

by measurements at the 8.36 μ band of the deuterium compound and the 8.59 μ 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 Fluoroölefins with Sulfur Trioxide

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β -Sultones have been synthesized in good yields by reaction of a variety of fluoroölefins 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 fluoroölefin 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 fluoroölefins 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 fluoroölefins 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-fluoroölefins. 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 (CFCI) 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-

(1) F. G. Bordwell, M. L. Peterson and C. S. Rondstvedt, Jr., *THIS JOURNAL*, **76**, 3945 (1954).

(2) S. Hsi-Kwei Jiang, *Hua Hsueh Hsueh Pao*, **23**, 330 (1957); *C. A.*, **52**, 15493b (1958).

(3) M. A. Dmitriev, G. A. Sokol'skil and I. L. Knunyants, *Khim. Nauka i Prom.*, **3**, 826-8 (1958); *Doklady Akad. Nauk S.S.S.R.*, **124**, 581 (1959); *C. A.*, **53**, 11211a (1959).

(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°.

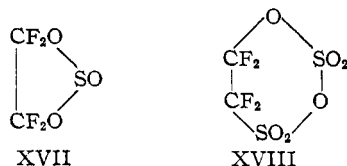
(5) The authors are indebted to a referee for unifying and expanding the mechanistic considerations contained in the original manuscript.

ylic acid. Good yields of the sultones XV and XVI were obtained from *n*-butyltrifluoroethylene and ω -hydroperfluoro-1-octene, respectively.

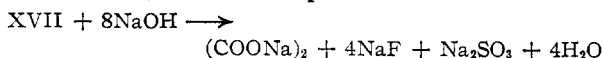
Several of the sultones in addition to I were treated with alcohols and amines to give derivatives of their rearrangement products. These compounds are also listed in Table I.

The importance of using *freshly distilled* sulfur trioxide in preparing the sultones must be emphasized. In our work with TFE, the use of Sulfan⁴ that had not been distilled prior to use almost invariably led to a mixture of products as discussed below. This was true whether Sulfan from a previously used or freshly opened ampoule was employed. Furthermore, in contrast to the reaction of TFE with freshly distilled sulfur trioxide, which could be scaled up manifold, all attempts to scale up the reaction with Sulfan in the Parr apparatus beyond about 0.2 mole quantities resulted in rapidly decreasing absorption of TFE and reaction soon became negligible. Since this inhibition was not appreciable in the atmospheric pressure apparatus, most of the experiments with TFE and Sulfan were conducted in this equipment.

The products obtained under these conditions consisted of a low-boiling mixture of two 1:1 adducts that could not be separated by distillation and a higher-boiling product. One component of the low-boiling mixture was clearly recognized as I by n.m.r. The other component was deduced to be the cyclic sulfite XVII on the basis of the following information: (a) in addition to the two



characteristic peaks of the sultone I, the n.m.r. spectrum of the mixture showed a pattern expected for structure XVII, assuming that the ring is non-planar; (b) neutral equivalent determinations on the mixture gave values between that established for the sultone (45) and that calculated for the sulfite (22.5) from the equation



Percentage compositions of mixtures estimated from n.m.r. spectra agreed closely with those based on neutral equivalent determinations; and (c) mixtures reacted with aniline and cyclohexylamine to give oxanilide and *N,N'*-dicyclohexylamide, respectively. These products were not obtained from pure I. In typical preparations, the sulfite was estimated to constitute about 15% of the low-boiling product. By careful fractional distillation, samples containing about 55% sulfite and 45% sultone were obtained, but pure sulfite was never isolated.

The higher-boiling product, which constituted about 30% of the total, was a fuming liquid. About half of it boiled at 100–108° and was shown by analyses to contain TFE and sulfur trioxide in approximately a 1:2 ratio. By analogy to

similar products obtained in this work, it is assumed to have structure XVIII. Neither this product nor the sulfite (XVII) was ever obtained from the reaction of TFE with freshly distilled sulfur trioxide.

The reaction of hexafluoropropene with Sulfan also gave a different product from that (XIV) obtained with distilled sulfur trioxide. This product contained two moles of sulfur trioxide and was presumably a cyclic sulfonate-sulfate anhydride.

The marked difference in results obtained with Sulfan before and after distillation may be caused by differences in the amount of polymeric sulfur trioxide present. It is known that monomeric liquid sulfur trioxide polymerizes quite readily and that this polymerization is promoted by water.⁸ In our work freshly distilled sulfur trioxide to which a small amount of water had been added showed greatly reduced reactivity toward TFE in the Parr apparatus and the product obtained contained some sulfite, XVII. Similar treatment of Sulfan completely inhibited its reaction with TFE under these conditions. Reaction of TFE with solid polymeric sulfur trioxide was very sluggish even at 100° and gave only a low yield of sultone and some sulfite. Another cause for the difference in reaction with Sulfan and freshly distilled sulfur trioxide could be the stabilizing agent used in Sulfan. Although the particular agent used is not known, one which has been disclosed,⁹ boric anhydride, did not affect the reactivity of freshly distilled sulfur trioxide.

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Experimental¹⁰

Reaction of TFE with Freshly Distilled Sulfur Trioxide.
(A) **Under Pressure.**—The bottle (400 ml.) of a Parr low-pressure hydrogenation apparatus was fitted with a two-hole rubber stopper through which were passed a thermocouple well made of 5-mm. glass tubing and a gooseneck made of 8-mm. heavy-walled glass tubing. The thermocouple well extended to within about 2 cm. of the bottom of the bottle. The gooseneck extended 1 cm. into the bottle and the other end was connected directly to a manifold system with heavy-walled Tygon polyvinyl chloride pressure tubing using screw clamps. Also attached to the manifold system through needle valves were a vacuum line, a storage cylinder of TFE, a pressure gage and a vent line.

The bottle was charged with 212 g. of freshly distilled sulfur trioxide (condensed at room temperature since cooling promotes polymerization) and clamped into the metal cage of the shaking apparatus. The bottle was evacuated briefly to remove most of the air present and was pressured to 2.7 atm. gage with TFE. A rapid, exothermic absorption of TFE began as soon as shaking was started. The tempera-

(8) H. V. Sidgwick, "The Chemical Elements and Their Compounds," Clarendon Press, Oxford, 1950, Vol. II, p. 901.

(9) H. G. McCann, U. S. Patent 2,458,718 (1949).

