TABLE I

ALKYLATE COMPOSITIONS

Alkylate composition, mole %	Experiment 1 Propylene	2 2-Methyl-2-butene	3 1-Pentene	4 4-Methyl-2-pentene	5 1-Hexene	6 Cyclohexene
Isopentane	3.1	36.2	31.6	22.4	8.3	1.3
n-Pentane	...	...	2.3	...	...	...
2,3-Dimethylbutane	2.4	5.7	1.2	3.3	0.7	1.2
2-Methylpentane	...	...	...	14.9	24.1	...
3-Methylpentane	...	1.3	0.1	4.5	12.8	...
n-Hexane	...	...	...	...	1.8	...
2,4-Dimethylpentane	21.9	1.5	0.5	2.1	1.0	...
2,3-Dimethylpentane, 2-methylhexane	52.2	1.8	0.2	3.5	0.3	...
Methylcyclopentane	...	...	...	...	...	30.5
Cyclohexane	...	...	...	...	...	...
2,2,4-Trimethylpentane	11.4	23.6	14.8	18.1	16.9	15.3
2,2,3-Trimethylpentane, 2,4- + 2,5-dimethylhexane	0.6	5.3	1.9	4.7	1.7	1.8
2,3,3- + 2,3,4-Trimethylpentane, 2,3-dimethylhexane	8.4	18.8	8.9	12.7	10.0	13.1
C_9	...	5.9	38.2	9.3	...	...
C_{10}	...	...	...	4.5	22.4	13.4[a]
Mole of paraffin[b]/mole of olefin	0.23	0.42	0.51	0.49	0.56	0.38
Mole of C_8/mole of olefin	0.16	0.57	0.38	0.78	0.40	0.23

[a] Possibly contains alkylated naphthenes. [b] Saturated paraffin having the same carbon number as the reactant olefin.

be an increase in octane formation. Since paraffins with the same carbon number as the reactant olefin are also formed by the alkylation–fission scheme, it is impossible to say how much is formed by this mechanism as compared to straight self-alkylation. It is clear, however, that considerably more alkylation–fission occurs with the isoolefins than with the normal olefins.

It is apparent from the preceding discussion that all the reaction products can be explained on the basis of classical carbonium ion reactions. However, the specific mechanistic route will depend to a large degree upon the reactant olefin. With normal olefins, the straight self-alkylation mechanism (reactions 2–5) appears to predominate. A normal hexene is particularly illustrative of this because alternative mechanisms would predict the formation of fairly large amounts of non-C_6 products. With isoolefins, an alkylation–fission sequence becomes increasingly important. This is borne out by the observed nonselectivity of the reactions with both the methylbutene and the methylpentene. Unfortunately, the general complexity makes it impossible to assess just how much of each mechanism is applicable to the different olefins.

Acknowledgment.—The author wishes to thank the Esso Research and Engineering Co. for permission to publish this work.

Identification of the Disultone from Sulfuryl Chloride and 1-Propanol

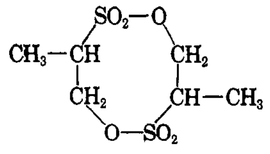
J. HODGE MARKGRAF,[1a] B. ANDES HESS, JR.,[1b] CHARLES W. NICHOLS,[1b] AND ROY W. KING[1c]

Departments of Chemistry, Williams College, Williamstown, Massachusetts, and Iowa State University, Ames, Iowa

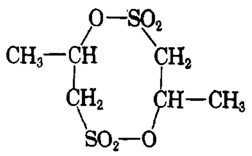
Received December 23, 1963

The crystalline product from the reaction of sulfuryl chloride with 1-propanol is assigned structure II on degradative and spectroscopic evidence. The mode of its formation is rationalized.

In 1952 Manecke[2] reported that sulfuryl chloride treatment of 1-propanol led to an eight-membered cyclic product to which he assigned structure I. Analytical and molecular weight data established the formula as $C_6H_{12}O_6S_2$, but it does not appear that alternate structures for the disultone were considered. Although hydrolytic and degradative reactions were reported, the structures of such products were not confirmed.



I



II

We have reinvestigated this reaction and established that the product is actually 4,8-dimethyl-1,5-dioxa-2,6-dithiacyclooctane 2,2,6,6-tetraoxide (II).[3] Repetition of Manecke's procedure afforded the same material in an over-all yield of 3% (the yield was not reported originally); modifications increased the yield

---

(1)(a) To whom inquiries should be addressed at Williams College; (b) based in part on the Honors theses of B.A.H., Jr. (1962), and C.W.N. (1960), Williams College; (c) Iowa State University.

(2) G. Manecke, *Chem. Ber.*, **85**, 160 (1952).

(3) The correct structure was originally proposed to us by Professor W. von E. Doering; his interest and encouragement in this work are gratefully acknowledged.

