

[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY OF THE GEORGIA INSTITUTE OF TECHNOLOGY, ATLANTA 13, GA.]

The Formation of Difluoromethylene from Difluoromethyl Phenyl Sulfone and Sodium Methoxide¹

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Difluoromethyl phenyl sulfone reacts with sodium methoxide in methanol at a rate much faster than would be expected for the S_N2 mechanism. The suggestion that the reaction involves an α -elimination to give difluoromethylene is supported by the following evidence: Difluoromethyl phenyl sulfone is relatively inert to sodium thiophenoxide alone, but in the presence of sodium methoxide reacts with it rapidly to give difluoromethyl phenyl sulfide, difluoromethyl methyl ether and sodium benzenesulfinate. The observation that the sulfone undergoes deuterium exchange at a rate quite rapid compared to its rate of consumption of alkali shows that the α -elimination reaction is a two-step process in which an intermediate carbanion is formed and not a concerted reaction like the formation of difluoromethylene from haloforms containing two fluorine atoms.

Introduction

In addition to the long-known homolytic processes that yield methylene intermediates,² a number of heterolytic reactions have been shown, in recent years, to form these interesting derivatives of divalent carbon. Most of these reactions involve α -dehydrohalogenation of a haloform³ or other organic halide,^{4,5} sometimes *via* an intermediate carbanion and sometimes by a concerted^{6,7} mechanism. In other examples α -dehalogenations⁸ and α -dehalodecarboxylations^{9,10} have been used. In each of these reactions a halide ion is liberated in the step in which the methylene is formed. It seemed plausible, however, that other reasonably stable anions could also be eliminated analogously, and for this reason we have studied difluoromethyl phenyl sulfone.

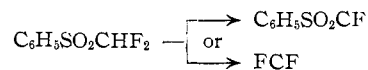
Results and Discussion

Difluoromethyl phenyl sulfone was prepared by the hydrogen peroxide oxidation of difluoromethyl phenyl sulfide that had been made from chlorodifluoromethane and sodium thiophenoxide in the presence of sodium methoxide.¹¹ It was found to undergo a kinetically second-order reaction with sodium methoxide in methanol at 50°. Satisfactory rate constants were obtained from the equation

$$k = \frac{2.303}{t(na - b)} \log \frac{b(a - x)}{a(b - nx)} \quad (1)$$

where a is the initial concentration of sulfone and b that of sodium methoxide, x is the change in sulfone concentration at time t (in seconds), and n , which is assumed to remain constant throughout the reaction, is the number of moles of methoxide used up per mole of sulfone. The value of the rate

constant obtained, 3.55×10^{-5} l. mole⁻¹ sec.⁻¹, constitutes strong evidence that the reaction proceeds *via* an intermediate methylene derivative. The only other plausible reaction path is the bimolecular nucleophilic displacement or S_N2 mechanism. Yet the rate constants for the displacement of fluoride ions from typical primary fluorides by the action of ethoxide ions in ethanol are around 5×10^{-8} l. mole⁻¹ sec.⁻¹ (extrapolated from data at higher temperatures¹²). Since α -arylsulfonyl¹³ and α -fluoro^{14,15} substituents both decrease S_N2 reactivity and since methoxide ions in methanol do not appear to be any more nucleophilic than ethoxide ions in ethanol,¹⁶ difluoromethyl phenyl sulfone would have been expected to be considerably less reactive than the primary fluorides if the S_N2 mechanism were operative. While an α -elimination reaction mechanism thus seems probable there are two such mechanisms possible, depending on whether the elements of hydrogen fluoride or of benzenesulfonic acid are eliminated from the reactant. The detection of



difluoromethyl methyl ether as a product of the reaction of the sulfone with sodium methoxide showed that difluoromethylene formation occurred and the isolation of difluoromethyl phenyl sulfide in 22% yield, difluoromethyl methyl ether in 38% yield and benzenesulfonic acid in 52% yield in the reaction with sodium thiophenoxide and sodium methoxide shows that difluoromethylene formation is the principal and perhaps sole reaction path. Even stronger evidence in support of the intermediacy of difluoromethylene is the fact that the difluoromethyl phenyl sulfide formed could not have arisen from the S_N2 attack of thiophenoxide ions on the sulfone. This follows from our observation that in the absence of sodium methoxide, difluoromethyl phenyl sulfone is almost inert to the

