tracted with ether. The ether was washed with water, dried, and removed to afford 283 mg of an oil which crystallized on standing. Recrystallization from hexane gave needles: mp 102–103°; λ_{max} 2.80 (OH), 7.43, 8.76 (SO_2), and 6.25, 6.70, and 12.5 μ (aromatic). The nmr spectrum showed the presence of five aromatic protons at 7.39, three singlet methyl groups at 0.80, 1.05, and 3.37, a widely spaced AB-type quartet centered at 3.10 for the CH_2SO_2, a multiplet at 4.10 for the CHOH proton, and the hydroxyl proton at 3.07 ppm (disappears upon addition of trifluoroacetic acid).

Anal. Calcd for $C_{17}H_{25}NO_3S$: C, 63.15; H, 7.74; S, 9.91. Found: C, 63.03; H, 7.57; S, 9.67.

Registry No.—**1**, 13144-39-3; **3**, 13131-57-2; **4'** 13131-58-3; **9**, 13144-40-6; **10**, 13131-59-4; **13**, 13144-41-7; **14**, 13144-43-9; **15**, 13144-44-0; **16**, 13144-45-1; **19**, 13144-46-2; **20**, 13144-47-3; **21**, 13137-33-2; **22**, 13144-48-4; **24**, 13144-49-5; **25**, 13144-50-8; **27**, 13131-60-7; **31**, 13144-51-9; **32**, 13144-52-0; **34**, 13144-53-1; **35**, 13144-54-2; **38**, 13144-55-3; sulfonamide (mp 87–88°), 13131-61-8; 3-*exo*-methyl-2-norbornanone, 3915-75-1; 3-*exo*-propyl-2-norbornanone, 13144-57-5; 4-methylisobornyl acetate, 13144-42-8.

"Aprotic" Solvolysis of p-Toluenesulfinic Esters[1]

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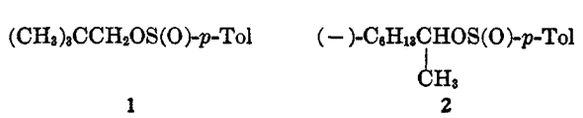
Alkyl p-toluenesulfinates undergo cleavage to unrearranged alcohols when heated in various aprotic, nucleophilic amide solvents. Particularly effective is N-methyl-2-pyrrolidone (NMP). The yields are good in this solvent and the process is first order in ester. Studies with the neopentyl ester **1** and the (−)-2-octyl ester **2** in NMP indicate that the cleavage is probably an S_N solvolysis where the solvent plays the roles both of attacking nucleophile and proton source, initiating cleavage by attack of the amide carbonyl on the sulfinate sulfur atom. Displaced alkoxide ion then, perhaps nearly concertedly, abstracts a proton from the α position of the amide leading to unrearranged alcohol product (when pertinent, with retention of configuration and optical purity). The cleavage is characterized by an extremely favorable activation enthalpy but a decidedly unfavorable activation entropy, reminiscent of $B_{Ac}2$ saponifications. Minor additional products observed from **1** in NMP are p-tolyl p-toluenethiolsulfonate (**3**) and the unusual salt N-methyl-2-pyrrolidonium tosylate (**4**). A side reaction involving dissociation of **1** is suggested as the source of these substances.

p-Toluenesulfinic esters are formed in the reaction of certain aldehyde tosylhydrazones with sodium methoxide in N-methyl-2-pyrrolidone (NMP) at 180°.[2] Such "aprotic" Bamford–Stevens reactions[3] ultimately lead to alcohols, and it was discovered that these esters were cleaved to alcohols without rearrangement by NMP under these reaction conditions. The present investigation was aimed at the elucidation of the mechanism of this cleavage.

Results

A number of p-toluenesulfinate esters were prepared in this study (see the Experimental Section), but the neopentyl ester **1** and the optically active (−)-2-octyl ester **2** were utilized most because of their obvious



1 **2**

mechanistic significance. Each ester was easily prepared by interaction of p-toluenesulfinyl chloride and the corresponding alcohol in ether–pyridine.[4] It was in the course of preparing and characterizing the sulfinic esters that the interesting nmr feature of magnetic nonequivalence of the methylene protons in the functionality $CH_2OS(O)$ was noticed and reported.[5]

It was quickly established that the use of hexadecane, another solvent often employed in aprotic Bamford–Stevens reactions, did not afford alcohols from sulfinic esters at 180°; thus the cleavage was not just a thermal process independent of solvent. Examination of a number of other aprotic solvents was then carried out. Neopentyl p-toluenesulfinate **1** was used as the test ester with the results given in Table I.