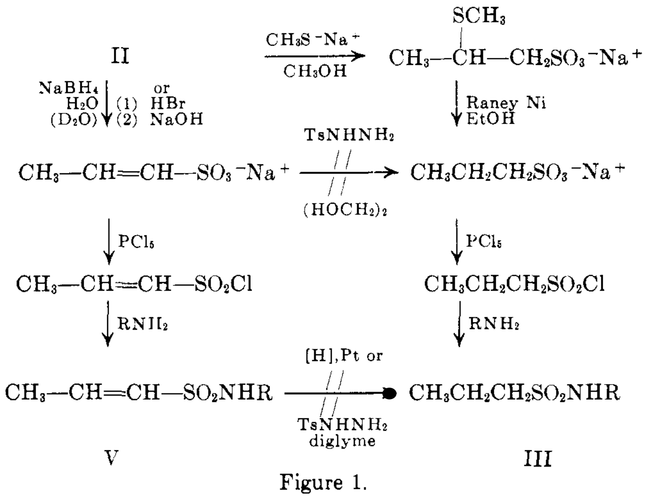


Figure 1.

to 25%. There is no doubt we have obtained the same compound, since analytical, molecular weight, and melting point data are in agreement. Manecke did not comment on the mode of formation of I, and it seemed to us that structure II may be mechanistically more reasonable.

Confirmation of structure II was obtained by degradation of the disultone to derivatives of 1-propanesulfonic acid. Authentic samples of sulfonamide derivatives (III and IV) of the isomeric propanesulfonic acids were prepared by known methods. Reductive

$$\underset{\text{III}}{CH_3CH_2CH_2SO_2NHR} \quad \underset{\text{IV}}{(CH_3)_2CHSO_2NHR}$$

a, R = *p*-tolyl
b, R = α-naphthyl

cleavage of the disultone with sodium borohydride appeared to be a satisfactory route to propanesulfonic acid derivatives. However, conversion of the sodium sulfonate to sulfonamide afforded material different from both III and IV. The infrared spectrum exhibited absorption similar to that for IIIb and, in addition, contained a peak at 10.5 μ characteristic of *trans* olefins.[4] The bromine test for unsaturation was positive. The compound was assigned the *trans*-N-aryl

$$\underset{\text{V}}{CH_3—CH{=}CH—SO_2NHR}$$

1-propene-1-sulfonamide structure (V) on the basis of its n.m.r. spectrum which was consistent only with a 1-propenesulfonamide: an ABX_3 system[5] similar to that worked out by Fessenden and Waugh.[6]

The chemistry of the 1-propenesulfonamide derivatives was interesting in regard to both the mechanism of generation and the resistance to reduction. Thus, hydrogenation of Vb → IIIb failed to occur with Adams catalyst. Furthermore, the attempted diimide reductions of Va and sodium 1-propene-1-sulfonate with tosylhydrazine by the method of van Tamelen[7] were unsuccessful; the unsaturated compound was recovered in each case. The fact that borohydride effected elimination rather than reduction raised the possibilities of a concerted process or a reversible formation of an intermediate carbanion. That the latter pathway was not operative was shown by the absence of deuterium in the product (*i.e.*, no $CH_3—CH{=}CD—SO_2NHR$) obtained from the disultone and sodium borohydride in deuterium oxide. This constitutes a sufficient condition for the concerted process since the degrees of freedom in the eight-membered ring permit a *trans* (E2) elimination to occur, regardless of the configuration (*vide infra*).[8,9] Hydrolysis of the disultone by hydrobromic acid also yielded the unsaturated acid. The generation of the olefinic linkage by acid catalysis must have occurred during ring opening because Marvel and Weil[10] used the same reagent to convert sodium 2-hydroxy-1-propanesulfonate to sodium 2-bromo-1-propanesulfonate.

Cleavage of the eight-membered ring without concomitant elimination was obtained with sodium methylmercaptide, which functioned as an effective nucleophile.[10] The resulting sodium 2-methylmercapto-1-propanesulfonate was converted to IIIa. These reactions are summarized in the accompanying flow chart (Fig. 1). Thus the assignment of structure II was unambiguous.[11]

