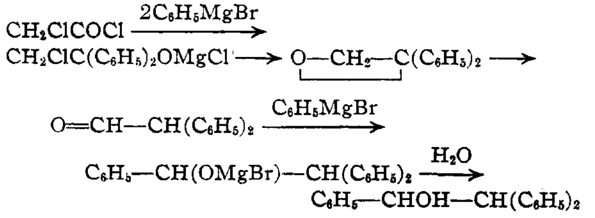
[CONTRIBUTION FROM THE KEDZIE CHEMICAL LABORATORY, MICHIGAN STATE COLLEGE]

The Reaction of α-Halocarbonyl Compounds with Grignard Reagents. I

BY R. C. HUSTON, R. I. JACKSON AND G. B. SPERO

With one exception, the products reported from the reaction of α-haloacid halides and α-haloacid esters with Grignard reagents have been tertiary alcohols,[1] ketones,[2,3] or anilides.[4]

A secondary alcohol, 1,2,2-triphenyl-1-ethanol, was obtained by Boyle, McKenzie and Mitchell[3] as one of the products of the reaction between chloroacetyl chloride and phenylmagnesium bromide. The following mechanism was proposed to explain its formation:



$$CH_2ClCOCl \xrightarrow{2C_6H_5MgBr} CH_2ClC(C_6H_5)_2OMgCl \longrightarrow \underbrace{O—CH_2—C}(C_6H_5)_2 \longrightarrow$$

$$O{=}CH—CH(C_6H_5)_2 \xrightarrow{C_6H_5MgBr} C_6H_5—CH(OMgBr)—CH(C_6H_5)_2 \xrightarrow{H_2O} C_6H_5—CHOH—CH(C_6H_5)_2$$

In the present investigation, chloroacetyl chloride, ethyl chloroacetate, bromoacetyl bromide and ethyl bromoacetate were allowed to react with an excess (four moles) of methylmagnesium bromide. Chloroacetyl chloride and bromoacetyl bromide were allowed to react with methylmagnesium iodide. In each case the only product isolated was 2-methyl-3-butanol.

According to the mechanism proposed by Boyle, McKenzie and Mitchell,[3] 1,2-epoxy-2-methylpropane would be one of the intermediates in the formation of 2-methyl-3-butanol. Henry[5] and Norton and Hass[6] report the formation of 2-methyl-2-pentanol when this compound reacts with diethylmagnesium and the formation of 2-methyl-3-pentanol when it reacts with ethylmagnesium bromide. Treatment of 1,2-epoxypropane with diethylmagnesium[6] or with ethylmagnesium bromide[6,7] gives 2-pentanol although in the last case there is some evidence of the simultaneous formation of 3-pentanol. When epoxyethane is treated with either diethylmagnesium or ethylmagnesium bromide, the main product is 1-butanol.[8] There is no evidence of formation of 2-butanol.

Mention should be made of the work of Winogradow[9] who found that 2-methyl-3-butanol was a product of the reaction of bromoacetyl bromide and three moles of dimethylzinc. The same acid halide gave with diethylzinc, 4-ethyl-3-hexanol. Molecular rearrangement was assumed to have taken place.

It has been shown by Fisher[10] and by Kohler and Tishler[11] that a number of α-bromoketones are dehalogenated when treated with one mole of Grignard reagent. We have found that bromoacetone reacts with an excess (2 moles) of methylmagnesium bromide or methylmagnesium iodide to give 2-methyl-3-butanol in yields approaching 20% of the theoretical.

We believe that a further study of the mechanism of the reactions in this formation of secondary alcohols from halides or esters of α-haloacids and from α-haloketones is justified and it is being continued in this Laboratory.

Preparation of the Grignard Reagents.—Methylmagnesium iodide was prepared in the usual manner. Methylmagnesium bromide was prepared by bubbling methyl bromide through a stirred mixture of magnesium and anhydrous ether. The methyl bromide was prepared from methyl alcohol, sodium bromide and concentrated sulfuric acid and washed with 30% sodium hydroxide and concentrated acid.

2-Methyl-3-butanol from the Haloacetyl Halides and Ethyl Haloacetates.—One mole of the ester or acid halide, dissolved in 500 cc. of anhydrous ether, was added to four moles of the Grignard reagent at such a rate that the mixture refluxed gently. When addition was complete, most of the ether was removed by distillation and the residue was heated on the steam-bath for twenty-four to thirty-six hours. The residue was broken up and hydrolyzed with ice and concentrated hydrochloric acid. The ether layer was separated and the water layer extracted three times with 200-cc. portions of ether. The combined layers were dried with a mixture of anhydrous sodium sulfate and anhydrous sodium carbonate and the ether was removed by distillation.

The residue was fractionally distilled and the 2-methyl-3-butanol collected at 110–113°. It was proved by the mixed melting points of the α-naphthyl urethan (m. p. 111–112°) and of the 3,5-dinitrobenzoyl esters (m. p. 74–75°) to be

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[1] Dalebroux and Wuyts, *Bull. soc. chim. Belg.*, **29**, 156 (1906); Blaise, *Compt. rend.*, **155**, 1252 (1912); Moreaux and Barrett, *Bull. soc. chim.*, [4], **29**, 993 (1921); Avy, *ibid.*, [4], **49**, 12 (1931).

[2] McKenzie and Boyle, *J. Chem. Soc.*, **119**, 1131 (1921).

[3] Boyle, McKenzie and Mitchell, *Ber.*, **70B**, 2153 (1937).

[4] Bodroux and Taboury, *Compt. rend.*, **144**, 1437 (1907); *Bull. soc. chim.*, [4], **1**, 911 (1907).

[5] Henry, *Compt. rend.*, **145**, 21 (1907).

