

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 reagent³ 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 C₁₄H₁₈O₃: 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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OLIVER GRUMMITT
DEAN MARSH

RECEIVED NOVEMBER 19, 1947

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>¹ 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 $[\alpha]^{20}_D -13.0^\circ$ 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 C₁₆H₂₀O₅: 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.² 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 $[\alpha]^{20}_D -81.9^\circ$ 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 C₁₆H₂₀O₅: C, 65.74; H, 6.90. Found: C, 65.86; H, 7.05.

CHEMISTRY LABORATORY
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RECEIVED OCTOBER 17, 1947

2,6-Di-*tt*-octyl-4-methylphenol¹

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-methylphenol² (b. p. 143–144° (10 mm.); n^{20}_D 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^{20}_D 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 C₂₃H₄₀O: 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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LELAND J. KITCHEN

RECEIVED NOVEMBER 7, 1947

1,4-Dimethoxy-2-butene^{1,2,3} and 1,4-Dimethoxy-3-chloro-2-butanol

1,4-Dimethoxy-2-butene.—A total of 69.1 g. of 1,4-dimethoxy-2-butyne⁴ 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 (Lespiau, *Ann. chim.*, [8] **27**, 172 (1912); Dupont, *ibid.*, [8] **30**, 492 (1913)).

sure. The calculated amount of hydrogen was taken up in a few minutes, with the evolution of appreciable amounts of heat. The catalyst was removed by filtration, the batches were combined, and distilled through a column until the b. p. reached 70°. Some low-boiling petroleum ether was added, causing separation of a lower layer, which was removed, and the solution dried. The solvent was removed and the residue distilled, which yielded the following fractions:

I	II	III
3.4 g.	b. p. 100–136°	n_D^{20} 1.4213
29.0	136–141°	1.4220
16.0	141–146°	1.4240

The analytical sample had the properties: b. p. 138–138.5°; n_D^{20} 1.4201; d_4^{20} 0.8958.

Anal. Calcd. for $C_6H_{12}O_2$: C, 62.03; H, 10.42. Found: C, 62.00; H, 10.39.

1,4-Dimethoxybutane has n_D^{15} 1.4031⁵; Johnson² reports n_D^{20} 1.4220 for (*trans*) 1,4-dimethoxy-2-butene. The percentage composition calculated by this author for this compound (C, 63.2; H, 8.8) is somewhat in error.

1,4-Dimethoxy-3-chloro-2-butanol.—A 0.68 molar solution of hypochlorous acid was prepared by passing chlorine

(5) Dionneau, *ann. chim.*, [9] 3, 259 (1915).

into a solution of 95 g. of sodium bicarbonate in 1140 cc. of water.⁶ One hundred-cc. portions of this solution were added with stirring to 72.9 g. of 1,4-dimethoxy-2-butene while cooling with ice, a total of 1080 cc. (theoretical 930 cc.) of the hypochlorous acid solution being added. After the addition was complete, the solution was stirred for one-half hour in the ice-bath, then for three and one-half hours at room temperature, and allowed to stand overnight. At this point, a potassium iodide test showed practically no oxidizing power in the solution, and it was saturated with sodium chloride, extracted three times with ether and the residue from the ether extract distilled. A total of 69.0 g. was collected as product in several fractions, b. p. 92–98.5° (8 mm.) most of it boiling at 96–98.5°; the analytical sample had the following properties: b. p. 97–97.5° (8 mm.), n_D^{20} 1.4542.

Anal. Calcd. for $C_6H_{10}ClO_3$: C, 42.74; H, 7.77. Found: C, 42.32; H, 7.41.

(6) Wohl and Schweitzer, *Ber.*, 40, 94 (1907).

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DEPARTMENT OF CHEMISTRY
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D. S. TARBELL
J. F. BURNETT⁷

RECEIVED NOVEMBER 17, 1947

COMMUNICATIONS TO THE EDITOR

THE CRYSTAL STRUCTURES OF AMMONIUM AND POTASSIUM MOLYBDOTELLURATES

Sir:

A structural study is now being made in this Laboratory of heteropoly ions of the general type $[XMo_6O_{24}]^{-n}$, in which the charge n depends on the metalloid X. The investigation is centered on the salts ammonium and potassium molybdotellurate, $(NH_4)_6TeMo_6O_{24} \cdot 7H_2O$ and $K_6TeMo_6O_{24} \cdot 7H_2O$, which have been described morphologically by Donnay and Mélon¹ as orthorhombic, homeomorphous and probably isostructural. A preliminary X-ray lattice study was reported by the writer to the Crystallographic Society in March 1947.² A more complete diffraction study since then has shown that the two salts are not isostructural, but possess entirely different and unrelated (though similar) symmetries. The final unit cell and space group data are as follows:

$(NH_4)_6TeMo_6O_{24} \cdot 7H_2O$, orthorhombic *mmm*; $a_0 = 14.62 \text{ \AA}$, $b_0 = 14.91$, $c_0 = 14.26$; space group *Pnaa* = C_{2h}^{10} ; 4 formulas (as above) per cell, density calcd. 2.82, found (Donnay and Mélon) 2.78.
 $K_6TeMo_6O_{24} \cdot 7H_2O$, orthorhombic *mmm*; $a_0 = 14.30 \text{ \AA}$, $b_0 = 14.95$, $c_0 = 14.26$; space group *Pbca* = C_{2h}^{15} ; 4 formulas per cell, density calcd. 3.15, found (Donnay and Mélon) 3.05.

The structure problem was attacked by the preparation of Patterson maps for the ammonium

(1) J. D. H. Donnay and J. Mélon, *Proc. Nat. Acad. Sci.*, 20, 327–335 (1934).

(2) H. T. Evans, Jr., *Am. Min.*, 32, 687 (1947).

salt projected on the three pinacoid faces, using diffraction intensities visually estimated from Weissenberg photographs. These maps showed sharp peaks revealing the positions of the tellurium and molybdenum atoms. Although these maps were greatly simplified by the presence of the heavy tellurium atom at a symmetry center, an ambiguity still remained which allowed the possibility of three different models. This ambiguity is represented by an indeterminacy of sign of the parameters of one of the three kinds of molybdenum atoms in the structure. Calculation of the structure factors for a certain class of reflections in each of the series $(hk0)$, $(0kl)$ and $(h0l)$ which is sensitive to this change of sign, shows that a reasonable check of observed and calculated intensities is obtained with only one of the three possible models. The correct parameters for the tellurium and molybdenum atoms in the ammonium crystals, and probably also the potassium crystals (with x and z interchanged), are

	x	y	z
Te	0	0	0
Mo _I	0	0.228	0
Mo _{II}	0.113	0.121	-0.168
Mo _{III}	0.113	-0.121	-0.168

The model accepted here is one originally proposed hypothetically by Anderson.³ In it, the molybdenum atoms lie in a hexagon about the tellurium atom at the center (Te–Mo and Mo–Mo distances 3.42 Å.); the oxygen atoms lie close-

(3) J. S. Anderson, *Nature*, 140, 850 (1937).