A mercury thermometer, 60 cm. in length and calibrated to 0.2° intervals, was used to measure the boiling points. It had been calibrated to 0.01° by the Bureau of Standards. Readings were recorded only when the thermometer was bathed in vapor above the mark representing the boiling point of the liquid, thus eliminating the necessity of a stem correction.

The observed vapor pressures in mm. can be represented adequately by the formula $\log_{10} p = A/T + B$, the values of $-A$ and B, together with the average deviation, being given in Table I.

Ketone	$-A$	B	Average deviation of p, %
Methyl ethyl ketone	1760.5	7.8746	1.06
Methyl isopropyl ketone	1830.9	7.8717	1.35
Methyl propyl ketone	1870.4	7.8642	1.27
Methyl isobutyl ketone	2009.5	8.0590	1.13
Methyl butyl ketone	2117.2	8.1852	0.80
Ethyl isopropyl ketone	1989.7	8.0277	1.95
Diisopropyl ketone	2021.4	7.9752	1.54
Propyl isopropyl ketone	2159.5	8.1930	0.87
Isopropyl isobutyl ketone	2221.9	8.1873	1.95
Isopropyl butyl ketone	2271.9	8.1827	0.86
Methyl cyclohexyl ketone	2418.7	8.2238	1.17
Ethyl cyclohexyl ketone	2512.5	8.2379	0.86

The boiling points of all the ketones were determined at several different pressures. These were all plotted against the boiling point of methyl isopropyl ketone at the same pressure. The points thus obtained for each ketone were found to lie on a straight line. When these lines were extended, it was found that they intersected at −440, −440, showing that the rule of Dühring[10] for predicting the vapor pressure curves from the boiling point at one pressure is applicable. Calculations of Trouton's constant show that the ketones are slightly associated, values of $\Delta H/T$ ranging from 22.7-24.

Summary

1. The vapor pressures of twelve ketones of the methyl, isopropyl and cyclohexyl series have been measured.

2. Dühring's rule applies to the ketones of the methyl, isopropyl and cyclohexyl series using methyl isopropyl ketone as standard.

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[10] White, *Ind. Eng. Chem.*, **22**, 230 (1930).

STATE COLLEGE, PA. RECEIVED AUGUST 13, 1934

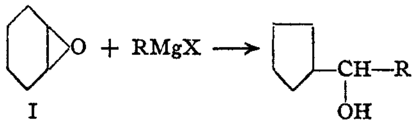
[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY OF THE UNIVERSITY OF MINNESOTA]

The Reaction of Dimethylmagnesium and of Diethylmagnesium with Cyclohexene Oxide

BY PAUL D. BARTLETT AND C. MANLY BERRY

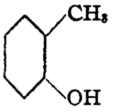
The reaction of ethylene oxide with Grignard reagents is a useful way of preparing alcohols containing the group $—CH_2CH_2OH$,[1] but with substituted ethylene oxides the reaction is often attended by rearrangements.[2] In the alicyclic series this has given rise to some confusion. Thus, Godchot and Bédos[3] originally reported that the single substance (phenylurethan, m. p. 71°) which they obtained from the action of methylmagnesium iodide on cyclohexene oxide (I) was the *cis*-2-methylcyclohexanol (II). A later careful study of the reduction products of *o*-cresol led to the characterization of two isomeric 2-methylcyclohexanols,[4] both different from the product of Godchot and Bédos.

An explanation was provided in the work of Godchot and Cauquil[5] and Vavon and Mitchovitch[6] who showed that the reaction of Grignard reagents with oxides or chlorohydrins of the cycloheptane and cyclohexane series led to ring contraction

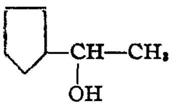


I

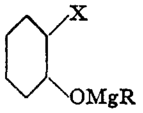
The supposed *cis*-2-methylcyclohexanol of Godchot and Bédos was accordingly methylcyclopentylcarbinol (III), which has been prepared in other ways and has the properties of this alcohol.



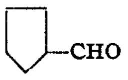
II



III



IV



V

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[1] "Organic Syntheses," John Wiley & Sons, Inc., New York, 1932, Coll. Vol. I, p. 299.

[2] For a number of examples, see Schlenk in Houben-Weyl, "Methoden der organischen Chemie," Georg Thieme, Leipzig, 1924, 2d. ed., Vol. IV, p. 781.

[3] Godchot and Bédos, *Bull. soc. chim.*, **37**, 1451 (1925).

[4] Gough, Hunter and Kenyon, *J. Chem. Soc.*, 2052 (1926).

[5] Godchot and Cauquil, *Compt. rend.*, **186**, 375, 955 (1928).

[6] Vavon and Mitchovitch, *ibid.*, **186**, 702 (1928).

