

oxide, oxygen, benzyl chloride, ethyl acetate and acetyl chloride with benzylmagnesium chloride on a larger scale has confirmed the results of previous investigators. Only acetyl chloride gave rearrangement.

3. The yield of rearranged product from the

addition of benzylmagnesium chloride to acetyl chloride was found to be much higher than that obtained from the addition of acetyl chloride to the Grignard reagent.

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

The Dehydration of Alcohols. XIX.¹⁻⁴ *t*-Amyl Alcohol and the Related Dimethylneopentylcarbinol

BY FRANK C. WHITMORE, C. S. ROWLAND,⁵ S. N. WRENN AND G. W. KILMER

Despite the amount of work done on the dehydration of alcohols since the discovery of ethylene by the four Dutch chemists in 1795, practically no generalizations of any value have been presented. This is largely because few, if any, cases have been studied with proper control of the variables involved. Moreover, the dehydration mixtures obtained from any but the simplest alcohols are likely to be so complex as to be unmanageable with ordinary equipment and techniques.¹ Even with a simple alcohol like *t*-amyl alcohol (I) the results in the literature are highly conflicting.⁶ In all this work the only consistent fact is that trimethylethylene (IV) is the chief product. The different proportions of olefins obtained by different investigators indicated that equilibrium conditions had not been obtained for the olefin mixture. The unasked question as to whether the olefin mixture obtained by dehydration of an alcohol is identical with the equilibrium mixture of the olefins has long existed. For strongly acid catalysts this question was answered in the affirmative in this Laboratory when essentially identical mixtures of olefins were obtained by passing the following over phosphoric acid on silica gel: (a) methyl-*t*-butylcarbinol, (b) *t*-butylethylene, (c) 1,1-methylisopropylethylene and (d) tetramethylethylene.⁷ Recently Cramer

and Glasebrook⁸ published their results with a less acidic catalyst, namely, activated alumina, in which they obtained high yields of *t*-butylethylene from methyl-*t*-butylcarbinol instead of the 3-5% of that olefin characteristic of the equilibrium mixture.^{7b} These results have been repeatedly checked in this Laboratory.⁹ The method of Cramer and Glasebrook⁸ is now recommended for the preparation of large quantities of *t*-butylethylene as more convenient than the pyrolysis of pinacolyl acetate.¹⁰

It may be mentioned in passing that making the catalyst even slightly alkaline prevents dehydration at anything below cracking temperatures.¹¹

Since 1930 there have been repeated indications in this Laboratory that the two alcohols *t*-amyl alcohol (I) and dimethylneopentylcarbinol (II) behave differently on dehydration. This is in spite of remarkable similarities in structure. Both are tertiary alcohols containing two methyl groups and a methylene group and both are dehydrated readily without rearrangement. In each, the proton for dehydration must come from one of the two methyl groups or from the methylene group. The only difference is that in one the methylene group is attached to methyl while in the other it is attached to *t*-butyl. Evidently this difference has a profound effect on the otherwise identical methylene groups.

(1) Whitmore and Karnatz, Diethylcarbinol (2-ethyl-1-butanol), *THIS JOURNAL*, **54**, 3461 (1932).

(2) Whitmore and co-workers, *ibid.*, **54**, 3717, 4011, 4392 (1932); **55**, 406, 812, 1106, 1119, 1528, 3428, 3721, 3732, 3809, 4153 (1933).

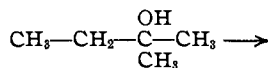
(3) Whitmore and co-workers, *ibid.*, (a) Homeyer, **55**, 4195 (1933); (b) Church, **56**, 176 (1934); (c) Rohrmann, **63**, 2033 (1941).

(4) Whitmore and Mosher, 3,5,5-Trimethyl-3-heptanol, *ibid.*, **63**, 1121 (1941).

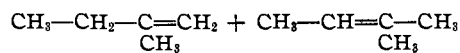
(5) Submitted in partial fulfillment for the M.S. degree.

(6) Kondakow, *J. prakt. Chem.*, [2] **54**, 454 (1896); Ipatiew, *Ber.*, **36**, 2002 (1903); Michael and Zeidler, *THIS JOURNAL*, **36**, 1002 (1914); Hibbert, *ibid.*, **37**, 1748 (1915); Church, *et al.*, *ibid.*, **56**, 176 (1934); Bourquel and Piaux, *Bull. soc. chim.*, **51**, 1051 (1932).

(7) (a) Whitmore and P. L. Meunier, *THIS JOURNAL*, **55**, 372 (1933). (b) Laughlin, Nash and Whitmore, *ibid.*, **56**, 1395 (1934).



(I)



(III)

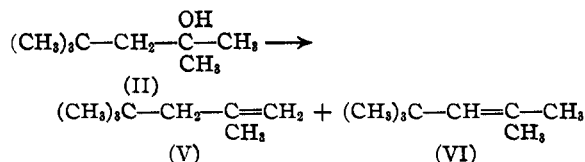
(IV)

(8) Cramer and Glasebrook, *ibid.*, **61**, 230 (1939).

