aryl-4-hydroxy-3-methyl-2-butanones. The variation in slope is less than that observed for the same compounds in aqueous solution. The observations of rate–acidity function correlation cover both reactions which do not follow H_0 in aqueous sulfuric acid (the halogenation of ketones and the dehydration of some hydroxyketones[26]) and reactions which do parallel the acidity function (the depolymerization of trioxane and pina col rearrangement[46]). From the fairly wide range of slopes observed, it is apparent that the interpretation of acidity dependence in anhydrous acetic acid needs to be approached with a great deal of caution. We conclude at the present time that the acidity function will be useful for correlating rates in acetic acid solvent, but that the acidity function will not be valuable as a criterion of detailed mechanism in this solvent. In other words, the usual result will be correlation with the measured acidity function regardless of the detailed mechanism for acid catalysis. If a reaction specificially involves water (as the hydrolysis of an ester) then deviations will be observed which may be correlated with the changing activity of water as reported by Noyce and Snyder.[45]

Further studies in 50% aqueous acetic acid would be useful.

(46) H. J. Gebhart and K. H. Adams, THIS JOURNAL, **76**, 3925 (1954).

BERKELEY 4, CALIF.

[CONTRIBUTION NO. 280 FROM THE RESEARCH DIVISION, JACKSON LABORATORY, ORGANIC CHEMICALS DEPARTMENT, E. I. DU PONT DE NEMOURS AND CO.]

The Preparation of Olefins from Arylsulfonate Esters of Alcohols[1]

BY HAROLD R. NACE[2]

RECEIVED MARCH 28, 1959

Dimethyl sulfoxide, hexamethylphosphoramide and, to a lesser extent, dimethyl- and diethylformamide, have been found to be excellent non-reacting solvents for the decomposition of (−)-menthyl, β-cholestanyl, cyclohexyl and 2-octyl arylsulfonates to the corresponding olefins.

The solvolysis of an aryl sulfonate ester of a secondary alcohol to give the corresponding olefin is a well-known and widely employed reaction.[3-7] However, the reaction is frequently complicated by nucleophilic attack of the solvent on the carbinol carbon, causing the formation of varying amounts of substitution product, and thus lowering the yield of olefin. Indeed, in certain cases the substitution product predominates.[4,6]

Several solvents are reported here which, while promoting decomposition to the olefin, appear to be non-nucleophilic with respect to the carbinol carbon and thus lead to high yields of olefins. These are the highly polar solvents dimethyl sulfoxide, hexamethylphosphoramide, dimethylformamide and diethylformamide.

Dimethyl sulfoxide has been known for some time as an excellent solvent[8] for many classes of organic compounds. In recent publications Kornblum[9] and Major and Hess[10] reported one of the few cases in which dimethyl sulfoxide reacted with the solute, *viz.*, the conversion of an α-bromoketone to the corresponding diketone. In all of the cases reported the halo-ketone was of the type

$$\text{aryl-}\overset{\overset{\text{O}}{\|}}{\text{C}}\text{–CHBr-aryl or aryl-}\overset{\overset{\text{O}}{\|}}{\text{C}}\text{–CH}_2\text{Br}$$

where elimination was not possible. Tien and Hunsberger[11] reported that ethyl bromoacetate and dimethyl sulfoxide reacted to give ethyl glyoxylate in excellent yield. Although the mechanism of this reaction is not well understood at present, Tien and Hunsberger[11] and Major and Hess[10] have presented evidence that the dimethyl sulfoxide was undergoing change in the reaction, since dimethyl sulfide and trimethylsulfonium bromide were isolated from the reaction mixture.

In the case of arylsulfonates of secondary alcohols, a smooth decomposition to the olefin is accomplished by simply heating, at temperatures in the neighborhood of 100°, a solution of the sulfonate ester in dimethyl sulfoxide. The progress of the reaction can be conveniently followed by titration of the arylsulfonic acid produced, and the olefin is readily isolated by adding the reaction mixture to water, and collecting the insoluble olefin by filtration or extraction. Isomerization or decomposition of olefins sensitive to sulfonic acids can be minimized by the addition of sodium bicarbonate to the reaction mixture in an amount at least equivalent to the quantity of sulfonate ester used.

The decomposition of (−)-menthyl arylsulfonates (Table I) in dimethyl sulfoxide afforded a mixture of (+)-Δ^2- and (+)-Δ^3-menthenes, in which the Δ^3-isomer predominated. The olefin

(1) H. R. Nace, *Chemistry & Industry*, 1629 (1958).

(2) Department of Chemistry, Brown University, Providence 12, R. I.

