[CONTRIBUTION FROM THE KNIGHT CHEMICAL LABORATORY, UNIVERSITY OF AKRON]

The Reaction of α,β-Dichloropropionaldehyde with a Number of Grignard Reagents

BY VAUGHN W. FLOUTZ

The research project here reported was undertaken to determine the behavior of representative Grignard reagents with α,β-dichloropropionaldehyde. Studies have shown that chloral and α,α,β-trichlorobutyraldehyde, commonly called butyl chloral, react normally with arylmagnesium halides, but abnormally with certain other Grignard reagents to give a primary alcohol by reduction of the aldehyde and an unsaturated hydrocarbon by oxidation of the Grignard reagent.[1,2] Unlike chloral and butyl chloral, α,β-dichloropropionaldehyde carries one chlorine atom on the alpha carbon rather than a maximum number. It was found that the reaction proceeds normally with phenylmagnesium bromide and gives a good yield of secondary alcohol. α,β-Dichloropropionaldehyde reacts with *n*-hexylmagnesium bromide, cyclohexylmagnesium bromide and β-phenylethylmagnesium bromide to give the secondary alcohols of normal addition in a smaller yield. In each case there is formed in addition to the secondary alcohol 2,3-dichloropropanol-1 (glycerol 2,3-dichlorohydrin) by the reduction of some of the aldehyde, and an unsaturated hydrocarbon by oxidation of some of the Grignard reagent. In the case of benzylmagnesium chloride no secondary alcohol was detected; the only reaction product identified was dibenzyl. It has been found that both chloral and butyl chloral exhibit this same behavior with benzylmagnesium chloride.[2]

TABLE I

REACTION PRODUCTS

	Secondary alcohol											Dibromo addition product yield		Primary alcohol $CH_2ClCHCl-CH_2OH$ yield	
						Analyses, %									
		Yield,		B. p.,		Calculated			Found						
RMgBr	Formula	G.	%	°C.	Mm.	C	H	Cl	C	H	Cl	G.	%	G.	%
C_6H_5MgBr[a]	$C_9H_{10}OCl_2$	35	68.3	150–151	10	52.71	4.92	34.58	52.39	4.89	34.36	..	..	...	..
$C_6H_{13}MgBr$[b]	$C_9H_{18}OCl_2$	19.5	36.6	139–141	12	50.71	8.51	33.27	50.41	8.61	33.32	10	16.4	6.5	20.2
$C_6H_{11}MgBr$[c]	$C_9H_{16}OCl_2$	13.5	25.6	144–146	12	51.20	7.64	33.59	51.30	7.66	33.50	14	23.1	8	24.8
$C_6H_5(CH_2)_2$-MgBr[d]	$C_{11}H_{14}OCl_2$	28.5	49	155–158	4	56.67	6.05	30.42	56.92	6.10	30.21	8	12.1	4	12.4

[a,b,c,d] In addition 1 g. of diphenyl, 3 g. of *n*-dodecane, 3 g. of dicyclohexyl and 1.5 g. of 1,4-diphenylbutane, respectively, were isolated.

Experimental[3]

α,β-Dichloropropionaldehyde and Phenylmagnesium Bromide.—In the preparation of this Grignard reagent, and also those subsequently considered, a 1-liter, three-necked flask, fitted with a mercury-seal stirrer, dropping funnel and condenser was employed. A 0.25 gram-atom portion of magnesium turnings was placed in the flask and covered with 250 ml. of anhydrous ether, and the reagent was formed by adding 0.25 mole of the halide dissolved in an equal volume of dry ether. The reagent was cooled and the aldehyde, dissolved in a like volume of dry ether, was added at a rate such that there was no refluxing of the ether. The product was poured slowly into a mixture of ice and water, and the resulting mixture was cleared by the addition of 5% aqueous acetic acid. The ether layer was removed, washed in turn with sodium bicarbonate solution, saturated sodium bisulfite solution, and water, and then dried over anhydrous sodium sulfate.

The ether solution from the reaction of α,β-dichloropropionaldehyde and phenylmagnesium bromide was subjected to distillation to remove the ether. The distillation was then continued under reduced pressure in an atmosphere of nitrogen to obtain the secondary alcohol 2,3-dichloro-1-phenylpropanol-1.