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(16) Ethyl bromide, at least, is about twice as reactive toward sodium ethoxide¹⁷ as toward sodium methoxide.¹⁴

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action of sodium thiophenoxide. On the other hand, a kinetic study showed that with sodium methoxide and sodium thiophenoxide the sulfone reacted at just the rate that would be expected if methoxide was the only reagent attacking the sulfone. The rate constant calculated from eq. 1 for a run in the presence of sodium thiophenoxide was 3.28×10^{-5} , within the experimental uncertainty of the value obtained in the absence of sodium thiophenoxide.

Further evidence for the intermediacy of difluoromethylene comes from the value determined for n , the number of moles of base used up per mole of sulfone. Previous work has shown that with difluoromethylene (generated from chlorodifluoromethane) the value of n increases with increasing alkoxide ion concentration.^{11,18} In methanol solution a value of 1.15 was found at an average sodium methoxide concentration of about 0.02 M and synthetic experiments showed that at an average concentration of 2.6 M the value was about 1.68.¹¹ The intermediate value, 1.45, that we have obtained at an intermediate average sodium methoxide concentration of 0.57 is therefore in the range to be expected for the intermediate difluoromethylene.

By use of the equation derived previously¹¹ (where the reaction of methoxide ions with difluoromethylene is neglected), the ratio k_T/k_M may be calculated thus

$$k_T/k_M = (2.3/\Delta[\text{MeO}^-]_t) \log ([\text{C}_6\text{H}_5\text{S}^-]_0/[\text{C}_6\text{H}_5\text{S}^-]_t) \quad (2)$$

where k_T is the second-order rate constant for the reaction of difluoromethylene with thiophenoxide ions and k_M is the first-order rate constant for reaction with methanol. In the present case a k_T/k_M value of 3.32 ± 0.44 was obtained at 50° in comparison with the value 4.47 ± 0.20 obtained previously at 35°. Because of the relatively large average deviations from these values and the assumptions involved in the derivation of eq. 2 the observed decrease in k_T/k_M may not be significant. It may, however, indicate that, contrary to our previous conclusion,¹¹ methoxide ions are significant competitors for the difluoromethylene intermediate. Nevertheless, since the average methoxide ion concentration was about the same in the present experiments at 50° as in the previous ones at 35° the relative magnitudes of the two values obtained for k_T/k_M should be significant. The observed decrease that accompanies a 15° temperature increase suggests that the reactions of difluoromethylene are becoming more random at the higher temperature.

In spite of the fact that all of the haloforms that contain two fluorine atoms appear to react with base to give difluoromethylene by a concerted mechanism,^{6,11,19} the difficulty with which RSO_2 groups are expelled as anions from organic molecules²⁰ and the ease with which sulfones give up α -hydrogens to form carbanions²¹ suggest that difluoromethyl phenyl sulfone should react with

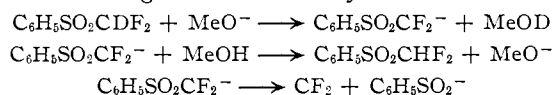
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sodium methoxide to give an intermediate carbanion. We have investigated this point by studying the deuterium exchange of the sulfone. When shaken with alkaline heavy water its infrared spectrum underwent a change that was completely reversed by shaking with alkaline water of ordinary isotopic content. Infrared techniques were then used to study the base-catalyzed hydrogen exchange of deuteriodifluoromethyl phenyl sulfone in aqueous and methanolic solutions. The exchange was much faster than the reaction in which base is consumed. Therefore the concentration of sodium methoxide did not change during the individual runs and satisfactory rate constants were obtained from the first-order rate equation. The first-order rate constants were found to be proportional to the concentration of the basic catalyst used, however, showing that the reactions are really second order. The mechanism, no doubt, involves a rate-controlling attack of methoxide ion to give a carbanion that is then rapidly protonated by a solvent molecule, only rarely losing a benzenesulfinate ion to give difluoromethylene. In Table I



is a summary of the rate constants for deuterium exchange and reaction with sodium methoxide.