The n.m.r. spectrum of the disultone was consistent with the assigned structure. Since both I and II would have the same coupling between protons, the chemical shift afforded the only basis for differentiation. In dimethyl sulfoxide the disultone showed a methyl doublet at τ 8.57 (J = 6.7 c.p.s.) and CH_2 and CH multiplets centered at τ 6.15 and 4.80, respectively. Irradiation of the methyl peak with a radiofrequency field of approximately 4.5 mgauss simplified the CH multiplet to four lines (Fig. 2). Their positions were found by replacing each one by a 1:3:3:1 quartet with the observed CH_3–CH coupling constant and thus assigning each peak of the original multiplet to its corresponding quartet. The four line positions obtained by averaging these quartets were analyzed with the methylene multiplet as an ABX system, giving ν_A = 233 c.p.s., ν_B = 229 c.p.s., ν_X = 312 c.p.s., J_{AB} = 14.8 c.p.s., J_{AX} = $\pm$1.3 c.p.s. and J_{BX} = $\pm$ 9.5 c.p.s. It was interesting that in this case, where $\nu_A - \nu_B$ was fortuitously equal to $^1/_2|J_{AX} - J_{BX}|$, one of the two quartets usually associated with the AB region collapsed to an intense singlet. In carbon tetrachloride solution the α-methylene protons of 1-propyl methanesulfonate and methyl 1-propanesulfonate appeared at τ 5.89 and 7.00, respectively, and the methine proton of 2-propyl methanesulfonate appeared at τ 5.15. The disultone methylene resonance at τ 6.15 might be consistent with either structure I or II. The methine protons, however, were at slightly lower field

---

[4] L. J. Bellamy, "The Infrared Spectra of Complex Molecules," John Wiley and Sons, Inc., New York, N. Y., 1956, p. 40.

[5] The vinyl–vinyl coupling constant (15.0 c.p.s.) showed these protons to be *trans* as in *trans*-propenylbenzene.[6]

[6] R. W. Fessenden and J. S. Waugh, *J. Chem. Phys.*, **30**, 944 (1959).

[7] E. E. van Tamelen, R. S. Dewey, M. F. Lease, and W. H. Pirkle [*J. Am. Chem. Soc.*, **83**, 4302 (1961)] successfully reduced allyl disulfide by this method; we thank Professor van Tamelen (private communication) for experimental details.

[8] E. L. Eliel, "Stereochemistry of Carbon Compounds," McGraw-Hill Book Company, Inc., New York, N. Y., 1962, pp. 253–254.

[9] The possibility of a two-stage mechanism involving formation of a carbanion in a rate-determining and irreversible step seems remote in the present case. Such an interpretation has been offered for *cis*-eliminations in some cyclic sulfones [H. L. Goering, D. I. Relyea, and K. L. Howe, *J. Am. Chem. Soc.*, **79**, 2502 (1957)], but not in the case of others [F. G. Bordwell and P. S. Landis, *ibid.*, **79**, 1593 (1957)].

[10] C. S. Marvel and E. D. Weil, *ibid.*, **76**, 61 (1954).

[11] Subsequent to the completion of this work a report appeared from which this structural assignment could be inferred. H. Schmitz, H. Grosspietsch, H. Kaltenhäuser, and H. Wendt [*Angew. Chem.*, **75**, 299 (1963)] observed that the barium salt of 1-hydroxy-2-propanesulfonic acid exhibited an infrared spectrum different from that of the hydroxypropanesulfonic acid obtained from the hydrolysis of "Manecke's" disultone. The latter compound was shown to be the isomeric 2-hydroxy-1-propanesulfonic acid.

than in 2-propyl methanesulfonate whereas, by analogy with the 1-propyl compounds, they should have been at considerably higher field if adjacent to sulfur instead of oxygen.

The preparation of a disultone from 1-propanol and sulfuryl chloride must proceed by the initial formation of 1-propyl chlorosulfonate (VI) as suggested by Manecke. We have isolated VI from the reaction

$$CH_3CH_2CH_2OH + SO_2Cl_2 \xrightarrow[-HCl]{0^\circ} \underset{VI}{CH_3CH_2CH_2OSO_2Cl} \quad (1)$$

mixture and subsequently converted the pure compound to II in enhanced yield. The transformation of VI to a system containing a primary carbon–sulfur linkage can be rationalized by an elimination–addition–dimerization sequence. The first two steps (eq.

$$VI \xrightarrow[\Delta]{} HCl + SO_3 + CH_3{-}CH{=}CH_2 \quad (2)$$

$$CH_3{-}CH{=}CH_2 \xrightarrow{SO_3} [CH_3{-}\overset{+}{C}H{-}CH_2{-}SO_2{-}O^-] \quad (3)$$

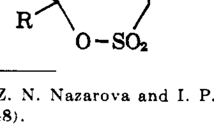
$$[CH_3{-}\overset{+}{C}H{-}CH_2{-}SO_2{-}O^-] \longrightarrow II \quad (4)$$