(3) (a) W. Hückel, *Ann.*, **533**, 1 (1937); (b) W. Hückel and W. Tappe, *ibid.*, **537**, 113 (1939); (c) W. Hückel, W. Tappe and G. Legutke, *ibid.*, **543**, 191 (1940); (d) W. Hückel and H. D. Sauerland, *ibid.*, **592**, 190 (1955); (e) J. von Euw and T. Reichstein, *Helv. Chim. Acta*, **29**, 654 (1946); A. Ruff and T. Reichstein, *ibid.*, **34**, 70 (1951).

(4) S. Winstein, B. K. Morse, E. Grunwald, H. W. Jones, J. Corse, D. Trifan and H. Marshall, THIS JOURNAL, **74**, 1127 (1952).

(5) R. E. Robertson, *Can. J. Chem.*, **31**, 589 (1953).

(6) H. R. Nace, THIS JOURNAL, **74**, 5937 (1952); N. Pappas, J. A. Meschino, A. A. Fournier and H. R. Nace, *ibid.*, **78**, 1907 (1956).

(7) R. T. Blickenstaff and F. C. Chang, *ibid.*, **80**, 2726 (1958).

(8) *Cf.* Technical Bulletin on dimethyl sulfoxide published by the Stepan Chemical Co.

(9) N. Kornblum, J. W. Powers, G. J. Anderson, W. J. Jones, H. O. Larsen, O. Levand and W. M. Weaver, THIS JOURNAL, **79**, 6562 (1957).

(10) R. T. Major and H. J. Hess, *J. Org. Chem.*, **23**, 1563 (1958).

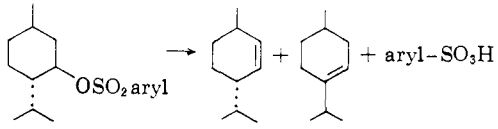
(11) J. M. Tien and I. M. Hunsberger, A.C.S. Abstracts, 134th National Meeting, September, 1958 p. 75-P.

TABLE I

DECOMPOSITION OF (−)-MENTHYL ARYLSULFONATES IN VARIOUS SOLVENTS

Sulfonate	Solvent	Temp., °C.	Time, hours	Yield of menthenes, %	Δ^2-, %	Racemization of Δ^3-, %
Benzene	Dimethyl sulfoxide	89–91	6	80	20.5	47
Benzene	Dimethyl sulfoxide plus 1 equiv. of $NaHCO_3$	100	5	80	39	14
p-Toluene	Dimethyl sulfoxide	100	10	78	35	73
p-Bromobenzene	Dimethyl sulfoxide	100	5	83	33	63
Benzene	Hexamethylphosphoramide	100	17	77	39	43
p-Toluene	Hexamethylphosphoramide	100	10	78	30	26
Benzene	Dimethylformamide	95–100	24	67	14	95
Benzene	Dimethylformamide	100	24	75	..	..
Benzene	Diethylformamide	100	23	60	..	..
Benzene	Pyridine	86–88	49.5	37	32	55

composition was determined by the method of Barton, Head and Williams.[12] This method at the same time allows the calculation of the amount of racemization of the Δ^3-menthene taking place during the elimination reaction. As can be seen



from Table I, there is considerable racemization, but this is markedly reduced in the one case studied by the addition of sodium bicarbonate. The racemization is undoubtedly due to reaction of the Δ^3-menthene with the arylsulfonic acid.[3c]

The olefin composition observed appears to eliminate the possibility that the reaction involves a *trans* elimination, since this would produce only Δ^2-menthene.

It was observed that the ease of decomposition with respect to the arylsulfonate group increased in the order *p*-toluenesulfonate < benzenesulfonate < *p*-bromobenzenesulfonate, suggesting that electronegative substituents on the aromatic ring facilitate the decomposition.

These results indicate that the *p*-toluenesulfonate esters, which are the most frequently used in synthetic work for olefin formation *via* solvolysis, are less desirable for this purpose than the benzenesulfonates.

In the case of 3β-cholestanyl arylsulfonates, a marked improvement in yield of olefins was obtained by the use of dimethyl sulfoxide (Table II) in place of methanol or *t*-butyl alcohol.[6] For comparison, 3β-cholestanyl *p*-toluenesulfonate in methanol required 72 hours for complete reaction and gave only 17% of a Δ^2- and Δ^3-cholestene mixture and 73% of 3α-cholestanyl methyl ether.[6]

The decomposition of cyclohexyl- and *sec*-octyl arylsulfonates (Table III) in dimethyl sulfoxide supply further examples of the utility of the reaction.

The substitution of hexamethyl phosphoramide, $[(CH_3)_2N]_3PO$, for dimethyl sulfoxide gave comparable reaction times and yields of olefins (Table I, II, III). In the case of (−)-menthyl arylsulfonates, the olefin composition was the same as that observed with dimethyl sulfoxide while the extent of racemization of the Δ^3-menthene appeared to be somewhat lower.

