ethylene glycol as determined by Gibson and Loeffler[14] together with the dielectric constant data of Akerlof[15] were used for the computation of the theoretical limiting slope for a uni-univalent electrolyte in this solvent. The value is 1970 cal.-kg.solvent-moles.$^{-1/2}$ The presence of 0.4% of moisture reduces the limiting slope by about 1%. The experimental limiting slopes are 1580 from equation (1) and 2502 from equation (5). The former value is to be recommended since it was obtained by a method specifically developed for the evaluation of such quantities. The probable error of the limiting slope of equation (1) has been calculated to be ±1188.[16] This value, although relatively large, indicates that the experimentally determined limiting slope is essentially in agreement with the theoretical slope.

A comparison of ΦL_2 values for sodium chloride in glycol with those in water[11b] in the concentration range studied shows that the heat effects in general are greater in glycol than in water by a factor of 5 or 6. This might have been anticipated from the theoretical limiting slopes (477 for water). The ΦL_2 curve for water shows a maximum in the neighborhood of $m^{1/2} = 0.4$. A maximum was not realized in glycol in the concentration range studied, although the shape of the curve (Fig. 2) indicates that a maximum might occur at $m^{1/2} = 0.6$ to 0.7.

It may be noted also that the ΦL_2 curve for aqueous solutions is below the limiting law curve over the complete concentration range, but that the curve for glycol is slightly above the limiting law in the lower concentrations (Fig. 2). The same is true for $\bar{L}_2$ values in the two solvents. This behavior with decreasing dielectric constant is in qualitative agreement with the behavior of hydrochloric acid in dioxane–water mixtures.[5]

Summary

Heats of dilution of sodium chloride in ethylene glycol have been measured from 0.17*m* to 0.0001*m* at 25°. Equations for the relative apparent molal heat content of the solute and for the relative partial molal heat contents of the solute and solvent have been derived.

The experimental limiting slope is in agreement with the theoretically calculated limiting slope.

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[14] R. E. Gibson and O. H. Loeffler, THIS JOURNAL, **63**, 898 (1941).

[15] G. Akerlof, *ibid.*, **54**, 4125 (1932).

[16] A. G. Worthing and Joseph Geffner, "Treatment of Experimental Data," John Wiley and Sons, Inc., New York, N. Y., 1943.

[CONTRIBUTION FROM THE GEORGE HERBERT JONES LABORATORY OF THE UNIVERSITY OF CHICAGO]

Factors Determining the Course and Mechanisms of Grignard Reactions. XII. The Effect of Cobaltous Chloride on the Reaction of Methylmagnesium Bromide with Alicyclic Chlorides

BY M. S. KHARASCH, FRANCES ENGELMANN AND W. H. URRY

Introduction.—It was recently shown[1] that, in the presence of cobaltous chloride, phenylmagnesium bromide reacts with aliphatic halides (methyl, ethyl, propyl, *n*-butyl bromides and *t*-butyl chloride) to yield biphenyl and the saturated and unsaturated hydrocarbons derived from the alkyl halide used. A free radical mechanism was postulated to explain these results. In order to study the behavior of alicyclic free radicals in solution, the reactions of a number of alicyclic chlorides with methylmagnesium bromide in the presence and in the absence of cobaltous chloride have now been investigated.

Procedure.—The Grignard reactions were carried out according to the directions of Kharasch, Lewis and Reynolds,[1] with two modifications: a trap cooled in dry-ice was placed between the reaction flask and the gas collector, and a 10% excess of Grignard reagent was used. Twenty-gram samples were used in reactions with bornyl and isobornyl chlorides. With *cis*- and *trans*-2-methylcyclohexyl chlorides and cyclohexyl chloride, 50-g. samples were used in the cobaltous chloride catalyzed reactions, and 25-g. samples in the control experiments. In the reactions catalyzed by cobaltous chloride, the mixtures were refluxed for five hours and allowed to stand overnight. In the control experiments where no cobaltous chloride was used, refluxing was continued for twenty-eight hours.

The reaction products were analyzed by procedures described in detail in the experimental part.

Results.—The results of the reactions between the alicyclic halides and methylmagnesium bromide (shown in Table I) indicate that the normal condensations are extremely slow, and that, consequently, the secondary reaction (elimination of hydrogen chloride and formation of the unsaturated compounds) predominates.

The reaction of methylmagnesium bromide and the alicylic halides takes an entirely different course when about 5 mole per cent. of cobaltous chloride is first added to the Grignard reagent. The results are summarized in Table II.

The column headed "Unsaturated Compound" refers to camphene and bornylene in experiments

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[1] Kharasch, Lewis and Reynolds, THIS JOURNAL, **65**, 493 (1943).

TABLE I

REACTION OF METHYLMAGNESIUM BROMIDE WITH ALICYCLIC CHLORIDES

Alicyclic chloride	Reaction,[a] %	Addition product	Unsaturated compound	Gas evolved
2-Methylcyclohexyl-(*trans*)	46	10	33	Pure methane
2-Methylcyclohexyl-(*cis*)	49	10	34	Pure methane
Bornyl	5			
Isobornyl	90		90	Pure methane

[a] The extent of the reaction was determined by halogen titration (Kharasch and Fields, THIS JOURNAL, **63**, 2316 (1941)).

