heptane, except for the chlorine–bromine inversion in the anisole excitation energies. In Figs. 1, 2 and 3 it is seen that the correspondence between increasing molar refraction and decreasing gas-phase excitation energy is in fact approximately linear. This linearity may be somewhat fortuitous since the two properties were not measured under rigorously identical conditions. Ideally, the molar refractions should also be measured in the gas phase, but this is experimentally impractical. However, there is clearly at least a qualitative parallelism between the two experimental quantities. It is therefore quite possible that the effect of the substituents upon dipolar electronic transitions and upon molar refraction is governed by similar factors.

SEATTLE 5, WASH.

[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT OF NORTHWESTERN UNIVERSITY]

The Hydrolysis of Sultones. The Effect of Methyl Groups on the Rates of Ring-opening Solvolyses

BY F. G. BORDWELL, C. EDWARD OSBORNE[1] AND RICHARD D. CHAPMAN[1]

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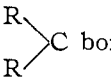
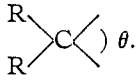
The rates of hydrolysis of eight primary, secondary and tertiary 5-membered ring sultones have been measured. Comparison of these hydrolysis rates among themselves, with those for sultones reported in the literature and with open-chain analogs has brought out a marked retardation effect caused by α- (to oxygen) and β-methyl groups. β-Methyl substitution greatly decreases the hydrolysis rate of these sultones, whereas an acceleration might have been anticipated on the basis of open-chain analogs. Although the net effect of α-methyl substitution is to enhance the rate, the increase in rate is not nearly as great as that expected, and an opposing rate retardation effect is clearly indicated. The effect of γ-methyl groups is less clear-cut, but also appears to be one of rate retardation in hydrolysis. The fact that in ring-openings the atoms formerly bonded cannot separate linearly, as is true in open-chain systems, but must rotate away from one another, is believed to be of fundamental importance in producing unusual and exaggerated effects of substituents in such reactions. The retarding effect of α-, β- and γ-methyl groups on the present ring-opening hydrolyses is believed to be caused by restriction of the required rotation by methyl substitution. The fact that the retardation effects of methyl groups on hydrolysis rates arise chiefly from a decrease in activation entropies is consistent with the idea that they are caused by steric hindrance to rotation. The possible extension of this idea to explain the striking effects of methyl groups on other ring openings is discussed.

It has been recognized for many years that methyl substitution promotes the formation or "stability" of ring compounds. Evidence for an effect of this kind was collected by Thorpe and Ingold and their students in the period 1915–1930.[2] An early explanation was offered[2b] that *gem*-dimethyl groups by mutual repulsion (B-strain in current terms) would cause an increase in the  bond angle and a decrease in the θ bond angle of  . If θ is part of a small ring this effect would result in ring stabilization ("Thorpe–Ingold effect"). However, the fact that the effect is by no means confined to small rings or to *gem*-dialkyl groups indicates that this factor is probably of minor importance. Furthermore, measurements of bond angles in open-chain systems have failed to confirm the decrease in θ predicted by the theory.

It is still uncertain as to whether or not methyl substitution leads to a greater thermodynamic stability for ring compounds than for open-chain analogs. However, there is abundant evidence that methyl substitution can lead indirectly to "stabilization" by accelerating the rate of ring closure.[3] A particularly striking example is the observation of Nilsson and Smith[4] that the rate of ring closure of chlorohydrins to epoxides is accelerated from 5- to 20-fold per methyl group, as the hydrogens of ethylene chlorohydrin are successively replaced by methyl groups.

It does not appear to have been generally appreciated that methyl groups may also "stabilize" the cyclic forms by retarding the rates of ring opening. However, the fact that methyl substituted glutaric anhydrides[2b] and methyl substituted cyclic adipic anhydrides[2i] are more stable to hydrolysis than the parent anhydrides clearly suggests this possibility.

The ability of methyl substituents to stabilize the cyclic form in systems where this form is believed to be in equilibrium with an open-chain isomer was the subject of many of the earlier papers.[2,5] It is evident that methyl substitution in such equilibrium systems may favor the cyclic form by increasing the rate of ring closure and/or by decreasing the rate of ring opening.

Several years ago T. Nilsson[6] made a careful

(1) Abstracted in part from the Ph.D. Dissertations of Richard D. Chapman (June, 1954) and C. Edward Osborne (June, 1956). Presented at the 7th Conference on Reaction Mechanisms at Chicago, Ill., Sept., 1958.

(2) (a) R. M. Beesley, C. K. Ingold and J. F. Thorpe, *J. Chem. Soc.*, **107**, 1080 (1915); (b) C. K. Ingold, *ibid.*, **119**, 305, 951 (1921); (c) G. A. R. Kon, A. Stevenson and J. F. Thorpe, *ibid.*, **121**, 650 (1922); (d) S. S. Deshapanda and J. F. Thorpe, *ibid.*, **121**, 1430 (1922); (e) C. K. Ingold, *ibid.*, **121**, 2676 (1922); (f) L. Bains and J. F. Thorpe, *ibid.*, **123**, 1206 (1923); (g) E. W. Lanfear and J. F. Thorpe, *ibid.*, **123**, 1683 (1923); (h) I. Vogel, *ibid.*, 594 (1927); (i) E. H. Farmer and J. Kracovski, *ibid.*, 580 (1927); (j) A. M. Quadrat-I-Kbuda, *ibid.*, 201, 713 (1929).

(3) See, for example, (a) G. W. Wheland, "Advanced Organic Chemistry," 2nd edition, John Wiley and Sons, Inc., New York, N, Y., 1949, p. 373; (b) E. L. Eliel, Chapter 2 of "Steric Effects in Organic Chemistry," edited by M. S. Newman, John Wiley and Sons, Inc., New York, N. Y., 1956, p. 119.

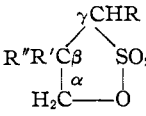
(4) H. Nilsson and L. Smith, *Z. physik. Chem.*, **166A**, 136 (1933).

(5) Data on these equilibria recently have been summarized and ably discussed by G. S. Hammond in Chapter 9 of ref. 3b, pp. 460-470.

