ferrous chloride was added to the slightly opaque solution and the mixture was stirred overnight without the bath. It was then added to a solution of 10 ml. of concentrated hydrochloric acid in 100 ml. of water, the aqueous layer and oil were extracted with chloroform, and the combined organic layers were dried and taken to dryness. The residue was distilled to remove unreacted β-hydroxyethylcyclopentadiene [1.35 g. (14%), b.p. 25–30° (0.2 mm.)], the distillation residue (6.52 g.) was dissolved in chloroform, and one-fourth of the solution was chromatographed on Florisil in benzene. Elution with benzene and benzene–ether was unfruitful, but subsequent elution with ether slowly removed 0.89 g. of colored material, which after two crystallizations from ether gave 0.59 g. (19%) of 1,1′-bis(β-hydroxyethyl)ferrocene, m.p. 43–45°.

Anal. Calcd. for $C_{14}H_{18}FeO_2$: C, 61.34; H, 6.62; Fe, 20.37. Found: C, 61.31; H, 6.76; Fe, 20.52.

Subsequent elution with acetone removed 0.45 g. of liquid, which was extracted with dry ether, the extract was taken to dryness, and the residue was extracted with 20 ml. of dry ether. Removal of solvent from the extract left 0.35 g. (13%) of amber oil, elemental analyses on which agreed fairly well for a compound containing four units of starting material (less two hydrogen atoms) per iron atom.

Anal. Calcd. for $C_{28}H_{38}FeO_4$: C, 68.01; H, 7.75; Fe, 11.30. Found: C, 67.48; H, 7.78; Fe, 10.83, 11.15.

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Pyrolytic Conversion of 7,7-Dichloronorcarane to Cycloheptatriene

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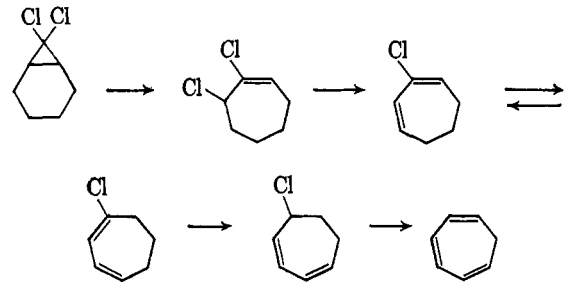
1,3,5-Cycloheptatriene is a versatile chemical intermediate used as a starting material for preparation of tropolone,[1] tropone,[2] and tropylium[3] salts. A convenient synthesis of high purity cycloheptatriene would facilitate work on these aromatic ring systems and on seven-membered ring compounds generally. Recent methods of synthesis of cycloheptatriene have involved reaction of diazomethane with benzene,[4] pyrolysis of 7,7-dichloronorcarane,[5] and pyrolysis of bicycloheptadiene.[6] The latter procedure is presently the most useful for large-scale preparations but gives a product contaminated with 7% toluene which is difficult to remove. Furthermore, the maximum yield is 45%.

The synthesis reported here is a modification of the 7,7-dichloronorcarane pyrolysis procedure of Winberg. Winberg passed 7,7-dichloronorcarane through a pyrolysis tube packed with short lengths of glass tubing heated at 490–520°. He obtained a 57% yield of hydrocarbon consisting of 35% cycloheptatriene and 65% toluene. The over-all cycloheptatriene yield was 14%. The origin of the toluene formed under Winberg's conditions was not established. It might have been a coproduct formed at the same time as the cycloheptatriene or it might have resulted from isomerization of cycloheptatriene.

The conditions chosen for our study of the pyrolysis of 7,7-dichloronorcarane were 444° over lump calcium oxide. These conditions were chosen to minimize any thermal or hydrogen chloride catalyzed isomerization of cycloheptatriene to toluene. Aerosol formation was a problem and some product was lost by entrainment during condensation of the pyrolysate. Examination of the crude condensate by gas–liquid chromatography showed a single hydrocarbon peak, a peak for unreacted dichloronorcarane, and twin peaks at an intermediate retention time. Separation of cycloheptriene by distillation gave 63% of a product having no toluene bands in its infrared spectrum. No toluene was detectable on gas–liquid chromatography. The procedure used would have detected 2% toluene. The distillation fraction corresponding to the twin peaks at intermediate retention time appeared from its infrared spectrum to be a mixture of chlorocycloheptadienes. This identification is consistent with the observed boiling point.

The mechanism by which cycloheptatriene is formed from 7,7-dichloronorcarane was not studied. The presence of two chlorocycloheptadienes in the crude product would be consistent with chlorocycloheptadienes serving as intermediates. The work of Kloosterziel[7] makes reasonable the occurrence of 1,5-hydrogen shifts in 1- and 2-chlorocycloheptadiene-1,3. This would permit isomerization of chlorine from a stable vinylic position to an allylic position where it could be readily eliminated as hydrogen chloride. The reaction sequence



is consistent with the known facts.