(12) D. H. R. Barton, A. J. Head and R. J. Williams, *J. Chem. Soc.*, 453 (1952).

TABLE II

DECOMPOSITION OF 3β-CHOLESTANYL SULFONATES IN VARIOUS SOLVENTS

Sulfonate	Solvent	Temp., °C.	Time, hr.	Yield of cholestenes, %
Benzene	Dimethyl sulfoxide	100	2.5	82
p-Toluene	Dimethyl sulfoxide	98–100	5	59
Methyl	Dimethyl sulfoxide	95–100	5	45
Benzene	Hexamethylphosphoramide	100	21	53
Benzene	Dimethylformamide	100	7	22

The use of dimethylformamide in place of the two above solvents indicated that it was the least useful of the three in promoting the elimination reaction. With (−)-menthyl benzenesulfonate, the yields were somewhat lower, while the time required for complete reaction was considerably longer (Table I). In view of this, the reactions of the 3β-cholestanyl, cyclohexyl and *sec*-octyl arylsulfonates in this solvent (Tables II, III) were only examined cursorily to determine whether or not a significant amount of elimination had occurred.

After this work had been completed, Chang and Blickenstaff[13] reported that under conditions somewhat different from those reported here, dimethylformamide and related acylamides reacted with steroid tosylates to give the inverted formate esters. In some cases, the substitution product was accompanied by varying amounts of olefins, and the amount of olefin formed appeared to increase if the reaction temperature was raised.

The relation of their work to the experiments with dimethylformamide reported here is not clear at present. However, it should be noted that (−)-menthyl benzenesulfonate and cyclohexyl *p*-toluenesulfonate both gave olefins in yields greater than 50%. No attempt was made to isolate the corresponding formates, and it is quite possible that they were present in the reaction mixture. Further study of the factors which determine whether substitution or elimination predominates in the reaction of dimethylformamide and related compounds with sulfonate esters seems desirable.

Pyridine and related heterocyclic amines have frequently been used[3a,7] for the decomposition of arylsulfonate esters to olefins and arylsulfonic acid. In order to provide a direct comparison with the solvents studied above, (−)-menthyl benzene-

(13) F. C. Chang and R. T. Blickenstaff, THIS JOURNAL, **80**, 2906 (1958).

TABLE III

REACTIONS OF VARIOUS SULFONATES

Sulfonate	Solvent	Temp., °C	Time, hr.	Product	Yield, %
Cyclohexyl benzene-	Dimethyl sulfoxide	90–95	2	Cyclohexene	65
Cyclohexyl *p*-toluene-	Dimethyl sulfoxide	90–95	5	Cyclohexene	61
Cyclohexyl *p*-toluene-	Hexamethylphosphoramide	100	6	Cyclohexene	62
Cyclohexyl *p*-toluene-	Dimethylformamide	100	5.5	Cyclohexene	55
2-Octyl benzene-	Dimethyl sulfoxide	100–107	0.75	Octene	52
2-Octyl benzene-	Dimethyl sulfoxide	100	1	Octene	58
2-Octyl 2-naphthalene-	Dimethyl sulfoxide	100	1	Octene	30
2-Octyl benzene-	Hexamethylphosphoramide	100	3	Octene	61.5

sulfonate was heated in pyridine solution. The reaction was considerably slower, and a much lower yield of menthenes was obtained (Table I). The olefin composition and degree of racemization of the Δ^3-menthene were similar to those obtained with the other solvents. Hence, it seems likely that pyridine and related bases also promote the decomposition of sulfonate esters by a solvolytic ionization route, although much less effectively.

In summary, the available evidence suggests that in the formation of olefins from sulfonate esters of secondary alcohols, dimethyl sulfoxide and hexamethyl phosphoramide function as highly polar non-reacting solvents, and promote the decomposition by an ionic path.