(6) T. Nilsson, Ph.D. Dissertation, University of Lund, Sweden, 1946.

TABLE I

KINETIC DATA FOR THE HYDROLYSIS OF PRIMARY SULTONES AND RELATED COMPOUNDS



Compound R	R′	R″	T, °C.	$k_1 \times 10^5$, sec.$^{-1}$	Relative rate (at 40°)	E_a, kcal./mole	ΔS^*, e.u. at 40°
A, H	H	H	20.0	13.0[a]			
			30.0	41.0[a]			
			40.0	121[a]	1.0	20.4 ± 0.1	−13.8
B, H	CH_3	H	40.0	25.3[a]	0.21		
			40.0	24[b]			
C, H	CH_3	CH_3	40.0	0.428[a]	0.0035	22.4 ± 0.1	−18.7
			50.0	1.30[a]			
			60.0	3.70[a]			
D, CH_2	H	H	20.0	20.3[a]			
			30.0	62.0[a]			
			40.0	170[a]	1.4	19.4 ± 0.3	−16.5
EtBr			55	18.3[c]			
$EtOSO_2C_6H_5$			60.0	501[d]	0.57	21.04	−12.9
$PrOSO_2C_6H_5$			50.1	130[d]	.38	21.09	−13.6
i-$BuOSO_2C_6H_5$			60.0	117.5[d]	.10	23.67	− 8.0
neo-Pen-$OSO_2C_6H_5$			60.0	54.8[d]	.04	24.98	− 5.6

[a] T. Nilsson.[6] [b] Present work (2.8% dioxane). [c] S. Winstein, E. Grunwald and H. W. Jones, THIS JOURNAL, **73**, 2700 (1951). [d] P. M. Laughton and R. E. Robertson, *Can. J. Chem.*, **33**, 1207 (1955).

study of the hydrolysis rates of a number of primary and secondary sultones, and of one tertiary sultone. The formation of a variety of 5-membered tertiary sultones[7] has allowed an extension of this work. Comparison of the hydrolysis rates of sultones among themselves and with open-chain analogs has made it possible for us to ascertain the effect of substituting methyl groups in the α-, β- and γ-positions of 5-membered ring sultones. We believe that these results may be of general significance as to the manner by which alkyl groups so dramatically affect the rates of ring opening and of ring closure for many reactions in solution.

Experimental

Kinetic Measurements.—The preparation and structural evidence for the sultones was reported earlier.[7] An 8–14 mg. sample of the sultone was dissolved in 5 ml. of purified dioxane.[8] The test-tube holding this solution, the conductivity cell and a 125-ml. erlenmeyer flask, into which 35 ml. of freshly distilled water had been pipetted, were allowed to equilibrate in a constant temperature bath for at least 15 minutes. One ml. of the dioxane solution then was pipetted into the water (2.8% dioxane by volume prior to mixing), the solution was swirled to ensure mixing and poured into the conductivity cell. The change in resistance was followed for about three half-lives, and the infinity reading was taken after more than ten half-lives. The temperature variation was ±0.05° except for the 0.1° bath (a 1-gal. Dewar flask filled with cracked ice and distilled water through which air was bubbled) which was not controlled as accurately.

Plots of $\ln R/(R - R_\infty)$ against time (read in seconds or minutes) gave excellent straight lines. Determination of the slope of the best straight line through the points (drawn by inspection) gave the first-order rate constant. The k_1 values given in Tables I–III are averages of at least two runs. In general, agreement between runs was better than 2%. The data for 2,3-dimethyl-2-phenyl-3-hydroxy-1-butanesulfonic acid sultone (K) are illustrative of the results obtained

T, °C.	k_1, sec.$^{-1}$ Run I	Run II	Average
20.1	7.78×10^{-5}	7.72×10^{-5}	7.75×10^{-5}
30.0	2.54×10^{-4}	2.50×10^{-4}	2.52×10^{-4}
40.0	7.65×10^{-4}	7.65×10^{-4}	7.65×10^{-4}

First-order rate constants in 2.8% dioxane were determined for three sultones reported by Nilsson[1] for pure water (B, E and G). Nilsson's value[6] for the primary sultone B is about 4% higher than ours. For the secondary sultone E his value is about 7% higher and for the tertiary sultone G about 11% higher. The rate for tertiary sultones H was also determined in solutions obtained by using 2 ml. and 3 ml. of dioxane to 35 ml. of water. Plots of the rates *vs.* weight per cent. dioxane were roughly linear, and extrapolation to pure water gave a rate increase of about 14%. These data show that the rates in 2.8% dioxane should be increased by about 5–15% to be strictly comparable with Nilsson's. However, this correction is relatively small for the comparisons made, and the observed rates are recorded in Tables I–III.

The rate for I was determined also in a solution 5.31×10^{-3} molar in sodium hydroxide and in sultone. In these runs the resistance increased with time (hydroxide ion neutralized) and $\ln R/(R_\infty - R)$ *vs.* time was plotted in order to evaluate the rate constant.

Activation energies were calculated from the rate constants obtained at different temperatures using the equation

$$E_a = 2.303R \frac{\log k_1 \text{ (at } T_1) - \log k_1 \text{ (at } T_2)}{(1/T_1 - 1/T_2)}$$

The individual activation energies calculated in this way for T_1 to T_2 and T_2 to T_3 agreed to within less than ±1 kcal. for sultones H-K, as did Nilsson's E_a-values. The average value and probable error are indicated in Tables I–III.

Activation entropies were calculated (using the rates at 40°) from Nilsson's data and from our data with the equation

$$-\Delta S^* = \left(\log \frac{kT}{h} - \log k_1 - \frac{E_a - RT}{2.303RT}\right) 2.303R$$

Results

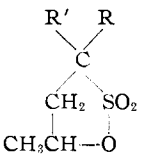
Tables I–III summarize the kinetic data obtained by Nilsson in pure water and our data for 2.8% dioxane–water. Suitable data on open-chain compounds are included for comparison.

(7) F. G. Bordwell, R. D. Chapman and C. E. Osborne, THIS JOURNAL, **81**, 2002 (1959).