(10) All boiling points and melting points are uncorrected. Nuclear magnetic resonance (n.m.r.) spectra were obtained by means of a high resolution nuclear magnetic resonance spectrometer and associated electromagnet, both manufactured by Varian Associates, Palo Alto, Calif., operating at 56.4 Mc. and approximately 14,000 gauss. Spectra were calibrated in cycles per second (c.p.s.) from the fluorine resonance of trifluoroacetic acid using the side-band technique. Positive signs refer to the high field side from the reference.

ture was kept below 80° by regulating the rate of addition of TFE and by cooling the vessel externally with a stream of ice-water. Absorption was complete in about 1 hr. The total gain in weight was 265 g. Distillation of the product gave 442 g. (93%) of 2-hydroxytetrafluoroethanesulfonic acid sultone (I), b.p. 42°, m.p. -35°. The fluorine n.m.r. spectrum showed two peaks of equal intensity at 768 and 1305 c.p.s. Fine structure showed each of these peaks to be a triplet.

Anal. Calcd. for $C_2H_4O_3S$: F, 42.2; S, 17.8; neut. equiv., 45.0. Found: F, 41.6; S, 18.0; neut. equiv., 44.9.

The reaction was repeated with 46.7 g. of sulfur trioxide to which two drops of water had been added to obtain 48 g. (46%) of product, b.p. 42°. The n.m.r. spectrum of this product showed the presence of a second component, subsequently identified as the sulfite XVII (see below). A considerable amount of higher-boiling material was also formed.

(B) *At Atmospheric Pressure.*—TFE was metered at a rate of 1 mole per hour into the top of a vertically mounted 25-mm. o.d. glass tube 20 inches long packed with short sections of 8-mm. glass tubing. Freshly distilled sulfur trioxide was added dropwise at the same rate. Near the bottom of the tube a hot spot of about 45° developed. The product was collected in a trap cooled in a bath of solid carbon dioxide in acetone. From 54 g. of sulfur trioxide there was obtained 53 g. (44%) of I, b.p. 42°, which was pure by n.m.r. Considerable sulfur trioxide polymer was formed. When TFE was bubbled through freshly distilled sulfur trioxide at atmospheric pressure in a moisture-protected flask, essentially no reaction was observed.

Reaction of TFE with Sulfan. (A) Under Pressure.—A 16-g. (0.2 mole) sample of Sulfan from a freshly opened ampoule absorbed 16 g. of TFE in the Parr apparatus in about 10 min. Distillation of the crude product gave 22 g. (61%) of 2-hydroxytetrafluoroethanesulfonic acid sultone, b.p. 42°, characterized by n.m.r. and neutral equivalent (found 45.5). Higher-boiling material was also found.

This result was duplicated in an immediately following experiment with sulfur trioxide from the same ampoule. All subsequent experiments on the 0.2-mole scale in the Parr apparatus gave sultone contaminated with the sulfite XVII, even with Sulfan from freshly opened ampoules. In runs made on a larger scale, absorption of TFE diminished rapidly and little product was obtained.

(B) *At Atmospheric Pressure.*—TFE and Sulfan (99 g.) were passed through the tube at the rate of one mole of each per hour. A hot spot of 38° developed near the bottom of the tube. Distillation of the product gave 95 g. (43%) of material, b.p. 36-40°, and 44 g. of material boiling at 40-109°. The fluorine n.m.r. spectrum of the product boiling at 36-40° showed a weak-strong-strong-weak combination of peaks at 106, 244, 348 and 486 c.p.s. (data taken at 30 Mc. and converted to 56.4 Mc.) in addition to the two peaks characteristic of I. This new combination of peaks is that predicted for the sulfite XVII, assuming a non-planar ring. On the basis of the spectrum, the mixture was estimated to contain approximately 85% I and 15% XVII. The neutral equivalent determined on the mixture was 30.0, from which a ratio of 84:16 for the two components was calculated.

Redistillation of the higher-boiling material gave 2 g. of a fuming liquid boiling at 100-108°. Analytical values were in fair agreement with those calculated for a TFE/2 SO₂ adduct (XVIII).

Anal. Calcd. for $C_2F_4S_2O_6$: S, 24.6; F, 29.2. Found: S, 23.8; F, 27.2.

By conducting this reaction at higher temperatures, products containing a higher proportion of the sulfite were obtained, although over-all yields were lower. Thus, TFE and Sulfan (99 g.) were passed through the tube at an external temperature of 378° to obtain 75 g. (34%) of product, b.p. 37-38°, neut. equiv., 34.7, and 25 g. of product boiling at 88-180°. From the neutral equivalent of the lower-boiling fraction, it was calculated to contain 29.5 g. of the sulfite. Redistillation of sultone-sulfite mixtures that had been stored in glass for several weeks gave fractions containing a higher proportion of sulfite and some high-boiling material. Precision distillation of one such sample gave a product, b.p. 44-45°, neut. equiv., 29.2, containing 55% sulfite and 45% sultone. Pure sulfite was never obtained.

Reaction of a Mixture of I and XVII with Aniline.—A solution of 18 g. (0.1 mole) of a mixture of I and XVII (ca.

85:15 by n.m.r.) in 75 g. of ether was added slowly with cooling in ice to a solution of 46.5 g. (0.5 mole) of aniline in 75 g. of ether. The reaction mixture was allowed to stand at room temperature overnight and the resulting slurry was diluted with 200 ml. of ether and filtered. The precipitate was washed well with ether and with methanol to obtain 4.5 g. of product, m.p. 253°, undepressed when mixed with an authentic sample of oxanilide, m.p. 255°. The remainder of the product was not isolated and characterized. No oxanilide was formed from pure I (see Table I).

Reaction of a Mixture of I and XVII with Cyclohexylamine.—A solution of 14.4 g. of a mixture of I and XVII (ca. 85:15) in 50 ml. of cyclohexane and 10 ml. of dry ether was added to a solution of 39.6 g. of cyclohexylamine in 50 ml. of cyclohexane. After standing overnight, the mixture was filtered and the solid was washed with ether. The dried solid (42 g.) was extracted with methanol and the insoluble portion, 9.4 g., was recrystallized from dimethylformamide, m.p. 274-275°, undepressed on admixture with an authentic sample of N,N'-dicyclohexylloxamide, m.p. 275-276°. ¹²

Evaporation of the original filtrate and ether washings gave 9 g. of solid. Evaporation of the methanol extracts gave 33 g. of solid that was washed with water to obtain 5 g. of insoluble product. These two samples were the same by melting point and mixed melting point (126-130°) and were combined. A portion recrystallized from benzene-petroleum ether melted at 129-133° and gave the correct analysis for N-cyclohexylcyclohexylsulfamylidifluoroacetamide.

