30.9.

4,4-Bis(trifluoromethylsulfonyl)-4-bromobutene-1 (**25**).—Using procedures described for **16**, bromination of 6 g (0.02 mol) of the dry potassium salt of the olefinic disulfone **11** with 2.7 g (0.02 mol) of bromine gave 4.9 g of **25**: bp 85–88° (5 mm); nmr ($CDCl_3$) τ 6.44 (d, 2, CH_2), 3.5–4.8 (m, 3, $CH{=}CH_2$); ir (neat) 6.08 μ (w, C=C).

Anal. Calcd for $C_6H_5BrF_6O_4S_2$: C, 18.1; Br, 20.0; F, 28.6. Found: C, 17.9; Br, 20.8; F, 28.3.

1,1-Bis(trifluoromethylsulfonyl)-3-bromo-5-chloropentane (**27**).—A mixture of 10 g (0.03 mol) of bis(trifluoromethylsulfonyl)bromomethane (**16**), 3.6 g (0.04 mol) of 4-chlorobutene-1, and 6 ml of methylene chloride (quartz flask) was irradiated at 25° for 4.0 hr using a 140-W Hanovia ultraviolet lamp. Distillation gave 8.8 g (70%) of **27**: bp 93–94° (0.05 mm); nmr ($CDCl_3$) τ 4.53 (m, 1, $CHCH_2$), 5.47 (m, 1, CHBr), 6.25 (t, 2, CH_2Cl), 7.10 (m, 2, $CHCH_2CHBr$), and 7.66 (q, 2, CH_2CH_2Cl, $J = 6.0$ Hz).

Anal. Calcd for $C_7H_8BrClF_6O_4S_2$: C, 18.7; Br, 17.8; F, 25.4. Found: C, 18.7; Br, 17.2; F, 25.4.

5,5-Bis(trifluoromethylsulfonyl)-3-bromovaleric Acid (**28**).—Using procedures described for the preparation of **27**, a mixture of 10 g (0.04 mol) of **16**, 3.5 g (0.04 mol) of 3-butenoic acid, and 6 ml of methylene chloride was irradiated for 6 hr. Filtration gave 6.0 g of **28**, mp 147–149°. Recrystallization ($CHCl_3$) gave mp 146.5–147.5°; nmr (CD_3CN) τ 4.17 (broad, 1, $CHCH_2$), 5.46 (m, 1, CHBr), 6.91 (m, complex, 4, $CH_2CHBrCH_2COOH$), 2.34 (s, 1, COOH).

Anal. Calcd for $C_7H_7BrF_6O_6S_2$: C, 18.9; H, 1.6; F, 25.6; neut equiv, 445.2 and 222.6. Found: C, 19.1; H, 1.8; F, 25.7; neut equiv, 468 and 225.

1,1-Bis(trifluoromethylsulfonyl)-3-bromononane (**29**).—The procedure described for **27** was used. Photolysis of 10 g (0.03 mol) of **16** and 3.5 g (0.03 mol) of distilled octene-1 followed by distillation gave 4.5 g of **29**: bp 97–98° (0.1 mm); nmr ($CDCl_3$) τ 4.48 (m, 1, $CHCH_2$), 5.72 (m, 1, CHBr), 7.17 (m, 2, $CHCH_2CHBr$), 8.10 (broad, 2, $CHBrCH_2CH_2$), 8.63 (broad, 8, $(CH_2)_4CH_3$, and 9.10 (t, 3, CH_3).

Anal. Calcd for $C_{11}H_{17}BrF_6O_4S_2$: C, 28.0; H, 3.6; Br, 17.0; F, 24.2. Found: C, 28.9; H, 3.6; Br, 16.2; F, 24.2.

The above distillation also gave a fraction, bp 94° (25 mm) to 77° (0.3 mm), which separated into two liquid phases. The lower phase (3.8 g) was **1** and the upper phase (1.5 g) after washing with 5% Na_2CO_3 was a mixture of bromooctenes **30a** and **30b** identified by ir and nmr.

Bromination of Toluene.—A mixture of 11.0 g (0.025 mol) of the dibromo disulfone **21**, 4.6 g (0.05 mol) of toluene, and 0.4 g of azobisisobutyronitrile was stirred at 75° for 20 hr. Distillation gave 0.7 g of toluene and 11.6 g of distillate, bp 85–89° (30 mm). The distillate (two phases) was separated and the upper phase was washed with 5% K_2CO_3 to give 4.9 g of benzyl bromide identified by infrared and nmr spectroscopy. The lower phase was mainly **1** (6.7 g). Distillation also afforded 1.5 g of benzal bromide, bp 65–67° (0.5 mm).

The above reaction of **21** and toluene was repeated using 0.3 g of hydroquinone instead of the azo catalyst; no appreciable reaction occurred at 80° (45 hr).

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[25] A 6 ft × 0.12 in. column (98°) composed of 10% SE-30 on 80–100 mesh "S" stainless was used. The injection port was at 180°.