(8) L. F. Fieser, "Experiments in Organic Chemistry," 2nd edition, D. C. Heath and Co., New York, N. Y., 1941, p. 368.

TABLE II

KINETIC DATA FOR THE HYDROLYSIS OF SECONDARY SULTONES AND RELATED COMPOUNDS



Compound R′	R	T, °C.	$k_1 \times 10^6$, sec.$^{-1}$	Relative rate (at 40°)	E_a, (kcal./mole	ΔS^*, e.u. at 40°
E, H	H	20.0	16[a]			
		30.0	52[a]			
		40.0	160[a]	1.3	21.2 ± 0.3	−10.6
		40.0	150[b]			
F, CH_3	CH_3	40.0	79[c]	0.7	18.4	−20.6
		50.0	205[c]			
i-PrBr		50.0	116[d]			
i-$PrOSO_2C_6H_5$		0.092	19.52[e]			
		20.01	345.8[e]		22.78	+ 5.5
		30.122	1243[e]			
		40.0	(3,680)[f]	(30)[f]		

[a] T. Nilsson.[6] [b] In 2.8% dioxane. We are indebted to Dr. Curtis W. Smith [see C. W. Smith, D. G. Norton and S. A. Ballard, THIS JOURNAL, **75**, 748 (1953)] for a sample of this sultone. [c] In 2.8% dioxane. These measurements were made by Mr. R. Wayne Ohline on a sample obtained through the kindness of Prof. Dr. A. Van Doramael and Dr. J. Willems [see J. Willems, *Bull. soc. chim. Belg.*, **64**, 409 (1955)]. [d] S. Winstein, E. Grunwald and H. W. Jones, THIS JOURNAL, **73**, 2700 (1951). [e] P. M. Laughton and R. E. Robertson, *Can. J. Chem.*, **33**, 1207 (1955). [f] Extrapolated.

Effect of α-Substitution.—Comparison of the first-order rate constants for the hydrolysis of the unsubstituted primary sultone A (3-hydroxypropanesulfonic acid sultone) with the open-chain analogs ethyl and *n*-propyl benzenesulfonates (see Table I) reveals a similar order of magnitude for the rates at 40°, the first-order rate constants being 69, 46 and 121 × 10^{-6} sec.$^{-1}$, respectively, for $EtOSO_2C_6H_5$,[9a] $PrOSO_2C_6H_5$[9b] and sultone A.

The primary benzenesulfonate esters and sultone A hydrolyze roughly ten times as rapidly as does ethyl bromide. α-Methyl substitution leads to about a 10-fold increase in hydrolysis rate for the bromide ($k_1^{i\text{-PrBr}}/k_1^{\text{EtBr}} \cong 10$) and an 80-fold increase for benzenesulfonate esters ($k_1^{i\text{-}PrOSO_2C_6H_5}/k_1^{n\text{-}PrOSO_2C_6H_5} \cong 80$). The larger increase in the latter instance has been attributed to more SN1 character, using the Hughes–Ingold notation,[9a] or to a closer approach to *Lim.* solvolysis using Winstein's classification.[10] The effect of α-methyl (to oxygen) substitution in sultones might have been expected to parallel that in benzenesulfonate esters,[9,10] but, surprisingly enough, the secondary sultone E hydrolyzes only 1.3 times as rapidly as does the primary sultone A.

The increase in rate of hydrolysis from *i*-PrBr to *t*-BuBr is of the order of 10^4 (see Tables II and III) to 10^5.[11] For solvolysis in formic acid the increase is of the order of 10^6, and this is a minimum figure for a *Lim.* type solvolysis.[11] Since the hydrolysis of open-chain secondary sulfonates appears to be more nearly *Lim.* than that of secondary bromides,[9,10] one might expect an increase in hydrolysis rate in going from a secondary to tertiary sulfonate ester (tertiary open-chain sulfonate esters are unknown) of at least 10^5. The increase in hydrolysis rate from the secondary ring sulfonate ester E to the tertiary ring sulfonate ester G is about 2 × 10^3. The over-all increase in hydrolysis rates from primary to tertiary in the bromides is a factor of about 10^5–10^6, as compared to about 10^3 in the sultone series. The effect of α-methyl substitution therefore results in a much smaller enhancement of hydrolysis rate of 5-membered ring sultones than expected.

Effect of β-Substitution.—Introduction of a β-methyl group into the primary sultone A causes a 5-fold retardation in hydrolysis rate (compare B in Table I). A second β-methyl group (sultone C) causes an additional 60-fold retardation so that the ratio of hydrolysis rates for C:B:A is about 1.0:60:300 at 40°. In the open-chain analogs, *neo*-$PenOSO_2C_6H_5$, *i*-$BuOSO_2C_6H_5$ and Pr-$OSO_2C_6H_5$ the relative hydrolysis rates at 60° are 1.0:2.1:6.5.[9b] The *neo*-$PenOSO_2C_6H_5$ to *i*-$BuOSO_2C_6H_5$ rate ratio in water is only 1.0:2.1 in contrast to 1.0:60 in the sultone series. Winstein and Marshall[12] report a *neo*-PenOTs to *i*-BuOTs rate ratio of 1.0:2.8 in acetic acid. The effect of β-methyl substitution on the behavior of sultones in water corresponds more closely to that of the open-chain sulfonate esters in solvents such as ethanol or ethanol–water, where nucleophilic attack of the solvent is emphasized.[10] For example, in ethanol the *neo*-PenOTs:*i*-$BuOSO_2C_6H_5$ ratio is 1.0:89[9b] and in 50% ethanol the *neo*-PenOTs:*i*-BuOTs ratio is 1.0:12.[12]

From these data it is apparent that substitution of one β-methyl group into a primary sultone has about twice as great an effect on the hydrolysis rate as expected by analogy with open-chain sulfonate esters,[9b] and that the effect of the second β-methyl group is about thirty times that expected.[9b] Furthermore, the changes in activation entropy are in the opposite direction.

