a mixture of the two dimers. Crystallization of the latter fraction from methanol, using a seed of dihydrovoacamine, yielded an additional quantity of the latter alkaloid. Thin layer chromatography indicated that the resulting mother liquors contained essentially uncontaminated dihydrovoacamidine. This material was converted to its hydrobromide salt which was crystallized from acetone; m.p. >300°.

Voacamidine (48) Hydrobromide.—The mother liquors from the voacamine synthesis were purified as described above. The hydrobromide salt was crystallized from acetone, m.p. >300°. Its Nujol mull infrared spectrum was identical with that of the hydrobromide salt of natural material.

Artifact Experiments.—A mixture of dregaminol (30 mg.) and voacangine (30 mg.) in methanol (3 ml.) was heated under reflux for 3 hr. and then evaporated to dryness on a steam bath. The

residue was dissolved in ethyl acetate and extracted twice with 5% aqueous acetic acid. Both fractions were neutralized with potassium carbonate, the aqueous phase was extracted with methylene chloride, and both organic phases were taken to dryness. Recrystallization of the ethyl acetate residue from · methanol–ether yielded pure voacangine (1) (infrared). Chromatography of the acetic acid residue on alumina (activity III) yielded pure voacangine (1) (infrared) and pure degraminol (32) (infrared). Thin layer chromatography of the crude mixtures showed only voacangine and dreganinol.

Structures of Sultones from Proton Magnetic Resonance Spectra

BY R. W. OHLINE,[1] A. L. ALLRED,[2] AND F. G. BORDWELL

Proton magnetic resonance spectroscopy has been used to confirm structure assignments for eighteen sultones.

The degradative method for structure proof for a sultone is particularly difficult since it inevitably requires isolation of the salts of sulfonic acids, and these are hard to separate and to characterize. As a result, rigorous structure assignments for most sultones have not been made. The present study has shown that proton magnetic resonance (p.m.r.) spectra can often be used to make unambiguous structure assignments to these compounds. Eighteen sultones have been characterized in this way. Many of these were prepared by the sulfonation of alkenes, a reaction involving skeletal rearrangement.[3] In every instance the structure proved to be that expected on the basis of the reaction course assumed previously.[3]

Experimental

Sources of Sultones.—The method of preparation for most of these sultones has been given in previous publications.[3,4] Soltones 9, 11, and 12 were obtained from the Shell Development Co., Emoryville, Calif., through the courtesy of Dr. Curtis Smith. The preparation of sultones 13–18 will be described in a separate publication.

Spectra.—The p.m.r. spectra were taken at 25 ± 2° with a Varian high-resolution spectrometer at 40 and/or 60 Mc./sec. Pyrex tubes (5-mm. o.d.) were filled to a height of approximately 8 cm. with chloroform solutions of the sultones. Two solutions of each sultone were prepared, one at approximately 4% concentration (by weight), and one at approximately 25%. The chemical shift data given in Table I and in the following section are from the 4% solutions. The variation of chemical shift with concentration over the 4 to 25% range was no more than 0.1 p.p.m. Chemical shifts were measured by the conventional side-band technique for all sultones relative to chloroform. The positive numbers in Table I refer to resonance at higher magnetic field, relative to the chloroform resonance; the line positions are accurate to within ±1 c.p.s. for δ's given to three significant figures.

Results and Discussion

It was anticipated that sultones 1, 2, and 3 would have simple spectra, since in the structures assigned no two adjacent carbon atoms hold hydrogen atoms, and

(1) Abstracted in part from the M.S. Thesis of R. W. Ohline, Northwestern University, August, 1958.

(2) Alfred P. Sloan Research Fellow.

(3) F. G. Bordwell, R. D. Chapman, and C. E. Osborne, J. Am. Chem. Soc., 81, 2002 (1959).

(4) F. G. Bordwell, C. E. Osborne, and R. D. Chapman, ibid., 81, 2698 (1959).

the possibility of proton spin coupling is thereby precluded. The appearance of three sharp peaks in the spectrum of 1 and of 3, and of four sharp peaks in the spectrum of 2, bears out this expectation. Judging from bond distances, one would expect five-membered sultone rings to be somewhat larger than cyclopentane rings. In sultones 1 and 3, as well as in 2, the hydrogen atoms, methyl groups, and oxygen atoms attached to adjacent ring atoms (carbon or sulfur) must then be staggered with respect to one another. The single sharp peaks in the spectra of 1, 2, and 3 are evidently average signals resulting from molecules undergoing rapid chair–chair interconversions.