2 and 3) have been postulated by Nazarova and Tsukervanik[12] to account for the product obtained from the thermal decomposition of 1-propyl chlorosulfonate (eq. 5).[13] From the gaseous products evolved

$$VI \xrightarrow[\substack{(2)\ H_2O \\ (3)\ PbCO_3}]{(1)\ 80^\circ} [CH_3{-}CH(OH){-}CH_2SO_3]_2Pb \quad (5)$$

from the similar decomposition of isobutyl chlorosulfonate, these same authors isolated isobutylene (dibromide derivative). The reaction of olefins with sulfur trioxide (eq. 3) has been studied extensively.[14] Repeated attempts were made to test the postulated sequence (eq. 2–4) by the reaction of 2-propanol with sulfuryl chloride. The crude 2-propyl chlorosulfonate (VII) could not be purified, and its thermal decomposition afforded no disultone. The instability of VII has been noted previously,[12] however, and the greater tendency for isopropyl derivatives of related systems to decompose has been observed.[12,15]

It is interesting to note that the disultone can exist as diastereomers. The configuration in which the methyl groups are *trans* is *meso* (onefold alternating axis of symmetry), while an enantiomeric pair is possible for the *cis* isomer (twofold axis of symmetry). Resolution studies were not undertaken with compound II.



VIII, R = R′ = H
IX, R = H; R′ = Ph
X, R = R′ = CH₃

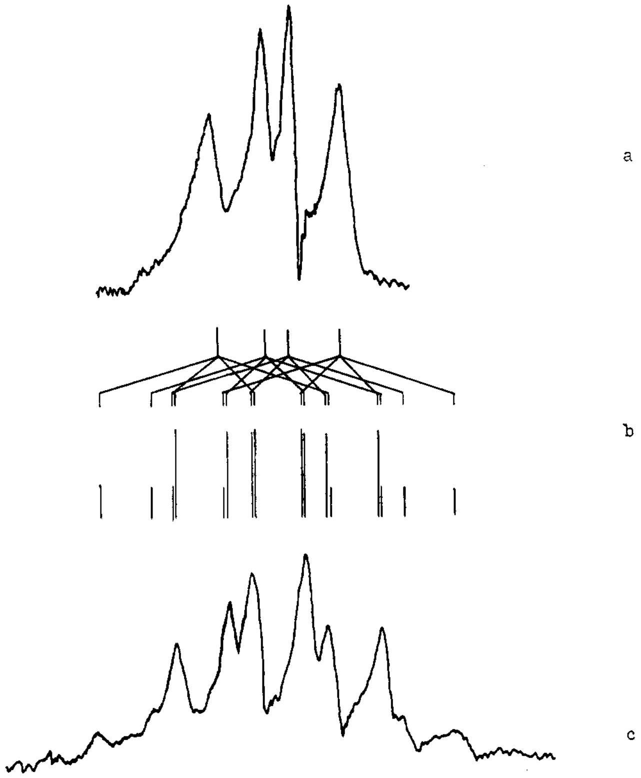


Fig. 2.—(a) N.m.r. spectrum at 60 Mc. of methine protons of disultone with CH_3 irradiated with 4.5 mgauss radiofrequency field; (b) theoretical spectrum of CH region; and (c) observed multiplet.

Only two other examples of eight-membered disultones have been reported. Manecke and Danhäuser[16] prepared the disultone of isethionic acid (VIII) by the vacuum distillation of bis(2-sulfoethyl) ether. Bordwell, *et al.*,[14b] isolated the relatively unstable compound IX from the sulfonation of styrene. From the thermal decomposition of isobutyl chlorosulfonate Nazarova and Tsukervanik[12] obtained the lead salt of a hydroxybutanesulfonic acid which, when allowed to stand 3 weeks over sulfuric acid, was reported to form an unidentified anhydride. The structure of this compound could be X, although their data were ambiguous.[17]

Experimental[18]

4,8-Dimethyl-1,5-dioxa-2,6-dithiacyclooctane 2,2,6,6-Tetraoxide (II). A.—The method of Manecke[2] was followed. To sulfuryl chloride (42.8 g., 0.317 mole) contained in a three-necked flask fitted with a drying tube, thermometer, and addition funnel, and cooled by an ice–salt bath, 1-propanol (19.7 g., 0.328 mole) was added dropwise with magnetic stirring. The reaction mixture, which was maintained below 0° during the addition, was permitted to warm to room temperature. After 5 days, excess water was added to the dark, two-phase system and crystalline material was formed. The solid was collected, washed with water, and dried in a vacuum desiccator to yield 1.1 g. (2.8%) of II. The crude material was recrystallized twice from absolute ethanol, m.p. 189.2–189.3° dec., lit.[2] m.p. 192–

---

[12] Z. N. Nazarova and I. P. Tsukervanik, *J. Gen. Chem. USSR*, **18**, 430 (1948).

[13] In one decomposition a white solid (m.p. 163°) was obtained; this material may have been crude disultone.