In the series of open-chain primary sulfonate esters Et:*i*-Bu:*neo*-Pen, β-methyl substitution causes a marked increase in the activation energies for solvolysis. In water the increase from $EtOSO_2C_6H_5$ (or $PrOSO_2C_6H_5$) to *neo*-$PenOSO_2C_6H_5$ is 4 kcal.[9b]; in ethanol,[9b] acetic acid[12] and formic acid[12] it is 7 kcal. In water, acetic acid and formic acid these large increases in activation energy are compensated, for the most part, by large *increases* in activation entropy, and the solvolysis rates are all of the same order of magnitude (see above). In contrast, the activation energy for the hydrolysis of the neopentyl-type sultone C is only 2 kcal. larger than for sultone A, and the entropy of activation for the hydrolysis *decreases* by 5 e.u. from A to C.

Substitution of β-methyl groups into the tertiary sultone G leading to the trimethyl sultone H and the tetramethyl sultone I also brings about a marked retardation in hydrolysis rate. The ratio of relative rates for G:H:I at 40° is 1.0:0.065:0.0058. This is totally unexpected from the behavior of open-chain analogs, since for solvolysis in 80% ethanol the rate ratio for $CH_3CH_2CH_2CCl$-

(9) (a) R. E. Robertson, *Can. J. Chem.*, **31**, 589 (1953); (b) P. M. Laughton and R. E. Robertson, *ibid.*, **33**, 1207 (1955).

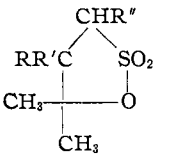
(10) S. Winstein, E. Grunwald and H. W. Jones, THIS JOURNAL, **73**, 2700 (1951).

(11) A. Streitwieser, *Chem. Revs.*, **56**, 571 (1956).

(12) S. Winstein and H. Marshall, THIS JOURNAL, **74**, 1120 (1952).

TABLE III

KINETIC DATA FOR THE HYDROLYSIS OF TERTIARY SULTONES AND RELATED COMPOUNDS[a]



Compound R	Compound R′	Compound R″	T, °C.	$k_1 \times 10^6$, sec.$^{-1}$	Relative rate (at 40°)	E_a, kcal./mole	ΔS^*, e.u. at 40°
G, H	H	H	0.1	3100[b]			
			5.03	6050[b]			
			10.06	11,500[b]	(3100)[c]	20.4 ± 0.3	+ 2.3
			0.1	2800			
H, CH_3	H	H	0.1	208			
			20.7	2780			
			29.7	6980	(170)[c]	19.2 ± 0.8	− 7.3
I, CH_3	CH_3	H	20.1	229			
			25.0	389			
			25.0	525[d]			
			30.0	687[e]			
			40.0	2130	18	20.3 ± 0.7	− 8.5
J, CH_3	H	CH_3	30.0	160			
			40.0	447	3.7	19.6 ± 0.1	−13.8
			50.1	1,180			
K, C_6H_5	CH_3	H	20.1	77.5			
			30.0	252			
			40.0	765	6.3	20.5 ± 0.5	− 9.8
t-BuCl			25.0	33,000[f]	(2200)[c]	23.8	+12.2
t-BuBr			25.0	750,000[g]	(40,000)[c]	22.5	+14

[a] Unless otherwise indicated the rates were determined in 2.8% aqueous dioxane. [b] T. Nilsson.[6] [c] Extrapolated. [d] Solution 5.3 × 10^{-3} molar in NaOH. [e] Measured by Mr. R. Wayne Ohline. [f] E. Grunwald and S. Winstein, THIS JOURNAL, **70**, 846 (1948). [g] Calculated using the Grunwald–Winstein equation, $\log k/k_0 = mY$.

Me_2: $(CH_3)_2CHCClMe_2$: $(CH_3)_3CCClMe_2$ is 1.0: 0.53:0.77,[13a] and for the corresponding bromides it is 1:0.7:1.[13b] When R in $RCClMe_2$ becomes larger (*t*-Pen, *neo*-Pen) enhancement of rate due to B-strain results,[13a] and for tertiary halides RR′R″-CCl with three branched R groups the solvolysis rates become very large due to B-strain[13b] and/or participation effects.[14] Instead of bringing about an acceleration of hydrolysis rate, β-methyl substitution in tertiary sultones causes a strong retardation of rate.

It is important to note that once again β-methyl substitution causes a decrease in activation entropy for hydrolysis. Again this contrasts sharply with the effect of β-methyl substitution in the open-chain analogs. For solvolysis of the tertiary chlorides $RCClMe_2$, β-methyl substitution, which changes R from Et to *i*-Pr to *t*-Bu, causes little change in either the rates,[13,15] activation energies or activation entropies (E_a's in this series are 22.9, 23.3 and 23.8 kcal., respectively).[15]

Effect of γ-Substitution.—Less information is available regarding the effect of γ-methyl substitution. In the primary series one γ-methyl substituent (compare D and A in Table I) increases the hydrolysis rate slightly (1.4 times). A slight decrease in activation entropy is more than compensated by a decrease in activation energy.

In the secondary sultone F a similar situation arises. Here introduction of two γ-methyl substituents leads to a decrease of about 2.5 kcal. in the activation energy of the hydrolysis reaction, but this is more than balanced by a sharp decrease in activation entropy, and the over-all result is a 50% retardation in rate.

In the tertiary sultone series introduction of a γ-methyl group into H, which already contains a β-methyl substituent, causes a sharp decrease in rate, due almost entirely to a decrease in activation entropy. The effect of one β- and one γ-methyl group is greater than that of two β-methyl groups.

Effect of Substitution on Olefin Production.—Nilsson[6] found that hydrolysis of primary sultone A gave no unsaturation, that the secondary sultone E gave 1% and that the tertiary sultone G gave 15% unsaturation.

The tertiary sultones G, H and I on hydrolysis appear to give somewhat smaller amounts of unsaturation than do the corresponding tertiary halides on solvolysis in 80% ethanol.[13b] However, the figures are roughly comparable. In the series $RCClMe_2$ the percentage unsaturation is 15, 33 and 34% when R is Me, Et and *n*-Pr as compared to 15% for G; 62% when R is *i*-Pr as compared to 38% for H; and 61% when R is *t*-Bu as compared to 62% for I. Bromide–bromate titrations on branched unsaturated sulfonic acids are likely to

(13) (a) H. C. Brown and R. S. Fletcher, THIS JOURNAL, **71**, 1845 (1949); (b) H. C. Brown and R. S. Fletcher, *ibid.*, **72**, 1223 (1950).