The signals for the three types of methylene groups possible for five-membered ring sultones appear in distinctly different regions of the spectrum and are useful for structure assignment. Thus, the average methylene signal for protons on the carbon atom α to oxygen ($-CH_2OSO_2-$) appears at 2.79 p.p.m., whereas the average signal for the protons on the carbon atom α to sulfur ($-CH_2SO_2O-$) is at 4.05 p.p.m., and that for the protons on the carbon atom β to oxygen (or sulfur; $-CH_2-C-OSO_2-C-$) is at 4.8 p.p.m. The average signals for the corresponding methine protons for these three positions are 2.54, 3.98, and 4.96, respectively. For methyl groups the average values are 5.80, 5.85, and 6.12, respectively. The assignments are summarized in Fig. 1. (Compounds containing halogen or phenyl groups are not included in arriving at these averages.)

Reference to Table I will show that a relatively large number of values are available for methylene groups α to sulfur, and for methyl groups on carbon atoms α or β to oxygen. The other values are less reliable. The chemical shifts for the corresponding methylene and methyl groups in the two six-membered ring sultones 2 and 12 are of comparable magnitude.

When one of the hydrogen atoms in one methyl of a *gem*-dimethyl group is replaced by a bromine or chlorine atom, as in 4, 14, 15, 16, or 18, the CH_2X signal is shifted downfield from that of the parent sultone (3, 13, or 17) to an extent anticipated on the basis of

Table I

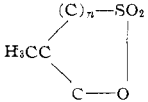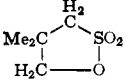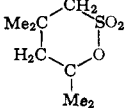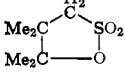Assignments of Proton Magnetic Resonance Peaks to Sultones (P.p.m. Relative to the Solvent Chloroform)[a]

Sultone	$HCOSO_2$	$HCSO_2O$	$HCCOSO_2$ (including both methylene and methine protons)	CH_3COSO_2	CH_3CSO_2O	$H_3CC-(C)_n-SO_2 \ / \ C-O$
1 — Me₂C(CH₂)SO₂ / H₂C—O	3.10	4.12				5.93
2 — Me₂C(CH₂)SO₂ / H₂C—O—Me₂		4.34	5.53	5.68		5.98
3 — Me₂C(CH₂)SO₂ / Me₂C—O		3.97		5.78		5.99
4 — Me₂C(CH₂)SO₂ / MeC(CH₂Br)—O		3.91	3.63 (–CH₂Br)	5.62		5.89
5 — H₂C(CH₂)SO₂ / Me₂C—O		~3.9 (t)	~4.8 (t)	5.71		
6 — MeCH(CH₂)SO₂ / Me₂C—O				5.74 / 5.85		6.10 (d)
7 — MeCH(MeCH)SO₂ / Me₂C—O		4.25 (quin)	4.96 (quin)	5.78 / 5.88	~5.87 (d)	~6.18 (d)
8 — C₆H₅C(Me)(CH₂)SO₂ / Me₂C—O		3.07 (d) / 3.84 (d)		5.50 / 5.62		6.04
9 — H₂C(CH₂)SO₂ / MeCH—O	2.5 (m)	~4.0 (m)	~4.8 (m)	5.78 (d)		
10 — H₂C(CMe₂)SO₂ / MeCH—O	2.58 (m)		4.88 / 5.22	5.81 (d)	5.76	
11 — H₂C(CH₂)SO₂ / H₂C—O	2.48 (t)	4.2 (m)	~4.8 (m)			
12 — H₂C(CH₂)SO₂ / H₂C—O—CH₂	2.48 (t)	4.2 (m)				
13 — Me₂C(CHMe)SO₂ / Me₂C—O		3.81 (q)		5.74 / 5.88	5.93 (d)	6.18 / 6.25
14 — Me₂C(CHMe)SO₂ / MeC(CH₂Cl)—O		3.80 (q)	3.55 (CH₂Cl)	5.59	5.90 (d)	6.06
15 — Me₂C(CHMe)SO₂ / MeC(CH₂Br)—O		3.81 (q)	3.72 (CH₂Br)	5.58	5.91 (d)	6.06

