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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Received March 6, 1961

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 $0.05M$ 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 $0.4M$ 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°).

CONTRIBUTION NO. 85
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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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Received March 6, 1961

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).

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