Anal. Calcd. for $C_{14}H_{24}F_2N_2O_3S$: N, 8.3; F, 11.2. Found: N, 8.6; F, 11.6.

Rearrangement of I to II.—The sultone I (180 g.) was placed in a 1-l. flask fitted with a stirrer and an efficient reflux condenser with drying tube attached. The sultone was cooled to about 0-10° in an ice-bath and 3 drops of triethylamine added through the condenser with stirring. After the rapid exothermic reaction had subsided, the material was distilled to give 162 g. (90%) of fluorosulfonyldifluoroacetyl fluoride (II), b.p. 29-30°. The fluorine n.m.r. spectrum of the product showed three peaks in the intensity ratio of 1:1:2 at -6724, -5663 and 1568 c.p.s. Fine structure showed the first two peaks (SO₂F and COF, respectively) to be triplets and the CF₂ peak to be a quadruplet. Peaks characteristic of the sultone were absent.

Anal. Calcd. for $C_2F_4O_2S$: neut. equiv., 45.0. Found: neut. equiv., 44.9.

Reaction of Hexafluoropropene with Freshly Distilled Sulfur Trioxide.—Distilled sulfur trioxide (28 g., 0.35 mole) and hexafluoropropene (52 g., 0.35 mole) were heated at 100° for 15 hr. in a Carius tube. The fuming mixture was distilled to obtain 68 g. (85%) of 2-hydroxy-1-trifluoromethyl-1,2,2-trifluoroethanesulfonic acid sultone (XIV), b.p. 46.5°. This structure was supported by n.m.r. and by the structure of its hydrolysis product described below. Fluorine n.m.r. showed a CF₂ peak at -150 c.p.s., a weak-strong-strong-weak combination for CF₂ at 309, 419, 645 and 756 c.p.s. and a CF peak at 4320 c.p.s.

Anal. Calcd. for $C_3F_6O_3S$: C, 15.7; S, 13.9; F, 49.5. Found: C, 15.6; S, 14.0; F, 48.7.

When the reaction was carried out in the Parr apparatus as described for TFE, absorption of hexafluoropropene was very slow. The product, b.p. 38.5°, appeared to be an azeotrope of sulfur trioxide with the sultone XIV in equimolar proportions.

Anal. Calcd. for $C_3F_6O_3S \cdot SO_2$: F, 36.8; S, 20.6; neut. equiv., 51.7. Found: F, 33.6; S, 20.2; neut. equiv., 50.0.

Reaction of Hexafluoropropene with Sulfan.—A mixture of 38 g. (0.04 mole) of Sulfan and 75 g. (0.05 mole) of hexafluoropropene was sealed in a stainless steel tube and heated to 60° for 5 hr. Distillation gave 55 g. of an unidentified mixture, b.p. 50-65°, which was not characterized, and a fraction (25 g., 17%) boiling at 114-115°. Analytical results for the high-boiling product suggest a cyclic sulfonate-sulfate anhydride structure.

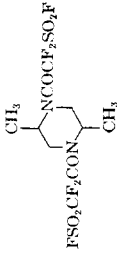
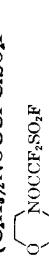
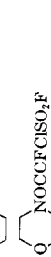
Anal. Calcd. for $C_3F_6O_6S_2$: F, 36.8. Found: F, 35.1.

This reaction proceeded very slowly in the Parr apparatus at 2.7 atm. gage pressure and gave the same product in slightly lower yield.

(11) J. Th. Boonwater, *Rec. trav. chim.*, **31**, 108 (1912).

(12) M. Grunfeld, *Compt. rend.*, **194**, 893 (1932).