Bédos has further elucidated the mechanism of this rearrangement[7] by showing that, as in the aliphatic series, the primary product of reaction between cyclohexene oxide and a Grignard reagent is the halohydrin derivative (IV), which gives the final rearranged product only after strong heating, presumably by way of cyclopentylformaldehyde (V). The latter was also obtained by heating cyclohexene oxide with magnesium bromide in dry ether.

If the halogen of the Grignard reagent plays a controlling part in bringing about this rearrangement, the halogen-free solution of a dialkylmagnesium,[8] which would be incapable of yielding the intermediate (IV), should give solely "normal" addition to cyclohexene oxide. We have found this actually to be the case. A solution of diethylmagnesium, in contrast to ethylmagnesium bromide, gave only 2-ethylcyclohexanol which was chiefly the *trans* form. Similarly, dimethylmagnesium gave a product consisting, apparently to the extent of 95%, of *trans*-2-methylcyclohexanol. The opening of the three-membered ring of cyclohexene oxide to give a *trans* substituted cyclohexane is in accord with the known hydrolytic cleavage of this ring to give mainly *trans*-cyclohexanediol.[9]

The two forms R_2Mg and RMgX of the Grignard reagent have been found to be quite equivalent in reactions of addition to the carbonyl group[8] and of reduction,[10] whereas Cope[11] has found that the two active forms of the Grignard reagent differ in the speed and course of their reaction with dimethyl sulfate. Such differences in behavior evidently may be expected toward any compound which can be acted upon by the magnesium halides themselves.

Because of the very small amount of dimethylmagnesium present in solutions of methyl Grignard reagents, this reaction is of no preparative value for methylcyclohexanol; for all other 2-alkylcyclohexanols, it is a useful synthetic method, and can probably be extended to other substituted ethylene oxides.

Experimental

Cyclohexene was prepared by passing cyclohexanol over silica gel at 280–300°, a procedure which requires much less time than the dehydration with either sulfuric or phosphoric acid. One kilogram of cyclohexanol yielded 603 g. (73%) of cyclohexene, the unchanged alcohol being added to the next run.

2-Chlorocyclohexanol and cyclohexene oxide were prepared according to the procedures of "Organic Syntheses.[12]

Dialkylmagnesium solutions were prepared by the method of Noller and Hilmer[13] except that the ether solutions were separated from the dioxane precipitate by centrifuging instead of filtration. The dialkylmagnesium content of our ethylmagnesium bromide solution was 60%, that of our methylmagnesium bromide solution 4%.

***Trans*-2-ethylcyclohexanol.**—To 18.5 g. of cyclohexene oxide 180 cc. of 1.04 *N* diethylmagnesium solution in dry ether was added. The ether was distilled off and the residue heated for one and one-fourth hours on the steambath under reflux. The reaction product was hydrolyzed with dilute hydrochloric acid, extracted with ether, and dried. Two distillations yielded, beside 5.5 g. of gummy residue, 10 g. of product boiling at 87–91° under 25 mm. This is a 42% yield, based on either reactant.

Trans-2-methylcyclohexanol was prepared in a similar manner, but with only one-tenth as much material.

Identification of the Alcohols.—Three derivatives of each alcohol were prepared and their melting points compared with those in the literature for the compounds in question. As an additional proof of the ring structure, 2-ethylcyclohexanol was oxidized to 2-ethylcyclohexanone and its semicarbazone prepared. The melting points indicate a persistent impurity, but the closeness of each melting point to that of the *trans* derivative in all cases where this melts higher than the *cis* derivative indicates that the product is largely (at least 95%) *trans*. The estimate of 95% for the purity of our *trans*-2-methylcyclohexanol was obtained from the mixed melting point tables of Vavon, Perlin and Horeau[15] for the acid phthalates and phenylurethans of the *cis* and *trans* isomers of this compound.

Melting Points of Derivatives of 2-Ethylcyclohexanol

Derivative	From oxide	*Cis*[14]	*Trans*[14]	Ethylcyclopentylcarbinol[14]
3,5-Dinitrobenzoate	104–105°	99	105	88–89
Phenylurethan	63	101.5	82–83	56–57
Acid phthalate	92–93	102–103	97	91–92
Semicarbazone of oxidation product	162–163	161	161	134

Melting Points of Derivatives of 2-Methylcyclohexanol

Derivative	From oxide	*Cis*[15]	*Trans*[15]	Methylcyclopentylcarbinol[16]
Phenylurethan	102	93–94	105	71–71.5
Acid phthalate	122–123	104–105	124–125	
p-Nitrobenzoate	60	55–56	65	

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[7] Bédos, *Compt. rend.*, **189**, 255 (1929).

[8] W. Schlenk and W. Schlenk, Jr., *Ber.*, **62**, 920 (1929).

[9] Van Loon, Thesis, Delft, 1919; Böeseken and van Giffen, *Rec. trav. chim.*, **39**, 184 (1920).

