The experimental portion describes one or two manipulative improvements in the standard synthesis of 3,4,6-triacetyl-β-methylglucopyranoside.[8,9] Nitration of the latter gave a triacetyl methylglucoside nitrate in an over-all yield of about 15% from glucose pentaacetate. The nitrate occurred as small prisms, m. p. 117–118° (cor.) and with a specific rotation of $[\alpha]^{25}\text{D}$ −1° in 3.69% chloroform solution. Since acyl wandering is unlikely during nitration, and was not observed during several similar substitutions,[8,9] the nitrate group was assigned to the second position in the triacetyl-β-methylglucoside molecule.

Experimental

2,3,4-Triacetyl-α-methylglucoside-6-nitrate.—Commercial α-methylglucopyranoside, 50 g., was condensed with triphenylmethyl chloride,[2] and the product was acetylated prior to isolation.[10] Although the purified triacetyl-6-trityl derivative, 81 g., analyzed correctly and had the accepted rotation of $[\alpha]^{20}\text{D}$ 137° in pyridine,[11] it melted at 143–145° (cor.) instead of at 136°.[2,11] A solution of 15 g. of the 6-trityl derivative in 75 cc. of chloroform was mixed, at 3 to 5°, with 6 g. of phosphorus pentoxide previously dissolved in 75 cc. of nitric acid.[12] This nitric acid was prepared by distilling a mixture of concentrated sulfuric and nitric acids (1:1) in an all-glass apparatus and was miscible without turbidity with chloroform. After being kept at 3 to 5° for ten to fifteen minutes, the nitration mixture was poured, with stirring, into 750 cc. of cracked ice and water. The chloroform layer was separated, washed with dilute sodium bicarbonate solution and with water, and dried over anhydrous sodium sulfate. Evaporation under reduced pressure left a solid, crystalline residue consisting of triphenylmethyl carbinol and the desired nitrate. This mixture was completely, or almost completely, dissolved in 75 cc. of warm, glacial acetic acid, and exactly 50 cc. of water was added, drop by drop with continuous shaking, in order to precipitate the carbinol. After the mixture had stood at room temperature for several hours, 6.1 g., or 88% of the carbinol was removed by filtration and the 6-nitrate was then precipitated by slowly adding 150 cc. of water to the mother liquor. An easy recrystallization from 50 cc. of hot benzene and 100 cc. of ligroin left 7.7 g. of practically pure material, which was recrystallized once more from methanol.

Anal. Calcd. for a triacetyl methylglucoside mononitrate, $C_{13}H_{19}O_{11}N$: C, 42.7; H, 5.2; N, 3.84. Found: C, 42.8, 42.8; H, 5.2, 5.1; N. 4.12, 4.15.

3,4,6-Triacetyl-β-methylglucoside-2-nitrate.—The trichloroacetyl group was removed from 20 g. of pure, recrystallized 2-trichloroacetyl-3,4,6-triacetyl glucopyranosyl chloride[8] by solution at 0° in 350 cc. of dry ether previously saturated with dry ammonia gas.[8] The crystalline aggregates of crude triacetyl glucosyl chloride that promptly separated were broken up by occasional shaking. They were then washed with ether, 25 cc., and benzene, 50 cc., and were suspended without previous drying in 160 cc. of dry benzene. This procedure retained the highly swollen, flocculent condition of the crystals and resulted in a semipermanent benzene suspension that gave reliable yields in the next operation. Suspensions of previously dried crystals gave erratic results. A slow stream of dry ammonia gas was passed through this suspension at room temperature for eight hours and benzene was occasionally added to replace that lost by evaporation. A rapid stream of gas greatly delayed the reaction because a quick evaporation of benzene chilled the mixture. Although it was easy to purify the crude 3,4,6-triacetyl anhydroglucose<1,5> <1,2>, 11.8 g., that was produced,[8,9] for present purposes it was sufficient to dissolve the sirup in 200 cc. of dry methanol. A nearly quantitative yield, 12 g., of 3,4,6-triacetyl-β-methylglucoside was isolated on the following day. Trituration of the crude product with 20 cc. of cold ether left 8.9 g., m. p. 93–94° (uncor.), whose specific rotation of 18.8° in methanol[9] showed that it was pure enough for nitration. Recrystallization from absolute alcohol was slow and difficult but better results were obtained with an alcohol–petroleum ether mixture. Yields, melting points and rotations given for all intermediates in the synthesis were confirmed.[8,9]

A solution of 5 g. of triacetyl methylglucoside in 50 cc. of chloroform was nitrated with 50 cc. of chloroform-soluble nitric acid and 6 g. of phosphorus pentoxide in the way already described. The crude product, 4.5 g. or 76% of calcd., crystallized readily and was recrystallized from 25 cc. of hot methanol. The physical properties given in the Introduction for 3,4,6-triacetyl-β-methylglucoside-2-nitrate were not changed by further recrystallization.

