

twenty minutes 12.5 g. (0.048 mole) of di-*p*-anisyl ketone (m. p. 140–142°) dissolved in 125 ml. of dry, warm thiophene-free benzene. After fifteen minutes of stirring at room temperature, a qualitative test for the Grignard reagent<sup>3</sup> was made to be certain that an excess had been used. Otherwise the product is difficult to purify because of the ketone present. The mixture was hydrolyzed by pouring it into 200 g. of ice and water containing 10 g. of ammonium chloride. The benzene-ether layer was separated and washed successively with 100-ml. portions of water, 2% sodium carbonate solution, and water. The solvent was removed under reduced pressure at 60° to give 10 g., 83% of the calculated yield melting 80–83°. Crystallization from 95% ethanol made alkaline to phenolphthalein with aqueous sodium hydroxide raised the melting point to 82–83.5°. To avoid dehydration the alcoholic solution was not heated above 60°.

*Anal.* Calcd. for C<sub>18</sub>H<sub>18</sub>O<sub>3</sub>: C, 74.80; H, 6.94; mol. wt., 258. Found: C, 74.90; H, 6.74; mol. wt. (cryoscopic in benzene), 265.

One gram of this compound was oxidized by refluxing one hour in a solution of 10 ml. of glacial acetic acid, 2 drops of concentrated sulfuric acid, and 1.8 g. of chromic acid. The yield of ketone was 0.7 g., melting 141–142°. A mixed melting point with authentic di-*p*-anisyl ketone showed no depression.

Di-(*p*-anisyl)-methylcarbinol is very readily dehydrated to 1,1-di-(*p*-anisyl)-ethylene. A sample of the pure compound standing on the shelf spontaneously formed the ethylene in less than two months, whereas diphenylmethylcarbinol and di-(*p*-chlorophenyl)-methylcarbinol are stable under the same conditions. Thus, it is important in this synthesis to avoid elevated temperatures and even traces of acid.

(3) Gilman and Schulze, *THIS JOURNAL*, **47**, 2002 (1925).

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#### 4-Benzyl-2,3-isopropylidene-D-mannosan<1,5>β<1,6> and 2-Benzyl-3,4-isopropylidene-D-galactosan<1,5>β<1,6>

**4-Benzyl-2,3-isopropylidene-D-mannosan<1,5>β<1,6>.**—Two and one-half grams of 2,3-isopropylidene-D-mannosan<1,5>β<1,6><sup>1</sup> was dissolved in 60 ml. of liquid ammonia in a three-necked flask (fitted with a mercury-sealed stirrer, a gas inlet tube and an outlet protected by a soda lime tube) cooled in a Dry Ice-acetone cooling bath. Three grams of sodium in small pieces was added in one portion and solution was completed by gentle stirring; the blue color imparted to the solution disappeared in a few minutes. Following the addition of 2.3 ml. (about 1.6 molecular equivalents) of benzyl chloride the flask was raised from the bath and the ammonia allowed to boil off slowly while standing at room temperature; dry air was then passed through the flask for two hours and the residue, which was easily scraped from the flask, was dried overnight in an evacuated desiccator. The reaction product was washed well with water and recrystallized from 5 parts of alcohol, forming large elongated plates which melted at 99–100° and rotated [α]<sub>D</sub><sup>20</sup> –13.0° in chloroform (*c*, 0.83). It is soluble in acetone, chloroform, pyridine and warm alcohol and nearly insoluble in water and petroleum ether.

*Anal.* Calcd. for C<sub>16</sub>H<sub>20</sub>O<sub>5</sub>: C, 65.74; H, 6.90. Found: C, 65.86; H, 7.07.

**2-Benzyl-3,4-isopropylidene-D-galactosan<1,5>β<1,6>.**—The procedure used for the benzylation of 3,4-isopropylidene-D-mannosan<1,5>β<1,6> was applied to 2.5 g. of 3,4-isopropylidene-D-galactosan<1,5>β<1,6> prepared by the pyrolysis of lactose.<sup>2</sup> The product remaining

(1) Knauf, Hann and Hudson, *THIS JOURNAL*, **63**, 1449 (1941).