TABLE II

REACTION OF METHYLMAGNESIUM BROMIDE WITH ALICYCLIC CHLORIDES IN THE PRESENCE OF COBALTOUS CHLORIDE[a]

Alicyclic chloride	Reaction, %	Dimer, %	Unsatd. compound, %	Satd. compound, %	Gaseous products, %		
					Methane	**Ethane**	**Ethene**
Cyclohexyl	86	26	29	27	85	9	6
2-Methylcyclohexyl-(*trans*)	87	27[b]	23	28	77	15	8
2-Methylcyclohexyl-(*cis*)	89	22	31	34	83	9	8
Bornyl	98	63	20	15	72	19	9
Isobornyl	94	31	44	19	77	15	8

[a] Cobaltous chloride (5 mole per cent.) was used in all experiments. [b] About 6% of an unidentified higher polymer was also isolated.

with bornyl and isobornyl chlorides, and to methylcyclohexene or cyclohexene in the experiments with the cyclohexyl chlorides. The "unsaturated compound" resulting from the reactions of bornyl and isobornyl chlorides is believed to be a mixture of camphene and bornylene because a 10% increase in unsaturation was observed when esterification was carried out under more drastic conditions.[2] Control samples of camphene gave the same unsaturation value when either method of esterification was used. The column headed "Saturated compound" refers to camphane in the bornyl and isobornyl chloride experiments, and to methylcyclohexane or cyclohexane, respectively, in the experiments with 2-methylcyclohexyl or cyclohexyl chloride.

Discussion

It is of considerable theoretical interest to note that in the uncatalyzed experiments the *cis*- and *trans*-forms of 2-methylcyclohexyl chloride react alike, while bornyl and isobornyl chlorides differ considerably in their stability. Isobornyl chloride reacts by elimination of hydrogen chloride to the extent of 90% in about one hour. Bornyl chloride is surprisingly stable in this respect.

In general, the catalyzed reactions are very much faster than the uncatalyzed ones. The reaction probably comes to an end while the reaction mixtures are allowed to warm from +5° to room temperature; they are certainly complete before the end of the first hour during which the mixture is kept at the boiling point of ether.[3]

This enhanced reactivity in the presence of cobaltous chloride is particularly striking in the case of bornyl chloride which, in the absence of cobaltous chloride, reacts only to the extent of 5%, even if the reaction mixture is heated for twenty-eight hours. These results are, in our estimation, best explained by a free radical chain reaction.

(1) $CH_3MgBr + CoCl_2 \longrightarrow CH_3CoCl + CoClBr$
(2) $CH_3CoCl \longrightarrow CH_3\cdot + CoCl\cdot$
(3) $RCl\ (\text{Alicyclic}) + CoCl\cdot \longrightarrow R\cdot + CoCl_2$
(4) $R\cdot \longrightarrow R_{-H} + R_{+H}$
(5) $R\cdot \longrightarrow R{:}R$[4]
(6) $CH_3\cdot + C_2H_5OC_2H_5 \longrightarrow CH_4 + C_2H_6 + C_2H_4$

However, the alicyclic free radicals differ significantly from the lower aliphatic free radicals (up to butyl) in that the reaction (5), the dimerization of the free radicals, does not occur with free aliphatic radicals, but takes place to the extent of 26% with the free cyclohexyl and 2-methylcyclohexyl radicals, and to the extent of 63% with the free bornyl radical. Since the free radicals derived from bornyl or isobornyl chloride are the same, the formation of 32% less dimer from the isobornyl chloride can be ascribed only to the greater ease of elimination of hydrogen chloride from that molecule. The formation of equal quantities of the saturated and unsaturated hydrocarbons in the reaction with bornyl chloride, and the preponderance of the unsaturated over the saturated compound (44 to 19%) in the reaction with isobornyl chloride is in full agreement with this view.

The non-dimerization of the simple free alkyl radicals which do not possess sufficient energy to react with the solvent, and the dimerization of the free alicyclic, benzyl and substituted benzyl radicals, supports the hypothesis previously submitted.[5b] In this connection, it is important to note that, although resonance stability in the free radical is important insofar as the tendency to dimerize is concerned, the dimerization of free alicyclic radicals and other radicals in which resonance (as currently interpreted) plays only a minor part must have a different origin. The facts cited are compatible, however, with the view that only free radicals derived from weakly electro-

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(2) Bredt and Hibbing, *J. prakt. Chem.*, **84**, 783 (1911).

(3) Kharasch and Fields, THIS JOURNAL, **63**, 2316 (1941).

(4) A detailed mechanism for the dimerization of free radicals in solution will be discussed in a future publication.

(5) For previous references see (a) Kharasch, Reinmuth and Mayo, *J. Chem. Ed.*, **13**, 7 (1936); (b) Kharasch and Kleiman, THIS JOURNAL, **65**, 491 (1943).

negative radicals dimerize, and that the free benzyl or substituted benzyl radicals, which stabilize themselves through resonance, are members of a larger class of free radicals derived from weakly electronegative radicals, in many of which resonance plays only a very minor part. In other words, other things being equal, resonance is a sufficient but not a necessary condition for dimerization.

