The Boiling Points of the Methylcyclohexanols—an Exception to the Conformational Rule

Ernest L. Eliel and Ralph G. Haber

Received July 28, 1958

The relationship between the physical properties of geometrical isomers and their configuration has long been of interest. Two empirical rules have been established, the von Auwers–Skita or Conformational Rule,[1–3a] and the van Arkel or Dipole Rule.[3c,4] These rules have recently been delineated in their area of application and restated by Allinger[3]: the Conformational Rule, applying to alicyclic epimers not differing in dipole moment, states that the isomer of smaller molecular volume and therefore higher density, index of refraction, and boiling point has the higher heat content, whereas the Dipole Rule, applying to geometrically isomeric olefins, states that the isomer of higher dipole moment has the higher boiling point, refractive index, and density.

In the cases which have been carefully studied,[3] it has been found that all three of the physical properties indicated follow the appropriate rule, although there is one instance—cyclodecene—where the refractive index and density of the *cis* and *trans* isomers follow the Dipole Rule[3c] but the boiling points of the isomers are identical.[5,6] We wish to report now that in the case of the epimeric 2-, 3- and 4-methylcyclohexanols, whereas the refractive index and density follow the Conformational Rule, the boiling points do not, as shown in Table I.

From the work of Skita and Faust[7] it is evident that in each series the diequatorial isomer, which is the more stable of the pair,[8] is also the isomer of lower enthalpy. Hence the Conformational Rule would lead one to predict that the diequatorial isomer (*trans*-2-, *cis*-3- and *trans*-4-methylcyclohexanol) should have a lower boiling point, refractive index, and density than its respective epimer.[9] The table shows that this is true of the refractive indices and densities but not of the boiling points. The Conformational Rule has been rationalized[3a] in terms of molecular volume, inasmuch as smaller molecular volume should lead to increased density, increased refractive index, and increased magnitude of dispersion forces (and therefore increased boiling point) on one hand and to increased internal repulsion and thus increased enthalpy on the other. We suggest that whereas in the case of the methylcyclohexanols the diequatorial isomers have smaller molecular volumes, there is superimposed on this a specific interaction due to intermolecular hydrogen bonding. Infrared spectral evidence suggests[10] that such intermolecular hydrogen bonding is greater in the diequatorial isomer than in the equatorial–axial isomer. In the latter, the hydroxyl function

TABLE I

Physical Constants of Methylcyclohexanols

Isomer	Conformation[a]	Boiling Point,[b] °C./Mm. Pressure	Refractive Index[c]		Density[c]		Heat of Combustion,[c] Cals./G.
			n_D	(Temp.)	G./Ml.	(Temp.)	
cis-2	e,a	165°/760 mm.	1.4648	(18.2)	0.9356	(18.0)	9127.9 ± 4
trans-2	e,e	166.5°/760 mm.	1.4613	(19.7)	0.9241	(19.7)	9047.5 ± 7
cis-3[d]	e,e	173°/745 mm.	1.4550	(20)	0.9145	(20)	9073.7 ± 7
trans-3[d]	e,a	168–169°/745 mm.	1.4564	(21.8)	0.9173	(21.8)	9119.2 ± 7
cis-4	e,a	168–169°/745 mm.	1.4543	(21.5)	0.9129	(21.5)	9080.5 ± 4
trans-4	e,e	172–173°/745 mm.	1.4531	(20.7)	0.9118	(20.7)	9038.2 ± 10

[a] a means axial, e means equatorial. [b] Data from this work, confirmed, in the case of the 2-isomer, by ref. 7. [c] Ref. 7. [d] For stereochemical assignment, see H. L. Goering and C. Serres, *J. Am. Chem. Soc.*, **74,** 5908 (1952); D. S. Noyce and D. B. Denney, *J. Am. Chem. Soc.*, **74,** 5912 (1952); S. Siegel, *J. Am. Chem. Soc.*, **75,** 1317 (1953).

---

(1) K. von Auwers, *Ann.*, **420,** 84 (1920); A. Skita, *Ber.*, **56,** 1014 (1923).

(2) R. B. Kelly, *Can. J. Chem.*, **35,** 149 (1957).

(3) N. L. Allinger, (a) *Experientia*, **10,** 328 (1954); (b) *J. Org. Chem.*, **21,** 915 (1956); (c) *J. Am. Chem. Soc.*, **79,** 3443 (1957); (d) *J. Am. Chem. Soc.*, **80,** 1953 (1958); (e) *J. Am. Chem. Soc.*, in press.

(4) A. E. van Arkel, *Rec. Trav. chim.*, **51,** 1081 (1932); **53,** 246 (1934).

(5) A. T. Blomquist, R. E. Burge, and A. C. Sucsy, *J. Am. Chem. Soc.*, **74,** 3636 (1952).

(6) We are aware of two other cases where there is some confusion about the application of the rules, *viz.* the case of the methyl and ethyl hexahydrophthalates, A. Skita and R. Rössler, *Ber.*, **72,** 265 (1939) and the case of the 3,5-dimethylcyclohexanols, A. Skita and W. Faust, *Ber.*, **72,** 1127 (1939). These cases should probably be reexamined. See also ref. 2.

(7) A. Skita and W. Faust, *Ber.*, **64,** 2878 (1931). The order of refractive indices and densities has been confirmed by several other investigators.

(8) E. L. Eliel and R. S. Ro, *J. Am. Chem. Soc.*, **79,** 5992 (1957).

(9) A complication is introduced by the fact that in the 3-methylcyclohexanol series the *cis*-(e,e) isomer of lower enthalpy has been reported to have a higher dipole moment by 0.16 debye units: A. Skita and W. Faust, *Ber.*, **72,** 1127 (1939). However, this difference is small, and the refractive index and density data suggest that in this case the Conformational Rule and not the Dipole Rule should be applied.

(10) E. E. Pickett and H. E. Ungnade, *J. Am. Chem. Soc.*, **71,** 1311 (1949); H. Goering, R. L. Reeves and H. H. Espy, *J. Am. Chem. Soc.*, **78,** 4926 (1956); E. G. Peppiat and R. J. Wicker, *J. Chem. Soc.*, 3122 (1955).

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.

Acknowledgment. This work was supported under Contract DA-11-022-ORD-2279 of the Office of Ordnance Research, U. S. Army.

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

---

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

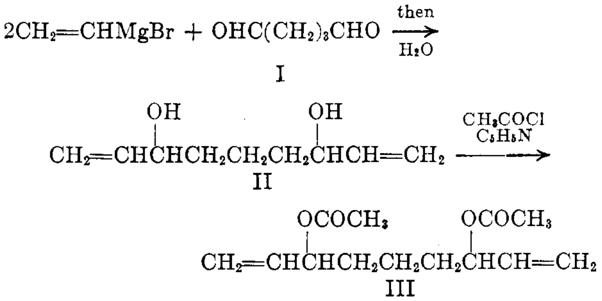
(12) Added in Proof: Three recent publications have dealt with the convenient preparation and analysis of methylcyclohexanols: W. Hückel and J. Kurz, *Chem. Ber.*, **91**, 1290 (1958); W. Hückel and A. Hubele, *Ann.*, **613**, 27 (1958); R. Komers, K. Kochloefl, and V. Bazant, *Chem. & Ind.* (*London*), 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*

Received July 30, 1958

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.



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

I

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

II

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

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]

---

* 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).