TABLE I

EFFECT OF SOLVENT ON CLEAVAGE OF NEOPENTYL p-TOLUENESULFINATE (1)[a]

Solvent	Neopentyl alcohol, %[b]
N-Methyl-2-pyrrolidone	84
N-Methyl-ε-caprolactam	52
N-Methyl-2-piperidone	27
N,N-Dimethylacetamide	31
N,N-Dimethylformamide	5
N,N-Dimethylpivalamide	5
γ-Butyrolactone	59[c]
Diethyl malonate	6.5
Cumene	0
Hexadecane	0

[a] At 180° normally for 15 min, except for the low conversion reactions which were heated for as long as 3 hr. [b] No t-amyl alcohol was found by glpc except in the case of γ-butyrolactone. The values represent the highest percentage in several experiments. [c] t-Amyl alcohol was also formed (11%).

The data indicated that tertiary amide solvents were effective, but only those in which the carbonyl group was flanked by a methyl or a methylene group (*i.e.*, "enolizable" amides). γ-Butyrolactone also cleaved the ester but here some rearranged alcohol was also produced. The involvement of the α position of the amide solvent was substantiated through use of 3,3-

(1) Taken from the M.S. Thesis of R. G. S., Loyola University, 1966, and from a portion of the Ph.D. dissertation of W. J. W., Loyola University, 1967.

(2) J. W. Wilt, C. A. Schneider, H. F. Dabek, Jr., J. F. Kraemer, and W. J. Wagner, *J. Org. Chem.*, **31**, 1543 (1966).

(3) W. R. Bamford and T. S. Stevens, *J. Chem. Soc.*, 4735 (1952).

(4) H. Phillips and J. Kenyon, *ibid.*, 2271 (1925).

(5) J. W. Wilt and W. J. Wagner, *Chem. Ind.* (London), 1389 (1964). Others had noted this earlier: J. S. Waugh and F. A. Cotton, *J. Phys. Chem.*, **65**, 562 (1961); M. Oki and H. Iwamura, *Bull. Chem. Soc. Japan*, **35**, 1428 (1962). We thank Professors Cotton and Iwamura for drawing our attention to their work.

$(CH_3)_3CCH_2OS(O)$-*p*-Tol $\xrightarrow[180°,\ D_2]{}$ $(CH_3)_3CCH_2OD$

dideuterio-N-methyl-2-pyrrolidone,[6] as shown. The neopentyl alcohol was hydroxyl deuterated as shown by nmr analysis. Furthermore, the ring size of the lactam solvents appeared to be a factor. Both the five- and seven-membered ring lactams were more efficacious solvents than the six-membered one.

The kinetics of the cleavage were determined *via* glpc using the best solvent (NMP) and the neopentyl ester **1**. The results are given in Table II. Though the order of the reaction with respect to the solvent was not determined, it was found that the use of equimolar ester **1** and NMP gave a 72% yield of alcohol. Therefore the reaction probably also involves 1 equiv of NMP.

TABLE II

KINETICS OF CLEAVAGE OF NEOPENTYL *p*-TOLUENESULFINATE (1) BY N-METHYL-2-PYRROLIDONE

Temp, °C[a]	k_1, sec^{-1} [b]	ΔH^* [c]	ΔS^* [d]
90	3.3×10^{-4}	10 ± 1	-22 ± 2
120	10.4×10^{-4}		
150	22.5×10^{-4}		

[a] ±2°. [b] Process first order in sulfinic ester **1** (5 g in 50 ml of NMP). The values are precise to about 10%. [c] In kcal/mole. [d] In eu.

Finally, the stereochemistry of the process was investigated by cleavage of (−)-2-octyl (±)-*p*-toluenesulfinate (**2**) in NMP. The (−)-2-octanol produced had 97% of its original optical purity; so the cleavage proceeded with over-all retention of configuration in the alcohol portion.

(−)-$C_6H_{13}CHOS(O)$-*p*-Tol $\xrightarrow[\Delta]{NMP}$ (−)-$C_6H_{13}CHOH$

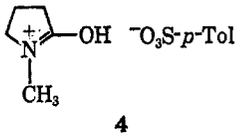
CH_3 CH_3

$[\alpha]^{25}D$ −21° (from alcohol with $[\alpha]^{25}D$ −9.1°) $[\alpha]^{25}D$ −8.81°

Heating ester **1** in less NMP again gave neopentyl alcohol but other products were also detected. *p*-Tolyl *p*-toluenethiolsulfonate (**3**) and the unusual compound N-methyl-2-pyrrolidonium tosylate (**4**) were also isolated, albeit in small yield (7–9%). The latter substance, apparently new, resulted easily upon ad-

p-$TolSO_2S$-*p*-Tol

3



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mixture of NMP and *p*-toluenesulfonic acid monohydrate as a white, crystalline salt, mp 121–122°.[7] While the infrared spectrum was inconclusive, the nmr spectrum indicated it to be enolic, so the proton appears to have added to the oxygen, as shown in **4**. No other major product was isolated and the fate of the solvent remains, unfortunately, largely unclear.