α,β-Dichloropropionaldehyde and *n*-Hexylmagnesium Bromide, Cyclohexylmagnesium Bromide and β-Phenylethylmagnesium Bromide.—The ether solution of the products from the reaction of the aldehyde with *n*-hexylmagnesium bromide was subjected to distillation to remove the ether and the hexene-1 formed in the reaction. The ether and larger portion of the hexene-1 were distilled by use of a hot water-bath; following this the residue was heated in an oil-bath to a bath temperature of 120°, and this additional distillate was added to the first portion. To determine more accurately the amount of hexene-1 produced, the hydrocarbon was converted into 1,2-dibromohexane; this was accomplished by treating the distillate in subdued light with a slight excess of bromine. The residue from the removal of ether and hexene-1 was distilled under diminished pressure to obtain the primary alcohol 2,3-dichloropropanol-1, and the secondary alcohol 1,2-dichlorononanol-3. The primary alcohol was further identified through its oxidation with fuming nitric acid to produce α,β-dichloropropionic acid.[4]

The reaction mixture from the cyclohexylmagnesium bromide, treated in a similar way, gave cyclohexene, determined as the dibromide, the primary alcohol and 2,3-dichloro-1-cyclohexylpropanol-1. That from β-phenylethylmagnesium bromide yielded styrene, determined as the dibromide, the primary alcohol and 1,2-dichloro-5-phenylpentanol-3.

α,β-Dichloropropionaldehyde and Benzylmagnesium Chloride.—The ether solution of the reaction products was distilled to remove the ether. The residual liquid on standing overnight deposited a considerable amount of non-crystalline solid. This substance had the characteristics of a polymerized material or a condensation product from the aldehyde, and was not identified. The liquid remaining from the removal of this solid was distilled under reduced pressure in an atmosphere of nitrogen. The only product isolated from the distillate was dibenzyl.

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[1] Floutz, THIS JOURNAL, **67**, 1615 (1945).

[2] Floutz, *ibid.*, **68**, 2490 (1946).

[3] A portion of the α,β-dichloropropionaldehyde was furnished through the courtesy of the Shell Development Company. That used in the initial studies was synthesized by the low temperature addition of chlorine to acrolein, according to the literature.

[4] Yarnell and Wallis, *J. Org. Chem.*, **4**, 270–283 (1939).

No secondary alcohol was detected; the larger part of the liquid began to decompose and carbonize at a bath temperature of 180° and pressure of 4 mm. An average of results from two runs gave amorphous solid, 12.5 g.; dibenzyl, 6.3 g.; tarry, carbonaceous residue, 14.5 g.

Table I provides essential data. Yields in each case are averages from two runs.

Summary

1. The reaction of α,β-dichloropropionaldehyde with phenylmagnesium bromide, *n*-hexylmagnesium bromide, cyclohexylmagnesium bromide, β-phenylethylmagnesium bromide and benzylmagnesium chloride has been studied.

2. The new secondary alcohols 2,3-dichloro-1-phenylpropanol-1, 1,2-dichlorononanol-3, 2,3-dichloro-1-cyclohexylpropanol-1 and 1,2-dichloro-5-phenylpentanol-3 have been prepared via the Grignard reaction.

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Cyclobutane Derivatives. IV. Ziegler Bromination[1a] of Methylenecyclobutane[1b,2]

BY EDWIN R. BUCHMAN AND DAVID R. HOWTON

In connection with another investigation,[3] we have studied the reaction,[1a] under a variety of conditions, between N-bromosuccinimide (NBS) and methylenecyclobutane (I). It was found that, although NBS reacted with I faster in the usually employed carbon tetrachloride[1a] than in benzene,[4] higher yields of allylic bromides, C_5H_7Br, were obtained in the latter solvent; in both cases the addition of small amounts of dibenzoyl peroxide[5] proved advantageous. A typical experiment carried out in benzene and with added peroxide gave the following products[6]: a C_5H_7Br fraction (14%), methylenecyclobutane dibromide[7] (56%), N-phenylsuccinimide[9] (15%) and succinimide (66%). In carbon tetrachloride and without added peroxide another minor product was encountered, apparently formed by direct 1:1 addition[8] of NBS to I.

The C_5H_7Br mixture (II + III) was investigated as indicated on the diagram. II and III were separated by virtue of the great difference in the rates at which they react with trimethylamine in benzene at room temperature. III reacted in a few minutes to precipitate the corresponding[10] allylic quaternary ammonium bromide (V) while the complete conversion of II to IV required several weeks; the relative amounts of IV and V isolated indicate a II:III ratio in the C_5H_7Br fraction of about 15:1.