TABLE I
KINETICS OF REACTIONS OF DIFLUOROMETHYL PHENYL SULFONE IN METHANOL

Initial concentrations, M		Temp., °C.	$10^5 k$, 1. mole ⁻¹ sec. ⁻¹
Sulfone ^a	Base		
0.1379 RH	0.2360 NaOMe	50.4	3.55 ± 0.07^b
.1379 RH	.2150 NaOMe	50.4	$3.28 \pm 0.15^{b,c}$
.0690 RD	.0237 NaOMe	0.0	97 ± 2^d
.0690 RD	.0711 NaOMe	.0	94 ± 4^d
.0062 RD	.00089 NaOH	.0	$6250 \pm 120^{d,e}$
.0062 RD	.00117 NaOH	.0	$5820 \pm 220^{d,e}$

^a R = $\text{C}_6\text{H}_5\text{SO}_2\text{CF}_2$. ^b Rate constant for the decomposition of the sulfone. ^c 0.1871 M sodium thiophenoxide also present initially. ^d Rate constant for deuterium exchange. ^e Run in aqueous solution.

Experimental²²

Difluoromethyl Phenyl Sulfone.—Difluoromethyl phenyl sulfide¹¹ (21.5 g., 0.13 mole) was dissolved in 60 g. of glacial acetic acid and kept at about 105° while 12 g. (0.33 mole) of 90% hydrogen peroxide was added dropwise over a period of 4 hours. After most of the acetic acid had been removed by distillation the reaction mixture was poured into water and the organic layer taken up in ether. The ether solution was then washed with alkali, dried with Drierite, and distilled. Fifteen grams (58%) of material, n_D^{20} 1.4999, d_4^{25} 1.3241, m.p. 24.7–25.0°, was collected at 115–120° (7 mm.). Infrared absorption maxima were found at 8.95, 7.38, 8.59, 9.24, 7.67, 8.46, 7.47, 12.09, 13.27, 13.82, 14.63, 13.45, 9.74, 9.98, 12.76 and 3.27 μ (in order of decreasing intensity) in carbon disulfide solution.

Anal. Calcd. for $\text{C}_7\text{H}_5\text{O}_2\text{F}_2\text{S}$: C, 43.70; H, 3.12; S, 16.66; F, 19.90. Found: C, 42.91; H, 3.24; S, 15.84, 16.99, 17.03; F, 22.11, 20.08, 20.36.

In order to calculate the expected molecular refraction of difluoromethyl phenyl sulfone, a value for the contribution of the sulfone group was needed. Since none seems to be available in the literature we sought data from which a value could be calculated. Reports on more than one

(22) All analyses by Clark Microanalytical Laboratories, Urbana, Ill.

hundred sulfones (most of which are solids) yielded only thirteen compounds for which densities and refractive indices had been determined.²³⁻²⁵ Using standard values for the other atomic and structural constants²⁶ the data on the ten sulfones that did not contain α,β -unsaturation gave a value of 8.60 ± 0.12 for the contribution of the sulfone group. Values of 8.72, 10.32 and 10.70 were obtained from the data on divinyl sulfone,²⁴ 2-chloroethyl 1-chlorovinyl sulfone, and 2-chloroethyl 2-chlorovinyl sulfone, respectively. Our experimental molecular refraction (40.88) is somewhat higher than the value (39.33) calculated from the average contribution of saturated sulfones but no higher than might be expected in view of the probability of exaltation due to conjugation of the sulfone group with the aromatic ring and the presence of two fluorine atoms on the same carbon.²⁷

Difluoromethyl 2-Naphthyl Sulfone.—By a method like that used previously in the preparation of difluoromethyl phenyl sulfide, 25 g. (0.16 mole) of 2-naphthalenethiol, 0.30 mole of sodium methoxide and excess chlorodifluoromethane in 500 ml. of methanol yielded 8 ml. of thick, oily difluoromethyl 2-naphthyl sulfide. The oxidation of 2 ml. of this oil with 5 ml. of 90% hydrogen peroxide in 10 ml. of acetic acid at 105° gave 1.5 g. of difluoromethyl 2-naphthyl sulfone, m.p. 57.2–58.0° (from methanol).