(6) C. Djerassi, A. M. Duffield, and H. Budzikiewicz, *J. Am. Chem. Soc.*, **86**, 5536 (1964).

(7) N-Methyl-2-pyrrolidone is a weak base (pK_a in H_2O = −0.2)[8] and forms a crystalline hydrochloride (mp 80–88°).[9]

(8) C. A. Streuli, *Anal. Chem.*, **31**, 1652 (1959); **32**, 985 (1960).

(9) "N-Methyl-2-pyrrolidone," General Aniline and Film Corp. Brochure No. AP-76-3, New York, N. Y., June 1963, p 10.

Small amounts of rapidly eluting material were evidenced in the glpc of the neopentyl ester cleavage. These were presumably the isomeric pentenes and they have some mechanistic significance (see later).

Discussion

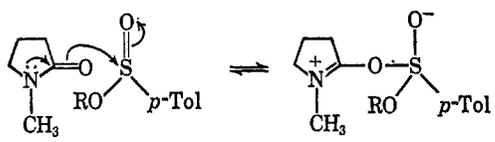
With the exception of γ-butyrolactone, the solvents that cleaved **1** did so without rearrangement of the alcohol product.[10] For these solvents, therefore, a solvolysis mechanism involving extensive dissociation of **1** to ions would appear unlikely as a major pathway in that considerable rearrangement to *t*-amyl product(s) would have occurred, as shown. The

$(CH_3)_3CCH_2OS(O)$-*p*-Tol $\xrightarrow[\text{not extensive}]{}$ $(CH_3)_3CCH_2^+ + {}^-O_2S$-*p*-Tol

$\downarrow$ fast

$(CH_3)_2\overset{+}{C}CH_2CH_3 \longrightarrow$ products

high retention of configuration observed in the cleavage of **2** even argues against product formation from ion-pair intermediates during the cleavage,[11] as also do the high polarity and dielectric constant of the solvents employed. It is more likely that the solvolytic cleavage observed is more a nucleophilic type (SN) rather than either of the above limiting (Lim) types. Indeed, the activation parameters ($\Delta H^* \sim 10$ kcal/mole, $\Delta S^* \sim -22$ eu) are close to those observed in typical $B_{Ac}2$ ester saponification reactions ($\Delta H^* \sim 11$ kcal/mole, $\Delta S^* \sim -25$ eu);[12] so the slow step of the cleavage is probably the nucleophilic attack of the carbonyl oxygen of the solvent upon the highly electrophilic sulfur atom of the ester,[13,14] as shown for the NMP case.



5

Such nucleophilic action by amides has been suggested for their decided catalytic action in alkylation reactions.[15] A nucleophilic attack upon the alkyl group R is unreasonable for steric reasons in the case of **1** and contrary to the evidence for configurational retention observed in the cleavage of **2**. Intermediate **5** is very similar in fact to that suggested for $B_{Ac}2$ saponification[16] and would be expected to be reversibly formed because the weakly basic NMP would in

(10) Earlier[2] cleavages of norbornyl-1-carbinyl and 1-bicyclo[2.2.2]octyl *p*-toluenesulfinates also proceeded without rearrangement.

(11) For studies of ion-pair formation in the solvolysis of arenesulfinic esters, *cf.* D. Darwish and R. McLaren, *Tetrahedron Letters*, 1231 (1962); D. Darwish and E. A. Preston, *ibid.*, 113 (1964).

(12) L. Smith and H. Ollson, *Z. Physik. Chem.*, **118**, 99 (1925). For some very recently determined activation parameters in saponifications, *cf.* D. D. Roberts, *J. Org. Chem.*, **31**, 4037 (1966).

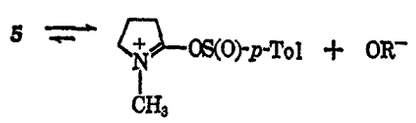
(13) Sulfinic esters are hydrolyzed rapidly by dilute base at 0° [I. B. Douglass, *ibid.*, **30**, 633 (1965)], presumably because of the high electrophilicity of the sulfur atom.

(14) The ester is written with S=O in view of the nmr studies of P. Haake, W. B. Miller, and D. A. Tyssee [*J. Am. Chem. Soc.*, **86**, 3577 (1964)] which indicate that this type of bonding exists in dimethyl sulfoxide and dimethyl sulfone.

(15) H. E. Zaugg, *ibid.*, **82**, 2903 (1960), and references therein.

