STUDIES OF POLYMERIZATION AND RING FORMATION. XVI. A POLYALCOHOL FROM DECAMETHYLENE DIMAGNESIUM BROMIDE

BY WALLACE H. CAROTHERS AND JAMES E. KIRBY

The action of bifunctional reactants on bifunctional Grignard reagents (e. g., on $BrMg(CH_2)_xMgBr$) presents the possibility of producing cyclic compounds of various types. Cyclopentanone,[1] cyclohexanone and methylcyclohexanol[2] have been prepared thus, and also 5- and 6-atom rings containing phosphorus, arsenic,[3] lead[4] and silicon.[5] Concerning larger rings it is recorded[2] that diacetyl reacts with pentamethylene dimagnesium bromide but yields very little of the product corresponding in composition with the expected 7-ring glycol. The same reagent is said[6] to react with dialdehydes and diketones to give ring compounds, though "not easily;" but none of these compounds are described. The rarity and obscurity of such allusions to reactions which might yield large rings is certainly not due to any difficulty of inducing reaction between —MgX and carbonyl or other groups. On the other hand, bifunctional reactions are not obliged to choose between ring formation and frustration or abortion; they may be, and in fact when the possibility of forming a ring of 5 or 6 atoms is absent, they generally are intermolecular, and they thus lead to linear polymeric chains.[7] The diversity of the Grignard reactions should permit the preparation of linear polymers of many different types. Complications due to the usual side reactions of the —MgX group are multiplied when two of these groups are present in the same molecule. Nevertheless, as the following example shows, it is possible by such reactions to prepare linear polymers which are homogeneous in their analytical and chemical behavior.

Methyl formate (0.2 mole) was added dropwise to an ethereal solution (250 cc.) of decamethylene dimagnesium bromide prepared from 0.2 mole of the bromide. Each drop of the formate immediately yielded a heavy, voluminous precipitate. After the addition of all the formate, the mixture was refluxed for one and one-half hours. A color test[8] then showed that C—MgX was absent from the ethereal layer but present in the insoluble precipitate. The mixture was treated with water and dilute hydrochloric

[1] V. Braun and Sobecki, Ber., 44, 1918 (1911).

[2] Grignard and Vignon, Compt. rend., 144, 1358 (1907).

[3] Grüttner and Wiernik, Ber., 48, 1473 (1915).

[4] Grüttner and Krause, ibid., 49, 2666 (1916).

[5] Bygden, ibid., 48, 1236 (1915).

[6] V. Braun, Chem. Zentr., II, 1993 (1909).

[7] See Carothers, THIS JOURNAL, 51, 2548 (1929), and subsequent papers of this series.

[8] Gilman and Schulze, ibid., 47, 2002 (1925).

acid, and the undissolved solid was separated by filtration. The yield was 88% of the theoretical. The product was completely freed of magnesium by triturating it with warm dilute hydrochloric acid. It dissolved readily in hot alcohol, acetic acid, or ethylene chloride, but not in acetone, ether or benzene. It melted at about 115–120°. More sharply melting samples (e. g., 120–121°) were obtained by repeated crystallization from alcohol, and higher and lower melting samples were obtained in other experiments. The melting points all varied with the rate of heating.

The analytical composition of this solid corresponds with the expected poly secondary alcohol, and its apparent molecular weight indicates an average formula —[(CH₂)₁₀—CHOH]₅—. The equation for the reaction may be represented as

$$\ldots-(CH_2)_{10}MgBr + O\!\!=\!\!C\!\!-\!\!OCH_3 + BrMg\!-\!\ldots \longrightarrow$$
$$|$$
$$H$$
$$\ldots-[-(CH_2)_{10}-CH(OMgBr)-]-\ldots$$
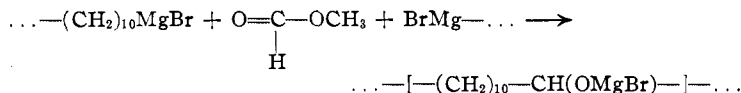
Anal. Calcd. for $C_{11}H_{22}O$: C, 77.65; H, 12.94. Found: C, 77.35, 77.40; H, 13.04, 12.79. Mol. wt., calcd. for $(C_{11}H_{22}O)_5$: 850. Found (in boiling ethylene chloride): 835, 879.

