will be the predominantly axial group[8,11] and will therefore be less accessible to intermolecular hydrogen bonding, leading to a decreased boiling point on the part of the equatorial–axial isomers, contrary to the Conformational Rule.

The boiling points here reported were found by fractionating commercial methylcyclohexanol mixtures through a four-foot Podbielniak column and identifying the fractions by their characteristic infrared spectra.[11] This is a convenient way of obtaining the pure epimers in this series.[12]

EXPERIMENTAL

Commercially available 2-methylcyclohexanol, 3-methylcyclohexanol, and 4-methylcyclohexanol (Eastman) were distilled through a 4′-Podbielniak column at a reflux ratio of 100:1 to 120:1. Of a charge of 300–500 g., about one third to one half was obtained as quite pure epimers (infrared evidence), the remainder being forerun, intermediate fractions, holdup and residue. In the case of the 2-isomer, a forerun of cyclohexanol was obtained, identified by infrared spectrum. It is necessary to use a charge free of the corresponding methylcyclohexanone, as the latter is not satisfactorily separated from the lower-boiling alcohol. Recent batches of EK methylcyclohexanols have been spectroscopically free of ketone.

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Department of Chemistry
University of Notre Dame
Notre Dame, Ind.

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[11] E. L. Eliel and C. A. Lukach, *J. Am. Chem. Soc.*, **79**, 5986 (1957).

[12] Added in Proof: Three recent publications have dealt with the convenient preparation and analysis of methylcyclohexanols: W. Hückel and J. Kurz, *Chem. Ber.*, **91**, 1290 (1958); W. Hückel and A. Hubele, *Ann.*, **613**, 27 (1958); R. Komers, K. Kochloefl, and V. Bazant, *Chem. & Ind.* (*London*), 1405 (1958). These communications have been anticipated by our earlier papers[8,11] to which none of them refers. Ref. 8 describes optimal preparative methods for pure methylcyclohexanols (though less convenient than the present distillation method). Ref. 11 describes analysis of methylcyclohexanol mixtures by infrared and gas chromatographic methods. After this note was submitted, a publication appeared by W. Hückel, M. Maier, E. Jordan, and W. Seeger, *Ann.*, **616**, 46 (1958) in which the anomalous boiling points of the alkylcyclohexanols are ascribed to intermolecular hydrogen bonding.

A Grignard Condensation of Glutaraldehyde[1]

R. G. Woolford*

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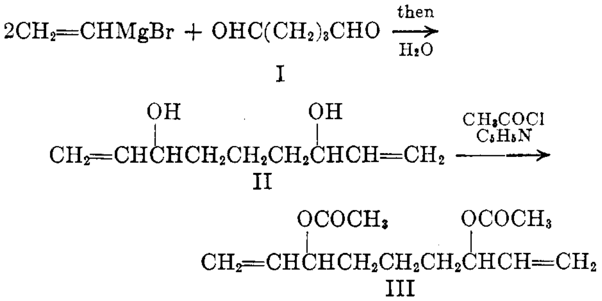
Continuing a study[2] of some of the reactions of vinylmagnesium bromide in an effort to prepare difunctional dienes, the condensation of vinylmagnesium bromide with glutaraldehyde (I) has been accomplished to give 60% yields of 3,7-dihydroxy-1,8-nonadiene (II). This diol (II) was easily acetylated with acetyl chloride and pyridine to give 3,7-diacetoxy-1,8-nonadiene (III) in 73% yield.



$$2CH_2{=}CHMgBr + OHC(CH_2)_3CHO \xrightarrow[H_2O]{\text{then}}$$

I

$$CH_2{=}CH\overset{OH}{\overset{|}{C}}HCH_2CH_2CH_2\overset{OH}{\overset{|}{C}}HCH{=}CH_2 \xrightarrow[C_5H_5N]{CH_3COCl}$$

II

$$CH_2{=}CH\overset{OCOCH_3}{\overset{|}{C}}HCH_2CH_2CH_2\overset{OCOCH_3}{\overset{|}{C}}HCH{=}CH_2$$

III

The preparation of 3,7-dihydroxy-1,8-nonadiene (II) marks the first successful condensation of an aliphatic dialdehyde with a Grignard reagent. Previous to this, the only Grignard reactions with dialdehydes were those in which the 1,2- 1,3- and 1,4-phthalaldehydes were used.[3–6] The Grignard reagent and the dialdehyde involved in this synthesis possess no unique structural features, so the reaction can probably be regarded as a general one for the preparation of aliphatic secondary diols.

Pyrolyses of the diacetate (III) in an effort to prepare the corresponding methylenebis(1,3-butadiene) gave only tarry products.