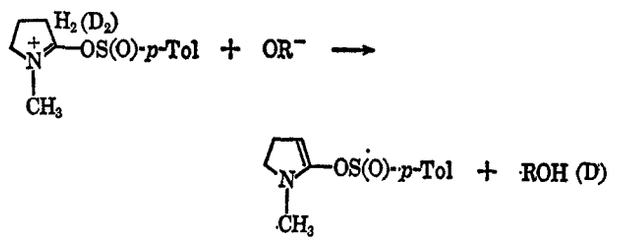
(16) M. L. Bender, *ibid.*, **73**, 1626 (1951).

turn be a good leaving group. Alternatively, **5** could eliminate alkoxide ion on occasion, probably reversibly as shown. From the results with deuterated NMP,



6

the alkoxide ion must then form the alcohol product by abstraction of an α proton (or deuteron) from either **6** or a solvent molecule. Two considerations suggest that **6** is the source of the proton, as shown. First,



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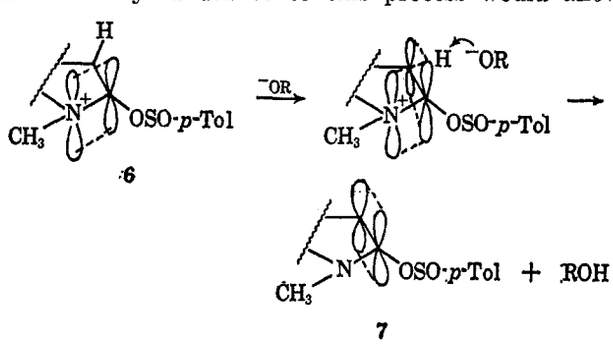
because of its immonium nature, **6** (and its analogs in the other ring sizes) would be decidedly more acidic than the lactam solvent and would be expected to react rapidly with the strongly basic alkoxide ion[17] upon expulsion of the latter from **5**. Second, the reaction of alkoxide ion with the α protons in structures like **6** would be expected to be subject to conformational effects because of stereoelectronic considerations, as shown. Any hindrance to this process would allow



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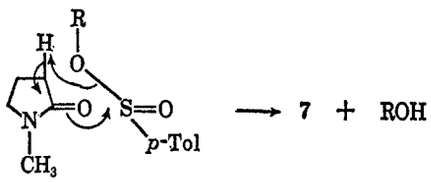
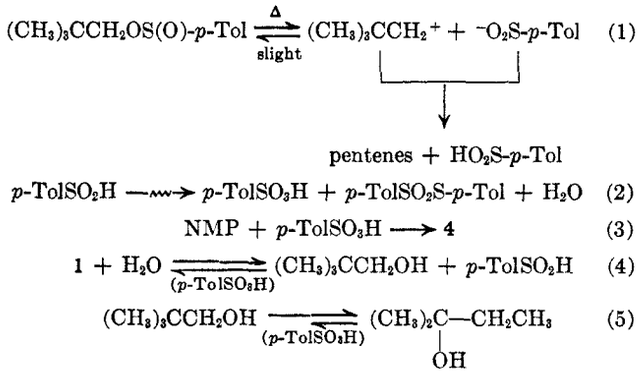
the equilibrium postulated above as $5 \rightleftharpoons 6 + OR^-$ to shift toward **5** and reduce the rate of alcohol production. Models indicate that the maximal overlap (and hence fastest rate) in the transition state for this process would be most easily achieved in the NMP instance, less so in the case of N-methyl-ϵ-caprolactam, and least so for N-methyl-2-piperidone because of the well-known conformational preferences existing in each ring size.[18] This would mean that *for a given reaction time* (*e.g.*, 15 min as in Table I) the yield of alcohol would decrease in the same order, as is indeed found. It is also possible that the attack by alkoxide ion on **6** is nearly synchronous with the attack by NMP on the sulfinic ester. This leads in the limit to a cyclic pathway, again as illustrated for the NMP reaction with the ester. Such a process might well possess



both the activation entropy and the ring-size effect in the lactam solvent found for this reaction, but the activation enthalpy expected for such a process would be higher.[19] Our data, however, do not allow a clear differentiation between this mode of cleavage and the earlier one of stepwise attacks, first by NMP on the sulfinic ester and next by alkoxide ion on **6**.

The detection of **3** and **4** under certain conditions (see earlier) of the cleavage of **1** as well as (presumably) pentenes and some neopentyl alcohol from **1** in solvents like DMF, malonic ester, and N,N-dimethylpivalamide suggests other decomposition pathways in addition to the major one previously mentioned. In addition, the concomitant formation of *t*-amyl and neopentyl alcohols from **1** in γ-butyrolactone warrants explanation. All these facts can be rationalized by assuming a slight dissociation[11] of **1** in polar solvents (but not in nonpolar ones like hexadecane or cumene where the cleavage failed totally), followed by the indicated reactions as shown. The products **3**, **4**,



and the pentenes can thus be explained by a combination of reactions 1, 2,[20] and 3. The slight formation of neopentyl alcohol in DMF, etc., can likewise be a consequence of reactions 1, 2, and 4. Reaction 4 is unlikely to be major in the basic amide solvents[7] where *p*-toluenesulfonic acid can be largely neutralized (*cf.* **4**). So the alcohol yield is low in these amide solvents that cannot cleave **1** by the SN mechanism. As the alcohol formation is low, isomerization *via* reaction 5 would be difficult to detect. The nonbasic γ-butyrolactone, on the other hand, would readily allow both reactions 4 and 5, and in this way afford rearranged product. *t*-Amyl alcohol should also have resulted from **1** in the nonbasic malonic ester solvent, but again the low alcohol yield could have precluded its observation. It should be stressed that reactions 1–5 are minor in the efficacious solvents like NMP, particularly when the

(17) The aprotic solvent environment would not solvate the alkoxide ion and its resulting basicity would be appreciably greater than normally observed (*e.g.*, in alcohol solvents).