Table I (Continued)

Sultone	HCOSO₂	HCSO₂O	HCCOSO₂	CH₃COSO₂	CH₃CSO₂O	$\begin{array}{c}(C)_n-SO_2 \\ H_3CC \qquad | \\ C\!-\!\!-\!\!-\!O\end{array}$
16	~3.7 (q)		1.37 (CHBr₂)	5.33	5.88 (d)	5.88 5.99
17	3.87			5.78 5.93		6.20
18	3.6		3.75 (CH₂Br)	5.55		5.95

[a] Peaks designated without parenthetical descriptions are singlets. (d, doublet; t, triplet; q, quartet; quin, quintet; m, multiplet).

Numbers refer to the center when more than one peak is indicated

Shoolery's constants.[5] The pattern observed is usually that of a double doublet, which is to be expected since the carbon atom at which the CH_2X group is attached is asymmetric.[6] The signal for the methyl group attached to this carbon atom is also shifted downfield slightly. The signal for the gem-dimethyl group in 4 might also be resolvable, in view of the adjacent asymmetric carbon atom, but this was not observed.

$$\text{(4.05)} \quad H_2C \overset{SO_2}{\diagdown} O$$
$$\text{(4.8)} \quad H_2C\!-\!\!-\!CH_2 \quad \text{(2.97)}$$
(methylene protons)

$$\begin{Bmatrix}CH_3, 5.85 \\ H, 3.98\end{Bmatrix} C \overset{SO_2}{\diagdown} O$$
$$\begin{Bmatrix}CH_3, 6.12 \\ H, 4.96\end{Bmatrix} C\!-\!\!-\!C \begin{Bmatrix}CH_3, 5.80 \\ H, 2.54\end{Bmatrix}$$
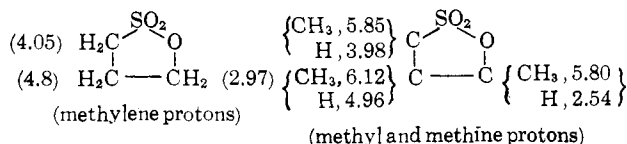(methyl and methine protons)

Fig. 1.—Average chemical shifts for methylene and for methyl and methine p.m.r. signals (in p.p.m. relative to chloroform).

The relative intensities of the peaks in the two triplets for 5 are not those expected by simple first-order theory. Analysis of this A_2B_2 system at 40 Mc./ sec. gave $J_{AB} = 7.2$ c.p.s. and $\nu = 35.2$ c.p.s.

In 6 the single methyl group attached to the β-ring carbon is spin coupled to the proton on this carbon atom ($J = 6.3$ c.p.s.). The geminal methyl groups are rendered nonequivalent by the adjacent asymmetric carbon atom,[6] and give rise to individual signals (at 5.75 and 5.85, $\delta = 0.13$). The methylene protons in 6 are also nonequivalent and the $-CH_2CHCH_3$ grouping constitutes an $ABCX_3$ system, which accounts for the complex multiplet pattern observed.

The complex absorption in the methyl region for 7 (Fig. 2) can be analyzed satisfactorily by analogy to 6.

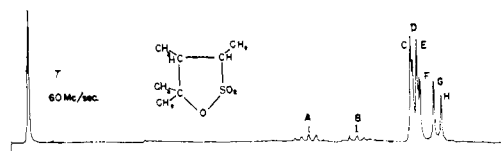Fig. 2.—P.m.r. spectrum at 60 Mc./sec. of 3,4-dimethyl-4-hydroxy-2-pentanesulfonic acid sultone (7).

The 5.78 and 5.88 p.p.m. peaks (C and E) are assigned to the gem-dimethyl group (compare the 5.75

(5) See L. M. Jackman, "Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry," Pergamon Press, New York, N. Y., 1959, Chapter 4.
(6) See ref. 5, pp. 99–103.

and 5.85 peaks for 6). Peaks G and H (367.3 and 374.1 c.p.s. at 60 Mc./sec.; $J = 6.8$ c.p.s.) are assigned to the (spin-coupled) methyl group on the β-carbon atom (compare with 363 and 369 c.p.s. and $J = 6.3$ c.p.s. for 6). This leaves peaks D and F for the remaining methyl group, which is also spin coupled (349.1 and 355.5 c.p.s.; $J = 6.4$ c.p.s.). The methine hydrogen atoms absorb in the regions of 4.25 and 4.96 p.p.m. and are spin coupled to each other and to a contiguous methyl group. All spin-coupling constants are 6.4 ± 0.4 c.p.s. This analysis was confirmed by examination of a spectrum taken at 40 Mc./sec.