[14] For a recent review see E. E. Gilbert, *Chem. Rev.*, **62**, 549 (1962). The following references are particularly pertinent: (a) C. M. Suter, P. B. Evans, and J. M. Kiefer, *J. Am. Chem. Soc.*, **60**, 538 (1938); (b) F. G. Bordwell, M. L. Peterson, and C. S. Rondestvedt, Jr., *ibid.*, **76**, 3945 (1954); (c) F. G. Bordwell and M. L. Peterson, *ibid.*, **76**, 3952 (1954).

[15] (a) F. W. Bushong, *Am. Chem. J.*, **30**, 212 (1903); (b) F. C. Wagner and E. E. Reid, *J. Am. Chem. Soc.*, **53**, 3407 (1931).

[16] G. Manecke and J. Danhäuser, *Angew. Chem.*, **70**, 745 (1958).

[17] The anhydride was reported only as $C_8H_{18}S_2O_6$ (mol. wt. 274). The disultone X requires $C_8H_{16}S_2O_6$ (mol. wt. 272). The anhydride or the isomeric sulfonate requires $C_8H_{18}S_2O_7$ (mol. wt. 290).

[18] Melting and boiling points are uncorrected. Infrared spectra were taken as chloroform solutions with a Perkin-Elmer Infracord Model 137 spectrophotometer. Analyses were made by Schwarzkopf Microanalytical Laboratory, Woodside 77, N. Y. and Galbraith Laboratories, Inc., Knoxville 21, Tenn.

193° dec. The molecular weight was determined cryoscopically in purified[19] *p*-dioxane.

Anal. Calcd. for $C_6H_{12}O_6S_2$: C, 29.50; H, 4.95; S, 26.25; mol. wt., 244. Found: C, 29.47; H, 5.15; S, 26.04; mol. wt., 253, 200, 247.

B.—The same procedure was followed for the addition of reagents. Directly after the addition, the reaction mixture was heated on the steam bath until a vigorous exothermic reaction ensued. Crystalline material was obtained upon the addition of water to the dark, viscous residue. Yields of II were 3–4% in a series of runs.

C.—Method B was modified. Careful application of a steam bath and cooling bath permitted the exothermic reaction to be moderate and self-sustaining with the liquid phase at 95°. Yields of II were increased to 25%.

1-Propyl Chlorosulfonate (VI).—The reaction solution obtained at 0° from the addition of 1-propanol (34.5 g., 0.574 mole) to sulfuryl chloride (75.0 g., 0.556 mole) was distilled *in vacuo* to yield 42 g. (48%) of 1-propyl chlorosulfonate, b.p. 52–53° (10 mm.), $n^{20}\mathrm{D}$ 1.4218; lit.[20] b.p. 53.2° (10 mm.), $n^{20}\mathrm{D}$ 1.422. 1-Propyl chlorosulfonate (29.5 g., 0.186 mole) was converted by method B to 1.7 g. (7.5%) of II.

Attempted Preparation of 2-Propyl Chlorosulfonate (VII).—The reaction solution obtained at 0° from the addition of 2-propanol (46 g., 0.77 mole) to sulfuryl chloride (100 g., 0.74 mole) was decomposed thermally by method C (above). Despite the cautious application of heat, violent bumping occurred under conditions that were adequate for VI. No crystalline material was obtained in a series of such reactions.

Several attempts were made to isolate the intermediate 2-propyl chlorosulfonate by vacuum distillation. Decomposition of the distilland occurred each time without distillation.

N-Aryl 1-Propanesulfonamides (III).—1-Propanesulfonyl chloride was prepared by the method of Pantlitshko and Salvenmoser.[21] A mixture of 1-bromopropane (55 g., 0.45 mole), ammonium sulfite (93 g., 0.69 mole), and water (170 ml.) was stirred and heated at reflux until the system was homogeneous (3.2 hr.). The solution was concentrated to dryness at reduced pressure. The residual ammonium 1-propanesulfonate was treated with phosphorus pentachloride (187 g., 0.90 mole) and the reaction mixture was worked up as described[21] to yield 2.6 g. (4.1%) of 1-propanesulfonyl chloride, b.p. 79–81° (15 mm.), $n^{25}\mathrm{D}$ 1.4524; lit.[22] b.p. 76–77° (12 mm.), $n^{20}\mathrm{D}$ 1.4540. The sulfonyl chloride was converted by the method of Mel'nikov, *et al.*,[23] to 1-propanesulfon-*p*-toluidide (IIIa), m.p. 68.2–69.0° from aqueous ethanol, lit.[24] m.p. 67.0–67.8°. The method of Shepherd[25] was used to convert the sulfonyl chloride to 1-propanesulfon-α-naphthylide (IIIb), m.p. 82.8–83.6° from aqueous ethanol, lit.[26] m.p. 84°.