(18) The ring-size effect could arise in the initial attack of the lactam on the ester. However, the catalytic effect of each of these three lactams in alkylations is nearly the same[15] and their basicities are in a different order (six- > seven- > five-membered ring) than that observed here.[15]

(19) Pyrolytic *cis* eliminations normally have Arrhenius E^{act} values some 30–40 kcal/mole higher than the ΔH^* observed in this work: C. H. DePuy and R. W. King, *Chem. Rev.*, **60**, 431 (1960). It is possible, however, that such reactions would have lower barriers in aprotic, high dielectric solvents if dipolar or ionic contributions in the transition state are important. Presumably the occurrence of the Cope amine oxide elimination in dimethyl sulfoxide at 0° is an illustration of this point: D. J. Cram, M. R. V. Sahyun, and G. R. Knox, *J. Am. Chem. Soc.*, **84**, 1734 (1962).

(20) This reaction has been studied in detail by J. L. Kice, G. Guaraldi, and C. G. Venier, *J. Org. Chem.*, **31**, 3561 (1966).

ester concentration is low. This is principally because the S_N cleavage is so fast under these conditions. Only when such solvents are used in limited amounts, or when the S_N process is precluded by the lack of proper structural features in the solvent, do these alternative decomposition paths then become significant.

Experimental Section

All melting points and boiling points are uncorrected for stem exposure. The former were taken on a calibrated Fisher-Johns block. Gas chromatography (glpc) was performed on either a Nester-Faust Anacro 1A or a Barber-Coleman No. 10 instrument; helium was used at 60 ml/min as the carrier gas. Nmr studies were done on both Varian A-60 and A-60A instruments. The resonances indicated are for the italicized protons and are relative to tetramethylsilane internal standard. The abbreviations used are s, singlet; d, doublet; t, triplet; and m, multiplet. The δ values given in italics are line positions. Otherwise they are true chemical shifts.[21] Infrared spectra were recorded on either a Beckman IR-5A or a Perkin-Elmer Infracord machine using sodium chloride optics. Optical activity was measured on neat liquids with a Rudolph No. 62 Standard Model polarimeter. Microanalyses were done by Micro-Tech Laboratories, Skokie, Ill., or by Abbott Laboratories, North Chicago, Ill. The preparations and reactions were carried out a number of times but only a representative procedure is given for each case.

Neopentyl *p*-toluenesulfinate (1) was prepared by dropwise addition of *p*-toluenesulfinyl chloride[22] (30 g, 0.17 mole) with stirring to neopentyl alcohol (Aldrich Chemical Co., Inc., 15 g, 0.17 mole) and pyridine (13.4 g, 0.17 mole) in dry ether (350 ml) at 0°. After 2 hr at this temperature the material was filtered and the filtrate was washed successively with hydrochloric acid (2 *N*), water, aqueous sodium bicarbonate solution (5%), and again with water. After being dried over magnesium sulfate, the solution was freed of ether and distilled. The ester was a colorless oil: 14.1 g (55.5%); bp 110–114° (0.5 mm); $n^{25}D$ 1.5115; $d^{23.5}_4$ 1.037; λ^{neat} 8.86 μ (S=O); δ^{CCl_4} 7.58 d, 7.38 d (Ar*H*, A_2B_2, J = 7 cps), 3.70 d, 3.18 d (CH_2OSO, AB, J = 10 cps), 2.42 s (ArCH_3), 0.89 s [$C(CH_3)_3$].

Anal. Calcd for $C_{12}H_{18}O_2S$: C, 63.68; H, 8.01. Found: C, 63.39; H, 7.76.

(−)-2-Octyl (±)-*p*-toluenesulfinate (2) was prepared similarly from (−)-2-octanol[23] [bp 86° (20 mm), $[\alpha]^{25}D$ −9.1°; lit.[4] $[\alpha]^{17}D$ −9.9°] and *p*-toluenesulfinyl chloride in ether containing pyridine. The ester (a mixture of diastereomers) was a colorless oil: 56%, bp 153–160° (1 mm), $n^{25}D$ 1.5068, $[\alpha]^{25}D$ −21° (lit.[4] $n^{25}D$ 1.5065, $[\alpha]^{22}D$ −22.16°), λ^{neat} 8.81 μ (S=O).