Experimental

Reagents.—Dow methyl bromide and Mallinckrodt magnesium turnings were used in the preparation of the Grignard reagent. The Grignard reagent was made by the method of Kharasch and Kleiman,[5b] filtered through a sintered glass disk, and titrated for basicity and halogen content immediately before use.

Anhydrous cobaltous chloride was prepared by heating the hydrated salt at 150° *in vacuo*.

The bornyl chloride was prepared according to the directions of Fisher.[6] The pinene used was first distilled over sodium; the fraction boiling between 153° and 156° was used in the preparation.

Isobornyl chloride was prepared from camphene (m. p. 41.2–41.6°) according to the directions of Meerwein and Van Emster.[7] Cyclohexyl and 2-methylcyclohexyl chloride (*cis*) were prepared according to the directions of Zelinski.[8] *trans*-2-Methylcyclohexyl chloride was prepared according to the method given for menthyl chloride by Cumming, Hopper and Wheeler.[9]

Analysis.—The reaction products from the bornyl and isobornyl chloride experiments were analyzed by the method of Hesse.[10] The amount of bibornyl was determined by distilling the ether from an aliquot portion of the ether extracts. The residue was heated on a steam-bath. A stream of air was blown over the warm material until the loss in weight per hour came to a small constant value. The weight of the remaining residue corrected for the known loss was taken as the weight of the bibornyl. In the analysis for camphene, ether from another aliquot portion was removed by fractional distillation through a 37-centimeter column filled with single-turn glass helices. The last of the ether was removed *in vacuo* while the residue was maintained at −18°. The camphene was converted to the ester according to the directions of Bertram and Walbaum.[11] The ester and mixed terpenes were dissolved in ether; the solution was washed with water and with sodium carbonate. The ether was removed as before. The saponification equivalent of the mixture was determined by the method of Shriner and Fuson.[12] The formation of the ester and the saponification were conducted in a closed flask to avoid loss of the highly volatile camphene and ester. Corrections, determined by blank runs, were made for hydrogen chloride removed from the bornyl and isobornyl chlorides during the saponification, and for losses due to the volatility of camphene. The amount of camphane was determined by difference.

Bibornyl and camphane were identified by their melting points (88–90° and 150°, respectively). Camphene was identified by conversion to the *p*-nitrobenzoyl ester of isoborneol (long needles, m. p. 133°). The melting point of this material was not lowered by admixture with a known sample of isobornyl *p*-nitrobenzoate.

In the reaction with cyclohexyl chloride and the 2-methylcyclohexyl chlorides, the products were separated by fractional distillation in a 12 plate concentric tube column.

The product of the reaction between cyclohexyl chloride and methylmagnesium bromide in the presence of cobaltous chloride was distilled and three fractions collected: (1) b. p. 81–84°, a mixture of cyclohexene and cyclohexane; (2) b. p. 83° at 110 mm., unreacted cyclohexyl chloride; and (3) b. p. 68° at 2 mm., bicyclohexyl. The product of the reaction between 2-methylcyclohexyl chloride and methylmagnesium bromide in the presence of cobaltous chloride was distilled and three fractions collected: (1) b. p. 63.5 to 67.5° at 140 mm.; b. p. 101–104° at 760 mm. (a mixture of methylcyclohexene and methylcyclohexane); (2) b. p. 101–102° at 133 mm. (unreacted 2-methylcyclohexyl chloride); (3) b. p. 104–106° at 3 mm. (2,2′-dimethylbicyclohexyl). The amounts of unsaturation in the cyclohexene–cyclohexane and methylcyclohexane–methylcyclohexene fractions were determined by bromide–bromate titration.[13]

The gas analyses were made according to the procedure of Kharasch, Lewis and Reynolds.[1] The gas collected was in all cases approximately 70% of the amount calculated from the amount of reaction determined by Volhard titration.

Summary

1. The reactions of some alicyclic chlorides with methylmagnesium bromide in the presence and in the absence of cobaltous chloride have been studied.

2. The significance of the formation of the dimers in the presence of cobaltous chloride is discussed.

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[6] Fisher, "Laboratory Manual of Organic Chemistry," John Wiley and Sons, Inc., New York, N. Y., 1920, p. 198.

[7] Meerwein and Van Emster, *Ber.* **55**, 2526 (1922).

[8] Zelinski, *ibid.*, **41**, 2679 (1908).

[9] Cumming, Hopper and Wheeler, "Systematic Organic Chemistry," Arnold Constable, London, 1937, p. 335.

[10] Hesse, *Ber.*, **39**, 1132 (1906).

[11] Bertram and Walbaum, *J. prakt. Chem.*, **49**, 8 (1894).

[12] Shriner and Fuson, "Systematic Identification of Organic Compounds," John Wiley and Sons, Inc., New York, 1941, p. 117.

[13] "Scott's Standard Methods of Analysis," N. H. Furman, Ed., Vol. II, D. Van Nostrand Co., New York, N. Y., 1939, p. 2253.