The effect of calcium oxide on the pyrolysis of bicycloheptadiene was studied qualitatively to see if the toluene content of the pyrolysate was reduced. No change in toluene content was detected. Since pyrolysis of 7,7-dichloronorcarane under identical conditions yielded toluene-free cycloheptatriene, the toluene in bicycloheptadiene pyrolysate must arise independently of cycloheptatriene. Klump and Chesick came to this same conclusion from comparing the pyrolysis rate of bicycloheptadiene with the rate of thermal rearrangement of cycloheptatriene to toluene.[8]

Experimental

Cycloheptatriene.—The apparatus consisted of a dropping funnel and a nitrogen inlet atop a Pyrex tube (30 × 2.8 cm.) charged with 140 g. of lump calcium oxide. The receiver train was an ice-cooled 50-ml. filter flask followed by a Dry Ice cooled U-tube. The calcium oxide was heated to 444° by a tube furnace. Then 50 g. (0.30 mole) of 7,7-dichloronorcarane was added from the dropping funnel during 1.5 hr., while maintaining a nitrogen

(1) W. von E. Doering and L. H. Knox, *J. Am. Chem. Soc.*, **72**, 2305 (1950).
(2) A. P. Ter Borg, R. Van Helden, and A. F. Bickel, *Rec. trav. chim.*, **81**, 177 (1962).
(3) A. P. Ter Borg, R. Van Helden, and A. F. Bickel, *ibid.*, **81**, 164 (1962).
(4) E. Muller and H. Fricke, *Ann.*, **661**, 38 (1963).
(5) H. Winberg, *J. Org. Chem.*, **24**, 264 (1959).
(6) W. G. Wood, *ibid.*, **23**, 110 (1958).
(7) A. P. Ter Borg, H. Kloosterziel, and N. Van Meurs, *Rec. trav. chim.* **82**, 717 (1963).
(8) K. N. Klump and J. P. Chesick, *J. Am. Chem. Soc.*, **85**, 130 (1963).

flow of 0.5 l./min. Some product was lost due to aerosol entrainment by the nitrogen flow. The pyrolysate amounted to 28 g. which on fractionation through a spinning-band column yielded 17.7 g. (63%) of cycloheptatriene, b.p. 61° (125 mm.). The remainder of the pyrolysate was a mixture of unchanged 7,7-dichloronorcarane and two partially dehydrochlorinated materials, b.p. 72–75° (26 mm.). Characteristic infrared bands at 3050, 1640, and 1614 cm.$^{-1}$ suggest these materials are chlorocycloheptadienes. The identity of the cycloheptatriene was verified by infrared examination and by gas–liquid chromatography on a silicone fluid column. The product contained less than 2% toluene, probably much less.

The Synthesis of 2,3,6-Tri-*O*-methyl-D-galactose and Its Derivatives[1]

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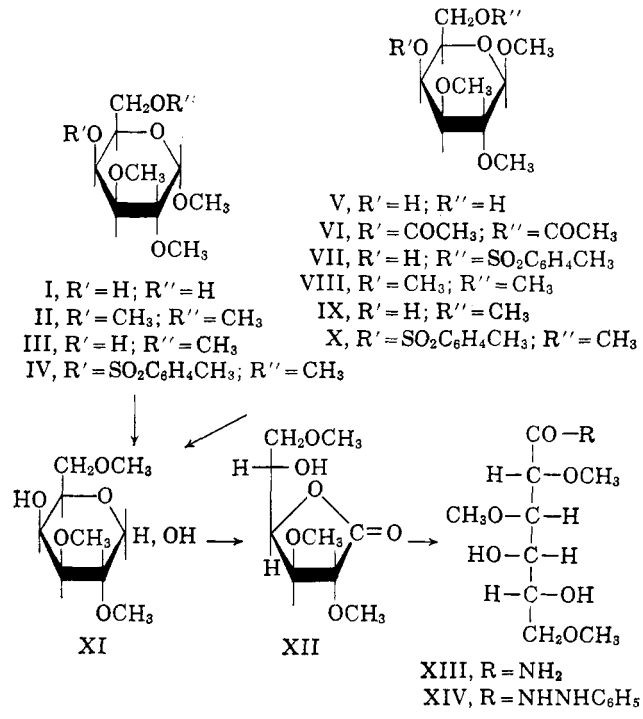
Application of the methylation procedure to the study of the chemical structure of glycoproteins[3,4] has shown the need for methylated derivatives of D-galactose as reference compounds, especially for the trimethyl ethers. Search of the literature to the present time (for review of literature to 1955, see ref. 5 and 6) showed that no synthesis of 2,3,6-tri-*O*-methyl-D-galactose (XI) had been devised, as far as we know. This sugar is known only by isolation from methylated polysaccharides. The present paper describes such a synthesis.