(2) Hann and Hudson, *ibid.*, **64**, 2436 (1942).

after removal of the ammonia was somewhat sticky and it was extracted with one 10-ml. and three 5-ml. portions of chloroform; the extract was evaporated and gave a mass of long fine needles which was stirred with 10 ml. of alcohol, cooled and filtered. The yield was 3.2 g. (89%). The compound was recrystallized from three parts of alcohol in the form of needles which melted at 84–85° and rotated [α]<sub>D</sub><sup>20</sup> –81.9° in chloroform (*c*, 0.85). The benzyl ether is soluble in acetone, ethyl acetate, ether, pyridine and warm alcohol and nearly insoluble in water and petroleum ether.

*Anal.* Calcd. for C<sub>16</sub>H<sub>20</sub>O<sub>5</sub>: C, 65.74; H, 6.90. Found: C, 65.86; H, 7.05.

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#### 2,6-Di-*tt*-octyl-4-methylphenol<sup>1</sup>

A mixture of 214 g. (2 moles) of *p*-cresol and an equal volume of diisobutylene was placed in an ice-bath and stirred for three hours during which were added additional diisobutylene to make a total of 896 g. (8 moles) and 21 g. of 45% boron trifluoride in ether as catalyst. The mixture then was let stand at 40–50° for fifteen hours. Catalyst was removed by agitation of the reaction mixture with 350 g. of 30% aqueous sodium hydroxide. Distillation through a column packed with Raschig rings (6 theor. plates) yielded a small amount of diisobutylene at atmospheric pressure, and then, at 10 mm., fractions containing approximately 581 g. of tetraisobutylene and 283 g. 2-*tt*-octyl-4-methylphenol<sup>2</sup> (b. p. 143–144° (10 mm.); *n*<sub>D</sub><sup>20</sup> 1.5105 (super-cooled); m. p. 47.0–47.8°, from petroleum ether). The viscous residue was distilled without fractionation to give 61 g. (9% yield) of crude 2,6-di-*tt*-octyl-4-methylphenol, a highly viscous yellow liquid, b. p. 168–195° (5 mm.) and *n*<sub>D</sub><sup>20</sup> 1.5036, which slowly crystallized. Recrystallized twice from alcohol, the long needles had m. p. 51.6–52.2° and b. p. 188° (10 mm.).

*Anal.* Calcd. for C<sub>23</sub>H<sub>40</sub>O: C, 83.07; H, 12.13; mol. wt., 332.55. Found: C, 82.81, 82.54; H, 12.24, 12.02; mol. wt. (micro-Rast), 338.

(1) The 1,1,3,3-tetramethylbutyl group is designated *tt*-octyl after Niederl and Ruderman, *THIS JOURNAL*, **67**, 1176 (1945).

(2) W. F. Hester, U. S. Patent 2,008,017.

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#### 1,4-Dimethoxy-2-butene<sup>1,2,3</sup> and 1,4-Dimethoxy-3-chloro-2-butanol

**1,4-Dimethoxy-2-butene.**—A total of 69.1 g. of 1,4-dimethoxy-2-butyne<sup>4</sup> was reduced in three equal batches, each dissolved in 100 cc. of methanol, with Raney nickel and hydrogen at room temperature and about 50 lb. pres-

(1) The work reported was done under a contract, recommended by the Committee on Medical Research, between the Office of Scientific Research and Development and the University of Rochester.

(2) This compound has been prepared by Johnson, *J. Chem. Soc.*, 1009 (1946). Dr. Johnson has pointed out in a private communication that the material obtained by him is undoubtedly the *trans* form, whereas the sample obtained by us by catalytic reduction must be the *cis* form.

(3) Cf. Campbell and O'Connor, *THIS JOURNAL*, **61**, 2897 (1939).

(4) This compound was prepared at Northwestern University by Professor C. D. Hurd and Dr. Otis Fancher, to whom we wish to express our appreciation. It was obtained by the action of chloromethyl methyl ether on the acetylenic Grignard (Lespieau, *Ann. chim.*, [8] **27**, 172 (1912); Dupont, *ibid.*, [8] **30**, 492 (1913)).