Sultone 8 corresponds in structure to 3, except that a phenyl group has replaced a methyl group on the β-carbon atom. By analogy to open-chain systems, the phenyl group should cause deshielding of the methyl and methylene protons attached to the β-carbon atoms of about 0.35 p.p.m.[7] Actually, one of the methylene protons is shifted only slightly downfield (by about 0.15 p.p.m.), whereas the other is shifted downfield by almost 1 p.p.m. A molecular model indicates that one of the methylene protons is held near the plane of the phenyl ring, which accounts for its unexpectedly strong deshielding. A characteristic AB pattern is observed for the methylene protons (peaks B–E in Fig. 3)
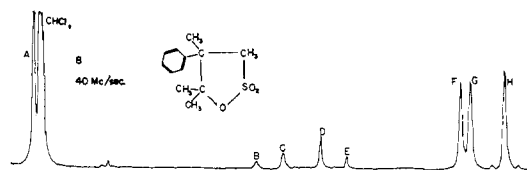
Fig. 3.—P.m.r. spectrum at 40 Mc./sec. of 2,3-dimethyl-3-hydroxy-2-phenylbutanesulfonic acid 1,3-sultone (8).

with $\delta = 0.77$ p.p.m. and $J_{AB} = 14$ c.p.s. The methyl group attached to the carbon atom holding the phenyl appears to be in a relatively unaffected region with respect to phenyl, and is assigned peak H. The geminal methyls are slightly deshielded (peaks F and G).

In the spectrum of 9 the methyl doublet ($J = 6.3$ c.p.s.) appears in the expected region and the remainder of the spectrum consists of an unresolved series of multiplets.
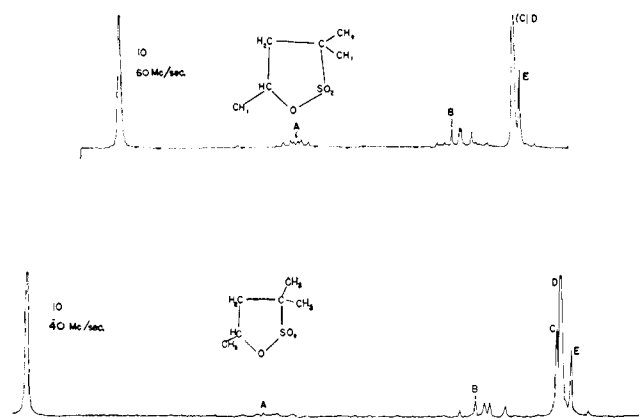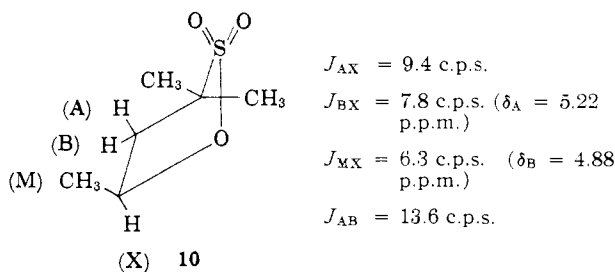
(7) See ref. 5, p. 53.

Fig. 4.—P.m.r. spectra at 40 and 60 Mc./sec. of 1-methyl-3-hydroxypentanesulfonic acid 1,3-sultone (10).

In the spectrum of 10 (Fig. 4) peaks C and E ($J = 7.8$ c.p.s.) are assigned to the doublet for the single methyl group by analogy with the assignment in 9. One of the components of the doublet overlaps with the sharp peak (D) assigned to the gem-dimethyl groups. One would expect the geminal methyl groups to be nonequivalent owing to the asymmetric carbon atom across the ring, but apparently the closeness of their chemical shifts precludes resolution of the peaks. The absence of peaks near 4.0 p.p.m. is consistent with the assigned structure,[3] since there are no protons α to sulfur (in contrast to all the other sultones in Table I). The $-CH_2-CHCH_3$ grouping constitutes an ABM_3X system. Analysis of both the 40- and 60-Mc. spectra were carried out to arrive at the parameters shown. In assigning

$J_{AX} = 9.4$ c.p.s.