It is undoubtedly mixed with traces of shorter and longer chains and with analogous derivatives of the coupling products $BrMg(CH_2)_{20}MgBr$, $BrMg(CH_2)_{30}MgBr$, etc., which are always formed in small amounts during the preparation of the reagent. The chains are probably all open, but there may be considerable variety in the nature of the terminal groups. However, its lack of homogeneity is probably no greater than that of a purified sample of polyvinyl alcohol,[9] of which it is a homolog.

The polyalcohol is readily converted into such acyl derivatives as bromobenzoyl, phthalyl, etc., but all of these products were obtained only in the form of oils or tars. The composition of an oily acetate prepared by refluxing the alcohol with acetic anhydride containing some sodium acetate confirms the empirical structure assigned to the alcohol.

Anal. Calcd. for —$(CH_2)_{10}$—CH—$(OCOCH_3)$— = $C_{13}H_{24}O_2$: C, 73.59; H, 11.32; saponification equivalent, 212. Found: C, 74.09, 73.61; H, 11.27, 11.33; saponification equivalent, 207, 223, 227.

Experiments in other directions remain incomplete.

The behavior of the polyalcohol in the molecular still is noteworthy. A sample melting at 110–113° was heated for a few hours at about 150° under a pressure less than 10^{-6} mm. A trace of crystalline solid melting at about 80° collected on the condenser which was within 1 cm. of the evaporating surface. The residue was a colorless, semi-transparent, very tough pliable mass. It was insoluble in the common solvents. On being heated, it gradually became completely transparent between 60 and 100°. At 215–220° it had become somewhat soft and sticky without losing its shape. Above this temperature it first became slightly yellow and finally, at about 250°, still darker with considerable decomposition. Its analytical composition was nearly the same as that of the alcohol from which it was derived. The change in properties indicates a considerable increase in molecular weight, and the absence of solubility and complete fusibility is consistent with the development of a three-dimensional polymeric molecular structure. This might readily occur, with very little change in composition, through cross-linking of the polyalcohol chains by occasional ether formation. When the polyalcohol is heated in the same way at ordinary pressure, it remains quite unchanged in its properties; so this example provides an even more striking illustration than those

⁹ Herrmann and Haehnel, *Ber.*, **60**, 1658 (1927); Staudinger, Frey and Starck, *ibid.*, **60**, 1782 (1927).

previously recorded[10] of the powerfulness of the molecular still as a tool for displacing chemical equilibria.

The description of these fragmentary experiments with bifunctional Grignard reagents is presented now because it has become necessary to suspend our work in this field.

Summary

A crystalline polydecamethylene carbinol has been prepared by the action of decamethylene dimagnesium bromide on methyl formate. Its properties are described. It is converted into a colorless, insoluble, tough, pliable mass when it is heated in a molecular still.

[10] Papers XI, XII, XIII and XIV.

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d-TALONIC ACID AND GAMMA-TALONOLACTONE

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Crystalline talonic acid has been described by Hedenburg and Cretcher.[1] In common with other monocarboxylic sugar acids talonic changes slowly in aqueous solutions to an equilibrium mixture of lactone and acid. The crystalline γ-lactone was isolated for the first time during the course of this investigation.

In a study of the mutarotation of aqueous solutions of sugar acids, Levene and Sims[2] found that for several hours the change in specific rotation is determined by the dextro or levo character of the δ-lactone, which forms nearly eight times as rapidly as the γ-lactone. d-Mannonic acid with a cis-configuration of the fourth and fifth hydroxyl groups gave rapidly increasing dextro readings during the first four hours, and subsequently showed a slow rise in dextro values. In the case of sugar acids which have the γ- and δ-hydroxyl groups in trans positions, Levene and Sims[2] and Rehorst[3] have observed that the values for specific rotation pass through an early maximum or minimum, corresponding to the formation of δ-lactone.

As Rehorst has noted—in accordance with Hudson's rule and in analogy with the behavior of similarly constituted acids—d-talonic acid solutions might be expected to give a series of increasing dextro readings[4] before

[1] Hedenburg and Cretcher, THIS JOURNAL, **49**, 478 (1927).

[2] Levene and Sims, J. Biol. Chem., **65**, 31 (1925).

[3] Rehorst, Ber., **63**, 2279 (1930).

[4] Freudenberg and Kuhn have questioned the validity of a generalization based on these premises and have presented an extensive analysis of rotational data [Freudenberg and Kuhn, Ber., **64**, 703 (1931)].