N-Aryl 2-Propanesulfonamides (IV).—Sodium 2-propanesulfonate monohydrate (15 g., 0.091 mole) was converted with phosphorus pentachloride (36 g., 0.18 mole) to 10 g. (80%) of 2-propanesulfonyl chloride. The crude sulfonyl chloride was converted to 2-propanesulfon-*p*-toluidide (IVa), m.p. 98.2–98.8° from aqueous ethanol.

Anal. Calcd. for $C_{10}H_{15}NO_2S$: C, 56.31; H, 7.09; N, 6.57; S, 15.03. Found: C, 56.50; H, 7.39; N, 6.31; S, 14.94.

The sulfonyl chloride was also converted to 2-propanesulfon-α-naphthylide (IVb), m.p. 133.8–134.8° from aqueous ethanol, lit.[26] m.p. 154°.

Anal. Calcd. for $C_{13}H_{15}NO_2S$: S, 12.86. Found: S, 13.16.

Degradation of Disultone (II). A. With Sodium Borohydride–Water.—To a magnetically stirred solution of sodium borohydride (0.31 g., 0.0082 mole) in 25 ml. of water at room temperature was added solid disultone (1.00 g., 0.0041 mole) over a 10-min. period; copious gas evolution accompanied the addition of each portion. The two-phase mixture was stirred until the system was homogeneous (1.3 hr.). The solution was stirred an additional hour at 90°, and then concentrated to dryness with a rotary evaporator at reduced pressure and steam bath temperature.

The residual white solid (1.27 g.) was treated with phosphorus pentachloride (2.08 g., 0.010 mole) in the manner previously described to give 0.40 g. (35%) of 1-propene-1-sulfonyl chloride.

The crude sulfonyl chloride was refluxed with α-naphthylamine (0.81 g., 0.0057 mole) in 15 ml. of dry benzene to give 0.28 g. (14% over-all from II) of 1-propene-1-sulfon-α-naphthylide (Vb), m.p. 104.4–107.4° from aqueous ethanol.

Anal. Calcd. for $C_{13}H_{13}NO_2S$: C, 63.13; H, 5.30; N, 5.66; S, 12.97. Found: C, 63.24; H, 5.50; N, 5.48; S, 13.17.

The bromine test for unsaturation was positive. The infrared spectrum contained absorption at 10.5 μ, not present in authentic IIIb.

B. With Sodium Borohydride–Deuterium Oxide.—In an analogous reaction, disultone (0.18 g., 0.0073 mole) was added to a stirred solution of sodium borohydride (0.056 g., 0.0015 mole) in 5 ml. of deuterium oxide (assay 99.7%; General Dynamics Corporation, Liquid Carbonic Division). Gas evolution was less vigorous, and homogeneity was not achieved until 3.5 hr. Work-up was by the previously described procedure.

The white residual solid was converted in the normal fashion to the sulfonyl chloride and then to 1-propene-1-sulfon-α-naphthylide (Vb), m.p. 104–106°, in 24% over-all yield from II. The bromine test for unsaturation was positive. The infrared spectrum, which contained no absorption characteristic of vinyl deuterium,[27] was identical with that for Vb prepared by method A.

C. With Hydrobromic Acid.—A mixture of disultone (0.69 g., 0.0028 mole), 47.5% hydrobromic acid (1.00 g., 0.0059 mole), and water (10 ml.) was stirred and heated at 95–100° until the system was homogeneous (4 hr.). The cooled reaction solution was titrated to a phenolphthalein endpoint with 1.000 *N* sodium hydroxide (11.0 ml., 0.0110 mole); the equivalents of base required for neutralization indicated the product was most likely 1-propene-1-sulfonic acid. The bromine test for unsaturation was positive.

D. With Sodium Methylmercaptide.—To a nitrogen-swept 5-ml. ampoule containing disultone (0.56 g., 0.0023 mole) was added a methanolic solution of sodium methylmercaptide prepared by the addition of sodium (0.10 g., 0.0043 mole) to 4 ml. of methanol containing methyl mercaptan (0.3 g., 0.006 mole). The sealed ampoule was heated at 95–105° for 25 hr. The reaction solution was concentrated to dryness at reduced pressure, and the white residual solid was dried in a vacuum desiccator over phosphorus pentoxide to give 0.65 g. (74%) of sodium 2-methylmercapto-1-propanesulfonate.

Desulfurization of the above compound was carried out by the procedure of Marvel and Weil.[10] To the solid (0.65 g., 0.0034 mole) were added Raney nickel[28] (approximate weight 6–8 g. in aqueous slurry, washed with absolute ethanol prior to use) and absolute ethanol (20 ml.). The reaction mixture was stirred and heated at reflux for 6.5 hr., filtered, and evaporated to dryness with a rotary evaporator at reduced pressure and steam bath temperature to give 0.43 g. (87%) of sodium 1-propanesulfonate.