$J_{BX} = 7.8$ c.p.s. ($\delta_A = 5.22$ p.p.m.)

$J_{MX} = 6.3$ c.p.s. ($\delta_B = 4.88$ p.p.m.)

$J_{AB} = 13.6$ c.p.s.

(X) 10

the labels A and B it is assumed that the molecule will be primarily in the conformation shown, and that the larger coupling constant is ascribable to the "diaxial" hydrogen pair (AX), rather than the "equatorial–axial" pair (BX).

The regions of absorption and complexity of the spectra for sultones 11 and 12 are consistent with expectations based on the other spectra. The $-CH_2O-$ group is spin coupled to the adjacent methylene group by 6.7 c.p.s. for 11 and 5.3 c.p.s. for 12.

Sultone 13 was first encountered as a by-product of a commercial hydration of a butene mixture with sulfuric acid.[9] Its p.m.r. spectrum is shown in Fig. 5.

It will be observed on examination of Fig. 5 that most of the absorption occurs in the methyl region. From the areas under the peaks it is clear that fifteen of the sixteen hydrogen atoms and five of the

(8) J. Willems, Bull. soc. chim. Belges, 64, 409 (1955).

(9) A small sample of this sultone was obtained through the courtesy of H. O. Mottern, Esso Laboratories, Linden, N. J., several years ago. From its chemical properties and carbon and hydrogen analysis it was known to be an octane sultone, $C_8H_{16}O_3S$, but not enough material was available to warrant further work toward structure assignment until the advent of p.m.r. spectroscopy.
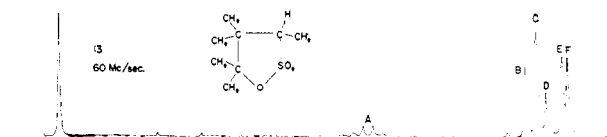

Fig. 5.—P.m.r. spectrum at 60 Mc./sec. of 3,3,4-trimethyl-4-hydroxy-2-pentanesulfonic acid sultone (13).

eight carbon atoms must be present as five methyl groups. The remaining three carbon atoms must then be contained in a five-membered sultone ring. The single remaining hydrogen atom gives a quartet centered at 3.81 p.p.m. (peaks at A). The quartet is consistent with the expected spin coupling of this hydrogen atom with the methyl group attached to the same carbon atom ($J = 7.0$ c.p.s.). The corresponding methyl doublet is not observable in Fig. 5 since one-half of the doublet is merged with another methyl signal in peak C. (Peak C was resolved in a 40-Mc./sec. spectrum, and also in a 60-Mc./sec. spectrum taken in hexadeuteriobenzene[10]; $J = 7.0$ c.p.s.)

The position of the signal for the single hydrogen atom at 3.81 p.p.m. corresponds closely to that of a hydrogen atom α to sulfur (see Table I and Fig. 1). The two alternative positions are ruled out by this observation, as well as by the positions of the methyl signals (see below). This leads to the unambiguous assignment of structure 13 for the sultone.[11]

Consistent assignments of the methyl peaks in 13 can be made on the basis of the structure arrived at above. Thus peak B and part of C (Fig. 5) at 5.74 and 5.88 p.p.m., respectively, are assigned to the gem-dimethyl group α to oxygen (Table I and Fig. 1). The appearance of individual peaks is understandable, since the carbon atom α to sulfur is asymmetric.[12] As mentioned above, part of peak C and peak D represent the methyl doublet. Peaks E and F are assigned to the gem-dimethyl group β to oxygen (compare Table I and Fig. 1).