The structure[11] of V (and indirectly that of IV) was established by relating it to the known[13] saturated quaternary bromide (IX). In this connection the applicability of a recently described[12] two-step reduction method was investigated. The addition of bromine to V yielded a single dibromo bromide to which structure VII must be assigned since on catalytic hydrogenation it was converted to a bromide identified (by comparison with an authentic sample[13]) as IX. However, the bromination of IV gave not only compound VI isomeric with VII (and yielding on reduction VIII isomeric with IX) but also, by a novel rearrangement, a nearly equal amount of bromide VII identical with the material originating from V.

A structure proof based on reactions not accompanied by possible rearrangements was achieved

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(1) (a) *Cf.* Ziegler, Späth, Schaaf, Schumann and Winkelmann' *Ann.*, **551**, 80 (1942); (b) *cf.* Ziegler bromination of ketene dimer' Blomquist and Baldwin, THIS JOURNAL, **70**, 29 (1948).

(2) Presented before the Pacific Division of the American Association for the Advancement of Science at the San Diego Meeting, June, 1947.

(3) See Paper V of this Series, to be published.

(4) *Cf.* Ettlinger and Fieser, *J. Biol. Chem.*, **164**, 451 (1946).

(5) *Cf.* Schmid and Karrer, *Helv. Chim. Acta*, **29**, 573 (1946).

(6) Yields based on NBS.

(7) Földi[8] obtained saturated dibromides from reactions of N-bromo-N-methylbenzenesulfonamide with certain olefins. In this Laboratory it has been found that I and cyclobutene,[3] which react slowly with NBS, give dibromides as major products (yield apparently independent of added peroxide but dependent on nature of solvent, see Experimental), while cyclohexene.[9] which reacts rapidly, gives only a small amount of dibromide.

The mechanism of formation of the dibromides remains obscure. Földi's unsubstantiated explanation that substituted derivatives of ethylenediamine and substituted dibromides are formed in equivalent amount obviously cannot apply in the present case. The possibility that hydrogen bromide (which would combine with NBS to make free bromine available, *cf.* Meystre, Ehmann, Neher and Miescher, *Helv. Chim. Acta*, **28**, 1252 (1945); Wieland and Miescher, *ibid.*, **30**, 1876 (1947); Barnes, THIS JOURNAL, **70**, 145 (1948)) is formed during the slow reaction is unsupported by experimental evidence; brominated reaction products from I appear to be stable and no loss of hydrogen bromide was noted during the Ziegler reaction or during the working-up procedure.

Cf. Buckles, Organic Division Abstracts, April, 1948, page 36L.

(8) *Cf.*. Földi, *Ber.*, **63**, 2257 (1930); Lichoscherstow, *et al.*, *Chem. Zentr.*, **109**, I, 3330 (1938); **110**, II, 66 (1939); **111**, 1. 3246 (1940); **111**, II, 198 (1940); Kharasch and Priestly, THIS JOURNAL, **61**, 3425 (1939); Fosdick, Fancher and Urbach, *ibid.*, **68**, 840 (1946); ref. 1a.

(9) *Cf.* Howton, THIS JOURNAL, **69**, 2060 (1947).

(10) The precipitated fractions are quite pure; we assume that III is the precursor of V and II of IV.

(11) As a possible aid in assigning structures to such compounds, it may be noted that there appears to be a degree of correspondence in m. p.'s between allylic quaternary picrates and the related saturated picrates, *e. g.*, picrates corresponding to V and IX melt at 127 and 117°, respectively, while for the IV–VIII pair the values are 215 and 245°; Howton[12] gives: 2-cyclohexenyltrimethylammonium picrate, m. p. 130°, and cyclohexyltrimethylammonium picrate, m. p. 125°; allyltrimethylammonium picrate, m. p. 220°, and *n*-propyltrimethylammonium picrate, m. p. 200°.

(12) Howton, THIS JOURNAL, **69**, 2555 (1947).

(13) (a) v. Braun, Fussgänger and Kuhn, *Ann.*, **445**, 201 (1925); see also (b) Demjanow and Dojarenko, *Ber.*, **55**, 2727 (1922); *Chem. Zentr.*, **94**, III, 746 (1923).