the acid layer was extracted with ether, and the combined ether and benzene–toluene solution was dried over anhydrous sodium sulfate followed by Drierite. The solution was distilled up to 140° and the residue was fractionated at 9 mm., collecting fractions at 72–130° and at 130–145°. To the residue was added the fraction boiling at 72–130° (9 mm.), and the mixture distilled, the material boiling at 129–149° (9 mm.) being collected and combined with the fraction boiling at 130–145 (9 mm.). Redistillation yielded 28.5 g. (52%) of ethyl benzoyldimethylacetate boiling at 132–135° (9 mm.). Some phenyl benzoate was recovered in the residues.

With hydroxylamine hydrochloride, the β-keto ester gave 3-phenyl-4-dimethylisoxazolone-5 (m. p. 69–70°)[5] in 90% yield. On ketonic hydrolysis by the acetic-sulfuric acid method,[6] the β-keto ester gave a 77% yield of phenyl isopropyl ketone (102–103° (15 mm.)); m. p. of 2,4-dinitrophenylhydrazone, 162–163°.[7]

In the Reformatsky reaction described above, in which approximately 80% of the zinc was used up, the zinc tended to become coated with a precipitate in the course of the reaction, and the yield was satisfactory only when the reaction mixture was stirred vigorously using zinc foil. With 20–30 mesh zinc 30% of the zinc was used up, giving an 18% yield of the β-keto ester. When magnesium turnings were used instead of zinc only an 18% yield of the β-keto ester was obtained even though practically all of the magnesium was used up.

In an experiment in which ethyl benzoate was used instead of phenyl benzoate, less than 10% of the zinc reacted, and the reaction was not further studied.

Other Reactions.—The following reactions were carried out essentially as described for the preparation of ethyl benzoyldimethylacetate.

Ethyl α-bromoisobutyrate with 4-phenylphenyl acetate[8] (m. p. 87–88°) gave an 11% yield of ethyl α,α-dimethylacetoacetate, b. p. 75–76° (14 mm.). When phenyl acetate was used instead of 4-phenylphenyl acetate, the β-keto ester could not be freed from the unreacted phenyl acetate. Ketonic cleavage by the acetic-sulfuric acid method,[6] gave a small amount of methyl isopropyl ketone, b. p. 93–95°; m. p. of 2,4-dinitrophenylhydrazone of the ketone, 118°.[9]

Ethyl bromoacetate with phenyl benzoate yielded a small fraction boiling at 141–143° (6 mm.) which apparently contained, in addition to phenyl benzoate, at least a trace of ethyl benzoylacetate since it gave the red enol test and the green copper salt.[10]

Ethyl bromoacetate with 4-phenylphenyl propionate[11] (m. p. 92.0–92.5°) yielded a small fraction of product boiling over a large range, giving the red enol test and the copper salt,[12] (m. p. 143–144°) of ethyl propionylacetate.

Summary

1. Phenyl benzoate has been found to undergo the Reformatsky reaction with ethyl α-bromoisobutyrate to form ethyl benzoyldimethylacetate in good yield.

2. Phenyl esters appear to be satisfactory as the carbonyl component for the Reformatsky reaction only when neither the phenyl ester nor the bromoester has α-hydrogens.

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[5] Renfrow and Hauser, This Journal, **60**, 464 (1938).

[6] Hudson and Hauser, *ibid.*, **63**, 3163 (1941).

[7] Huntress and Mulliken, "Identification of Pure Organic Compounds," John Wiley and Sons, New York, N. Y., 1941, p. 391.

[8] This ester was prepared in 74% yield from 4-phenylphenol and acetic anhydride essentially as described for the corresponding propionate, see ref. 11.

[9] Huntress and Mulliken, *op. cit.*, p. 375.

[10] Huntress and Mulliken, *ibid.*, p. 268.

[11] Abramovitch and Hauser, This Journal, **64**, 2272 (1942).

[12] Beilstein, "Handbuch der organischen Chemie," Julius Springer, Berlin, 1921, Vol. III, p. 671.

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NOTES

2,3,4-Triacetyl-α-methylglucopyranoside-6-nitrate and 3,4,6-Triacetyl-β-methylglucopyranoside-2-nitrate

By E. K. Gladding[1] and C. B. Purves

Although these two compounds were synthesized, apparently for the first time, by conventional methods as an incident in a larger research, it seems advisable to make a brief, separate record of their preparation and their properties.

The nitration of 2,3,4-triacetyl-6-trityl-α-methylglucoside[2] produced a crystalline residue consisting of triphenylmethyl carbinol and the desired 6-nitrate in equimolecular amount.[3] A fractional crystallization, carried out exactly as specified below, resulted in a 79% yield of pure 2,3,4-triacetyl-α-methylglucoside-6-nitrate, which occurred as well formed prisms having m. p. 112–113° (cor.). No wandering of acetyl groups occurred during the nitration because the same nitrate was obtained by heating 2,3,4-triacetyl-6-iodo-6-desoxy-α-methylglucopyranoside[4] with excess silver nitrate in acetonitrile. Conversely, the 6-iodo compound was produced in 91% yield by heating the nitrate with excess sodium iodide dissolved in acetonylacetone.[5] The specific rotation of the nitrate in 1.11% chloroform solution was $[\alpha]^{20}\text{D}$ 132°, and this value, in conjunction with that of −14.3° found for triacetyl-β-methylglucopyranoside-6-nitrate,[6] leads to a molecular rotation difference of 53,400. The fact that this difference is very close to that of 53,900, accepted for tetraacetyl α- and β-methylglucoside[7] supports the conclusion that the two isomeric nitrates differ only in the configuration of the glycosidic carbon atom.

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[1] Du Pont Post-Doctoral Research Fellow, 1942–1943. Present address, Magnolia Petroleum Company, Field Research Department, Dallas, Texas.

[2] Haworth, Owen and Smith, *J. Chem. Soc.*, 88 (1941).

[3] *Cf.* Oldham and Bell, This Journal, **60**, 323 (1938).

[4] Compton, *ibid.*, **60**, 395 (1938).

[5] Murray and Purves, *ibid.*, **62**, 3194 (1940).

[6] Oldham, *J. Chem. Soc.*, 2840 (1925).

[7] Hudson and Dale, This Journal, **40**, 997 (1918).

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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(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).

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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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[1] Present address, Hercules Powder Company, Wilmington, Delaware.

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