Experimental

Solvolysis of (−)-Menthyl Benzenesulfonate in Dimethyl Sulfoxide.—A solution of 29.6 g. (0.10 mole) of (−)-menthyl benzenesulfonate in 150 ml. of dimethyl sulfoxide (Stepan Chemical Co.) was heated (solution temperature 89–91°) under reflux for 6 hours. On allowing the solution to cool to room temperature, two layers formed. The mixture was extracted with 50 ml. of ligroin (b.p. 66–75°), which dissolved the upper layer. The lower layer was poured into an equal volume of a mixture of ice and water, and the resulting mixture was extracted with two 50-ml. portions of ligroin. All of the ligroin extracts were combined, washed with two 50-ml. portions of water, 50 ml. of saturated brine and then filtered through anhydrous sodium sulfate. The ligroin was removed by distillation through a 7" Vigreux column and the residue was fractionated with an efficient semi-micro column.[14] Five fractions were collected and combined to give 10.5 g. (76%) of mixed menthenes, b.p. 60–61.5° (17–19 mm.), $n^{25}D$ 1.4495 − 1.4500, $[\alpha]D$ +85° (1% in $CHCl_3$); reported[15] for a mixture containing 24% Δ^2-menthene, b.p. 64.5–65° (22 mm.), $n^{25}D$ 1.4500, $[\alpha]D$ +117° (1% in $CHCl_3$). The residue (1.53 g.) solidified and a mixture m.p. with (−)-menthyl benzenesulfonate (m.p. 79–79.5° (cor.)) was 77–79°. The yield of menthenes was 80% based on recovered starting material.

A 500-mg. sample of the menthenes was racemized with hydrogen chloride in chloroform[12] and had $[\alpha]D$ +27° (1% in $CHCl_3$) after racemization, corresponding to 20.5% of Δ^2-menthene in the original mixture.

Solvolysis of β-Cholestanyl Benzenesulfonate in Dimethyl Sulfoxide.—A mixture of 250 mg. (0.46 millimole) of β-cholestanyl benzenesulfonate and 2.5 ml. of dimethyl sulfoxide was heated at 100° (a clear solution resulted soon after heating) for 150 minutes. When the solution was allowed to cool to room temperature a colorless oil separated which partially solidified on standing. The mixture was added to a mixture of ice and water, this mixture was neutralized with sodium bicarbonate, and the white solid which formed was collected by filtration, washed well with water, and recrystallized from aqueous ethanol. A yield of 139 mg. (82%) of a mixture of Δ^2- and Δ^3-cholestene was obtained, m.p. 69.5–70.5° (cor.).[6]

Solvolysis of Cyclohexyl Benzenesulfonate in Dimethyl Sulfoxide.—A solution of 24 g. (0.10 mole) of cyclohexyl benzenesulfonate in 100 ml. of dimethyl sulfoxide was heated in a distillation flask under a nitrogen atmosphere at 90–95° (130–160 mm.) for 2 hours. The receiver was cooled in a Dry Ice–acetone-bath, and when the reaction was complete, the receiver contents were fractionated through a semi-micro distillation column.[14] A yield of 5.34 g. (65%) of cyclohexene was obtained, b.p. 81–82.5°, $n^{25}D$ 1.4440–1.4444.

(14) C. W. Gould, Jr., G. Holzman and C. Niemann, *Anal. Chem.*, **20**, 361 (1948).

(15) H. R. Nace, D. G. Manly and S. Fusco, *J. Org. Chem.*, **23**, 687 (1958).

WILMINGTON 98, DEL.

[CONTRIBUTION FROM THE BOUND BROOK LABORATORIES, RESEARCH DIVISION, AMERICAN CYANAMID CO.]

Aliphatic Disulfinic Acids; The Unique Stability of 1,4-Butanedisulfinic Acid[1]

BY MICHAEL T. BEACHEM, JOHN T. SHAW, G. DANN SARGENT, ROBERT B. FORTENBAUGH AND JASON M. SALSBURY

RECEIVED JANUARY 9, 1959

The preparation of the first stable, crystalline, aliphatic disulfinic acid, 1,4-butanedisulfinic acid, is described. Other disulfinic acids are also described and their reactions with various α,β-unsaturated systems are reported. The preparation of 1,4-bis-(hydroxymethylsulfonyl)-butane and its reactions with various amides and aromatic amines are also reported.

This article reports the preparation and isolation of a stable, crystalline, aliphatic disulfinic acid, 1,4-butanedisulfinic acid. All of the lower aliphatic monosulfinic acids[2] are unstable and are usually prepared by the reduction of the corresponding sulfonyl chlorides with sodium sulfite under neutral or slightly alkaline conditions.[3] In 1948, Marvel and Johnson[4] prepared for the

(1) Presented before the Division of Organic Chemistry at the 133rd National Meeting, American Chemical Society, San Francisco, Calif., April 16, 1958.

(2) The chemistry of aliphatic sulfinic acids has been reviewed by (a) P. Allen, *J. Org. Chem.*, **7**, 23 (1942); (b) W. E. Truce and A. N. Murphy, *Chem. Revs.*, **48**, 69 (1951); (c) Houben-Weyl "Methoden der Organischen Chemie," 4th edition, George Thieme, Stuttgart, 1955, pp. 285–299.

(3) H. Bredereck and E. Bäder, *Chem. Ber.*, **87**, 129 (1954).

(4) C. S. Marvel and R. S. Johnson, *J. Org. Chem.*, **13**, 822 (1948).