TABLE I: REACTIONS OF FLUOROOLEFIN-SULFUR TRIOXIDE DERIVATIVES

R reactant (mole)	SO ₃ deriv. (mole)	Solvent (ml.)	Method	Product	Yield, %	M. p. or b. p., °C. (mm.)	#D	Calculated— F S N	Found— F S N
Sodium methoxide (0.2)	I (0.2)	Ether (200)	R to I, 10°	CH ₃ OCCF ₂ SO ₂ F	50	118 (atm.)	1.3500	29.7 16.7	29.8 16.0
Isopropyl alc. (0.15)	I (0.15)	Ether (200)	I to R, 10°	C ₃ H ₇ OCCF ₂ SO ₂ F	30	133-134 (atm.)	1.3571	25.9 14.5	25.7 14.5
Isopropyl alc. (0.13)	II (0.12)	Ether (200)	R to II, 10°	C ₃ H ₇ OCCF ₂ SO ₂ F	47	132-134 (atm.)	1.3572	110 (N.E.)	113 (N.E.)
Octanol-1 (0.2)	I (0.2)	Ligroin (400)	I to R, 0°	C ₈ H ₁₇ OCCF ₂ SO ₂ F	70	88 (5)	1.3597	20.3 11.7	19.3 11.7
2-Ethylhexanol-1 (0.4)	VII-VIII (0.4)	Ligroin (150)	VII-VIII to R, 0°	C ₂ H ₅ CH ₂ OCCF ₂ SO ₂ F*	14	71-74 (2.5)	1.3978	11.7	19.7 10.5
2-Ethylhexanol-1 (0.1)	XIV (0.1)	Ligroin (240)	R to XIV, 0°	C ₂ H ₅ CH ₂ OCCF ₂ (CF ₂)SO ₂ F	63	92-94 (8)	1.3855	28.9 9.7	26.9 9.4
Trichloroethanol (0.25)	II (0.25)	Ligroin (100)	R to II, 0°	Cl ₃ CCH ₂ OCCF ₂ SO ₂ F	48	111-113 (55)	1.4171	Cl 34.4 10.3	Cl 36.4 10.1
Octafluoroamyl alc. (0.1)	I (0.1)	Ether (200)	I to R, 10°	H(CF ₂) ₇ CH ₂ OCCF ₂ SO ₂ F	30	98-99 (30)	1.3334	53.3 8.2	55.7 8.0
Ethylene glycol (0.2)	I (0.4)	Ligroin (300)	I to R, 10°	(CH ₂ OCCF ₂ SO ₂ F) ₂	51	124-125 (7)	1.3830	29.5 16.7	30.7 16.9
Phenol (0.5)	I (0.5)	None	I to R, 10°	C ₆ H ₅ OCCF ₂ SO ₂ F	36	91.5-92.5 (30)	1.4350	22.4 12.6	20.9 12.7
Benzenethiol (0.25)	II (0.25)	Ether (150)	R to II, 10°	C ₆ H ₅ SOCCF ₂ SO ₂ F	42	98-99 (5.5)	1.4931	21.1 23.7	21.1 23.8
NaSCN (0.25)	I (0.75)	None	R to I, 25°	SCNOCF ₂ SO ₂ F	5	87 (106)	1.4567	26.0 29.2	6.4 26.0 29.2 6.2
Butylamine (0.8)	I (0.4)	Ether (16)	I to R, 10°	C ₄ H ₉ HNOCCF ₂ SO ₂ F	15	97-97.5 (4)	1.4076	24.4 13.7	6.0 24.3 13.5 5.8
Octylamine (0.6)	I (0.3)	Ether (400)	R to I, 10°	C ₈ H ₁₇ HNOCCF ₂ SO ₂ NHC ₄ H ₉	10	190-191 (4) ^b	1.4524	13.3 11.2	9.8 13.1 10.7 9.7
Aniline (0.4)	I (0.1)	Ether (125)	I to R, 10°	C ₆ H ₅ HNOCCF ₂ SO ₂ NHC ₈ H ₁₇	27	163-164 (20)	1.4237	19.7 11.1	4.8 19.0 10.9 4.9
Aniline (0.2)	I (0.2)	Ether (400)	I to R, -80°	C ₆ H ₅ HNOCCF ₂ SO ₂ H ₂ NC ₄ H ₉	35	250-270 (20)	1.4561	9.6 8.0	7.0 8.3 8.3 7.2
					84	218-219	11.0 9.3	8.1 10.8 9.2 8.2	344 (N.E.) 340 (N.E.)
					98	107-108	22.5 12.6	5.5 22.9 12.6 5.6	
2,5-Dimethylpiperazine (0.6)	I (0.6)	Ether (250)	R to I, 0°		64	212-214	26.3 14.8	6.5 26.4 14.0 6.5	
N-Methylaniline (0.6)	I (0.3)	Ether (160)	R to I, 10°	C ₆ H ₅ N(CH ₃)OCCF ₂ SO ₂ F	70	69-71	21.3 12.0	5.2 21.5 12.0 5.4	
N-Methylaniline (0.2)	XIV (0.1)	Ether (240)	R to XIV, 0°	C ₆ H ₅ N(CH ₃)OCCF ₂ (CF ₂)SO ₂ F	62	108-110 (2)	1.4598	183.5 (N.E.) 136.6 (N.E.)	136.6 (N.E.)
p-Anisidine (0.6)	I (0.15)	Ether (125)	I to R, 10°	p-CH ₃ OCC ₆ H ₄ HNOCCF ₂ SO ₂ H-p-CH ₃ OCC ₆ H ₄ NH ₂	33	201-203	6.9	4.4 29.2	5.0 7.0
Diethylamine (0.8)	I (0.4)	Ether (300)	R to I, 10°	p-CH ₃ OCC ₆ H ₄ HNOCCF ₂ SO ₂ NHCH ₂ CH ₃ -p-CH ₃ OCC ₆ H ₄ NH ₂	25	177-179	7.3	7.3	7.3
Diethylamine (0.6)	VII-VIII (0.3)	Ether (240)	R to VII-VIII, 10°	(C ₂ H ₅) ₂ NOCF ₂ SO ₂ F	63	120-121 (20)	1.4092	24.4 13.8	386 (N.E.) 395 (N.E.)
Diethylamine (0.1)	III (0.05)	Ether (50)	R to III, -10°	(C ₂ H ₅) ₂ NOCF ₂ (CF ₂)SO ₂ F	20	107-110 (10)	1.4411	24.4 13.8	116.5 (N.E.) 118 (N.E.)
Morpholine (0.6)	I (0.3)	Ether (300)	R to I, 10°		45	72-73	23.1 13.0	5.7 23.3 12.8 5.5	
Morpholine (0.6)	VII-VIII (0.3)	Ether (200)	R to VII-VIII, 10°		30	70-74	14.2 (Cl)	13.8 (Cl)	
Diphenylamine (0.25)	I (0.25)	Ether (200)	R to I, 10°	(C ₆ H ₅) ₂ NOCF ₂ SO ₂ F	10	90-92	13.5 (Cl)	13.8 (Cl)	
Urea (0.4)	I (0.4)	Ligroin (400)	I to R, 25°	H ₂ NCOHNOCF ₂ SO ₂ F	50	75-76	17.3 9.7	4.1 15.7 9.7 4.3	
					96	150-152	25.8 14.5	12.7 23.6 13.9 12.9	

* A higher-boiling product containing chlorine was isolated but not purified. ^b M. p. 39-42°.

Rearrangement of XIV. 2-Fluorosulfonyl-2,3,3,3-tetrafluoropropionyl Fluoride.—Five drops of triethylamine was added to 41 g. of XIV and the mixture was heated to reflux for 0.5 hour. Distillation gave 38 g. (93%) of 2-fluorosulfonyl-2,3,3,3-tetrafluoropropionyl fluoride, b.p. 44.5°, characterized by n.m.r. which showed an SO_2F peak at -7332 c.p.s., a COF peak at -6157 c.p.s., a CF_2 peak at -194 c.p.s. and a CF peak at 4738 c.p.s.

Anal. Calcd. for $\text{C}_2\text{F}_6\text{SO}_2$: F, 49.6; S, 13.9. Found: F, 49.7; S, 14.1.

Hydrolysis of XIV. 1,2,2,2-Tetrafluoroethylsulfonyl Fluoride.—The sultone XIV (80 g.) was added dropwise to 200 g. of ice with stirring while maintaining the temperature below 10° . Stirring was continued for 3 hr. at room temperature after the addition was complete. Gas was evolved during this period. The lower layer was separated, dried over magnesium sulfate and distilled to obtain 40.1 g. (62.5%) of 1,2,2,2-tetrafluoroethylsulfonyl fluoride, b.p. $62-63^\circ$, characterized by n.m.r., infrared spectra and elemental analyses. The fluorine n.m.r. peaks appeared at -7239 (SO_2F), -248 (CF_2) and 4670 c.p.s. (CF).