Other *p*-toluenesulfinic esters[24] were also prepared in this way. The yield of **methyl ester** was 65%; $n^{11}D$ 1.5458; d^{27}_4 1.156; λ^{neat} 8.80 μ (S=O); δ^{CCl_4} 7.45 d, 7.24 d (Ar*H*, A_2B_2, J = 8 cps), 3.29 s ($SOOCH_3$), 2.38 s (ArCH_3), [lit.[25] bp 129–130° (14 mm)]. The yield of **cyclopropylcarbinyl ester** was 40.5%; $n^{14}D$ 1.5447; d^{25}_4 1.127; λ^{neat} 8.81 μ (S=O); δ^{CCl_4} 7.60 d, 7.35 d (Ar*H*, A_2B_2, J = 7 cps), 3.83 m, 3.49 m (CH_2OSO, *ABX*, J_{AB} = 10 cps), 2.42 s (ArCH_3), *1.37–0.33* m (cyclopropyl *H*'s).

Anal. Calcd for $C_{11}H_{14}O_2S$: C, 62.82; H, 6.71. Found: C, 63.04; H, 6.75.

The yield of **benzyl ester** was 52%; $n^{12}D$ 1.5863; d^{22}_4 1.168; λ^{neat} 8.83 μ (S=O), δ^{CCl_4} 7.49 d, 7.19 d (Ar*H*, A_2B_2, J = 8 cps), 7.13 s ($C_6H_5CH_2$), 4.87 d, 4.33 d (CH_2OSO, AB, J = 11 cps), 2.38 s (ArCH_3) (lit.[25] mp 22–24°). The **neophyl ester** was crude material which decomposed on attempted distillation: *ca.* 30%, λ^{neat} 8.83 μ (S=O); δ^{CCl_4} 7.02 d, 7.38 d (Ar*H*, A_2B_2, J = 8 cps), 7.08 s (C_6H_5), 3.90 d, 3.31 d (CH_2OSO, AB, J = 10 cps), 2.35 s (ArCH_3), 1.28 s [$C(CH_3)_2$–]. The **norbornyl-1-carbinyl** and **1-bicyclo[2.2.2]octyl esters** which have been described earlier[2] were also prepared.

p-**Tolyl *p*-toluenethiolsulfonate** (3) was prepared by oxidation of *p*-tolyl disulfide (Aldrich Chemical Co.) with hydrogen peroxide in acetic acid as reported:[26] mp 75–77°, λ^{Nujol} 7.52, 8.75 μ (SO_2) (lit.[26] mp 77–79°).

N-Methyl-2-pyrrolidonium tosylate (4) was obtained by the addition of *p*-toluenesulfonic acid monohydrate (19 g, 0.1 mole) to NMP (39.9 g, 0.3 mole). Heat was evolved, after which the solution was heated at 100° for 15 min, chilled in ice, and treated with hexadecane (75 ml). The precipitated solid was collected, washed with ether, and recrystallized from ethanol several times: 14.2 g (52.5%), mp 121–122°; λ^{CHCl_3} 2.73 (very weak, OH ?), 5.99 (strong, amide C=O or C=N+), 8.50 μ (broad, strong, SO_3^-); δ^{CDCl_3} 15.66 s (enolic *H*, appears to be too deshielded for either N^+H or SO_3H[27]), 7.74 d, 7.19 d (Ar*H*, A_2B_2, J = 8 cps), 3.60 t (5-CH_2, J = 8 cps), 2.96 s (=N^+CH_3), 2.85 t (3-CH_2, J = *ca.* 8 cps; these protons are more deshielded than the analogous ones in NMP, suggesting a modification in the adjacent carbonyl structure), 2.36 s (ArCH_3), *2.22–1.99* m (4-CH_2).

Anal. Calcd for $C_{12}H_{17}NO_4S$: C, 53.11; H, 6.32; N, 5.16; O, 23.59; S, 11.82. Found: C, 53.19; H, 6.29; N, 5.09; O, 23.30; S, 11.65.

Aprotic Solvent Preparation and/or Purification.—**N-Methyl-2-pyrrolidone** (NMP, a generous gift from the General Aniline and Film Corp.) was purified from the minor contaminant γ-butyrolactone by treatment with aqueous base followed by neutralization with sodium bisulfate and eventual distillation.[28] The lactam was homogeneous on several glpc columns and had bp 204–205° (1 atm). **3,3-Dideuterio-N-methyl-2-pyrrolidone** was prepared as described:[6] bp 205° (1 atm); $n^{25}D$ 1.4672; λ^{neat} 4.52, 4.7 μ (CD); δ^{CDCl_3} 3.41 t (5-CH_2, J = 7 cps), 3.0 s (NCH_3), 2.01 t (broad, 4-CH_2, J = 7 cps). From the nmr spectrum the NMP was over 95% 3,3-d_2. **N-Methyl-ε-caprolactam** was prepared by methylation of ε-caprolactam (a gift from the Abbott Laboratories) with dimethyl sulfate, as described:[29] bp 110° (16 mm), $n^{25}D$ 1.4812 [lit.[29] bp 120° (19 mm), $n^{25}D$ 1.4818]. **N,N-Dimethylpivalamide** was synthesized from pivalyl chloride (Aldrich Chemical Co.) and anhydrous dimethylamine in ether as reported:[30] very minty odor, bp 183–185° (1 atm), $n^{25}D$ 1.4385 [lit.[30] bp 185–186° (750 mm), $n^{25}D$ 1.4431–1.4428]. All the other solvents in Table I were commercial chemicals redistilled to glpc homogeneity prior to use in this study.