(14) (a) P. D. Bartlett, *J. Chem. Ed.*, **30**, 22 (1953); (b) P. D. Bartlett and M. S. Swain, THIS JOURNAL, **77**, 2801 (1955); (c) P. D. Bartlett and E. B. Lefferts, *ibid.*, **77**, 2804 (1955).

(15) E. D. Hughes, C. K. Ingold, R. J. L. Martin and D. F. Meigh, *Nature*, **166**, 679 (1950).

give high values,[7] so the values for G and H may be high. The reaction of I with bromide–bromate leads to a bromosultone,[7] and the 62% value is more accurate. In the presence of strong alkali compound I gave larger amounts of unsaturated product (about 80%). The formation of unsaturated sulfonates is indicative of C–O cleavage since S–O cleavage would lead to hydroxyalkanesulfonates, which would not dehydrate in alkaline medium.

Discussion

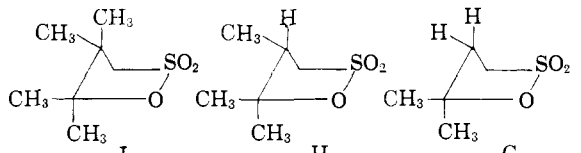
Methyl Substitution in Tertiary Sultones.—It is apparent from the results reported in the previous section that the effect of methyl groups on the rate of hydrolysis of cyclic sulfonate esters (sultones) is frequently much different from their effect on the rate of hydrolysis of open-chain analogs. More information is available for the effects of substitution in 5-membered ring tertiary sultones than for other types, so the discussion will be developed using these as a basis.

The extensive work on the effect of substitution on the rates of solvolysis of tertiary halides, RR'R''CX, provides a background for visualizing the types of effects that may be expected. In tertiary chlorides, $RCClMe_2$, substitution of one or two β-methyl groups in R has but little effect on the rate, the ratio of rates for the solvolysis in 80% ethanol of $CH_3CH_2CH_2CClMe_2$, $(CH_3)_2CHCClMe_2$ and $(CH_3)_3CCClMe_2$ being 1.0:0.53:0.77.[13a] It is difficult to say anything about the causes for such minor rate variations, but from data on the effect of change of *m*- and *p*-R groups on the solvolysis rates of alkylphenyldimethylcarbinyl chlorides[16] it would seem that hyperconjugative stabilization of the carbonium ion is more important than inductive stabilization, and that substitution of methyl groups for β-hydrogens leads to a surprisingly small decrease in hyperconjugation. The change in hyperconjugative or inductive effects in the series Et, *i*-Pr, *t*-Bu is small.[16] There is no reason to expect a ring structure to alter greatly the relative polar effects of alkyl groups on hydrolysis rate, so the marked retardation produced by substitution of the β-hydrogens of tertiary sultone G by methyl groups is difficult to rationalize in terms of inductive or hyperconjugative effects. Only a moderate change in hydrolysis rate of tertiary sultones on β-methyl substitution would be anticipated from these polar effects. A steric effect is thereby implicated.

Extensive branching of the alkyl groups of tertiary halides leads to acceleration of the solvolysis rates. For solvolysis in 80% ethanol some approximate relative rates are[13]: $EtCClMe_2$, 1.0; Et_2CClMe, 1.6; *t*-$PenCClMe_2$, 3.4; *t*-BuCClMeEt, 4.1; *neo*-$PenCClMe_2$, 12; $(i\text{-Pr})_2CClMe$, 14; $(neo\text{-Pen})_2CClMe$, 320. Although it is possible to attribute most of these accelerations to polar factors[11,17] and/or participation,[14,17] most investigators agree that B-strain[13] is also important.[11,14] The failure to observe rearrangement during the solvolysis of halides such at *t*-$BuCClMe_2$,[18] *t*-$PenCClMe_2$,[19] and *t*-BuCClEtMe[19] renders acceleration of rate by methyl participation unlikely in these systems, although this factor is probably at least partly responsible for the very large rate accelerations in highly branched systems.[14b,c]

It is remarkable that in the tertiary sultone series two β-methyl substituents produce a 170-fold *retardation* of rate (compare I and G) whereas similar substitution in open-chain tertiary chlorides produces a slight rate *acceleration* in solvolysis rate (in 80% ethanol *t*-$PenCMe_2$ solvolyzes 3.6 times as rapidly as does *n*-$PrCClMe_2$). The effect of β-alkyl substitution on the solvolysis rate of the ring compounds is, therefore, much greater in magnitude and opposite in direction.

If the 5-membered rings in sultone G were planar, the substitution of a methyl group (giving H) should introduce a strain energy due to replacement of a hydrogen to methyl opposition by a methyl to methyl opposition of about 5 kcal. per mole.[20] Similarly, compound I should then possess a strain energy about 10 kcal. greater than that of G. Since this could lead to a very large *acceleration* of the hydrolysis rate of H and I compared to G, whereas experimentally a large *retardation* in rate actually is observed, it seems clear that these rings are not planar. Inasmuch as the cyclopentane ring is not planar,[20] it is perhaps not surprising that the larger 5-membered heterocyclic ring of sultones can be puckered so as to permit the groups attached to the ring to achieve staggered positions with respect to one another, as shown for G, H and I.[21]



	I	H	G
Rel. hydrol. rates	1.0	9.5	170

Effect of Ring Structure.—It seems likely that the key to the explanation of the unusual and exaggerated effects of methyl groups on the rates of sultone hydrolyses resides in one essential difference in the solvolyses of open-chain and ring compounds. For open-chain compounds the ions of the ion pair formed on initial cleavage of the C–X or C–O bond may separate *linearly*. This is impossible in a ring-opening reaction unless it is accompanied by bond bending to widen the ring angles. As a result, *ring-opening solvolyses are accomplished primarily by rotation around the bonds of the ring atoms in order to allow separation of the two atoms between which bond rupture has occurred.* Using this concept it is possible to visualize several ways in which methyl

(16) H. C. Brown, J. D. Brody, M. Grayson and W. H. Bonner, THIS JOURNAL, **79**, 1897 (1957).