Anal. Calcd. for $C_{11}H_8F_2SO_2$: C, 54.54; H, 3.31; F, 15.70; S, 13.22. Found: C, 54.83, 54.78; H, 3.45, 3.60; F, 15.68, 15.69; S, 12.96, 12.71.

Reaction of Difluoromethyl Phenyl Sulfone with Sodium Methoxide and Sodium Thiophenoxide.—When 12 g. (0.53 mole) of sodium had dissolved in 300 ml. of methanol, 23 g. (0.21 mole) of thiophenol and 26.5 g. (0.138 mole) of difluoromethyl phenyl sulfone were added and the mixture was kept at about 50° for 24 hours. After an additional 24 hours at about 64° the reaction was stopped and a sample withdrawn for a titration that showed 0.16 mole of sodium methoxide and 0.15 mole of sodium thiophenoxide to be unreacted. In a Dry Ice-cooled trap attached to the reaction flask was found more than 4 ml. of material shown to be difluoromethyl methyl ether by its infrared spectrum.¹¹ This corresponds to 4.4 g. (38%), but some of this volatile (b.p. -4°) material was undoubtedly lost.

About 170 ml. of methanol was distilled from the reaction mixture which was then poured into water and the organic layer separated. Two ether extracts of the aqueous layer were combined with the organic layer and the combined material distilled to give 4.98 g. (22%) of difluoromethyl phenyl sulfide, b.p. 65° (10-mm.), identified by its infrared spectrum.¹¹

The aqueous layer was acidified with hydrochloric acid to a pH of 5 and the thiophenol extracted with two portions of ether. Additional acid was added until the pH was 0.5 and after the solution had stood at 0° overnight, 2.50 g. of benzenesulfonic acid, m.p. 81.5–82.5°, neutralization equivalent 143, had separated. By ether extraction of the aqueous solution 7.8 g. of less pure acid, m.p. 72–74°, was obtained for a total yield of 52%.

Kinetics of Reactions with Sodium Methoxide and Sodium Thiophenoxide.—In a typical run 20 ml. of sodium methoxide solution was pipetted into 60 ml. of a solution of thiophenol in methanol. After this material had been in a 50° bath for at least 30 minutes, 2.00 ml. of difluoromethyl phenyl sulfone was added by syringe. At various time intervals 10-ml. samples were removed by pipet and titrated to the *p*-nitrophenol end-point with standard hydrochloric acid. The thiophenol concentration was then determined by titration with standard base using thymol blue as the indicator. This method for the determination of the thiophenol concentration was made necessary by the interference of benzenesulfonic acid with the iodometric method used previously.¹¹ The runs in the absence of sodium thiophenoxide were carried out similarly except that no thiophenol determination was necessary.

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Calculation of Rate Constants.—The value of term n in eq. 1 increases with increasing sodium methoxide concentration.^{11,18} Experiments on chlorodifluoromethane have shown that n is 1.15 at a sodium methoxide concentration of 0.02 M ¹¹ and experiments on difluoromethyl phenyl sulfone have given a value of 1.45 in the presence of 0.57 M sodium methoxide. We have therefore chosen an intermediate value of 1.30 for our experiments carried out at intermediate average sodium methoxide concentration of around 0.2 M . The results of synthetic experiments^{11,19} show that the presence of RS^- anions does not greatly change the number of moles of total base reacting per mole of difluoromethylene. Therefore in the experiments where sodium thiophenoxide was present it was assumed that 1.30 moles of total base reacted per mole of sulfone. Since direct measurements showed that 62.4% of the total base that reacted was methoxide ion, an n -value of 0.811 was used in calculating the rate constants in this case. Our method of arriving at n , particularly in the presence of sodium thiophenoxide, may easily produce a 10% error in the rate constant that we have obtained. Kinetic data on a reaction between sodium methoxide, sodium thiophenoxide and difluoromethyl phenyl sulfone are shown in Table II.