Cleavage of Neopentyl *p*-Toluenesulfinate (1).—A flask containing a solution of 1 (1 g) in NMP (10 ml) was immersed in a bath at 180° under reflux. After 15 min the dark solution was cooled in ice and analyzed for neopentyl alcohol by glpc [175°, 6 ft × 3/8 in. column of Dow Corning silicone oil (25%) and ethylene glycol (6%) on firebrick]. The alcohol yield varied from 65 to 85% over several experiments, as determined by integration of its peak area in comparison with standards. Cleavages in other solvents were performed in the same way, though on one-half the scale of the experiment described. Only neopentyl alcohol and solvent peaks were observed in the glpc of these cleavages, except for small forepeaks that had the retention times of pentenes (obtained for comparison by dehydration of *t*-amyl alcohol) and in the case of γ-butyrolactone a resolved peak confirmed as *t*-amyl alcohol. For other solvents this cleavage gave the alcohol yields listed in Table I, though in those solvents where little or no conversion occurred the heating at 180° was continued for as long as 3 hr. The infrared spectrum of 1 was unchanged after its recovery from attempted cleavages in hexadecane and cumene solvents.

Cleavage of 1 (5 g) in less NMP (5 ml) than above but otherwise as before, gave neopentyl alcohol (68%) but, in addition, from the chilled reaction mixture there precipitated *p*-tolyl *p*-toluenethiolsulfonate 3 (200 mg, 6.6%, mp 74–75°, authenticated by comparison of spectra and mixture melting point with synthetic material). From another cleavage of 1 (2.26 g, 0.01 mole) in an equivalent of NMP (0.99 g, 0.01 mole) in hexadecane (10 ml) at 180° for 15 min, a 72% yield of alcohol was obtained (glpc). Again the chilled reaction material deposited a solid which was triturated with pentane and recrystallized from ethanol. This

(21) The patterns were mostly AB or A_2B_2 and the midpoints of the doubled doublets were chosen for δ.

(22) F. Kurzer, "Organic Syntheses," Coll. Vol. IV, John Wiley and Sons, Inc., New York, N. Y., 1963, p 937.

(23) J. Kenyon, "Organic Syntheses," Coll. Vol. II, John Wiley and Sons, Inc., New York, N. Y., 1950, p 418.

(24) Some of these were purified by molecular distillation, and so their boiling points were not determined.

(25) A. H. Wragg, J. S. McFadyen, and T. S. Stevens, *J. Chem. Soc.*, 3603 (1958).

(26) O. Hinsberg, *Ber.*, **41**, 2836 (1908).

(27) $>N^+H$ (δ 7.7–7.1 in trifluoroacetic acid) and $-SO_3H$ (δ 12–11) are listed in J. R. Dyer, "Applications of Absorption Spectroscopy of Organic Compounds," Prentice-Hall, Inc., Englewood Cliffs, N. J., 1965, p 85.

(28) H. E. Clements (to Monsanto Chemical Co.), U. S. Patent 2,964,535 (Dec 13, 1960); *Chem. Abstr.*, **55**, 8432g (1961).

(29) R. E. Benson and T. L. Cairns, *J. Am. Chem. Soc.*, **70**, 2115 (1948).

(30) L. Franchimont, *Rec. Trav. Chim.*, **6**, 241 (1904).

solid (240 mg, 9% based on NMP,[31] mp 121.5–123°) was identified as N-methyl-2-pyrrolidonium tosylate **4** by spectral comparison and mixture melting point with authentic material.

Anal. Calcd for $C_{12}H_{17}NO_4S$: C, 53.11; H, 6.32; N, 5.15; O, 23.59; S, 11.82. Found: C, 52.58; H, 6.12; N, 5.11; O, 24.02; S, 12.12.

Cleavage of 1 in Deuterated NMP.—Ester **1** (31 mmoles) was dissolved in 3,3-dideuterio-N-methyl-2-pyrrolidone[6] (133 mmoles) and held at 150° for 20 min. An aliquot was then treated *via* glpc [175°, 6 ft × 3/8 in. column of silicone L-46 (20%) on Chromosorb W—no hydroxylic substrate was used to prevent exchange] and the eluted neopentyl alcohol was collected in carbon tetrachloride. Nmr analysis showed the neopentyl alcohol was hydroxyl deuterated (integration and correspondence of spectra with *bona fide* neopentyl alcohol O-D).

