enediamine dihydrochloride was found to be 0.86 c./m./mg. This indicates that 2.6% of the succinic acid radioactivity was in the methylene carbon atoms.

Oxidation of Malic Acid.—To a solution of 109.7 mg. of C^{14}-labeled malic acid (275 c./m./mg. or 30,100 c./m. total.) in 10 ml. of 1.0 N sulfuric acid in a 100-ml. flask equipped with nitrogen inlet bubbler, reflux condenser and dropping funnel was added 20 ml. of 0.15 M chromic acid solution during two hours on the steam-bath.

The carbon dioxide evolved was collected in carbonate-free sodium hydroxide solution and precipitated with barium chloride to give 326 mg. (101%) of barium carbonate. The specific activity was found to be 81.5 c./m./mg. or 26,600 c./m. total. Acetic acid was obtained from the residual solution upon steam distillation. It was converted to barium acetate (80% yield based on titer of steam distillate) which was recrystallized from water. From the specific activity (2.0 c./m./mg.) and the theoretical yield (112 mg.), the activity in the α and β carbon atoms of the malic acid, 224 c./m., can be determined accurately without interference from carboxyl activity. Incomplete recovery of the carbon dioxide and overoxidation of the malic acid is assumed to have caused the loss of carboxyl activity.

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Acetylation of D-Psicose

BY W. W. BINKLEY[1] AND M. L. WOLFROM

In connection with our studies[2] on the chromatography of acetylated molasses fractions, it became of interest to investigate the behavior of the rare ketose D-psicose (synonyms D-allulose and D-erythrohexulose) under mild acetylating conditions since Zerban and Sattler[3] have shown that this ketose may be a constituent of some molasses fractions. Under conditions of mild acetylation the ketoses may form acetates of the cyclic or acyclic types.[4] In the work herein described D-psicose was acetylated at low temperature with zinc chloride and acetic anhydride and the resultant product was subjected to chromatographic analysis. Five fractions (Table I) were obtained and from the major fraction there was isolated the previously described[5] crystalline *keto*-D-psicose pentaacetate. The main product then of the direct acetylation of D-psicose under mild conditions is the acyclic acetate.

TABLE I

CHROMATOGRAM OF ACETYLATED D-PSICOSE

Zone	Approx. time, sec., for distinct zone formation	Zone position in mm. from top of column	Zone yield, g.
Top	60	0–3	0.017
1	180	21–27	.064
2	180	63–73	.095
3	30	115–122	.183
4	10	126–129	.037
		Total	.396 (84.6%)

Experimental

The D-psicose sirup obtained from the deacetylation of 500 mg. of *keto*-D-psicose pentaacetate[5] was treated with 10 ml. of acetic anhydride and 0.3 g. of freshly fused zinc chloride for twenty hours at 0–3°. The reaction mixture was then poured onto 40 g. of ice and water under good agitation and after thirty minutes of stirring the *p*H of the mixture was adjusted to 6 with sodium bicarbonate. The mixture was then extracted with three 25-ml. portions of chloroform. A sirup was obtained on solvent removal; yield 470 mg.

The above sirup (468 mg.), dissolved in 10 ml. of benzene, was added at the top of a 170 × 44 mm. (diam.) column of 100 g. of 5 parts Magnesol[6]/1 part Celite (by wt.) pre-wet with benzene. The chromatogram was developed with 600 ml. of 100 parts benzene/1 part ethanol (by vol.). Five zones were detected on the extruded column with the permanganate streak indicator (1% potassium permanganate in 2.5 N sodium hydroxide) and were eluted with acetone (Table I). Well-formed elongated prisms were obtained from a 95% ethanolic solution of zone 3 and were identified as *keto*-D-psicose pentaacetate; yield 90 mg., m. p. 64–65° (mixed melting point unchanged), $[\alpha]^{23}\text{D}$ −21.0° (c 4, chloroform). Accepted values[5] for *keto*-D-psicose pentaacetate are: m. p. 63–65°, $[\alpha]^{29}\text{D}$ −21.5° (c 3, chloroform). No crystalline products were obtained from the other zones.

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[1] Sugar Research Foundation Fellow of The Ohio State University Research Foundation (Project 190).

[2] W. W. Binkley, M. Grace Blair and M. L. Wolfrom, THIS JOURNAL, **67**, 1789 (1945); W. W. Binkley and M. L. Wolfrom, *ibid.*, **69**, 664 (1947); **70**, 290 (1948).

[3] F. W. Zerban and L. Sattler, *ibid.*, **64**, 1740 (1942); *Ind. Eng. Chem.*, **34**, 1180 (1942).

[4] See, for example, M. L. Wolfrom and A. Thompson, THIS JOURNAL, **56**, 880 (1934); Yvonne Khouvine and G. Aaragon, *Bull. soc. chim.*, [5] **5**, 1404 (1938); Yvonne Khouvine and Y. Tomoda, *Compt. rend.*, **205**, 1414 (1937).