TABLE II
REACTION OF DIFLUOROMETHYL PHENYL SULFONE WITH SODIUM METHOXIDE AND SODIUM THIOPHENOXIDE AT 50.4°^a

Time, sec.	[NaSC ₆ H ₅]	[NaOMe]	$10^5 k$, l. mole ⁻¹ sec. ⁻¹	k_T/k_M , l. mole ⁻¹
0	0.1871	0.2150		
27,840	.1776	.1962	3.15	2.77
69,960	.1663	.1722	3.50	2.76
86,560	.1580	.1680	3.25	3.61
109,620	.1533	.1621	3.07	3.77
156,480	.1449	.1453	3.35	3.67

Av. 3.28 ± 0.15 3.32 ± 0.44

^a $[C_6H_5SO_2CHF_2]_0 = 0.1379 M$.

Deuteriodifluoromethyl Phenyl Sulfone.—When difluoromethyl phenyl sulfone was shaken with alkaline heavy water its infrared spectrum changed in a manner to be expected from deuteration. This interpretation was supported by the fact that the spectral change could be entirely reversed by shaking the deuterated sulfone with ordinary aqueous alkali. The material used in our work had absorption maxima at 7.39, 8.86, 8.70, 8.36, 9.28, 12.76, 14.61, 13.29 and 13.76 μ (in the order of decreasing intensity in carbon disulfide solution). This material absorbed only 17% as strongly at 12.09 μ as did the protium compound. If all of this absorption is due to protium compound present as impurity in the deuterated material the isotopic purity is 83%. If the deuteriodifluoromethyl phenyl sulfone itself absorbs significantly at 12.09 μ its isotopic purity is greater than 83%. In the kinetic runs isotopic analyses were made

TABLE III
SODIUM METHOXIDE-CATALYZED DEUTERIUM EXCHANGE OF $C_6H_5SO_2CDF_2$ IN METHANOL AT 0°^a

Time, sec.	% D ^b	$10^5 k$, sec. ⁻¹
1,800	83.3	^c
3,600	73.4	7.04
7,530	51.2	6.65
10,800	45.4	6.75
14,430	38.7	6.08
18,000	27.8	6.77

Av. 6.66 ± 0.23 ^d

^a $[C_6H_5SO_2CDF_2]_0 = 0.069 M$; $[NaOMe] = 0.0711 M$.

^b Relative to the deuterium content of the starting material. ^c This was used as the "zero point" in that 1800 sec. were subtracted from the times listed and 83.3% was used as the initial deuterium content in the calculation of rate constants.

^d By dividing by the sodium methoxide concentration this is changed to the second-order rate constant $(94 \pm 4) \times 10^{-6}$ l. mole⁻¹ sec.⁻¹.

by measurements at the 8.36μ band of the deuterium compound and the 8.59μ band of the protium compound.

Kinetics of Deuterium Exchange.—In a typical run 0.5 ml. of deuteriodifluoromethyl phenyl sulfone was pipetted into 50 ml. of 0.0237 *M* sodium methoxide in methanol at 0° and the reaction flask shaken. At various recorded times 10-ml. samples were pipetted into 70 ml. of 0.2 *M* hydrochloric acid and extracted with 1.5 ml. of carbon disulfide. After drying with a little silica gel, the carbon disulfide solutions were analyzed for the isotopic content of the sulfone they contained.

Since the deuterium exchange is quite rapid compared to the rate of consumption of sodium methoxide the reaction is first order within a given run. As we have shown previously we need to know only the base concentration and the deuterium content at time *t* relative to that present initially. Ignorance of the absolute deuterium content,

variations in sample size, incomplete (but isotopically non-selective) extraction, spillage of extract, etc., will have no effect on the values of the rate constants obtained. Table III gives data on one of the deuterium exchange runs.