Cleavage of (−)-2-Octyl (±)-*p*-Toluenesulfinate (2).—A large-scale cleavage of ester **2** (45 g, 0.168 mole) in NMP (39.6 g, 0.40 mole) at 165° for 30 min was processed by preparative glpc (silicone oil–glycol column) to obtain sufficient alcohol for optical purity studies. (−)-2-Octanol (4.6 g, $n^{25}D$ 1.4248, infrared spectrum correct, 21%) was collected, though the actual yield was considerably higher, and it showed $[\alpha]^{25}D$ −8.81° (97% retention based on original purity of alcohol used to make **2**).

Kinetic Study.—Ester **1** (5 g, 22 mmoles) in NMP (50 ml) was heated at a constant temperature (see Table II). Aliquots (20 μl) were taken every 3 min and analyzed for neopentyl alcohol by glpc on the silicone oil–glycol column. Its peak area was divided by that obtained from 20 μl of a solution of 22 mmoles of neopentyl alcohol in 50 ml of NMP. In this way the percentage alcohol formed in a given time was obtained. The pseudo-first-order rate constant was then obtained by plotting ln [100/(100 − per cent alcohol)] *vs.* time and calculating the slope of the visually best straight-line fit. With the exception of the first points, good first-order kinetics were observed. An Arrhenius plot gave E^{act} which was taken to be, within ±10% error, ΔH^* also. ΔS^* was then calculated from the Eyring equation. The data for the 120° run are given in Table III.

TABLE III

KINETICS OF CLEAVAGE OF 1 IN NMP AT 120°

Time, sec	Peak area, cm^2 [a]	% alcohol (x)	Ln 100/(100 − x)	10^4k_1, sec^{-1}
180	0.16	3.5	0.040	...[b]
360	1.28	28.0	0.322	9.0
540	2.05	44.5	0.588	10.9
720	2.42	52.6	0.746	10.4
900	2.77	60.2	0.920	10.2

[a] 100% alcohol = 4.6 cm^2. [b] Neglected.

(31) If all the sulfonic acid arose from sulfinic acid by eq 2 this yield would be 27% based on ester **1**.

Registry No.—**1**, 13146-08-2; **2**, 13146-09-3; **3**, 2943-42-2; **4**, 13146-11-7; methyl *p*-toluenesulfinate, 672-78-6; cyclopropylcarbinyl *p*-toluenesulfinate, 13146-12-8; benzyl *p*-toluenesulfinate, 13146-13-9; neophyl *p*-toluenesulfinate, 13146-14-0; 3,3-dideuterio-N-methyl-2-pyrrolidone, 932-07-0.

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The Overoxidation of Carbohydrates with Sodium Metaperiodate[1]

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The periodate oxidation of 1,4-anhydroallitol (I), which serves as a model for the periodate oxidation of naturally occurring oligosaccharides, has been examined in the pH range 3–7.5. The overoxidation process which occurs has been shown to require the prior formation of 2,3-dihydro-6-formyl-3-hydroxy-1,4-dioxine (IV), which is hydroxylated by periodate to give a product which is further oxidized in a normal fashion. Compound IV has a strong absorption band in the ultraviolet (E^{M}_{278} = 2.49 × 10^4 at pH 8.5) which can be used as an index of the presence of this compound during the oxidation. The structure of IV in solution has been examined by nmr spectroscopy and its rate of formation and oxidation have been shown to be consistent with its being an important intermediate in the overoxidation of I.

Oxidation with sodium metaperiodate is one of the most useful tools for the exploration of the structures of carbohydrates and compounds containing oxidizable functions α to each other. Normal oxidations involve adjacent hydroxyl, amino, carbonyl, or carboxyl functions in any combination, and the consumption of 1 molar equiv of periodate results in the cleavage of the carbon–carbon bond between the functional groups and the oxidation of each group to the next highest oxidation state. When only normal oxidation occurs, it is possible to deduce from the consumption of periodate and the quantities of the various oxidation products a great deal about the structure of the compound being oxidized. However, a number of structural features have been found which react with periodate in atypical ways leading to considerable ambiguity in the interpretation of the results of periodate oxidations. Some of these structural features are readily discernible, and the abnormal oxidation associated with them can be taken into account. For example, sulfur-containing compounds can consume periodate with the formation of sulfoxides or sulfones with or without cleavage of carbon–carbon bonds.[2,3] The presence of sulfur is readily detected, and its presence requires that consideration be given to its consumption of oxidant. Other structural features are not associated with such an obvious marker and can severely limit the utility of the periodate method. The most important of these is the active methylene group which is produced as a result of normal oxidations of a variety of carbohydrates and which is almost always produced in the oxidation of naturally occurring

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