In the preparation of methyl 2-acetamido-2-deoxy-3,6-di-*O*-methyl-α-D-galactopyranoside,[7] it was found that the hydroxyl at C-4 of methyl 2-acetamido-2-deoxy-3-*O*-methyl-α-D-galactopyranoside was quite resistant to methylation. Such resistance may be ascribed to the axial configuration of the hydroxyl group and to the influence of the vicinal methoxyl group at C-3. In a similar fashion, sirupy methyl 2,3-di-*O*-methyl-α-D-galactopyranoside (I)[8,9] was treated with methyl iodide and silver oxide. The resulting sirupy mixture was fractionated by column chromatography on silica gel, giving 12% of sirupy methyl 2,3,4,6-tetra-*O*-methyl-α-D-galactopyranoside (II),[10,11] 7% of a mixture of II and III, 33% of sirupy methyl 2,3,6-tri-*O*-methyl-α-D-galactopyranoside (III), and 24% of a mixture of III and starting material I. The trimethylgalactoside III was characterized by a crystalline 4-tosylate IV. Hydrolysis with hydrochloric acid of III gave sirupy 2,3,6-tri-*O*-methyl-D-galactose (XI).[12,13] Attempts to prepare crystalline derivatives of XI with α-benzyl-α-phenyl-, toluene-*p*-sulfonyl-, *p*-bromophenyl-, and 2,4-dinitrophenylhydrazine, or with aniline, were not successful. Characterization was obtained by oxidation of XI into 2,3,6-tri-*O*-methyl-D-galactonic acid, characterized by the crystalline lactone XII,[12,14–17] amide XIII,[14,15] and phenylhydrazide XIV. The sirupy starting material I had been obtained from crystalline methyl 4,6-*O*-benzylidene-2,3-di-*O*-methyl-α-D-galactopyranoside,[8,9,18] and characterized by the crystalline 4,6-dinitrate.[9]



An alternate route to the synthesis of 2,3,6-tri-*O*-methyl-D-galactose (XI) was also investigated, using the β-galactoside derivatives. From the crystalline methyl 4,6-*O*-benzylidene-2,3-di-*O*-methyl-β-D-galactopyranoside,[18,19] sirupy methyl 2,3-di-*O*-methyl-β-D-galactopyranoside (V) was prepared. It was characterized by crystalline, low-melting 4,6-diacetate VI, and by the crystalline 6-monotosylate VII. Methylation of V with methyl iodide and silver oxide followed by fractionation on silica gel column gave 7% of crystalline methyl 2,3,4,6-tetra-*O*-methyl-β-D-galactopyranoside (VIII),[10,20] 63% of sirupy methyl 2,3,6-tri-*O*-methyl-β-D-galactopyranoside (IX), and 17% of starting material V. The trimethylgalactoside IX was characterized by crystalline 4-tosylate X. Hy-

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(2) To whom inquiries should be addressed.

(3) R. W. Jeanloz and E. H. Eylar, *Intern. Symp. Makromol. Chem., Wiesbaden, West Germany, 1959*, Sektion V., A 8.

(4) R. W. Jeanloz and A. M. Closse, *Federation Proc.*, **22**, 538 (1963).

(5) D. J. Bell, *Advan. Carbohydrate Chem.*, **6**, 11 (1951).

(6) G. G. Maher, *ibid.*, **10**, 273 (1955).

(7) D. K. Stearns, R. G. Naves, and R. W. Jeanloz, *J. Org. Chem.*, **26**, 901 (1961).

(8) G. J. Robertson and R. A. Lamb, *J. Chem. Soc.*, 1321 (1934).

(9) D. J. Bell and G. D. Greville, *ibid.*, 1136 (1955).

(10) D. J. Bell, *ibid.*, 1543 (1940).

(11) F. Micheel and O. Littmann, *Ann.*, **466**, 115 (1928).

(12) W. N. Haworth, H. Raistrick, and M. Stacey, *Biochem. J.*, **31**, 640 (1937).

(13) J. J. Connell, R. M. Hainsworth, E. L. Hirst, and J. K. N. Jones, *J. Chem. Soc.*, 1696 (1950).

(14) P. Andrews, L. Hough, and J. K. N. Jones, *ibid.*, 806 (1954).

(15) W. N. Haworth, H. Raistrick, and M. Stacey, *Biochem. J.*, **29**, 2668 (1935).

(16) W. N. Haworth, E. L. Hirst, and M. Stacey, *J. Chem. Soc.*, 2481 (1932).

(17) E. Pacsu, S. M. Trister, and J. W. Green, *J. Am. Chem. Soc.*, **61**, 2444 (1939).

(18) F. Reber and T. Reichstein, *Helv. Chim. Acta*, **28**, 1164 (1945).

(19) J. W. H. Oldham and D. J. Bell, *J. Am. Chem. Soc.*, **60**, 323 (1938).

(20) H. H. Schlubach and K. Moog, *Ber.*, **56**, 1957 (1923).