Anal. Calcd. for $\text{C}_2\text{HF}_4\text{SO}_2$: C, 13.1; H, 0.6; S, 17.4; F, 51.6. Found: C, 13.1; H, 0.7; S, 17.3; F, 53.6.

Reaction of Chlorotrifluoroethylene with Sulfur Trioxide.—This reaction was exactly analogous to the reaction of TFE with distilled sulfur trioxide and was carried out in the same way in the Parr apparatus. From 46.5 g. (0.58 mole) of distilled sulfur trioxide there was obtained 97 g. (85%) of product, b.p. $76-78^\circ$. Nuclear magnetic resonance indicated that the product was an equimolar mixture of the two possible sultones, 2-hydroxy-1-chloro-1,2,2-trifluoroethanesulfonic acid sultone (VII), and 2-hydroxy-2-chloro-1,1,2-trifluoroethanesulfonic acid sultone (VIII). The fluorine n.m.r. peaks appeared at -287 c.p.s. (doublet, CF), a weak-strong-strong-weak combination for CF_2 at 296, 391, 520 (doublet) and 615 c.p.s. (doublet), another weak-strong-strong-weak combination for CF_2 at 703, 857, 963 (doublet) and 1117 c.p.s. (doublet) and a CF peak at 1418 c.p.s. (doublet).

Anal. Calcd. for $\text{C}_2\text{ClF}_3\text{O}_2\text{S}$: F, 29.0; Cl, 18.1; S, 16.3; neut. equiv., 49.1. Found: F, 30.0; Cl, 18.0; S, 16.7; neut. equiv., 49.1.

A small amount of higher-boiling residue was not distilled or characterized.

Rearrangement of a Mixture of VII and VIII.—A mixture of VII and VIII (83 g.) prepared as described in the preceding experiment was placed in a 200-ml. still-pot attached to a 12-inch distillation column (0.5-inch diameter, packed with glass helices) protected from moisture by a calcium chloride drying tube. The mixture was cooled to -10° , stirred with a magnetic stirrer and 5 drops of triethylamine was added. The mixture was then allowed to warm spontaneously with stirring. After 2 hours without external heating, it was refluxing vigorously (pot temperature about 75°). When refluxing subsided, the product was carefully distilled to obtain 6.5 g. (8.3%), b.p. 30° , which was characterized by fluorine n.m.r. as II; 57.5 g. (73.2%), which was collected as several fractions over the range $73-76^\circ$; and 14.5 g. (18.5%) distilling mostly at $110-150^\circ$. A mid-fraction of the material boiling between 73 and 76° corresponded in composition to, and gave the expected fluorine n.m.r. pattern for, a mixture of IX and X.

Anal. Calcd. for $\text{C}_2\text{ClF}_3\text{O}_2\text{S}$: F, 29.0; Cl, 18.1; S, 16.3. Found: F, 29.2; Cl, 18.0; S, 16.9.

A fraction boiling at $73-74^\circ$ was nearly pure IX as shown by fluorine n.m.r. peaks of equal intensity at -6646 (SO_2F), -5628 (COF) and 2090 c.p.s. (CF). A fraction boiling at 76° was nearly pure X, showing two peaks in the intensity ratio of 1:2 at -5910 (COF) and 1371 c.p.s. (CF_2). The fluorine n.m.r. spectrum of the material boiling at $110-150^\circ$ contained two fluorine peaks, one of which was attributable to a COF group.

Conversion of X to II by Reaction with Amine Hydrofluorides.—A mixture of IX and X (18 g.) was added rapidly to 7 g. of triethylamine hydrofluoride through the side arm of a flask attached to a 12-inch distillation column (0.5-inch diameter, packed with glass helices) protected from moisture by a calcium chloride drying tube. An exothermic reaction occurred and II began to distill at 30° . When the reaction had subsided, the flask was heated to obtain 6.0 g. of II, 2 g. of intermediate mixture and 4.5 g. of

unchanged IX, b.p. $73-74^\circ$. These compounds were characterized by fluorine n.m.r. Near the end of the distillation some decomposition occurred in the flask. When diethylamine hydrofluoride was used in place of triethylamine hydrofluoride, decomposition occurred after about 2 g. of II (characterized by boiling point and fluorine n.m.r.) had been collected.

Reaction of 1,2-Dichloro-1,2-difluoroethylene with Sulfur Trioxide.—To 55 g. of 1,2-dichloro-1,2-difluoroethylene in a flask cooled with an ice-bath and fitted with an ice-cooled reflux condenser was added dropwise with stirring over a period of 10 min., 33 g. of freshly distilled sulfur trioxide. The mixture was stirred at room temperature for 1 hr. and distilled to obtain 4 g. of unreacted fluoroolefin and 65.7 g. (80%) of 2-hydroxy-1,2-dichloro-1,2-difluoroethanesulfonic acid sultone (III), b.p. $110-113^\circ$. The fluorine n.m.r. spectrum indicated the product to consist of an equimolar mixture of the *cis* and *trans* isomers showing peaks of equal intensity (all doublets) at -890 , -601 , 691 and 979 c.p.s.

Anal. Calcd. for $\text{C}_2\text{F}_2\text{Cl}_2\text{SO}_3$: Cl, 33.3; S, 15.0; F, 17.8; neut. equiv., 52.3. Found: Cl, 32.2; S, 13.4; F, 16.0; neut. equiv., 53.2.

Continued distillation gave 7 g. of material, b.p. $140-145^\circ$, which is presumed to be the impure cyclic sulfonate-sulfate anhydride.

Anal. Calcd. for $\text{C}_2\text{F}_2\text{Cl}_2\text{S}_2\text{O}_6$: neut. equiv., 49.0. Found: neut. equiv., 42.8.

Rearrangement of III. Chlorosulfonylchlorofluoroacetyl Fluoride (IV).—Five drops of triethylamine was added to 30.5 g. of III and the mixture was heated to reflux for 2 hr. Distillation gave 19 g. (62%) of chlorosulfonylchlorofluoroacetyl fluoride (IV), b.p. 113° , characterized by n.m.r. and neutral equivalent. Fluorine n.m.r. peaks (doublets) of equal intensity occurred at -5832 (COF) and 1676 c.p.s.

Anal. Calcd. for $\text{C}_2\text{F}_2\text{Cl}_2\text{SO}_2$: neut. equiv., 53.2. Found: neut. equiv., 52.2.

