reduced with platinum oxide catalyst at room temperature and atmospheric pressure. The hydrogen uptake was 191 cc. (S.T.P.) or 1.01 molar equivalents. Filtration, removal of solvent, and distillation yielded (+)-cyclohexylmethylcarbinol, n^{25}D 1.4631, [α]^{25}D +5.36° (homogeneous).

The (–)-1-Cyclopentenylmethylcarbinol.—Equivalent amounts of the *dl*-hydrogen phthalate of 1-cyclopentenylmethylcarbinol and brucine were dissolved in refluxing dry acetone and the hot solutions mixed, filtered and allowed to cool. The resulting crystals of brucine salt together with those obtained by evaporation of the acetone to one-half volume, were recrystallized from acetone to constant rotation. The pure brucine salt melts at 154–155° with decomposition, [α]$^{29.8}$D –31.9°, (*c* 4.3, $CHCl_3$). The salt was decomposed and reduced exactly as described for the cyclohexenyl analog to yield (–)-1-cyclopentenylmethylcarbinol: b.p. 89.2–90.4° (36 mm.), n^{25}D 1.4707, d^{25}_4 0.9438, [α]^{25}D –10.21° (homogeneous). The observed rotations at different temperatures are given in Table I.

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[CONTRIBUTION FROM THE DIVISION OF AGRICULTURAL BIOCHEMISTRY, UNIVERSITY OF MINNESOTA]

A Reinvestigation of the Preparation of β-Methyl Lactoside[1,2]

BY F. SMITH AND J. W. VAN CLEVE

Pure crystalline β-methyl lactoside has been prepared. Its structure has been proved by oxidation with periodic acid and by methylation followed by hydrolysis and identification of the methylated monosaccharides.

In 1902, Ditmar[3] reported the preparation of crystalline β-methyl lactoside and the corresponding crystalline heptaacetyl β-methyl lactoside but since then there seems to have been no further mention of the preparation of either of these compounds in the crystalline form. It is perhaps of some interest to note that Hudson[4] deduced from the Isorotation Rules and the specific rotation quoted by Ditmar for his acetate that the latter was probably impure.

Pure β-methyl lactoside, prepared as described herein by the interaction of α-acetobromolactose[5] with methanol to give heptaacetyl β-methyl lactoside followed by deacetylation with sodium methoxide according to the method of Zemplén,[6] crystallizes as a monohydrate, m.p. 206°, [α]^{20}D +5.6° in water. The specific rotation is in close agreement with that calculated by Hudson[4] from the Isorotation Rules. The m.p., however, is more than thirty degrees higher than that quoted by Ditmar.[3] The structure of the β-methyl lactoside was proved by methylation studies and by periodate oxidation. The crystalline heptamethyl-β-methyl lactoside was hydrolyzed and the resulting methylated cleavage fragments, 2,3,4,6-tetramethyl-D-galactose and 2,3,6-trimethyl-D-glucose, were separated by column chromatography[7,8] using methyl ethyl ketone–water azeotrope as the solvent and identified in the usual way. The heptaacetyl derivative of β-methyl lactoside could not be induced to crystallize either when prepared directly from the α-acetobromolactose or by acetylation of crystalline β-methyl lactoside.

Experimental

Preparation of β-Methyl Lactoside.—Lactose octaacetate (18.0 g.) was converted to acetobromolactose (yield 15.2 g.) by the method of Fischer.[9] To a solution of the acetobromolactose (not recrystallized) in absolute methanol (200 ml.) was added an excess of dry silver carbonate and the mixture was shaken for 16 hours. The solution was treated with a little charcoal, filtered and evaporated under reduced pressure giving heptaacetyl β-methyl lactoside as a sirupy residue which failed to crystallize. It was redissolved in absolute methanol (*ca.* 100 ml.) and a small piece of sodium was added to effect deacetylation.[6] The solution was refluxed for 30 minutes and then allowed to cool. The crude β-methyl lactoside which separated while the reaction mixture was being heated was filtered off and recrystallized from hot 95% ethanol (yield 5.1 g.); [α]^{26}D +5.6° in water (*c* 3); m.p. 206°. Ditmar[3] has recorded a melting point of 172° for this substance. His preparation, for which he failed to give a specific rotation, was evidently impure.

Anal. Calcd. for $C_{13}H_{24}O_{11} \cdot H_2O$: C, 41.7; H, 7.0; $-OCH_3$, 8.3. Found: C, 41.9; H, 6.8; $-OCH_3$, 8.6.

When the monohydrate was heated at 150° *in vacuo* for one hour, 1 molecule of water was lost (tested by weighing) and the product showed [α]^{23}D +6.3° in water (*c* 3.5). Hudson[4] has calculated a value of [α]^{20}D +6.0° (in water) for β-methyl lactoside.