[6] Norton and Hass, THIS JOURNAL, **58**, 2147 (1936).

[7] Henry, *Compt. rend.*, **145**, 453 (1907).

[8] Huston and Agett, *J. Org. Chem.*, **6**, 127 (1941).

[9] Winogradow, *Ann.*, **191**, 125 (1878).

[10] Fisher, THIS JOURNAL, **52**, 5038 (1930).

[11] Kohler and Tishler, *ibid.*, **54**, 1594 (1932).

identical with a sample obtained from a reliable manufacturer.

2-Methyl-3-butanol from Bromoacetone.—The same procedure was used except that one mole of bromoacetone[12] was added to two moles of the Grignard reagent.

Methylmagnesium bromide with chloroacetyl chloride gave a 51% yield of 2-methyl-3-butanol; with ethyl chloroacetate, 40%; with bromoacetyl bromide, 21%; with ethyl bromoacetate, 32%; with bromoacetone, 18%.

Methylmagnesium iodide with chloroacetyl chloride gave a 48% yield; with bromoacetyl bromide, 16%; with bromoacetone, 12%.

Summary

2-Methyl-3-butanol has been prepared from the reactions of methylmagnesium bromide and methylmagnesium iodide with chloroacetyl chloride, ethyl chloroacetate, bromoacetyl bromide, ethyl bromoacetate and bromoacetone.

EAST LANSING, MICHIGAN RECEIVED DECEMBER 26, 1940

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[12] Levene, "Organic Syntheses," Vol. X, p. 12.

[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY AND PHYSICS OF THE PENNSYLVANIA STATE COLLEGE]

Polymerization of Olefins. IV.[1] The Nonenes from the Dehydration and Copolymerization of *t*-Butyl and *t*-Amyl Alcohols[2]

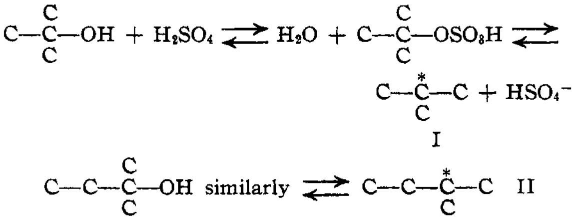
BY FRANK C. WHITMORE AND L. W. MIXON[3]

The present study was undertaken to throw additional light on the mechanism of the polymerization of olefins. Two tertiary alcohols were chosen because the related olefins polymerize with extraordinary ease in the presence of acid catalysts.

The dehydration of an equimolar mixture of *t*-butyl alcohol and *t*-amyl alcohol with 65% sulfuric acid at 80° gave the following percentage yields: isobutylene, 0.5; isoamylenes, 30; diisobutylenes, 22; nonenes, 17; diamylenes, 6; triisobutylenes, 6; higher polymers, 1.5. Satisfactory separation of the isomeric nonenes could not be effected by repeated fractionation through a column equivalent to 23 theoretical plates. The identification of the nonene mixture was effected by ozonolysis of the mixture and subsequent separation and identification of the products of ozonolysis, namely, formaldehyde, acetaldehyde, acetone, trimethylacetaldehyde, dimethylethylacetaldehyde, pinacolone, methyl neopentyl ketone and 3,4,4-trimethyl-2-pentanone.

From the nature and amounts of the ozonolysis products, the nonenes were concluded to be the following with the indicated percentages of the total nonenes: 2,3,4,4-tetramethyl-1-pentene (V, 50%), and its -2-isomer (VI, 10%), 3,5,5-trimethyl-2-hexene (VII, 23%), and its -3-isomer (VIII, 5%), and 2,4,4-trimethyl-2-hexene (IX, 10%).

The course of nonene formation may be pictured as follows, the asterisk indicating a carbon with only six electrons[4]:



$$\mathrm{C{-}\overset{C}{\underset{C}{C}}{-}OH} + \mathrm{H_2SO_4} \rightleftarrows \mathrm{H_2O} + \mathrm{C{-}\overset{C}{\underset{C}{C}}{-}OSO_3H} \rightleftarrows \mathrm{C{-}\underset{C}{\overset{*}{C}}{-}C} + \mathrm{HSO_4^-} \quad \mathrm{I}$$

$$\mathrm{C{-}C{-}\overset{C}{\underset{C}{C}}{-}OH} \text{ similarly } \rightleftarrows \mathrm{C{-}C{-}\underset{C}{\overset{*}{C}}{-}C} \quad \mathrm{II}$$

The electronically deficient fragments are not to be considered as ions capable of continued existence. Their half life is more probably of the order of 10^{-13} second. Essentially as rapidly as they are formed they undergo changes to more stable arrangements.

The yields indicate that 88% of the nonenes are formed by addition of a *t*-butyl fragment to an amylene or its equivalent as compared with 12% formed by the addition of a *t*-amyl fragment to isobutylene. This is related to the fact that only 0.5% isobutylene was found as compared with 30% isoamylenes.

The ratio of V to VI indicates that the loss of a proton from two methyl groups takes place about five times as easily as the loss of the tertiary proton which is part of a neopentyl system. This recalls the ratio in which the two isomeric diisobutylenes occur.[5] It is interesting that the reactivity of a tertiary hydrogen under these conditions appears to be somewhat less than that of two sec-

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[1] For Paper III of this series see THIS JOURNAL, **63**, 1120 (1941). Original manuscript received February 15, 1940.

[2] Presented at the San Francisco meeting, August, 1936.

[3] Present address, Standard Oil Company of Indiana, Whiting, Indiana.

[4] Whitmore, THIS JOURNAL, **54**, 3274 (1932); *Ind. Eng. Chem.*, **26**, 94 (1934).

[5] Whitmore and Church, *ibid.*, **54**, 3711 (1932).