Anal. Calcd. for $C_{13}H_{19}O_{11}N$: C, 42.7; H, 5.2; N, 3.84. Found: C, 42.6, 42.5; H, 5.2, 5.7; N, 3.90, 3.87.

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RESEARCH LABORATORY OF ORGANIC CHEMISTRY
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CAMBRIDGE, MASS.
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The Alkylation of *o*- and *p*-Xylene

BY DOROTHY NIGHTINGALE AND J. R. JANES[1]

Our experiences with various catalysts for the alkylation of *m*-xylene[2] indicated that it would be worth while to study their efficiency with *o*- and *p*-xylene, especially since one of these catalysts, boron trifluoride, is less likely to promote migration or rearrangement of alkyl groups already on the ring. *t*-Butyl compounds were selected as alkylating agents since they are more reactive than their isomers and the *t*-butyl radical does not undergo rearrangement.

o-Xylene alkylated readily with *t*-butyl chloride and anhydrous ferric chloride and with *t*-butyl alcohol and boron trifluoride to form 1,2-dimethyl-4-*t*-butylbenzene in good yield.

As might be expected *p*-xylene did not alkylate as readily as the *o*- and *m*-xylenes. It did not alkylate at all with *t*-butyl alcohol and 80% sulfuric acid, *t*-butyl chloride and ferric chloride, or isobutylene and ferric chloride. With boron trifluoride and *t*-butyl alcohol, the product distilled over a 45° range and no one compound could be isolated from the mixture. Toluene alkylated readily with isobutylene and ferric chloride so the failure of *p*-xylene to alkylate was not due to the reagents.

Experimental

Alkylation of *o*-Xylene with Ferric Chloride and *t*-Butyl Chloride.—*t*-Butyl chloride (25 g.) was added during one hour and with stirring to 150 g. of *o*-xylene and 12.5 g. of anhydrous ferric chloride in a one-liter round-bottom

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(8) Brigl, *Z. physiol. Chem.*, **116**, 39 (1921); **122**, 262 (1922).

(9) Hickinbottom, *J. Chem. Soc.*, 3140 (1928); 1681 (1929); 1338 (1930).

(10) *Cf.* Müller, *Ber.*, **64**, 1820 (1931).

(11) Helferich and Becker, *Ann.*, **440**, 1 (1924).

(12) *Cf.* Behrend and Roth, *ibid.*, **331**, 359 (1904).

(1) Present address, Hercules Powder Company, Wilmington, Delaware.

(2) Nightingale, Radford and Shanholtzer, THIS JOURNAL, **64**, 1662 (1942).

three-necked flask equipped with a reflux condenser and motor stirrer. The temperature was maintained at −3 to 10° during the total reaction time of seven hours. The mixture was decomposed by pouring into 100 cc. of hydrochloric acid and 100 g. of cracked ice. The upper layer was extracted with petroleum ether (28–38°), washed and dried.

After removal of the solvent and excess *o*-xylene, the product (44 g.) distilled at 83–85° (3 mm.). Fractionation of this material yielded 30.5 g. (70%) of 1,2-dimethyl-4-*t*-butylbenzene, $n^{25}D$ 1.4970.

Anal. Calcd. for $C_{12}H_{18}$: C, 88.89; H, 11.11. Found: C, 88.83; H, 11.45.

Oxidation of 1,2-Dimethyl-4-*t*-butylbenzene.—The hydrocarbon (5 g.) was dissolved in 40 cc. of pyridine in a 3-necked conical flask and water added until the solution became slightly turbid. The flask was heated to 80° in a water-bath. Potassium permanganate (15 g.) was added with stirring during one hour and the mixture stirred an additional six hours. The manganese dioxide was separated by filtration. The filtrate was acidified with concentrated hydrochloric acid and the acid collected on a filter. Crystallization from dilute alcohol yielded 2 g. of white needles, m. p. 140–141°, the melting point recorded in the literature for 2-methyl-4-*t*-butylbenzoic acid.[3,4]

Anal. Calcd. for $C_{12}H_{16}O_2$: C, 75.00; H, 8.33; n. e., 197. Found: C, 74.60; H, 8.44; n. e., 197.

Alkylation of *o*-Xylene and Boron Trifluoride and *t*-Butyl Alcohol.—*o*-Xylene (102 g.) and 19 g. of *t*-butyl alcohol were placed in a 500-cc. three-necked conical flask equipped with a motor stirrer, gas inlet and outlet tubes for the boron trifluoride. The boron trifluoride (14 g.) was added according to the procedure previously described.[2] The product was worked up in the usual manner; yield of 1,2-dimethyl-4-*t*-butylbenzene 34.5 g., b. p. 76–81° (3 mm.), $n^{26}D$ 1.4970.