Reaction of 1,1-Dichloro-2,2-difluoroethylene with Sulfur Trioxide.—Freshly distilled sulfur trioxide (56 g., 0.075 mole) was added to 11 g. (0.083 mole) of 1,1-dichloro-2,2-difluoroethylene in a Carius tube cooled in a solid carbon dioxide-bath. The tube was sealed, heated overnight on the steam-bath, cooled in solid carbon dioxide and opened. The contents were distilled to obtain 9 g. (56%) of product, b.p. $110-112^\circ$. The fluorine n.m.r. spectrum, which showed a single peak at 107 c.p.s., supported the structure 2-hydroxy-1,1-dichloro-2,2-difluoroethanesulfonic acid sultone (V).

Anal. Calcd. for $\text{C}_2\text{Cl}_2\text{F}_2\text{SO}_3$: Cl, 33.3; F, 17.8; S, 15.0; neut. equiv., 53.2. Found: Cl, 32.7; F, 18.0; S, 16.0; neut. equiv., 53.2.

Further structural proof was provided by an examination of the rearrangement product as described below.

Rearrangement of V. Fluorosulfonyldichloroacetyl Fluoride (VI).—Six drops of triethylamine was added to 6 ml. of V. The mixture was refluxed for 30 min. and distilled. Essentially all of the material boiled at 110° . The fluorine n.m.r. spectrum showed two peaks (doublets) of equal intensity at -6535 (SO_2F) and -5609 (COF) c.p.s. and, thus, was in agreement with structure VI.

Anal. Calcd. for $\text{C}_2\text{F}_2\text{Cl}_2\text{SO}_2$: neut. equiv., 53.2. Found: neut. equiv., 53.4.

Reaction of Trifluoroethylene with Sulfur Trioxide.—This reaction was run in the Parr apparatus as described for TFE. Freshly distilled sulfur trioxide (48 g., 0.6 mole) rapidly and exothermally absorbed 41 g. (0.5 mole) of trifluoroethylene. The crude product was distilled to obtain 49.5 g. (61%) of 2-hydroxy-1,2,2-trifluoroethanesulfonic acid sultone (XI), b.p. 103° . The structure was established by the fluorine n.m.r. spectrum of the sultone and its rearrangement product described below. The fluorine n.m.r. showed a weak-strong-strong-weak combination of peaks for CF_2 at 254, 362, 564 and 674 c.p.s. and a CHF peak (doublet) at 5123 and 5172 c.p.s.

Anal. Calcd. for $\text{C}_2\text{F}_3\text{SO}_2\text{H}_2$: F, 35.2; S, 19.8; neut. equiv., 40.5. Found: F, 35.0; S, 19.9; neut. equiv., 40.9.

Continued distillation gave 29 g. (24%) of material, b.p. $156-157^\circ$, which may be the cyclic sulfonate-sulfate anhydride XIII.

Anal. Calcd. for $\text{C}_2\text{F}_3\text{HS}_2\text{O}_6$: F, 23.5; S, 26.4; neut. equiv., 60.5. Found: F, 24.9; S, 26.1; neut. equiv., 56.5.

Rearrangement of XI. Fluorosulfonylfluoroacetyl Fluoride (XII).—Three drops of triethylamine was added to 25 g. of XI and the mixture was refluxed for 30 min. Distillation gave 18.5 g. of product boiling mostly at 103°. The fluorine n.m.r. spectrum was consistent with that expected for fluorosulfonylfluoroacetyl fluoride (XII) in that it showed an SO₂F peak at -7141 c.p.s., a COF doublet at -6274 and -6240 c.p.s. and eight peaks for CHF due to splitting by hydrogen and both of the other fluorine atoms. These peaks occurred at 5881, 5888, 5913, 5921, 5926, 5934, 5951 and 5965 c.p.s.

Synthesis of ω -Hydroperfluoro-1-octene.—This compound was prepared according to a known method¹³ for preparation of terminal fluoroolefins. A solution of ω -hydroperfluorononanoic acid¹⁴ (80 g.) in 100 ml. of water was neutralized with sodium hydroxide to a phenolphthalein end-point. The resulting solution was placed in a crystallizing dish and dried in a vacuum oven at 90° for 60 hr. The dried salt (79 g.) was transferred to a still-pot attached to an 18-inch spinning-band still and heated to about 350° (thermocouple between heating mantle and still-pot) to obtain 57 g. (88%) of ω -hydroperfluoro-1-octene, b.p. 66° at 130 mm., n_D^{25} 1.2960.

Reaction of ω -Hydroperfluoro-1-octene with Sulfur Trioxide.—A mixture of 25 g. (0.065 mole) of ω -hydroperfluoro-1-octene and 3 ml. (5.7 g., 0.07 mole) of freshly distilled sulfur trioxide was sealed in a glass tube, heated overnight on a steam-bath, and distilled to obtain 27.4 g. (90%) of 2-hydroxy-1-(ω -hydroperfluorohexyl)-1,2,2-trifluoroethanesulfonic acid sultone (XIV), b.p. 76° at 22 mm. Assignment of this structure is based on analogy to the formation of XIV from perfluoropropene.

Anal. Calcd. for C₈H₉F₁₀O₅S: F, 61.8; S, 6.9. Found: F, 63.7; S, 7.1.

Reaction of Butyltrifluoroethylene with Sulfur Trioxide.—Freshly distilled sulfur trioxide (20 g., 0.25 mole) was added dropwise with stirring to butyltrifluoroethylene¹⁵ (27.6 g., 0.2 mole) in a flask cooled with an ice-bath. The mixture was allowed to warm to room temperature and distilled at reduced pressure to obtain 31.4 g. (72%) of 2-hydroxy-1-butyl-1,2,2-trifluoroethanesulfonic acid sultone (XV), b.p. 63–65° at 20 mm. This structure is proposed by analogy to the formation of XIV from perfluoropropene.

Anal. Calcd. for C₈H₉F₃O₃S: F, 26.1; S, 14.7. Found: F, 26.6; S, 15.0.

Reaction of Vinylidene Fluoride with Sulfur Trioxide.—In the Parr apparatus, freshly distilled sulfur trioxide (127 g., 1.6 moles) rapidly and exothermally absorbed 46 g. (0.72 mole) of vinylidene fluoride after which the reaction stopped. The product was a crystalline solid that may be a cyclic sulfonate-sulfate anhydride based on the molar ratio of the reactants. On standing overnight at room temperature in the sealed reaction vessel, the product was converted to a dark amber liquid. Only about one-half of this oil could be distilled at reduced pressure. It was not further characterized.