EXPERIMENTAL[7]

Glutaraldehyde (*anhydrous*) (I). The 25% aqueous glutaraldehyde obtained from the Union Carbide Chemical Company was saturated with sodium chloride and extracted five times with ether. The ether extract was dried over anhydrous magnesium sulfate for 24 hr. and distilled. After a small forerun, a large main fraction boiling at 83–85° (15 mm.), n_D^{25} 1.4338, was obtained. [Longley and Emerson[8] give: b.p. 75–81° (15 mm.), n_D^{25} 1.4330.]

This dialdehyde reacted at room temperature to give a quantitative yield of glutaraldehyde bis(2,4-dinitrophenylhydrazone), m.p. 192–193° [literature[9] m.p. 192.5–193.3°].

3,7-Dihydroxy-1,8-nonadiene (II). Using vinyl bromide (75.0 g., 0.70 mole), magnesium (17.0 g., 0.70 mole) and tetrahydrofuran (300 ml.), a solution of vinylmagnesium bromide was prepared in the usual manner.[2]

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[*] Address after Jan. 1, 1959: Chemistry Dept., Waterloo College, Waterloo, Ont., Canada.

[1] This work was supported by a grant from the National Science Foundation for polymer research.

[2] C. S. Marvel and R. G. Woolford, *J. Org. Chem.*, **23**, 1658 (1958).

[3] M. S. Kharasch and O. Reinmuth, *Grignard Reactions of Nonmetallic Substances*, Prentice-Hall Inc., New York, 1954, p. 278.

[4] F. Nelken and H. Simonis, *Ber.*, **41**, 986 (1908).

[5] R. Deluchat, *Ann. chim.* [11], **1**, 181 (1934).

[6] H. W. Johnston and J. L. R. Williams, *J. Am. Chem. Soc.*, **69**, 2065 (1947).

[7] We are indebted to Mr. J. Nemeth of the University of Illinois for the microanalytical data and to Mr. Paul McMahon for the infrared spectra.

[8] R. I. Longley, Jr., and W. S. Emerson, *J. Am. Chem. Soc.*, **72**, 3079 (1950).

[9] A. C. Cope, H. L. Dryden, Jr., C. G. Overberger, and A. A. D'Addiecio, *J. Am. Chem. Soc.*, **73**, 3416 (1951).

A solution of freshly distilled glutaraldehyde (25.0 g., 0.25 mole) in tetrahydrofuran (100 ml.) was added dropwise with stirring to a vinylmagnesium bromide solution at such a rate as to maintain gentle reflux. After the addition, the reaction mixture was stirred for 4 hr. and hydrolyzed with a saturated solution of ammonium chloride. The tetrahydrofuran layer was distilled to yield 3,7-dihydroxy-1,8-nonadiene, b.p. 148–150° (12 mm.), n_D^{25} 1.4755. This was a colorless, hygroscopic, very viscous liquid (23.3 g., 60% yield).

Anal. Calcd. for $C_9H_{16}O_2$: C, 69.19; H, 10.32. Found: C, 69.12; H, 10.55.

An infrared spectrum of this diol yielded the following major bands (cm.$^{-1}$): 3065, 1842, 1642, 1428, 990, 918 (vinyl); 3300–3400 (hydroxyl); 1170 (C—O); 2920, 2860, 1462, 1320 (—$CH_2CH_2CH_2$—).

3,7-Diacetoxy-1,8-nonadiene (III). A solution of 3,7-dihydroxy-1,8-nonadiene (17.0 g., 0.109 mole), pyridine (27.7 g., 0.35 mole) and anhydrous ether was stirred vigorously while acetyl chloride (23.6 g., 0.30 mole) was added dropwise at a rate to maintain gentle reflux. After the addition was complete the mixture was heated under reflux overnight (16 hr.).

The reaction mixture was poured into water and extracted three times with ether. The ether extracts were washed with dilute hydrochloric acid (twice), saturated sodium carbonate (twice) and water (once) and dried over anhydrous magnesium sulfate. Distillation yielded 19.2 g. (73%) of 3,7-diacetoxy-1,8-nonadiene, b.p. 150–151° (12 mm.), n_D^{25} 1.4439.

Anal. Calcd. for $C_{13}H_{20}O_4$: C, 64.98; H, 8.39. Found: C, 65.32; H, 8.64.

An infrared spectrum of this diacetate yielded the following major bands (cm.$^{-1}$): 3062, 1643, 1430, 990, 924 (vinyl); 1738 (ester carbonyl); 1238 (acetate); 1370, 1020 (C—O); 2930, 2860, 1464 (—$CH_2CH_2CH_2$—). No absorption above 3062 was noted (no hydroxyl).

THE NOYES CHEMICAL LABORATORY
UNIVERSITY OF ILLINOIS
URBANA, ILL.