(9) Unpublished results of R. K. Smith and N. C. Cook and others.

(10) Whitmore and Rothrock, *THIS JOURNAL*, **55**, 1107 (1933); unpublished results of V. C. Meunier and N. C. Cook.

(11) Unpublished results of M. R. Fenske and co-workers.



This pair of alcohols was chosen for study because of the facts given above. Moreover, they are both dehydrated by refluxing with an excess of 15% sulfuric acid. This allows dehydration under almost identical conditions and avoids the vigorous treatment required to dehydrate primary or secondary alcohols. The olefins III and IV are readily separable in a 60-plate column.¹² This Laboratory had long been familiar with olefins V and VI, the well-known diisobutylenes.¹³

Repeated dehydrations of the alcohols, I and II, with 15% sulfuric acid and careful study of the resulting olefin mixtures indicate that *t*-amyl alcohol (I) gives 1,1-methylethylethylene (III) and trimethylethylene (IV) in the ratio 1:7 while dimethylneopentylcarbinol (II) gives 1,1-methylneopentylethylene (V) and 1,1-dimethyl-2-*t*-butylethylene (VI) in the ratio 4.5:1. Thus, a methylene group attached to methyl loses a proton about 30 times as readily as a methylene attached to *t*-butyl. In other words, an ethyl group loses a proton much more readily than does a neopentyl group. This greater activity of the ethyl group has been observed repeatedly in this Laboratory.^{3b} The sluggishness of the neopentyl group in this respect is well illustrated by the dehydration of diethylneopentylcarbinol, which takes place 90% from the ethyl group to yield 2,2-dimethyl-4-ethyl-4-hexene.^{3c} The dehydration of 3,5,5-trimethyl-3-heptanol indicates an even more sluggish behavior for the neohexyl group (*t*-amylcarbinyl).⁴

A good example of the difficulty of drawing generalizations regarding the dehydration of alcohols is given by a comparison of dimethylneopentylcarbinol and methylneopentylcarbinol.^{3a} As stated above, the former gives dehydration from the two methyl groups and the one neopentyl group in the ratio of 4.5:1. It might thus be argued that *one* methyl group would give up a proton about twice as readily as one neopentyl group. This is contrary to the fact^{3a} that methylneopentylcarbinol undergoes dehydration from the one methyl group and the one neopentyl group

(12) Rose, *Ind. Eng. Chem.*, **33**, 594 (1941); Fenske, Tongberg, Quiggle and Cryder, *ibid.*, **28**, 644-5 (1936).

(13) Whitmore and co-workers, *THIS JOURNAL*, **53**, 3156 (1931), **54**, 3706, 3710 (1932).

in the ratio of about 1:4:5. The fallacy here lies in comparing a tertiary alcohol with a secondary alcohol, the one being dehydrated with excess 15% sulfuric acid at about 100° and the other with a small amount of 100% sulfuric acid at perhaps 135°.

In connection with the present work it should be noted that the ratio 4.5:1 for the olefins V and VI checks with the equilibrium present in the diisobutylenes.¹³ The equilibrium between III and IV is being studied. It has been found that 15% sulfuric acid does not isomerize either III or IV.

The dehydration of alcohols and the study of equilibrium relations of the resulting olefin mixtures is being continued.

We thank Dr. W. A. Mosher of the Hercules Powder Co. for help in the preparation of this paper.

Experimental

Materials.—Commercial *t*-amyl alcohol, Sharples, was fractionated through a 15-plate column to give material of b. p. 101° (742 mm.), n_D^{20} 1.4049. Dimethylneopentylcarbinol was prepared by the action of methylmagnesium bromide on methyl neopentyl ketone, n_D^{20} 1.4038. The product, after decomposition in the usual manner, was fractionated through a 10-plate column to give material of b. p. 70.5° (43 mm.), n_D^{20} 1.4286.

Dehydration of *t*-Amyl Alcohol.—*t*-Amyl alcohol, 319 g., was dissolved in 395 ml. of 15% sulfuric acid and refluxed under a column of 60 theoretical plates while the olefins formed distilled out. The yield of olefin was 97.8% allowing for 16.7 g. of recovered alcohol. The olefin mixture, 227 g., was dried over potassium carbonate and fractionated through a 60-plate column with 0.5 g. of potassium carbonate in the still pot to prevent isomerization. Ice-water was circulated through the condenser and receiver system while dry-ice traps protected all outlets. The loss on distillation was 2%.

Two olefins were found on fractionation: 2-methyl-1-butene, 27 g., 33-35° (740 mm.), 1.3788, 11.9%; and 2-methyl-2-butene, 195 g., 39.5° (740 mm.), 1.3870, 85.9%. The structures were confirmed by ozonolysis.