Oxidation of β-Methyl Lactoside with Periodic Acid.—To a solution of β-methyl lactoside monohydrate (0.0522 g.) in water (150 ml.) was added 20 ml. of 0.1 *N* periodic acid and the mixture was diluted with water to 200 ml. and kept at 5°. After 95 hours titration of an aliquot of the reaction mixture with standard sodium arsenite solution in the usual way[10] showed that 3.1 moles of periodic acid had been consumed per mole of β-methyl lactoside.

Methylation of β-Methyl Lactoside.—β-Methyl lactoside monohydrate (5.0 g.) was methylated with 30% sodium hydroxide and methyl sulfate.[11] After one methylation the crude sirupy product (6.0 g.) was methylated to completion by dissolving it in anhydrous toluene, digesting with metallic sodium and treating the sodio derivative so formed with methyl iodide.[12] After filtering off the sodium iodide from the reaction mixture, concentration of the filtrate gave a sirup which crystallized spontaneously in the flask. Two recrystallizations from boiling petroleum ether gave heptamethyl-β-methyl lactoside in the form of long, colorless needles, m.p. 86–86.5°; [α]^{19}D –22.2° in ethanol (*c* = 2.1). Haworth and Leitch[11] who obtained heptamethyl-β-methyl lactoside by direct methylation of lactose followed by fractional distillation of the product, reported a melting point of 77–82° and a specific rotation of [α]^{20}D –16.9° in ethanol for this substance.

Anal. Calcd. for $C_{20}H_{38}O_{11}$:. C, 52.9; H, 8.4; $-OCH_3$, 54.6. Found: C, 52.9; H, 8.6; $-OCH_3$, 54.8.

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(1) From a thesis submitted to the graduate faculty of the University of Minnesota in partial fulfilment of the requirements for the degree of Doctor of Philosophy by John W. Van Cleve.

(2) Paper No. 2710, Scientific Journal Series, Minnesota Agricultural Experiment Station.

(3) R. Ditmar, *Ber.*, **35**, 1951 (1902).

(4) C. S. Hudson, THIS JOURNAL, **47**, 268 (1925).

(5) W. Koenigs and E. Knorr, *Ber.*, **34**, 957 (1901).

(6) G. Zemplén, *ibid.*, **59**, 1258 (1926).

(7) L. Boggs, L. S. Cuendet, M. Dubois and F. Smith, in press.

(8) L. Hough, J. K. N. Jones and W. H. Wadman, *J. Chem. Soc.*, 2511 (1949).

(9) E. Fischer and H. Fischer, *Ber.*, **43**, 2521 (1910).

(10) P. Fleury and J. Lange, *J. Pharm. Chim.*, [8] **17**, 107 (1933).

(11) W. N. Haworth and G. C. Leitch, *J. Chem. Soc.*, **113**, 195 (1918).

(12) E. Pacsu and S. M. Trister, THIS JOURNAL, **61**, 2442 (1939).

Hydrolysis of Heptamethyl-β-methyl Lactoside.—The heptamethyl-β-methyl lactoside (0.95 g.) was dissolved in 1 *N* sulfuric acid (5 ml.) and the solution was heated on the boiling water-bath for 2.5 hours. The hydrolysate was diluted with water to 75 ml., neutralized with barium carbonate and filtered. The filtrate was evaporated *in vacuo* (bath temp., 50–60°) to yield a sirupy mixture of 2,3,6-trimethyl-D-glucose and 2,3,4,6-tetramethyl-D-galactose which was separated into its constituents by means of partition chromatography on a column of cellulose[7] using methyl ethyl ketone–water azeotrope as the partitioning solvent,[13] and an automatic fractionating device.[7]

The 2,3,6-trimethyl-D-glucose so obtained as the slower moving component showed m.p. and mixed m.p. 115–117°[14] after recrystallization from benzene–petroleum ether and once from benzene.

The 2,3,4,6-tetramethyl-D-galactose, the faster moving component to emerge from the column was distilled (b.p. (bath temp.) 160°, 0.5 mm.) and converted directly to the anilide; m.p. and mixed m.p. 196–197° (after recrystallization from ethyl acetate).[15]

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[13] L. A. Boggs, L. S. Cuendet, I. Ehrenthal, R. Koch and F. Smith, *Nature*, **166**, 520 (1950).

[14] W. S. Denham and H. Woodhouse, *J. Chem. Soc.*, **105**, 2357 (1914).

[15] H. H. Schlubach and K. Moog, *Ber.*, **56**, 1957 (1923).

