Thus the original solution was found to contain 0.427 mole of 2-chloroethyl hydrogen sulfate. This corresponds to a 43.4% yield of 2-chloroethyl hydrogen sulfate.

The above yields of bis(2-chloroethyl)sulfate and 2-chloroethyl hydrogen sulfate are calculated on the basis of consumed chlorine.

Preparation of bis(2-chloroethyl)sulfate. In the apparatus previously described was placed 170.2 g. of 98% sulfuric acid. Chlorine was passed into the acid at a rate of 19.2 g. per hour and ethylene simultaneously at a rate of 8.02 g. per hour. After 4 hr. chlorine and ethylene were discontinued and nitrogen passed through the mixture for 30 min. Chlorine (2.7 g.) and ethylene dichloride (5.5 g.) were collected in the cold trap.

The reaction mixture (245.4 g.) was extracted once with 108 ml. of benzene. The benzene layer was washed with distilled water to remove 2-chloroethyl hydrogen sulfate, dried over anhydrous magnesium sulfate, the benzene removed under vacuum and the bis(2-chloroethyl)sulfate isolated by distillation under vacuum. In this manner 25.6 g. (0.115 mole, 22.0% yield) of bis(2-chloroethyl)sulfate was obtained.

The sulfuric acid layer from the above extraction was found to contain 13.3 g. (0.0595 mole, 11.4% yield) of bis-(2-chloroethyl)sulfate and 51.8 g. (0.354 mole, 33.9% yield) of 2-chloroethyl hydrogen sulfate.

The above yields of bis(2-chloroethyl)sulfate and 2-chloroethyl hydrogen sulfate are calculated on the basis of consumed chlorine.

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The Camphenilanic and Camphenanic Acids

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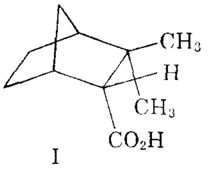
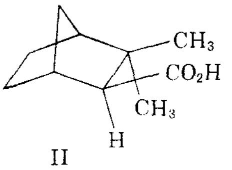
The relationship of camphenilanic acid, m.p. 65°, isocamphenilanic acid, m.p. 118°, camphenanic acid, m.p. 95°, and isocamphenanic acid, m.p. 74°, has remained obscure for many years.[1] Alder,[2] however, has recently demonstrated that pure camphenilanic acid (I) melts at 92°[3] and has suggested that the camphenilanic acid, m.p. 65°, obtained by earlier investigators was a mixture of I and isocamphenilanic acid (II).[4] An obvious corollary to these observations, which we have now verified, is that camphenanic acid is pure I while isocamphenanic acid is a mixture of I and II.



I



II

The oxidation of camphene with potassium permanganate in glacial acetic acid[5] afforded, in 9–15% yield, a mixture of camphenanic acids which on fractional recrystallization gave a camphenanic acid, m.p. 91–92°, whose properties correspond exactly with those cited for pure I.[2] The homogeneity of this acid was confirmed by elution chromatography and by its smooth conversion with lithium aluminum hydride to *endo*-isocamphanol, m.p. 83–84°.[2,6]

Chromatography of the solid found in the mother liquors after removal of camphenanic acid demonstrated it was a mixture of I and II.

The neutral fraction from the permanganate oxidation of camphene was composed of camphenilone, isolated in 20–35% yield, and small amounts of higher boiling unidentified carbonyl compounds. It should be noted that the R-homocamphenilones[7] were not detected among these products.

EXPERIMENTAL

The potassium permanganate oxidation of Camphene. A mixture of 100 g. (0.74 mole) of camphene, 145 g. (0.92 mole) of potassium permanganate, and 350 ml. of acetic acid was stirred at 0° for 4 hr., kept at room temperature overnight and then heated on a steam bath for 4 hr. The mixture was steam distilled and the distillate was extracted with ether. The ether solution was extracted with aqueous sodium carbonate, dried, and distilled affording *ca.* 40 g. of camphenilone, contaminated by appreciable amounts of camphene and tricyclene, b.p. 72–90°/*ca.* 15 mm., m.p. 39.5–41°[8]; and *ca.* 1.0 g. of a liquid b.p. 95–102°/15 mm. Chromatography of the 2,4-dinitrophenylhydrazone derivatives derived from the higher boiling fraction demonstrated the presence of camphenilone and at least three other unidentified carbonyl compounds.