[5] M. L. Wolfrom, A. Thompson and E. F. Evans, THIS JOURNAL, **67**, 1793 (1945).

[6] W. H. McNeely, W. W. Binkley and M. L. Wolfrom, *ibid.*, **67**, 527 (1945).

DEPARTMENT OF CHEMISTRY
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Rearrangement of Alkyl Sulfites to Alkanesulfonate Esters

BY WILLIAM E. BISSINGER, FREDERICK E. KUNG AND CHARLES W. HAMILTON

Although a number of references on the formation of *salts* of alkanesulfonic acids from the reaction of alkyl sulfites with sodium or potassium hydroxides have appeared,[1,2,3,4] only one direct conversion of an alkyl sulfite to an *ester* of an alkanesulfonic acid has been described.[3] In that case, only a very small amount of methyl methanesulfonate resulted when dimethyl sulfite and excess methyl iodide were heated in a sealed tube for twelve hours. We have now found that *catalytic* amounts of tertiary amines, such as tri-*n*-butylamine, are excellent agents for promoting the rearrangement of dimethyl sulfite to methyl methanesulfonate, in yields as high as 56%. Dimethyl ether and sulfur dioxide were the other products. Diethyl sulfite, with the same amine, gave lower yields of either ethyl ethanesulfonate or

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[1] Warlitz, *Ann.*, **143**, 72 (1867).

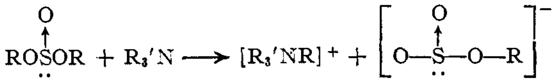
[2] Rosenheim and Liebnicht, *Ber.*, **31**, 405 (1898).

[3] Arbuzov, *J. Russ. Phys.-Chem. Soc.*, **41**, 429 (1909).

[4] Baggesgaard and Rasmussen, *Ber.*, **52B**, 1069 (1919).

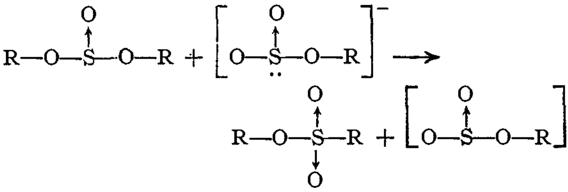
ethanesulfonic acid, depending on the reaction conditions. Butanesulfonic acid or its ester could not be isolated from a similar reaction with *n*-butyl sulfite, the only products formed being *n*-butyl alcohol, di-*n*-butyl ether and probably *n*-butene. Efforts to rearrange 2-chloroethyl sulfite were also unsuccessful.

A possible mechanism[5] for this rearrangement involves, as the first step, the formation of a quaternary ammonium alkyl sulfite.



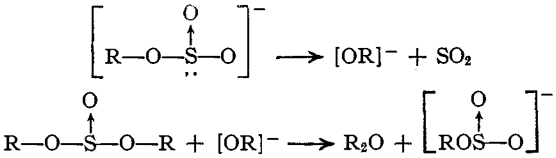
$$\mathrm{RO\underset{\cdot\cdot}{\overset{\overset{O}{\uparrow}}{S}}OR} + \mathrm{R_3'N} \longrightarrow [\mathrm{R_3'NR}]^+ + \left[\mathrm{O{-}\underset{\cdot\cdot}{\overset{\overset{O}{\uparrow}}{S}}{-}O{-}R}\right]^-$$

This negative ion then reacts with a second alkyl sulfite molecule to form the ester of an alkanesulfonic acid with the propagation of another alkyl sulfite ion, which may continue the reaction.



$$\mathrm{R{-}O{-}\underset{\cdot\cdot}{\overset{\overset{O}{\uparrow}}{S}}{-}O{-}R} + \left[\mathrm{O{-}\underset{\cdot\cdot}{\overset{\overset{O}{\uparrow}}{S}}{-}O{-}R}\right]^- \longrightarrow \mathrm{R{-}O{-}\underset{\underset{O}{\downarrow}}{\overset{\overset{O}{\uparrow}}{S}}{-}R} + \left[\mathrm{O{-}\overset{\overset{O}{\uparrow}}{S}{-}O{-}R}\right]^-$$

The formation of sulfur dioxide and an ether in the reaction can result from the decomposition of the alkyl sulfite ion, $\mathrm{ROSO_2^-}$, to an alkoxide ion and sulfur dioxide. The alkoxide ion then reacts with a neutral alkyl sulfite molecule to produce an ether.



$$\left[\mathrm{R{-}O{-}\underset{\cdot\cdot}{\overset{\overset{O}{\uparrow}}{S}}{-}O}\right]^- \longrightarrow [\mathrm{OR}]^- + \mathrm{SO_2}$$

$$\mathrm{R{-}O{-}\overset{\overset{O}{\uparrow}}{S}{-}O{-}R} + [\mathrm{OR}]^- \longrightarrow \mathrm{R_2O} + \left[\mathrm{RO\overset{\overset{O}{\uparrow}}{S}{-}O}\right]^-$$

Thus, by this mechanism, the amine serves essentially as an initiator of the reaction, although its presence in the mixture is probably soon lost, through formation of the quaternary salt.