The rate constants calculated in the usual manner showed a tendency to fall as the reaction proceeded. We believe that this is due to an increase in the reaction temperature brought about while removing the flask from the ice-bath for vigorous shaking at the beginning of the reaction. To correct for this we have used the first point taken as a "zero point."

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Reactions of Fluoroolefins with Sulfur Trioxide

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β -Sultones have been synthesized in good yields by reaction of a variety of fluoroolefins with sulfur trioxide. Other products including a cyclic sulfite from tetrafluoroethylene and adducts believed to be six-membered cyclic sulfonate-sulfate anhydrides are also obtained depending on the structure of the fluoroolefin and the reaction conditions. The sultones rearrange in the presence of bases to give derivatives of sulfodihaloacetic acids, and the mechanism of this rearrangement is considered.

Reactions of olefins with sulfur trioxide have been rather extensively studied. These reactions are generally quite vigorous and must be moderated by use of inert diluents or by use of complexes of sulfur trioxide with pyridine or dioxane. In only one case, *i.e.*, the reaction of styrene with sulfur trioxide, has the isolation of a β -sultone been reported.¹

In contrast, it has recently been reported^{2,3} that a number of fluoroolefins react with sulfur trioxide in the absence of any complexing agent or diluent to give β -sultones and, under some conditions, cyclic sulfonate-sulfate anhydrides. In studies extending over a period of several years, we have also been examining the behavior of fluoroolefins toward sulfur trioxide and are prompted to submit a detailed account of our findings, since they are at variance with those already reported in some respects and serve to extend and clarify them in many others.

Tetrafluoroethylene (TFE) reacted rapidly and exothermically with *freshly distilled* sulfur trioxide⁴ in a modified Parr low-pressure hydrogenation apparatus to give β -hydroxytetrafluoroethanesulfonic acid sultone (I) in nearly quantitative yield. The reaction temperature was kept below 80° by external cooling and by regulating the rate of addition of TFE. The reaction could

also be run at atmospheric pressure by passing a mixture of TFE and sulfur trioxide through a Pyrex tube packed with short sections of Pyrex tubing. Under these conditions, a mildly exothermic reaction occurred and distillation of the product gave pure I in 44% yield. Attempts to accomplish the reaction by bubbling TFE through liquid sulfur trioxide at atmospheric pressure were unsuccessful. The sultone I is a fuming liquid that boils at 42°. Its structure was established from elemental analyses, neutral equivalent determinations and the fluorine nuclear magnetic resonance spectrum (n.m.r.).

Sultones were also prepared from several chloro-fluoroolefins. For example, reaction of *sym*-dichlorodifluoroethylene with distilled sulfur trioxide at atmospheric pressure with mild heating gave the sultone III in 80% yield. *unsym*-Dichlorodifluoroethylene reacted with sulfur trioxide to give V as the sole product. However, chlorotrifluoroethylene gave approximately equal amounts of the two possible isomeric sultones VII and VIII. These products codistilled but the fluorine n.m.r. spectrum of the mixture was readily interpreted as consisting of a single peak (CFCl) and a weak-strong-strong-weak combination (CF₂ in an unsymmetrical ring) for each of the two isomers present.

Treatment of the sultones with a catalytic amount of base, such as triethylamine, brought about rapid and quantitative rearrangement to sulfonic-carboxylic acid halides. A possible mechanism for this rearrangement is proposed as⁵ In the first step, triethylamine would be expected to attack at the sulfur atom as shown and ring-

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(4) "Sulfan," purchased in 2-lb. ampoules from General Chemical Division, Allied Chemical Corp., and described in their trade literature as "stabilized sulfur trioxide," was used in this work. In our hands, this material distilled practically quantitatively at 46°.

(5) The authors are indebted to a referee for unifying and expanding the mechanistic considerations contained in the original manuscript.