(17) E. D. Hughes, C. K. Ingold and V. J. Shiner, *J. Chem. Soc.*, 3827 (1953).

(18) J. D. Roberts and J. A. Yancey, THIS JOURNAL, **77**, 5558 (1955).

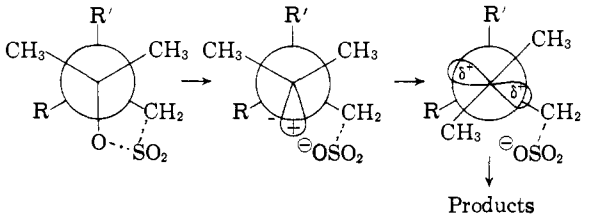
(19) H. C. Brown and Y. Okamoto, *ibid.*, **77**, 3619 (1955).

(20) See the discussion by W. G. Dauben and K. S. Pitzer in Chapter 1 of reference 3b.

(21) Even in the cyclopentane series there is evidence that two *trans* groups on adjacent carbon atoms can achieve a conformation approaching the axial-axial relationships of similar groups on a cyclohexane ring; see F. V. Brutcher, Jr., T. Roberts, S. J. Barr and N. Pearson, THIS JOURNAL, **78**, 1507 (1956); J. Weinstock, S. N. Lewis and F. G. Bordwell, *ibid.*, **78**, 6072 (1956); H. L. Goering and K. L. Howe, *ibid.*, **79**, 6542 (1957).

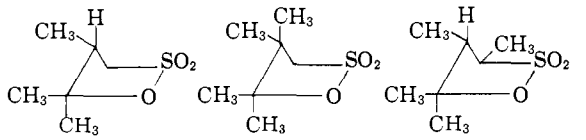
substitution may sterically retard the rate of ring opening of 5-membered ring sultones.

Steric Hindrance to Rotation.—Assuming a staggered conformation for the ground state, the hydrolysis of the tertiary sultones may be pictured as involving ion-pair formation and rotation around C_α–C_β, as shown, to allow separation of the ions. Examination of Fisher–Hirschfelder models



indicates that even when R and R are hydrogen it is almost impossible to accomplish the separation *by this rotation alone*, because of interferences between the α-methyl groups and the sulfonate group. By rotation around *both* C_α–C_β and C_β–C_γ the separation readily is accomplished. Rotation around S–C_γ is completely ineffective in providing separation, since three symmetrical oxygens are present on sulfur, and rotation to separate one from $C_\alpha^\oplus$ merely brings another into bonding distance. When R is H and R′ is CH_3 (sultone H) rotation around C_α–C_β is definitely restricted, and when both R and R′ are CH_3 (sultone I) rotation around C_α–C_β is very difficult. In this situation the separation of the ions is dependent almost entirely on rotation around C_β–C_γ. A model for sultone I in which C_α is made trigonal, so as to approximate a planar carbonium ion, relieves the restriction to rotation around C_α–C_β, but causes more hindrance between the α-methyls and sulfonate group on rotation and makes rotation around C_β–C_γ more difficult. Steric hindrance to rotation appears to be about equal using either a trigonal or tetrahedral carbon atom for C_α.

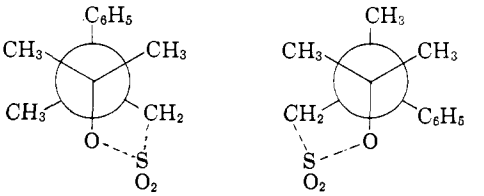
It appears possible to explain most of the retarding effects of methyl groups on hydrolysis rates of the sultones studied thus far in terms of steric hindrance to rotation. As mentioned above, restriction of rotation around C_α–C_β probably occurs even in the simplest tertiary sultone (G), and may be the cause of its smaller than expected solvolysis rate. The much greater restrictions of C_α–C_β rotation present in sultones H and I can be used



	H	I	J
Rel. hydrol. rates	1.0	0.11	0.022
ΔS^*	−7.3	−8.5	−13.8

similarly to rationalize the slow rates of these sultones relative to G. The larger retarding effect produced by replacing a γ-hydrogen of sultone H by methyl (giving sultone J) than replacing a β-hydrogen of H by methyl (giving sultone I) is also explicable in this way, since it is not unreasonable that restriction of rotation around C_β–C_γ of H by γ-methyl substitution might be more effective than further restriction around C_α–C_β by β-methyl substitution, since the C_α–C_β bond rotation is already highly hindered. This hypothesis is consistent with the larger decrease in entropy of activation from H to J than from H to I.

It is noteworthy that substitution of a β-hydrogen in H by phenyl causes an even larger drop in the rate of hydrolysis and entropy of activation than does β-methyl substitution (the rate for sultone K is one-third that of I and $\Delta S^* = -9.8$ e.u.). Analysis of the products from K shows that phenyl migration occurs during hydrolysis.[7] The phenyl group is in position to participate in one of the conformations probable for sultone K. However if



conformations for sultone K

such participation is realized it is buried in the much larger decelerating effect, which we ascribe to steric hindrance to rotation.

Correlation of Sultone Solvolysis Rates and Entropies of Activation.—One of the strong pieces of evidence which indicates that methyl substitution in sultones is producing a different kind of effect on hydrolysis rates than in open-chain analogs is the fact that β-methyl (and γ-methyl) substitution generally leads to a substantial *decrease* in activation entropy in the ring compounds (primary, secondary or tertiary sultones), whereas in the open-chain analogs there is either no change in ΔS^* (β-methyl substitution in tertiary halides) or a substantial *increase* in ΔS^* (β-methyl substitution in primary benzenesulfonates).