The white crystalline solid (0.43 g., 0.0029 mole) was treated with phosphorus pentachloride (0.73 g., 0.0035 mole) in the normal manner. The crude sulfonyl chloride was converted to 0.21 g. (21% over-all from II) of 1-propanesulfon-*p*-toluidide (IIIa), m.p. 66.6–67.5° from aqueous ethanol, m.m.p. 67.4–68.4° with authentic IIIa. The infrared spectrum was identical with that for authentic IIIa.

Attempted Reductions of 1-Propenesulfonic Acid Derivatives. A. Sodium 1-Propene-1-sulfonate.—The diimide reduction procedure of van Tamelen was used.[7] The white residual solid (0.82 g., containing 0.59 g., 0.0041 mole of sodium 1-propene-1-sulfonate), obtained from the reaction of the disultone with aqueous sodium borohydride solution, was dissolved in 25 ml. of warm ethylene glycol. To the stirred solution at 80–90° was added solid *p*-toluenesulfonyl hydrazine (2.29 g., 0.0123 mole) over a 30-min. period; gas evolution accompanied the addition of each portion. The stirred reaction solution was heated at 85° for an

---

(19) K. B. Wiberg, "Laboratory Technique in Organic Chemistry," McGraw-Hill Book Co., Inc., New York, N. Y., 1960, p. 245.

(20) W. W. Binkley and E. F. Degering, *J. Am. Chem. Soc.*, **60**, 2810 (1938).

(21) M. Pantlitschko and F. Salvenmoser, *Monatsh.*, **89**, 285 (1958).

(22) G. Geisler and P. Laue, *Chem. Ber.*, **95**, 867 (1962).

(23) N. N. Mel'nikov, E. M. Sokolova, and P. P. Trunov, *Zh. Obshch. Khim.*, **29**, 529 (1959).

(24) P. H. Latimer and R. W. Bost, *J. Org. Chem.*, **5**, 24 (1940).

(25) R. B. Shepherd, *ibid.*, **12**, 275 (1947).

(26) M. Duguet, *Bull. Acad. Roy. Belg.*, 87 (1906); *Chem. Zentr.*, 1529 (1906).

(27) M. F. Zinn, T. M. Harris, D. G. Hill, and C. R. Hauser, *J. Am. Chem. Soc.*, **85**, 71 (1963).

(28) (a) Kindly supplied by Dr. R. E. Boucher, Anken Chemical & Film Corporation. (b) Contrary to most specifications for freshly prepared Raney nickel, this sample had been stored 9 months under tap water at pH 8.3.

additional 2.5 hr. The solvent was removed by distillation at reduced pressure. The residual solid was extracted exhaustively with ethyl ether, and the remaining white solid (0.49 g.) was dried in a vacuum desiccator. The solid was converted by the normal procedures to the N-*p*-tolylsulfonamide derivative, m.p. 53–55°. The infrared absorption and elemental analysis indicated that the compound was 1-propene-1-sulfon-*p*-toluidide (Va).

Anal. Calcd. for $C_{10}H_{13}NO_2S$: C, 56.85; H, 6.20; N, 6.63; S, 15.18. Found: C, 57.13; H, 6.40; N, 6.67; S, 15.06.

B. 1-Propene-1-sulfon-*p*-toluidide (Va).—The diimide reduction of Va was unsuccessful. A solution of Va (0.22 g., 0.0010 mole) and *p*-toluenesulfonyl hydrazine (0.39 g., 0.0021 mole) in 13 ml. of freshly distilled diglyme was refluxed for 1.5 hr. The solvent was removed at reduced pressure, and the residual oil was chromatographed in chloroform on alumina. No material corresponding to IIIa was recovered.

C. 1-Propene-1-sulfon-α-naphthylide (Vb).—The catalytic hydrogenation of Vb was unsuccessful. A solution of Vb in absolute ethanol was shaken with Adams catalyst for 3.5 hr. in a Parr apparatus under 2.5 atm. of hydrogen. Starting material was recovered unchanged.

1-Propyl Methanesulfonate.—The product, b.p. 103° (12 mm.), lit.[29] b.p. 115° (21 mm.), was obtained in 60% yield by the method of Ross and Davis.[29]

Methyl 1-Propanesulfonate.—The product, obtained in 7% yield by the same procedure,[29] was distilled *in vacuo* twice, b.p. 93° (12 mm.), and chromatographed in chloroform on alumina.

Anal. Calcd. for $C_4H_{10}O_3S$: S, 23.20. Found: S, 23.30.