The sodium carbonate extract mentioned above was acidified affording 15 g. of a crystalline mixture of the camphenanic acids. A portion of this mixture was recrystallized five times from petroleum ether affording *camphenanic acid,* m.p. 87–89° (reported,[5] m.p. 87–91°). The melting point of this acid was raised to 91–92.5° by chromatography on silica gel and recrystallization from methanol. Further chromatography or recrystallization from methanol, petroleum ether, or water failed to alter this melting point.

Lithium aluminum hydride reduction of camphenanic acid afforded a solid which on sublimation *in vacuo* afforded *endo*-isocamphanol, m.p. 83–84° (reported,[6] m.p. 83°).

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(1) For a historical review of these $C_{10}H_{16}O_2$ acids derived from camphene see J. L. Simonsen, *The Terpenes,* University Press, Cambridge, 1949, p. 294.

(2) K. Alder and W. Roth, *Ber.,* **90,** 1830 (1957).

(3) W. Hückel and H. Rohrer, *Ber.,* **91,** 198 (1958), claimed to have isolated pure I, m.p. 55–56°, for the first time. The homogeneity of this acid was not rigorously established, nor was a satisfactory explanation offered for the acid melting *ca.* 40° lower than that described by Alder.[2] Hückel's acid was probably a mixture of I and II.

(4) Henderson [*J. Chem. Soc.,* **99,** 1887 (1911)] found that recrystallization of camphenilanic acid, m.p. 65°, from petroleum-ether afforded a solid, m.p. 86°, and therefore postulated that I had rearranged to II. It seems more reasonable to conclude that Henderson had isolated relatively pure I; I certainly does not isomerize to II on recrystallization from petroleum-ether.

(5) O. Aschan, *Chem. Abstr.,* **6,** 3414 (1912).

(6) W. Huckel and H. Schultz, *Ann.,* **575,** 32 (1952).

(7) J. Wolinsky, *J. Org. Chem.,* **26,** 704 (1961).

(8) Camphene apparently does not depress the melting point of camphenilone.

The *isocamphenanic acid,* m.p. 68–74°, recovered from the mother liquors after the separation of camphenanic acid, was placed on silica gel and eluted with chloroform affording the following fractions: (a) camphenilanic acid (I), m.p. 75–80° to 78.5–80°, whose melting point was raised to 90–91° by recrystallization from petroleum ether; (b) mixtures of (I) and (II), m.p. 55–65°, 47–52°, and 71–79°; and (c) isocamphenilanic acid (II), m.p. 87–90° and 96–105°, whose melting point was raised to 118.5–119.5° by recrystallization from methanol.

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A Convenient Laboratory Preparation of *p*-Diacetylbenzene

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A method for preparing 50-g. samples of *p*-diacetylbenzene in yields of 82% has been developed.

The air oxidation of *p*-diethyl- or *p*-diisopropylbenzene to *p*-diacetylbenzene usually results in a mixture of products.[1,2] The presence of oxidation products formed from *o*- and *m*-dialkylbenzenes, usually present in commercial samples of the *p*-dialkylbenzenes, helps to make this mixture complex.

Riemschneider[3] concluded, after reviewing the literature, that all prior syntheses of *m*- and *p*-diacetylbenzenes were long, difficult, and low in yield. He then described a procedure for the buffered permanganate oxidation of *p*-ethylacetophenone on a 0.05*M* scale, using essentially a 1:1 molar ratio of permanganate to *p*-ethylacetophenone. Yields of *p*-diacetylbenzene were 55%.

Sladkov and Vitt[4] prepared *p*-diacetylbenzene in 50% yield by the buffered permanganate oxidation of 0.1 mole of *p*-ethylacetophenone. They used a 2:1 molar ratio of permanganate to monoketone in a slightly acidic medium.