The decrease in ΔS^* accompanying β- and γ-substitutions in tertiary sultones has been discussed in the preceding section. In primary sultones (compare A, B and C) ΔS^* decreases by about 5 e.u. from A to C, whereas in the hydrolysis of the corresponding benzenesulfonates there is an increase in ΔS^* of about 8 e.u. from propyl to neopentyl. The limited amount of data on γ-methyl substitution in primary and secondary sultones indicate similar trends. In going from from primary sultone A to its γ-methyl analog ΔS^* decreases by about 3 e.u., and in going from secondary sultone E to its γ,γ-dimethyl analog F there is a drop in ΔS^* about 7 e.u. However, unlike β-methyl substitution, these decreases in ΔS^* for γ-methyl substitution fail to manifest themselves in rate retardations.

Assuming that in the sultone hydrolyses the atoms attached to the ring are brought from a staggered relationship in the ground state to a more nearly opposed relationship in the transition state as a consequence of ring opening, an entropy decrease with methyl substitution is explicable since

as these groups are brought into opposition their rotations (*e.g.*, C–C–CH_3) will be hindered, these restrictions becoming more serious with progressive substitution. It is possible, then, to correlate the decrease in ΔS^* for hydrolysis brought about by β-methyl substitution in tertiary or primary sultones with increased restrictions of bond rotation in the transition state.

For the hydrolysis of open-chain benzenesulfonate esters and halides α-methyl substitution leads to large rate enhancements which are accompanied by appreciable increases in ΔS^*.[22] For the change $PrOSO_2C_6H_5$ to i-$PrOSO_2C_6H_5$ an 80-fold increase in hydrolysis rate is accompanied by an increase in E_a of 1.7 kcal. and an increase in ΔS^* of 14 e.u. (Tables I and II). In the sultone series the change from primary to secondary (sultones A and E) causes a 1.3-fold increase in hydrolysis rate. The increase in E_a is about the same as for the benzenesulfonates (1 kcal.), but ΔS^* increases by only 3 e.u. It seems possible that the factor responsible for the usual increase[22] in ΔS^* is being counteracted in the sultone series by a factor which decreases ΔS^*. The latter could be increased rotational restriction in the transition state. In the sultone series the secondary–tertiary change (sultones E and G) leads to a 2×10^3 increase in hydrolysis rate, which is due largely to an increase of about 13 e.u. in ΔS^* (E_a decreases by about 1 kcal.). It is possible that this increase in ΔS^* is not as large as would be encountered in an open-chain analog, since the rate increase in the sultone series is several orders of magnitude less than might be expected. However, no comparable data for open-chain analogs are available. In the halide series ΔS^* for hydrolysis increases by 21 e.u. from EtBr to t-BuBr (data on i-PrBr not available), but the change in the nature of the anion makes comparison with this series hazardous.

Steric Hindrance to Solvation.—It seems probable that solvation forces may be of importance in producing or putting into effect some of the unusual effects on sultone hydrolyses caused by methyl substitution. Steric hindrance to solvation has been mentioned several times[10,13a] as a factor in determining the rates of solvolysis reactions, but no evidence to demonstrate its importance in such reactions appears to have been forthcoming. However, in other types of ionization reactions steric hindrance to solvation may exert a considerable effect.[23] It seems possible that steric hindrance to solvation might assume unusual significance in ring-opening solvolyses. However, it would be anticipated that ΔS^* would *increase* with increased steric hindrance to solvation, so the general tendency of ΔS^* to *decrease* for sultones as the number of methyl groups is increased does not fit an *a priori* theory based on solvation effects.

(22) The reasons for these increases in ΔS^* are not clear. See R. E. Robertson, *Can. J. Chem.*, **35**, 613 (1957), and S. Winstein and A. H. Fainberg, THIS JOURNAL, **79**, 5937 (1957), for discussions.

(23) See D. H. Everett and W. F. K. Wynne-Jones, *Trans. Faraday Soc.*, **35**, 1380 (1939); G. S. Hammond and D. H. Hoegle, THIS JOURNAL, **77**, 338 (1955); H. K. Hall, Jr., *ibid.*, **79**, 5441, 5444 (1957); B. M. Wepster, *Rec. trav. chim.*, **76**, 357 (1957).

Methyl Space-excluding Effects.—An alternative way to explain the effect of methyl groups in retarding the rates of hydrolysis of sultones is to use the approach originated by Kirkwood and Westheimer[24] to account for the unusual effect of methyl groups on the first and second dissociation constants of dicarboxylic acids. Using Bartlett's qualitative description of the effect,[14a] the methyl groups may be visualized as producing a "space-excluding" effect, which results in an intensification of polar interactions within the molecule. For sultone hydrolyses this would mean stronger attraction between the $C_\alpha^\oplus$ and $^-OSO_2$ ions of the ion pair with increasing alkyl substitution. The failure of similar effects to develop in the similarly shaped $RCClMe_2$ molecules with increased alkyl substitution could be ascribed to an exaggeration of the effect in the ring compounds by the fact that escape from the sphere is possible for the chloride ion, but *not* for the sulfonate ion. The effect of alkyl substitution would have to be assessed from estimates of the change in the size and shape of the "sphere" brought about by various types of alkyl substitutions.

Application to Other Ring-opening Reactions.—It seems likely that steric hindrance to rotation may be of importance in determining the effect of alkyl substitution on the rates of certain other ring-opening reactions. However, it is entirely possible that the effect may be much exaggerated in solvolysis reactions by the possibility of internal and external return from various ion pairs produced.[25] Ring openings occurring by other mechanisms, such as E2 or SN2, may not be so markedly affected by methyl substitution.[26] However, ring openings such as the hydrolysis of cyclic dicarboxylic acid anhydrides are probably comparable to sultone hydrolyses. The available qualitative evidence on these hydrolyses suggests rate retardation of hydrolysis by alkyl substitution. Glutaric anhydride hydrolyzes readily, but β,β-dimethylglutaric anhydride may be boiled for several hours with but little change, and α,β,β-trimethylglutaric anhydride crystallizes from water with a molecule of water of hydration.[2b] Similarly, the cyclic anhydride of adipic acid hydrolyzes readily, $\beta,\beta,\beta'\beta'$-tetramethyladipic anhydride is more stable to hydrolysis and $\alpha,\alpha,\alpha'\alpha'$-tetramethyladipic anhydride is not hydrolyzed by boiling water or aqueous sodium bicarbonate.[2i]

The effect of alkyl groups on a number of systems where there is a presumed equilibrium between an open-chain and ring form were investigated by the Thorpe–Ingold school,[2] and recently have been discussed by Hammond.[5] These systems include: hemiacetal ⇆ hydroxy ketone or aldehyde; pseudo acid ⇆ keto acid or aldehydo acid; cyclic aldol or ketol ⇆ dicarbonyl compound; pseudo acid chloride ⇆ diacid chloride; cyclico rtho ester ⇆ hydroxy ester; lactone ⇆ eneoic acid. Alkyl substituents appear to have a general effect of stabilizing

(24) J. G. Kirkwood and F. H. Westheimer, THIS JOURNAL, **60**, 505 (1938).