[10] Noller, This Journal, **53**, 635 (1931).

[11] Cope, *ibid.*, **56**, 1578 (1934).

[12] "Organic Syntheses," Coll. Vol. I, pp. 151 and 179.

[13] Noller and Hilmer, This Journal, **54**, 2506 (1932).

[14] Vavon and Mitchovitch, *Bull. soc. chim.*, **45**, 966–968 (1929).

[15] Vavon, Perlin and Horeau, *ibid.*, **51**, 644 (1932).

[16] Edwards and Reid, This Journal, **52**, 3236 (1930).

One of us is indebted to the Graduate School of the University of Minnesota for a grant from its research funds in support of a part of this work.

Summary

Diethylmagnesium and dimethylmagnesium, prepared from solutions of ethyl- and methylmagnesium bromides by the method of Schlenk, react with cyclohexene oxide without rearrangement to give, respectively, *trans*-2-ethyl- and *trans*-2-methylcyclohexanol. This is in contrast to the behavior of ethylmagnesium bromide, which undergoes a different mode of addition to the oxide ring, leading to ethylcyclopentylcarbinol.

MINNEAPOLIS, MINN. RECEIVED AUGUST 15, 1934

[CONTRIBUTION FROM THE RESEARCH LABORATORY OF THE BONEFF MANUFACTURING COMPANY, GABROVO, BULGARIA]

Synthesis and Reactions of 1,4-Hydroxy Ketones. Derivatives of 5-Hydroxyhexanone-2 and 2,5-Dimethyl-4,5-dihydrofuran

BY GEORGI POJARLIEFF

In effecting the synthesis of 5,6-dihydroxyhexanone-2 (IIa) from epichlorohydrin and ethyl acetoacetate, Traube and Lehmann[1] obtained the lactone (Ib) as an intermediate product. (IIa) is prepared by boiling the lactone with half a mole of potassium carbonate. To obtain (IIb) from the same lactone, the ring must be broken. In aqueous suspension this reaction can be brought about by the use of mineral acid, in which (IIb) is unstable. A better yield and a purer product can be obtained in the following way. In a methyl alcohol solution with a small quantity of hydrogen chloride gas at ordinary temperature the lactone (Ib) gives, in the first place, the lactolide (VIIb). On distillation, especially if acids are present, methyl alcohol is eliminated with the formation of the ester of dihydrofurancarboxylic acid (VIIIb). The latter can be saponified with one mole of sodium hydroxide to give (IXb), which in a free state can easily be purified by recrystallization from water. When heated, the acidified aqueous solution of the free acid liberates carbonic acid and (IIb) is formed.

This method of synthesis of (IIb) seems to be generally applicable. In quite an analogous way (IIc) was obtained from epimethyline and ethyl acetoacetate.

5-Hydroxy-6-chlorohexanone-2 shows a great tendency to undergo internal condensation. This occurs with the elimination of water, as in the internal condensation of (IIa), which was first observed by Hibbert and Timm.[2] The methoxyl analog (IIc) is more stable. When heated with a trace of concd. sulfuric acid (1:1000) for four minutes at 150° about 50% is condensed and the mixture of unaltered ketone and its anhydride (Vc) can be distilled in high vacuum. On the other hand, (IIb) and (IIc) are resinified by similar treatment.

Levene and Walti[3] have shown that in all probability with the internal condensation of (IIa) an intermediate product—furan (Va) or pyran (VI)—was formed and the condensation was caused by the presence of the double bond. They believe the sensitivity of the glucals (which are closely related to the desoxy sugars) toward acids is likewise due to the presence of a double bond in the 2,3-position. However, the esters of dihydrofurancarboxylic acid (VIIIb and VIIIc) are very stable, which seems to indicate that a double bond in the 2,3-position is not alone sufficient to cause polymerization. Bergmann and Pojarlieff[4] expressed the opinion that the sensitivity of the glucals and of the intermediate product formed in the internal condensation of (IIa) toward acid was the result of the presence of both a double bond and of hydroxyl groups.

When heated with a trace of concentrated sulfuric acid, the methyl lactolide[3] of (IIa) likewise undergoes internal condensation with the elimination of methyl alcohol. I have found that this lactolide consists chiefly of the tetrahydrofuran (IVa). This suggests that the dihydrofuran (Va), which is probably the intermediate product of the condensation, also possesses a tendency to polymerize. A comparison with the dihydro-

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[1] W. Traube and E. Lehmann, *Ber.*, **34**, 1971 (1901).

[2] H. Hibbert and J. A. Timm, THIS JOURNAL, **45**, 2433 (1923).

[3] P. A. Levene and A. Walti, *J. Biol. Chem.*, **88**, 771 (1930).

[4] M. Bergmann and G. Pojarlieff, *Naturwiss.*, **18**, 1114 (1930); *Collegium*, **244**, 1931.