Dehydration of Dimethylneopentylcarbinol.—The alcohol, 150 g., was dehydrated by refluxing with an equal weight of 15% sulfuric acid under a 10-plate column and distilling off the olefins as formed. Taking 33 g. of recovered carbinol into account, the yield of olefin was 96%. Distillation of the olefin through a 60-plate column gave 2,4,4-trimethyl-1-pentene, 77.2 g., 78%, 103° (742 mm.), 1.4086-8; and 2,4,4-trimethyl-2-pentene, 17.7 g., 17%, 106.5 (740 mm.), 1.4152-5. The identity of these olefins has been repeatedly checked by ozonolysis in this Laboratory.

Summary

1. The difficulty in drawing generalizations on the dehydration of alcohols is emphasized.

2. The relation of acidity of the dehydrating catalyst to the equilibrium in the resulting olefin mixture is considered.

3. Two closely related tertiary alcohols have been dehydrated under mild but definitely acidic

conditions. In *t*-amyl alcohol and dimethylneopentylcarbinol, under similar conditions, the ethyl group yields a proton in dehydration about thirty times as readily as does the neopentyl group.

STATE COLLEGE, PENNSYLVANIA RECEIVED JULY 23, 1942

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

Factors Determining the Course and Mechanism of Grignard Reactions. V. The Effect of Metallic Halides on the Reaction of Grignard Reagents with Benzalacetophenone and with Benzophenone

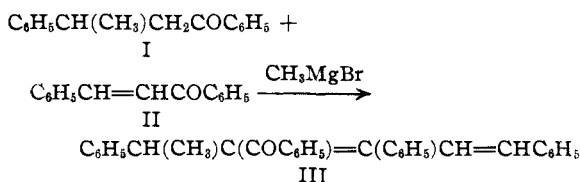
BY M. S. KHARASCH AND D. C. SAYLES

It has been shown that small amounts of some metallic halides exert a profound effect on the reactions of Grignard reagents with many compounds.¹ The present paper describes the results obtained when methyl- and ethylmagnesium bromides react with benzalacetophenone (chalcone) and benzophenone in the presence of ferric chloride, cuprous chloride, manganous chloride or cobaltous chloride.

The structures of the products formed by the addition of Grignard reagents to some α,β -unsaturated aldehydes and ketones have been determined by Kohler and his co-workers.² They report that, with chalcone, phenyl- and ethylmagnesium bromides give, respectively, 94 and 99% of the 1,4-addition product.^{2c} The reaction between ethylmagnesium bromide and chalcone has not been investigated, but Kohler reports that ethylmagnesium bromide reacts with benzalacetophenone to give 70% of the 1,4-addition product. Smith and Hanson,³ on the other hand, record only the 1,2-addition product of benzalacetophenone and ethylmagnesium iodide.

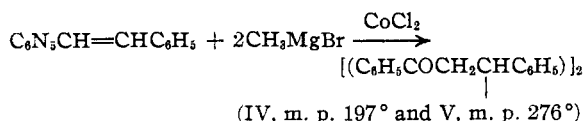
It is desirable to elucidate the conditions under which an optimum yield of β -phenylbutyropenone (the 1,4-addition product) is obtained by condensation of ethylmagnesium bromide with chalcone. Kohler and Peterson^{2d} state explicitly that an excess of Grignard reagent is necessary to prevent the formation of "secondary" products, but they do not mention the exact

proportion of the reagents employed. In the experiments here reported in detail, a 40% excess of Grignard reagents was used, and (Table I) large quantities of 1,3,5-triphenyl-4-benzoylhexadiene-1,3 (m. p. 176°) (III) were produced, probably according to the equation



The structure of III was confirmed by independent syntheses from I and II where pyridine, trimethylamine or sodium ethylate was used as condensing agent. Other experiments showed that in order to avoid completely the formation of III, a very large excess of the Grignard reagent (200%) was required.

Although (Table I) no one of the metallic halides (2 to 5 mole per cent.) has any effect on the ratio of the 1,2 and 1,4 addition of ethylmagnesium bromide to chalcone, yet they profoundly influence the nature of the products formed in the reaction. This effect is most marked with cobaltous chloride. In the presence of this metallic halide the Grignard reagent does not add to the chalcone, but acts as a reducing agent leading to the formation of two products which melt at 197 and 276°, respectively.



These two substances (IV and V) were shown by analyses, molecular weight determinations and the melting points of mixtures to be identical

(1) (a) Kharasch, Kleiger, Martin and Mayo, *THIS JOURNAL*, **63**, 2305 (1941); (b) Kharasch and Lambert, *ibid.*, **63**, 2315 (1941); (c) Kharasch and Tawney, *ibid.*, **63**, 2308 (1941); (d) Kharasch and Fields, *ibid.*, **63**, 2316 (1941).

(2) (a) Kohler, *Am. Chem. J.*, **31**, 642 (1904); (b) *ibid.*, **37**, 369 (1907); (c) *ibid.*, **38**, 511 (1907); (d) Kohler and Peterson, *THIS JOURNAL*, **55**, 1073 (1933).

(3) Smith and Hanson, *ibid.*, **57**, 1376 (1935).