Experimental

Methyl Methanesulfonate.—Fifty-five grams (0.5 mole) of dimethyl sulfite,[6] b. p. 125–126° (735 mm.), was refluxed with 1.9 g. (0.01 mole) of tri-*n*-butylamine (Eastman Kodak Co.) for nineteen hours. The reflux temperature increased from 126 to 207°. During this time, 20.8 g. of volatile products were collected in a Dry Ice trap connected to the reflux condenser.

Distillation of the reaction product through a Vigreux column gave 26.8 g. (49% yield) of methyl methanesulfonate, b. p. 100.5–101.5° (25 mm.), 198–198.6° (732 mm.), n^{20}D 1.4140.

Anal. Calcd. for $C_2H_6SO_3$: S, 29.1. Found: S, 29.8.

A viscous residue of 3.8 g. remained. No dimethyl sulfite was recovered.

The material in the Dry Ice trap was vaporized and repeatedly passed over a hot sodium hydroxide solution to remove sulfur dioxide; analysis of this solution iodometrically showed the presence of 9.8 g. (30% yield) of sulfur dioxide. The effluent gases, free of sulfur dioxide, were condensed in a second Dry Ice trap. This liquid, 5.7 g. (26% yield), boiled at −23 to −20° and was dimethyl ether.

When the above reaction was repeated, using 500 g. of dimethyl sulfite, 17.1 g. of amine, and a reflux period of twenty-six hours, a 56% yield of methyl methanesulfonate was obtained.

Ethyl Ethanesulfonate.—A mixture of 69 g. (0.50 mole) of diethyl sulfite[6] and 1.9 g. (0.01 mole) of tri-*n*-butylamine was heated under reflux for twenty-five and one-half hours, during which time the reflux temperature decreased from 150 to 109°. Collected in the Dry Ice trap was 3.0 g. of liquid, of which 1.9 g. was identified as sulfur dioxide.

Distillation of the reaction product through a 1.0 × 30-cm. Fenske column gave 49.0 g. of diethyl sulfite (71% recovery) and 4.2 g. (0.03 mole) of ethyl ethanesulfonate, b. p. 101.5–102.5° (18 mm.), n^{20}D 1.4212.

Anal. Calcd. for $C_4H_{10}SO_3$: S, 23.2. Found: S, 23.7.

This represented a 21% yield of ethyl ethanesulfonate, based on the ethyl sulfite not recovered.

Ethanesulfonic Acid.—Using the same quantities of reactants as above, the diethyl sulfite and tri-*n*-butylamine were heated in a flask attached to a short Vigreux column so as to remove the low boiling reaction products. The mixture was then heated at 150–160° for twenty-one hours during which time a non-condensable gas passed through the attached Dry Ice trap. It decolorized bromine water and probably was ethylene.

Distillation of the product remaining in the reaction flask gave 9.0 g. (16% yield) of ethanesulfonic acid, b. p. 136–140° (2 mm.), n^{20}D 1.4335.

Anal. Calcd. for $C_2H_6SO_3$: S, 29.1; neut. equiv., 110. Found: S, 29.7; neut. equiv., 116.

No diethyl sulfite was recovered.

The volatile products liberated during the reaction, and condensed in the receiver and Dry Ice trap, consisted of 0.29 mole (58% yield) of sulfur dioxide, and 0.24 mole (48% yield) of diethyl ether.

Attempted Rearrangement of Dibutyl Sulfite.—A mixture of 87 g. (0.5 mole) of di-*n*-butyl sulfite[6] and 1.9 g. (0.01 mole) of tri-*n*-butylamine was heated for sixty-five hours at 150–160° in a flask attached to a short Vigreux column. A total of 10.6 g. of volatile products was evolved, of which 7.6 g. (0.12 mole) was identified as sulfur dioxide; the remaining material may have been *n*-butene, although this was not conclusively established.

Distillation of the reaction product gave 19.9 g. of material, b. p. 43–47° (30 mm.), n^{20}D 1.4000, which was a mixture of *n*-butyl alcohol and probably di-*n*-butyl ether.

Anal. Calcd. for C_4H_9OH: OH, 23.0. Found: OH, 5.7.

The *n*-butyl alcohol in this fraction was identified as its α-naphthylurethan, m. p. 68°. On continued distillation, 49.2 g. (0.28 mole) of unreacted dibutyl sulfite was recovered, and a residue of 3.9 g. remained.

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Halogen–Lithium Interconversion with Iodothiophenes

BY E. CAMPAIGNE AND WILLIAM O. FOYE

In connection with the preparation of 2,5-diphenylthiophene, the reaction of 2,5-diiodothiophene with phenyllithium was observed. Lithium–halogen interchange was found to occur, which conforms with previous results in which lithium has been introduced into heterocyclic nuclei without further reaction with the halogen compound

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[5] This was suggested by Dr. P. D. Bartlett.

[6] A commercial product of this Division, used without further purification.