The assignments for 13 were strengthened by examination of the spectra of its chloro, bromo, and dibromo derivatives (14, 15, and 16, respectively). In 14 and 15 part of peak C disappears, as it should ($CH_3 \rightarrow CH_2X$), and a new peak for CH_2X appears downfield (at 3.55 p.p.m. for 14 and 3.72 p.p.m. for 15). In each instance the quartet for the single hydrogen atom continues to be centered near 3.8, and peaks B shift to 5.59 and 5.58 p.p.m., respectively. Peaks E and F are shifted slightly downfield and are merged (at 6.06 p.p.m. for both 14 and 15). The positions of peak D and the remaining part (one-third) of C are essentially unchanged in each instance [doublet centered at 5.90 for 14 ($J = 7.2$ c.p.s.); doublet centered at 5.91 for 15 ($J = 7.0$ c.p.s.)]. The downfield shifts for B, E, and F are expected by analogy with the shifts observed in the positions of comparable methyl groups in 3 when it is converted by comparable substitution to 4. The failure of C and D to move supports the conclusion that this methyl group is in a position

(10) We wish to thank Dr. K. W. Bartz, Humble Oil and Refining Co., Baytown, Texas, for this spectrum.

(11) It would be anticipated on the basis of previous work[3] that a sultone of this structure would be formed by sulfonation of 3,4,4-trimethyl-2-pentene. Dr. J. Schaeffer (unpublished results) has indeed obtained 13 in good yield by this reaction.

(12) It is of interest to note that the difference in chemical shifts is large enough here (0.14 p.p.m.) to give rise to separate peaks whereas in 10, which also has an asymmetric carbon atom across the ring from a gem-dimethyl group, only one peak is observed.

α to sulfur, rather than β to sulfur (where it would be closer to the halogen atom).

The trends in chemical shifts noted for **14** and **15** are continued in the spectrum of the dibromo derivative **16**. The CHBr$_2$ singlet is at 1.37 p.p.m. and the quartet for the single ring hydrogen atom is at about 3.7 p.p.m. Peak B is shifted to 5.33, whereas peaks C and D remain essentially fixed [doublet centered at 5.88 ($J = 7.0$ c.p.s.)]. Peaks E and F are now resolved, as in the parent sultone **13**, but are shifted downfield to 5.88 and 5.99 p.p.m. They are separated by a chemical shift ($\delta = 0.11$ p.p.m.) comparable in magnitude to that observed in **13** ($\delta = 0.07$ p.p.m.).

Sultone **17** was prepared by the sulfonation of 1-t-butylcyclohexene.[3] The structure assigned on the basis of the expected course of reaction[3,4] is that shown. This assignment is supported by the p.m.r. spectrum,

which can be compared with that of **13**. Structurally, **17** differs from **13** by the fact that the cyclohexane ring has replaced one methyl group on each of the carbon atoms α and β to oxygen. The structural features held in common (gem-dimethyl group α to oxygen, methyl group β to oxygen, and single hydrogen atom γ to oxygen) give rise to closely similar p.m.r. signals (Table I). The chemical shifts observed in changing from **17** to **18** should be, and are, comparable to those in changing from **13** to **15**.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, NORTHWESTERN UNIVERSITY, EVANSTON, ILLINOIS]

The Effect of the Carbonyl and Related Groups on the Reactivity of Halides in Sn2 Reactions

BY F. G. BORDWELL AND W. T. BRANNEN, JR.

RECEIVED JUNE 25, 1964

The rates of reaction of potassium iodide in acetone solution with several series of compounds of the type Y(CH$_2$)$_n$Cl ($n = 1$ to 5) have been measured. The strong deactivating effects of F$_3$C and C$_6$H$_5$SO$_2$ groups when attached to the α-carbon atom are attributed to steric and field effects, their inductive effects being assumed to be mildly rate enhancing. The C$_6$H$_5$SO group was found to have a mild retarding effect. Neither these groups nor related groups, such as C$_6$H$_5$S, C$_6$H$_5$CO, or CN, exhibit much effect of any kind from β or more remote positions. The mild activating effect of the β-C$_6$H$_5$CO group is the one exception. The methanolysis rates for C$_6$H$_5$S(CH$_2$)$_n$Cl ($n = 1$ to 5) have been measured.