Reactions of I and II with Water. Fluorosulfonyldifluoroacetic Acid.—A solution of 94 g. of fluorosulfonyldifluoroacetyl fluoride (II) in 200 ml. of petroleum ether (b.p. 30–60°) was stirred and cooled to -10° and 9.5 g. of water was added dropwise. When addition was complete, the product (86 g.) was separated as a heavy lower layer from petroleum ether. Distillation gave 70 g. (75%) of fluorosulfonyldifluoroacetic acid, b.p. 88–90° at 45 mm., n_D^{25} 1.3604. Both fluorine and hydrogen n.m.r. spectra were in agreement with this structure.

Anal. Calcd. for C₂H₂F₃SO₄: F, 32.0; S, 18.0; neut. equiv., 59.3. Found: F, 30.4; S, 17.3; neut. equiv., 62.8.

Reaction of 90 g. of β -hydroxytetrafluoroethanesulfonic acid sultone (I) in 300 ml. of petroleum ether (b.p. 30–60°) with 18 g. of water in the same way as described above gave 56 g. (62%) of fluorosulfonyldifluoroacetic acid.

Hydrolysis of Fluorosulfonyldifluoroacetic Acid. Carboxydifluoromethanesulfonic Acid.—Fluorosulfonyldifluoroacetic acid (17.8 g., 0.1 mole) was added to a solution of 12 g. (0.3 mole) of sodium hydroxide in 500 ml. of water

and the mixture was allowed to stand for 18 hr. at room temperature. An ion-exchange column was prepared by packing a 30 × 1 inch glass tube with Amberlite IR-120 and washing it with distilled water until the effluent was colorless and pH 6. The above solution was slowly passed through this column followed by distilled water until the pH of the effluent changed from less than 1 to 5. The total effluent (about 2 liters) was evaporated at room temperature over a period of 12 days to a sirupy residue (24 g.). A sample (10 g.) placed in an evaporating dish in a vacuum desiccator over phosphorus pentoxide for 48 hr. gave 7.75 g. of hygroscopic solid, m.p. 45–47°, characterized as carboxydifluoromethanesulfonic acid containing 1.5 moles of water of crystallization by elemental analyses and by examination of its n.m.r. and infrared spectra.

Anal. Calcd. for C₂H₂F₂SO₃·1.5H₂O: F, 18.7; S, 15.8. Found: F, 18.8; S, 15.7.

A sample of the hydrated acid (4.06 g.) in 25 ml. of water was added to a clear solution of 6.31 g. of barium hydroxide octahydrate in 100 ml. of water. The mixture was filtered to remove a little gelatinous precipitate and evaporated in air at room temperature. The crystalline white residue was dried in a vacuum desiccator over phosphorus pentoxide to give 6.25 g. (95%) of a monohydrated barium salt of carboxydifluoromethanesulfonic acid, which was soluble in cold water.

Anal. Calcd. for C₂F₂O₅SBa·H₂O: Ba, 41.7; S, 9.7. Found: Ba, 41.0; S, 9.9.

Similar treatment of a 2.03 g. (0.01 mole) sample of the hydrate dissolved in 25 ml. of distilled water with 1.0 g. (0.01 mole) of calcium carbonate gave 2.6 g. (97%) of a trihydrated calcium salt of carboxydifluoromethanesulfonic acid.

Anal. Calcd. for C₂F₂O₅SCa·3H₂O: Ca, 14.9; H₂O, 20.2. Found: Ca, 14.3; H₂O, 20.9.

Reaction of II with Benzene.—One mole (180 g.) of fluorosulfonyldifluoroacetyl fluoride (II) was dissolved in 1000 g. of carbon disulfide, the solution was chilled to 0° and 2 moles (267.2 g.) of aluminum chloride was added gradually with vigorous stirring. The mixture was stirred for approximately 2 hr. in an ice-bath to form a smooth yellow slurry. Approximately 3 moles (225 g.) of sodium-dried benzene was added slowly with vigorous stirring. After addition was complete, the reaction mixture was allowed to come to room temperature. Bubbling occurred, fumes were given off, and the mixture became black. After standing overnight, the mixture was refluxed for 2 hr. and poured into 1500 g. of cracked ice to which 200 ml. of concd. hydrochloric acid had been added. The mixture was extracted repeatedly with ether, the extracts were dried over anhydrous MgSO₄, and the solvent was removed by distillation. The tar-like residue was distilled at reduced pressure to yield: (1) 49.5 g. of a liquid boiling at 65–183° at 9–3 mm., and (2) 23.0 g. of a white solid which collected in the distillation column and fraction cutter.

Redistillation of the liquid yielded 25 g., b.p. 96–98° at 40 mm., n_D^{25} 1.4943. Nuclear magnetic resonance and infrared spectra showed that this liquid was a mixture of two components, one of which appeared to be difluoroacetophenone. A small quantity of the liquid was treated with 2,4-dinitrophenylhydrazine to give a yellow solid (approximately 35% yield), m.p. 216°, undepressed on admixture with an authentic sample of the 2,4-dinitrophenylhydrazone of difluoroacetophenone.¹⁶

Separation of the components was accomplished by shaking the liquid mixture with 10% sodium bisulfite in which the difluoroacetophenone (approximately 35%) dissolved. The insoluble portion, b.p. 98–99° at 40 mm., n_D^{25} 1.4940, n_D^{20} 1.4956, was identified as chlorodifluoroacetophenone (lit. values,¹⁷ b.p. 95–97° at 37 mm., n_D^{20} 1.4954). Our observations substantiate the report¹⁶ that the chloro compound does not form a dinitrophenylhydrazon.

The solid product was identified as benzoyldifluoromethyl phenyl sulfone, m.p. 78–80°.

Anal. Calcd. for C₁₄H₁₀F₂O₂S: C, 56.75; H, 3.37; F, 12.84; S, 10.81. Found: C, 57.39; H, 3.73; F, 12.81; S, 10.60.

(16) J. H. Simons and D. F. Herman, *THIS JOURNAL*, **65**, 2064 (1943).

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(13) A. M. Lovelace, D. A. Rausch and W. Postelnek, "Aliphatic Fluorine Compounds," Reinhold Publishing Corp., New York, N. Y., 1958, p. 107.