The acid obtained by oxidation of this hydrocarbon melted at 139–140° (n. e., 198) and did not depress the melting point of the acid described above.

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[3] Effront, *Ber.*, **17**, 2333 (1884).

[4] Baur, *ibid.*, **33**, 2569 (1900).

DEPARTMENT OF CHEMISTRY
UNIVERSITY OF MISSOURI
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RECEIVED OCTOBER 4, 1943

Pyrazine–Water Azeotrope

By HARRY F. PFANN[1]

In the course of an investigation involving the purification of pyrazine by fractional distillation, it was observed that an azeotrope was formed with water. This was found to distil at 95.5° (uncor.) at 760 mm., to have a refractive index $n^{25}D$ 1.4510, density of 1.06 at 25°, and a composition of 60% pyrazine—40% water. The mole ratio of 1:3.38 approaches the 1:3.31 ratio for the pyridine–water azeotrope, for which the boiling point is variously given as 92.6–94.0°.[2,3,4] The refractive index of pyrazine–water solutions appears to be a linear function of weight concentration. The pyrazine taken for this work had a melting range of 50–52° and boiling range 114–115°. Values in the literature[5,6] range from m. p. 47–54° and b. p. 111–118°.

The minimum boiling mixture was obtained from solutions containing an excess of either pyrazine or water. Essentially dry pyrazine resulted from fractionation of mixtures containing more than 60% pyrazine, the water being removed as the azeotrope. No azeotrope was observed with methyl or ethyl alcohols.

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[1] Present address: Koppers United Company, Butadiene Division, Monaca, Pa.

[2] E. Baud, *Bull. soc. chim.*, **5**, 1022–1033 (*C. A.*, **4**, 703 (1910)).

[3] Lange, "Handbook of Chemistry," 4th edition, p. 1210.

[4] Lecat, "La Tension de Vapeur des Melanges des Liquids," Brussels, 1913.

[5] Beilstein, Vol. XIII, p. 91.

[6] Aston, Peterson and Holowchak, THIS JOURNAL, **56**, 153–154 (1934).

STAMFORD RESEARCH LABORATORIES
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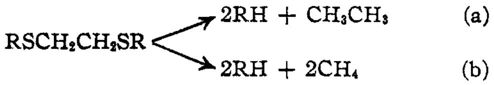
Carbon–Carbon Cleavage in the Hydrogenolysis by Raney Nickel Catalyst of Ethylenedithiol and its Ethers

By H. R. SNYDER and GEORGE W. CANNON

In the determination of the structure of ω,ω′-bimethionine [$HO_2CCH(NH_2)CH_2CH_2SCH_2CH_2SCH_2CH_2CH(NH_2)CO_2H$] the *bis*-phenylhydantoin obtained from the substance was subjected to hydrogenolysis by Raney nickel catalyst.[1] This treatment converts a monosulfide (RSR′) into the two molecules RH and R′H,[2] and accordingly was expected to convert the *bis*-phenylhydantoin into two molecules of *dl*-3-phenyl-5-ethylhydantoin and one molecule of ethane. The first of these products was isolated in good yields.[1] However, analysis of the gas produced during the hydrogenolysis has shown that not only ethane but also methane is formed. The occurrence of these two hydrocarbons indicates that the hydrogenolysis of ethers of 1,2-dithiols may take two courses.



$$RSCH_2CH_2SR \rightarrow 2RH + CH_3CH_3 \quad (a)$$
$$RSCH_2CH_2SR \rightarrow 2RH + 2CH_4 \quad (b)$$

To determine whether carbon–carbon cleavage may be expected of other similar substances ethylenedithiol and certain of its ethers have been subjected to the hydrogenolysis. The hydrogenolyses were run as described by Mozingo, Wolf, Harris and Folkers[2] and the evolved gases were passed through a tower containing 20% aqueous sodium hydroxide into a liquid-air trap. At the end of each reaction the collection tube was connected momentarily to a vacuum pump while still immersed in liquid air, and the residual liquid was allowed to vaporize into gas sample tubes. The gas then was analyzed by standard methods.[3] The results are shown in the table.

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[1] Snyder, Cannon, Howe and Nyman, THIS JOURNAL, **65**, 2211 (1943).

[2] Mozingo, Wolf, Harris and Folkers, *ibid.*, **65**, 1013 (1943).

[3] The authors are indebted to Mr. Cameron D. Lewis for certain of the gas analyses.