2-Propyl Methanesulfonate.—The product, b.p. 86–88° (12 mm.), n^{25}_D 1.4219, was prepared by the same procedure.[29]

N.m.r. Spectra.—Measurements were obtained with a Varian HR-60 instrument at 60 Mc. and 14,100 gauss. Tetramethylsilane was used as internal standard. Spin decoupling experiments were done by a modification of the method of Johnson.[30]

Acknowledgment.—The authors are indebted to Professor C. H. DePuy for assistance with the n.m.r. spectra. We thank Mr. N. E. Fersen, Williams College, for Russian translations.

(29) W. C. J. Ross and W. Davis, *J. Chem. Soc.*, 2420 (1957).

(30) L. F. Johnson, "Proton-proton Spin Decoupling Using the Varian V-3521 Integrator," Varian Associates, Palo Alto, Calif., 1962.

Skeletal Rearrangement Accompanying the Reaction of 2-Phenyl-1-propanol, 1-Phenyl-2-propanol, and 2-Phenyl-ethanol-1-C^{14} with Brominating and Chlorinating Reagents[1]

HERMAN PINES AND FREDERICK SCHAPPELL[2]

Ipatieff High Pressure and Catalytic Laboratory, Department of Chemistry,
Northwestern University, Evanston, Illinois

Received November 6, 1963

Under conventional brominating procedures employing phosphorus tribromide or aqueous hydrobromic acid, 2-phenyl-1-propanol is shown to produce up to 85% 1-phenyl-2-bromopropane. Bromination of 1-phenyl-2-propanol yields only small amounts of isomeric bromides. The mechanism of the rearrangement is discussed. The reaction product of 2-phenylethanol-1-C^{14} with the brominating agents consisted of 2-phenyl-1-bromoethane-1-C^{14} containing 0.1 to 6.3% of the rearranged bromide, 2-phenyl-1-bromoethane-2-C^{14}. 2-Phenyl-1-propanol upon treatment with thionyl chloride and pyridine produced 9.3% of the rearranged product, 1-phenyl-2-chloropropane. The same alcohol on reaction with phosphorus trichloride formed the normal and rearranged products in a ratio of 1.3 to 1.

In conjunction with the study of some base-catalyzed reactions being carried out in this laboratory it became necessary to synthesize 2-phenyl-1-bromopropane. The usual procedure for converting alcohols to bromides consists of reacting the alcohol with phosphorus tribromide or with concentrated aqueous hydrobromic acid in the presence of sulfuric acid. When applied to secondary alcohols this reaction is accompanied by isomerization. It was found that either 2- or 3-pentanol gives a mixture of 2- and 3-bromopentanes.[3,4]

These procedures were considered to be safe for the synthesis of primary bromides although Whitmore and Rothrock[5] reported that neopentyl alcohol underwent extensive rearrangement to pentyl bromides when treated with hydrobromic acid.

In the present study we found that the primary alcohol, 2-phenyl-1-propanol, undergoes extensive rearrangement upon bromination with either phosphorus tribromide or 48% hydrobromic acid; however, the secondary alcohol, 1-phenyl-2-propanol, rearranges very little upon treatment with either reagent.

In order to determine the effect the methyl group in 2-phenyl-1-propanol may have upon the extent of skeletal isomerism, it was decided to study the reaction of 2-phenylethanol-1-C^{14} with phosphorus tribromide and hydrobromic acid.

Results

I. 2-Phenyl-1-propanol and 1-Phenyl-2-propanol with Phosphorus Tribromide and with Hydrobromic Acid. 1. Reactions with Phosphorus Tribromide.—The bromination of 2-phenyl-1-propanol by conventional procedures[6,7] yields, besides 2-phenyl-1-bromopropane, from 16 to 34% 1-phenyl-2-bromopropane (Table I). The other isomeric bromides, which would be expected to be formed had the rearrangement proceeded by carbonium ion mechanisms 1 and 2, were essentially absent (see p. 1504).

The tertiary bromide, 2-phenyl-2-bromopropane, which would be produced by mechanism 1, was found to be unstable in the presence of water or base, or on

---

(1) This research was supported in part by the National Science Foundation Grant NSF-G14503.

(2) Monsanto Chemical Co. Predoctoral Fellow, 1962–1963.

(3) H. Pines, A. Rudin, and V. N. Ipatieff, *J. Am. Chem. Soc.*, **74**, 4063 (1952).

(4) J. Cason and J. J. Correia, *J. Org. Chem.*, **26**, 3645 (1961).

(5) F. C. Whitmore and H. S. Rothrock, *J. Am. Chem. Soc.*, **71**, 3431 (1932).

(6) C. R. Noller and R. Dinsmore, "Organic Syntheses," Coll. Vol. II; John Wiley and Sons, Inc., New York, N. Y., 1943, p. 358.

(7) P. A. Levene, R. E. Marker, and A. Rothen, *J. Biol. Chem.*, **100**, 589 (1953).