(14) R. M. Joyce, Jr., U. S. Patent 2,559,628 (1951).

(15) S. Dixon, *J. Org. Chem.*, **21**, 400 (1956).

It formed a 2,4-dinitrophenylhydrazone, m.p. 188–190°. *Anal.* Calcd. for $C_{20}H_{14}F_2N_4O_6$: N, 11.76. Found: N, 11.87.

Reactions of I and II with Other Reagents.—These reactions are summarized in Table I. In general, they were very

exothermic and were moderated by using diethyl ether or petroleum ether as solvent. The products were usually washed with water and distilled. Regardless of whether the sulfone or its rearrangement product was used, the same product was obtained.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF WASHINGTON, SEATTLE 5, WASH.]

Alkyl Substituents. VII. Solvent Dependence of the Baker–Nathan Effect in the Solvolysis of *m*-Alkylbenzhydryl Chlorides¹

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Values of k , ΔH^\ddagger and ΔS^\ddagger have been determined conductimetrically for the solvolysis of 3,5-dimethyl- and 3,5-di-*t*-butylbenzhydryl chloride in "80%" acetone and "80%," "87%" and "90%" ethanol. Where literature data were unavailable, kinetic parameters for the solvolysis of benzhydryl chloride and *m*-methyl and *m-t*-butylbenzhydryl chloride also were determined. The Baker–Nathan effect on the rate constants has been found to be both temperature and solvent dependent. The changes in kinetic parameters brought about by the introduction of the second *m*-methyl and the second *m-t*-butyl groups follow the predictions of the hypothesis that the Baker–Nathan effect is due to steric hindrance to solvation in the vicinity of bulky alkyl substituents.

In chemical transitions in solution that place a high electron demand on an alkyl substituent bonded to an unsaturated system, rate constants tend to take the order $Me > Et > i\text{-}Pr > t\text{-}Bu$.^{3,4} This experimental phenomenon has been termed the Baker–Nathan effect. The hypothesis of Baker and Nathan, that this is due to C–H hyperconjugative electron release (in the order of the number of α -hydrogens) becoming predominant over inductive release (in the opposite order)^{5,6} when the electron demand placed on the alkyl substituent is sufficiently large, has enjoyed widespread acceptance and stimulated much research.^{3,4} However, it has been recognized more recently that the hypothesis is unable to account satisfactorily for a number of facts presumably within its domain and suggestions for its modification⁶ or complete replacement^{1,7,8} have appeared.

A typical instance of the Baker–Nathan effect is found in the rate constants for the solvolysis of *p*-alkylbenzhydryl chlorides, e.g., in 80% acetone (Table I). Hughes, Ingold and Taher considered these results to be in support of the hypothesis of Baker and Nathan.⁹ However, Schubert and Sweeney have pointed out that the orders of the rate constants and heats of activation, as well as the order of the entropies of activation, are equally consistent with their hypothesis that, even in the face of high electron demands, the inherent stabilizing effect of alkyl is in the inductive order, and that steric hindrance to solvation in the vicinity of bulky alkyl groups acts to invert the order of

the heats of activation, hence also to invert the rate order.^{7,10,11} Direct support for this hypothesis has been found in the principal electronic transition energies of *p*-alkylnitrobenzenes and acetophenones, in the gas phase and in a variety of solvents.¹²

A mild Baker–Nathan effect is found in the rate constants for the solvolysis of *m*-alkylbenzhydryl chlorides in "80%" acetone (Table V)¹³ and for the solvolysis of *m*-alkylphenyldimethylcarbinyl chlorides in "90%" acetone.¹⁴ Brown, Brady, Grayson and Bonner, and Berliner and Chen have attributed these results to a slight predominance of C–H hyperconjugative over inductive release from the *m*-position.¹⁵ Schubert and Sweeney have pointed out that these results are equally consistent with mild steric hindrance to ring solvation, acting to invert an inherent inductive order of stabilization of the polar transition state relative to the ground state. It is presumed that a bulky substituent will be less efficient in shielding ring solvation when it is *meta* than when it is *para*. When *meta*, the alkyl group is somewhat removed from the sites of greatest electron deficiency in the ring, i.e., the *o*- and *p*-positions. When *para*, the alkyl group is directly on one of the sites of greatest electron deficiency.

Shiner and Verbanic have observed that for the solvolysis of *m*-methyl- and *m-t*-butylbenzhydryl chloride at 0°, the rate constants are in the induc-

(1) Preliminary results were reported at the Hyperconjugation Conference, Bloomington, Ind., June 2, 1958; see *Tetrahedron*, **5**, 194 (1959).

(2) National Science Foundation predoctoral Fellow, 1956–1958.

(3) J. W. Baker, "Hyperconjugation," Oxford University Press, London, 1953.

(4) Hyperconjugation Conference, *Tetrahedron*, **5**, 107 (1959).

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(6) V. J. Shiner, Jr., *THIS JOURNAL*, **76**, 1603 (1954); *Tetrahedron*, **5**, 243 (1959).

(7) (a) W. A. Sweeney and W. M. Schubert, *THIS JOURNAL*, **76**, 4625 (1954); (b) *J. Org. Chem.*, **21**, 119 (1956).

(8) A. Burawoy and E. Spinner, *J. Chem. Soc.*, 3752 (1954).

(9) E. D. Hughes, C. K. Ingold and N. A. Taher, *ibid.*, 949 (1940).

(10) The position taken by these authors has sometimes been misunderstood. They do not maintain that C–H hyperconjugative release is necessarily inoperative; only that the total stabilizing effect of alkyl substituents on electron deficiencies, even when these deficiencies are large, is in the inductive order.

(11) Steric hindrance to solvation acts to raise both ΔH^\ddagger and ΔS^\ddagger leading to cancelling effects on the rate constant. It is assumed that $\Delta H^\ddagger/T$ is increased more than ΔS^\ddagger .^{7b}

(12) W. M. Schubert, J. Robins and J. L. Haud, *THIS JOURNAL*, **79**, 910 (1957).

(13) E. Berliner and M. M. Chen, *ibid.*, **80**, 343 (1958).

(14) H. D. Brown, J. D. Brady, M. Grayson and W. H. Bonner, *ibid.*, **79**, 1897 (1957).

(15) It is to be noted that *m*-alkyl substitution increases the rate constant only slightly, much less than does *p*-alkyl substitution. This can be taken as an indication that the electron demand placed on the *m*-alkyl substituent in the transition state is small.