On scaling up the procedure of Sladkov and Vitt to a 0.4*M* scale, the present authors obtained 70–76% yields of *p*-diacetylbenzene. Changing the molar ratio of permanganate to monoketone to 5:2 gave an 82% yield of the diketone with complete conversion of the *p*-ethylacetophenone.

Several attempts to oxidize 1.2-molar batches of *p*-ethylacetophenone resulted in approximately 20% yields of the diketone. However, this scaled-up process was not thoroughly studied.

EXPERIMENTAL[5]

Magnesium oxide, 40 g. (1.0 mole), 1034 ml. of water, 135 ml. of concd. nitric acid (*d.* 1.4; 2.1 moles), and 158 g. (1.0 mole) of potassium permanganate were charged to a 2-l., three-neck, round-bottom flask fitted with a mechanical stirrer, dropping funnel, and reflux condenser. A thermometer, suspended through the condenser, dipped into the solution.

The oxidizing mixture was stirred rapidly and heated to 60° on a steam bath. *p*-Ethylacetophenone,[6] 59.3 g. (0.40 mole), was added dropwise to the oxidizing mixture during 30 min. while maintaining a reaction temperature of 60 ± 1°. Cooling may be necessary. The mixture was then stirred at 60 ± 2° for an additional 4.5 hr. The mixture of product and manganese dioxide was cooled, filtered by vacuum, and dried. The powdered residue was taken up and stirred vigorously with refluxing benzene to extract the product. This mixture was filtered hot by vacuum using a steam-heated funnel. The residual manganese dioxide was thoroughly washed in a similar manner with more hot benzene. The benzene filtrates were combined and stripped to dryness under reduced pressure, leaving 57.2 g. (88% yield) of residue having no odor of unchanged *p*-ethylacetophenone. This residue was slurried with 250 ml. of cold anhydrous diethyl ether, filtered, and dried to give 53.2 g. (82.1% yield) of white, crystalline product, m.p. 112.4–113.4° (reported,[4] 113–114°).

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[1] R. Mittag, Ger. Patent **767,389** (July 31, 1952).

[2] A. J. Harding and A. W. C. Taylor, Brit. patent **784,681** (October 16, 1957).

[3] R. Riemschneider, *Gazz. chim. ital.*, **77**, 607 (1947); *Chem. Abstr.*, **42**, 5876e (1948).

[4] A. M. Sladkov and S. V. Vitt, *Zhur. Obshchei Khim.*, **26**, 1130 (1956); *Chem. Abstr.*, **50**, 16704c (1956).

[5] All melting points and boiling points are uncorrected.

[6] Prepared according to the procedure of D. T. Mowry, M. Renoll, and W. F. Huber, *J. Am. Chem. Soc.*, **68**, 1107 (1946); b.p. 125.5–126.8°/20 mm., n_D^{25} 1.5277.

Ethyl 2-*S*-Ethyl-1,2-dithio-5-*aldehydo*-α-D-*xylo*(*lyxo*)pentodialdofuranoside

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Schneider, Sepp, and Stiehler[2,3] prepared alkyl 1-thio-α-D-glucosides by treating an aqueous solution of dialkyl dithioacetal at room temperature with one mole of mercuric chloride and neutralizing the acid formed with alkali. Green and Pacsu[4] obtained alkyl glucosides when the reaction was effected in alcoholic solution and from the rotation values and ease of hydrolysis of the products, considered that they were furanosides. This ring assignment was

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[1] Postdoctoral fellows supported by Grant No. CY-3232(C3) from the Department of Health, Education, and Welfare, U. S. Public Health Service, National Institutes of Health, Bethesda, Md. (O.S.U.R.F. Proj. 759C).

[2] W. Schneider and Johanna Sepp, *Ber.*, **49**, 2054 (1916).

[3] W. Schneider, Johanna Sepp, and Ottilie Stiehler, *Ber.*, **51**, 220 (1918).

[4] J. W. Green and E. Pacsu, *J. Am. Chem. Soc.*, **59**, 1205 (1937).