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Registry No.—**1**, 428-76-2; **1** potassium salt, 33249-12-6; **1** morpholine salt, 31322-96-1; **1** diethylamine salt, 40906-76-1; **1** *N*-methylaniline salt, 40906-77-2; **1** piperidine salt, 31323-01-0; **1** guanidine salt, 31322-97-1; **2**, 29214-37-7; **3**, 29214-34-4; **4**, 31253-33-5; **4** triethylamine salt, 40906-78-3; **4** potassium salt, 40906-79-4; **5**, 40906-80-7; **6**, 40906-81-8; **7**, 40906-82-9; **8**, 40906-83-0; **9**, 40906-84-1; **10**, 40906-85-2; **11**, 30354-36-0; **11** potassium salt, 40906-86-3; **12**, 29214-36-6; **13**, 31139-48-7; **14**, 30354-37-1; **15**, 29269-32-7; **16**, 30354-38-2; **16** sodium salt, 30354-42-8; **16** potassium salt, 30354-43-9; **17**, 29214-39-9; **17** potassium salt, 40906-87-4; **18**, 31322-84-6; **21**, 40906-88-5; **22**, 40906-89-6; **23**, 40906-90-9; **25**, 40906-91-0; **27**, 30354-40-6; **28**, 30416-82-1; **29**, 30354-41-7; **30a**, 40906-92-1; **30b**, 25466-54-0; methylmagnesium chloride, 676-58-4; trifluoromethanesulfonyl fluoride, 335-05-7; nonafluorobutanesulfonyl fluoride, 375-72-4; methylmagnesium bromide, 75-16-1; heptadecafluorooctanesulfonyl fluoride, 307-35-7; ethylmagnesium bromide, 925-90-6; benzylmagnesium chloride, 6921-34-2; allyl bromide, 106-95-6; benzyl chloride, 100-44-7; ethylene oxide, 75-21-8; bromine, 7726-95-6; chlorine, 7782-50-5; 4-chlorobutene-1, 927-73-1; 3-butenoic acid, 625-38-7; octene-1, 111-66-0; toluene, 108-88-3; benzyl bromide, 100-39-0; benzal bromide, 618-32-6.

Mechanisms of Elimination Reactions. XIX. Rates and Product Proportions in the Reactions of 2-Methyl-2-butyl Halides with Thiolate Ions[1]

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Rates of reaction of 2-chloro-2-methylbutane with various thiolates have been determined in ethyl, isopropyl, and *tert*-butyl alcohols. The proportions of 2-methyl-1-butene and 2-methyl-2-butene in the products have been determined under the same conditions. Some experiments have also been done with 2-iodo- and 2-bromo-2-methylbutane, and with alkoxide, phenoxide, and phenylselenoxide bases. The elimination is faster with the sulfur than with the oxygen bases. The Brønsted β values for the reaction of substituted thiophenoxides with 2-methyl-2-butyl chloride run 0.13 to 0.16, reflecting a low sensitivity of rate to pK_b. The orientation also is little affected by changes in the basicity or steric requirements of the thiolates, showing a strong preference for the Saytzev-rule product in all cases. The nature of the transition state for elimination is discussed in the light of these results.

A problem of long standing in discussions of the effect of the nature of the base on rates and product proportions in eliminations is that the base is usually the conjugate base of the solvent. A change in base thus entails a change in solvent as well. If the base is changed without changing the solvent, the possibility remains that conjugate base of the solvent, in equilibrium with the added base, will be the actual reactant. Only when the added base is much weaker than the conjugate base of the solvent is this problem minimized.

Because thiolates are much weaker bases than the corresponding alkoxides or phenoxides, and because thiolates are reported to react more rapidly than alkoxides with tertiary alkyl halides,[3,4] we chose the reaction of thiolates with 2-methyl-2-butyl halides in alcoholic media as a means of studying steric and electronic effects of the base on rates and product proportions in eliminations from 2-methyl-2-butyl halides. Observed rate constants are recorded in Table I. To the rate constants used in the Brønsted correlations (see below), a small correction for accompanying solvolysis was applied where necessary.[5] The corrected values are given in Table II. The proportions of 2-methyl-1-butene in the olefinic products were determined by glpc and are recorded in Table III. No correction for solvolysis is necessary. The solvolysis gives primarily substitution product, and control experiments showed that the olefin composition is not affected by changing the thiolate concentration.

The low sensitivity of the relative yields of 2-methyl-1-butene and 2-methyl-2-butene (Table III) to the nature of the thiolate indicates a rather loose transition state, in which the base has not interacted strongly enough with the substrate for differences in base strength to have an appreciable effect. Particularly striking is the apparent absence of any steric effect along the series *n*-BuSH, *sec*-BuSH, *t*-BuSH. Although few other examples of variation of base without concomitant variation of solvent are known, it is certainly not true that orientation is generally insensitive to the nature of the base under such circumstances. The phenoxide gives substantially more 1-ene than the thiophenoxide (Table III), and substituted phenoxides with 2-butyl tosylate give a decrease in 1-ene with decreasing basicity of the phenoxide.[6] A slight trend in the same direction is noted with the substituted thiophenoxides in the present work, but the variation is barely outside experimental error.

There is somewhat more variation of product proportions with change of solvent and leaving group. While results in ethyl and isopropyl alcohols are similar, there is a marked increase in 1-ene and decrease in rate in *tert*-butyl alcohol. Perhaps the base is less hydrogen bonded, and therefore stronger, in *tert*-butyl than in

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