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF OKLAHOMA]

Studies of Non-aqueous Solvates. VI. The Preparation of Magnesium Amide Bromide

BY H. H. ROWLEY AND LEONARD N. DEVONSHIRE

The ammonolysis of ethylmagnesium bromide has been carried out in solutions of ethyl ether or benzene saturated with ammonia. The slightly soluble product obtained has been identified as magnesium amide bromide, $Mg(NH_2)Br$, rather than the possible imido or nitrilo ammonobasic salt. The existence of two ammoniates of magnesium amide bromide has been indicated. The diammoniate is apparently formed at room temperatures when excess ammonia is present, the monoammoniate resulting from partial desolvation of the diammoniate. The diammoniate of magnesium amide bromide has been found to be relatively stable under dry atmospheric conditions, but may be changed to the monoammoniate by gentle heating at lower pressures. The decomposition to the completely desolvated magnesium amide bromide requires heating at higher temperatures and preferably reduced pressure. The desolvated product has been found to be stable to over 200°. An attempt to prepare ethyl etherates of magnesium amide bromide was not successful.

The existence of ammonobasic salts of the magnesium halides has been previously reported but no study has been made of their preparation or properties. Meunier,[1] Oddo and Calderaro,[2] Cornell,[3] Pickard[4] and others have reported the formation of ammonobasic salts when various Grignard reagents and addition compounds of the Grignard reagent were decomposed with ammonia. Usually, the apparently inorganic precipitates were not extensively analyzed or investigated.

As a continuation of a study of non-aqueous solvates of magnesium bromide and related compounds,[5a–g] it was decided to investigate the precipitates obtained by the ammonolysis of Grignard reagents. Preliminary work indicated that the precipitates obtained in ketimine formation[4] were not of sufficient purity to be used in the investigation. It was therefore decided to undertake the preparation of pure magnesium amide bromide and to study some of its properties.

Experimental

The experimental procedure in general involved the preparation of ethylmagnesium bromide followed by the ammonolysis of the Grignard reagent. The product was obtained as a fine white precipitate which was separated from the liquid medium. This product was analyzed, and some reactions such as desolvation and reaction with other solvents were studied.

Preparation and Ammonolysis of the Grignard Reagent.—A filtered solution of the ethylmagnesium bromide was prepared from 25 ml. of pure ethyl bromide, 15 g. of magnesium turnings and 150 ml. of ethyl ether. Preliminary work indicated a much better product could be obtained by the slow addition of the Grignard reagent to a relatively inert solvent such as benzene or ethyl ether saturated with ammonia. Mechanical stirring during the addition was also found advisable.

Anhydrous ammonia was introduced into the reaction flask containing 200 ml. of benzene or ethyl ether by means of a gas inlet tube which extended well below the surface of the inert liquid. A slow stream of nitrogen was also passed over the reaction mixture. A gas outlet tube allowed the escape of excess ammonia, nitrogen and ethane formed during the ammonolysis of the Grignard reagent. The product was obtained as a fine white suspension. When ether was used as an inert solvent, it was necessary to add additional ether during the reaction to keep the mixture from becoming too thick. With benzene, the loss of solvent was less noticeable.

Isolation of Product.—The product, suspended in the inert solvent, was transferred from the reaction flask by filtering through a sintered glass filter in an anhydrous nitrogen atmosphere. The cake formed by gentle suction was then easily broken up with a spatula and dried to a fine powder.

Since all of the solvent was not removed by the filtration procedure, and since experimental results indicated the possibility that rather stable ammoniates were formed, it was found necessary to heat the original product to obtain the desolvated product. The most satisfactory procedure was to use low pressures during the heating. The original filtered product was placed in a flask, connected to an oil-pump vacuum, and evacuated 5–10 minutes until most of the excess solvent had evaporated. The flask was then immersed in a hot wax-bath kept at 180°. After 4 hours the original sample was completely desolvated. An additional 10 hours evacuation at 180° showed no appreciable change in composition. The product was a fine, faintly gray powder.

Several other methods were tried including extraction of ammonia from the solid suspended in benzene using anhydrous calcium chloride. Desolvation was also attempted by heating at atmospheric pressure in a stream of dry nitrogen. The latter method was also slow since too rapid heating sometimes resulted in partial fusion of the solid.

Analysis.—Early experience showed that the products being analyzed liberated ammonia at a rapid rate when treated with water or absolute ethanol and that some am-

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[1] L. Meunier, *Compt. rend.*, **136**, 758 (1903).

[2] C. Oddo and E. Calderaro, *Gazz. Chim. Ital.*, **53**, 94 (1923).

[3] E. F. Cornell, THIS JOURNAL, **50**, 3314 (1928).

[4] P. L. Pickard and D. J. Vaughan, *ibid.*, **72**, 5017 (1950).

[5] H. H. Rowley, (a) *ibid.*, **72**, 3305 (1950); (b) *ibid.*, **63**, 1908 (1941); (c) *Proc. Iowa Acad. Science*, **47**, 159 (1940); (d) THIS JOURNAL, **61**, 1949 (1939); (e) *ibid.*, **59**, 631 (1937); (f) *ibid.*, **58**, 1337 (1936); (g) *ibid.*, **52**, 3523 (1930).