Conant, Kirner, and Hussey first called attention to the profound influence of Y groups on the reactivity of YCH$_2$Cl type halides toward potassium iodide in acetone.[1] The powerful activating effect of the carbonyl, cyano, and related groups in this and other Sn2 reactions has since been the subject of much study and speculation.[2] Our interest in this effect was first aroused several years ago by the observation that the activating effect of the carbonyl group, not only is not shared, but is actually *reversed*, by the sulfonyl group. This is surprising since the carbonyl and sulfonyl groups exert the same type of inductive and resonance effects as judged by their σ-constants.[3] It was suggested that the retarding effect of sulfonyl group was of steric origin.[2e,4] We decided to extend the study to the sulfinyl and trifluoromethyl groups, since these groups exhibit closely similar inductive and resonance

effects, and these are of the same general type as those of the carbonyl and sulfonyl groups, as judged by σ-constants.[5,6] On the other hand, C$_6$H$_5$SO and F$_3$C groups were expected to offer additional variation with regard to steric effects and field effects.

A further point that appeared to be worthy of additional investigation was the fact that the activating effect of the carbonyl group is apparently still operative when the group is attached to the β-carbon atom or the γ-carbon atom (C$_6$H$_5$COCH$_2$CH$_2$Cl and C$_6$H$_5$-COCH$_2$CH$_2$CH$_2$Cl were reported to be 80 and 230 times as reactive, respectively, as BuCl[1]). The effect of the C$_6$H$_5$SO, F$_3$C, and C$_6$H$_5$SO$_2$ groups was therefore determined, not only at the α-carbon atom, but also at the β-, γ-, δ-, and, in some instances, the ϵ-carbon atom.

Although use of the reaction of potassium iodide in acetone as a measure of Sn2 reactivity has been subjected to some criticism,[7] it offers the advantages of wide applicability, relative freedom from side reactions, and simplicity in measurement of rates. The difficulties in the use of the Andrew's titration method for the determination of iodide[8] were obviated by using amperometric and potentiometric titration methods. All

(1) J. B. Conant, W. R. Kirner, and R. E. Hussey, *J. Am. Chem. Soc.*, **47**, 488 (1925).

(2) (a) J. W. Baker, *J. Chem. Soc.*, 1148 (1932); (b) E. D. Hughes, *Trans. Faraday Soc.*, **37**, 603 (1941); (c) J. W. Baker, *ibid.*, **37**, 643 (1941); (d) M. J. S. Dewar, "The Electronic Theory of Organic Chemistry," Oxford University Press, London, 1949, p. 73; (e) F. G. Bordwell and G. D. Cooper, *J. Am. Chem. Soc.*, **73**, 5184 (1951); (f) R. G. Pearson, S. H. Langer, F. V. Williams, and W. J. McGuire, *ibid.*, **74**, 5130 (1952); (g) A. Streitwieser, Jr., "Solvolytic Displacement Reactions," McGraw–Hill Book Co., Inc., New York, N. Y., 1962, p. 28; (h) P. D. Bartlett and E. N. Trachtenberg, *J. Am. Chem. Soc.*, **80**, 5808 (1958); (i) W. Reeve, E. L. McCaffery, and T. E. Kaiser, *ibid.*, **76**, 2280 (1954).

(3) F. G. Bordwell and G. D. Cooper, *ibid.*, **74**, 1058 (1952).

(4) The statement made . . . "one would expect only a small steric effect for the sulfonyl group, unless it is assumed that the partial negative charge on the oxygen atoms would greatly extend their effective radius in blocking an incoming nucleophilic reagent" . . . was meant to include a field effect with the steric effect. Recently, C. Y. Meyers, *Tetrahedron Letters*, **No. 24**, 1125 (1962), has suggested that the field effect is the dominating factor.

(5) F. G. Bordwell and P. J. Boutan, *J. Am. Chem. Soc.*, **79**, 717 (1957); H. H. Szmant and G. Suld, *ibid.*, **78**, 3400 (1956); J. D. Roberts, R. 1. Webb, and E. A. McElhill, *ibid.*, **72**, 411 (1950).

(6) See R. W. Taft, Jr., "Steric Effects in Organic Chemistry," M. S. Newman, Ed., John Wiley and Sons, Inc., New York, N. Y., 1956, p. 595, and R. W. Taft, Jr., and I. C. Lewis, *J. Am. Chem. Soc.*, **81**, 5343 (1959), for discussions of the relative magnitudes of inductive and resonance contributions for these groups.

(7) See ref. 2g, pp. 17 and 18.

(8) K. L. Senior, R. R. Hetrick, and J. G. Miller, *J. Am. Chem. Soc.*, **66**, 1987 (1944).