(25) See S. Winstein and G. C. Robinson, THIS JOURNAL, **80**, 169 (1958), and previous papers for a discussion of the importance of internal return and external ion pair return in solvolysis reactions.

(26) This point is under investigation.

the ring form. In at least some instances this may be due to steric hindrance to ring opening by the alkyl groups, as discussed. Of course the rate of ring closure must also be considered in deciding the position of equilibrium.

The data concerning the effect of methyl substitution on the rates of ring opening reactions of sultones should also prove helpful in understanding the reverse (ring closing) reactions. However, it seems best not to speculate about ring closures until more information on ring openings becomes available.[26]

Acknowledgment.—It is a pleasure to acknowledge the help derived in several discussions of this problem with Professor Ralph G. Pearson and with Dr. J. C. Martin of the University of Illinois. We are grateful to the Research Corporation and the Nitrogen Division of the Allied Chemical and Dye Corporation for financial assistance.

EVANSTON, ILL.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, PURDUE UNIVERSITY]

Heterogeneity as a Factor in the Alkylation of Ambident Anions: Phenoxide Ions[1,2]

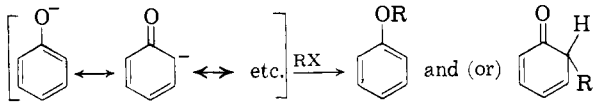
BY NATHAN KORNBLUM AND ARNOLD P. LURIE[3]

RECEIVED OCTOBER 29, 1958

Sodium and potassium salts of phenol and *p*-*t*-octylphenol have been alkylated with benzyl and allyl halides in a variety of solvents. Quantitative yields of the ether (oxygen alkylation) are obtained whenever the reaction is conducted in solution. In addition, it is demonstrated that the truly heterogeneous reaction gives exclusively carbon alkylation. Reactions carried out with the phenolic salt present as a solid phase ordinarily give both carbon and oxygen alkylation, but this result is clearly a consequence of incursion by the homogeneous process. The factors, other than heterogeneity, which may influence the course of phenoxide alkylations are briefly discussed. An explanation is offered for the fact that heterogeneity confers an essentially irresistible preference for carbon alkylation.

In a recent paper[4] the alkylation of ambident anions, *i.e.*, ions wherein covalent bond formation can take place at either of two alternative positions, was discussed; in particular, attention was directed toward the influence of electrical effects on the reaction course.

The present study is concerned with phenoxide ions, which, being ambident anions, are capable of undergoing alkylation either on carbon[5] or on oxygen

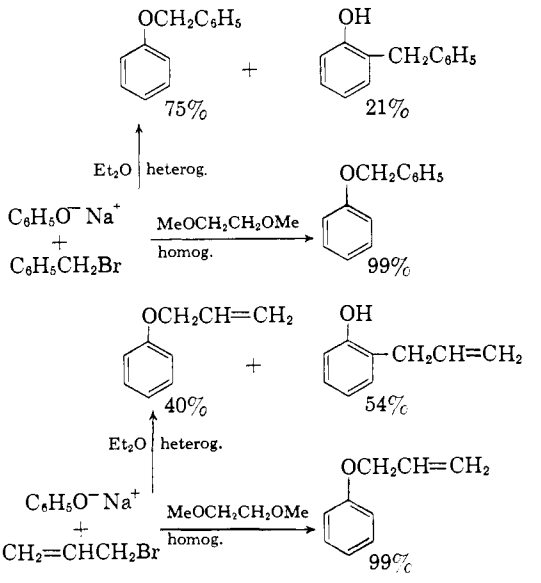


Our initial intention of studying the influence which electrical effects have on the course of phenoxide alkylations was temporarily set aside when it became clear that a new factor, heterogeneity *vs.* homogeneity, is of paramount importance; the present investigation is concerned with this new factor.

The demonstration that heterogeneity is a factor which must be reckoned with consists of two parts. The first rests upon divergences resulting from conducting reactions in anhydrous ether on the one hand and ethylene glycol dimethyl ether on the other. The second part of the demonstration is based on a study of the alkylation process in a single solvent—toluene.

The experiments summarized in Chart I were conducted at 35°; they derive their significance from the fact that sodium phenoxide has a low

CHART I



solubility in anhydrous ethyl ether but dissolves readily in the dimethyl ether of ethylene glycol; in the first solvent we deal with a heterogeneous system while in the second the reaction occurs in solution. It will be seen that alkylations in ethyl ether (heterogeneous) give substantial yields of carbon alkylated phenols[6] whereas the same alkylations, conducted homogeneously in ethylene glycol dimethyl ether, give no carbon alkylated products.[7]

(1) This research was supported by the United States Air Force under Contract No. AF49(638)-324 monitored by the A. F. Office of Scientific Research of the Air Research and Development Command and by the Purdue Research Foundation.

(2) Presented at the San Francisco Meeting of the American Chemical Society, April, 1958.

(3) From the doctoral dissertation of Arnold P. Lurie, Purdue University, June, 1958.

(4) N. Kornblum, R. A. Smiley, R. K. Blackwood and D. C. Iffland, THIS JOURNAL, **77**, 6269 (1955).

(5) The dienone produced by carbon alkylation is not usually isolated since, by proton removal, it is rapidly transformed into the salt of the *o*-alkylated phenol.

(6) Allyl phenyl ether does not isomerize to *o*-allylphenol under the conditions of this experiment (*cf.* Experimental).

(7) Here, and throughout, care was taken to conduct comparative reactions at the same temperature and concentration.