44.9; found, 45.0, phenylurethan m. p. 58–59°, *α-naphthylurethan* m. p. 76.5–77.5°.

Anal. Calcd. for $C_{20}H_{27}O_2N$: N, 4.47. Found: N, 4.52.

Reaction of Trimethylacetyl Chloride with Ethylmagnesium Bromide.—The reaction of 2.54 moles of acid chloride with 6.1 moles of the Grignard reagent gave 26.1% of diethyl-*t*-butylcarbinol,[3] b. p. 59.2° (35 mm.), $n^{20}\text{D}$ 1.4230 and 60% of ethyl-*t*-butylcarbinol,[3] b. p. 73° (24 mm.), $n^{20}\text{D}$ 1.4424–6. No neopentyl alcohol was found.

Reaction of *t*-Butylacetyl Chloride with Isopropylmagnesium Bromide.—The reaction of 1 mole of acid chloride with 4 moles of Grignard reagent gave 32.7% of isopropyl neopentyl ketone, b. p. 61° (26 mm.), $n^{20}\text{D}$ 1.4120–9, 2,4-dinitrophenylhydrazone m. p. 128–129°, semicarbazone m. p. and mixed m. p. 168–9° and 26.7% of isopropylneopentylcarbinol, b. p. 76.7° (32 mm.), $n^{20}\text{D}$ 1.4283–1.4302, d_{20} 0.825, mol. ref. calcd., 45.0; found, 45.2; *α-naphthylurethan* m. p. 88–90°.

Anal. Calcd. for $C_{20}H_{27}O_2N$: N, 4.47. Found: N, 4.49.

Attempted Reaction of the Methyl Ester of Methyl-*t*-butylneopentylacetic Acid with Methylmagnesium Bromide.—The ester was made from methanol and the acid chloride[6] in 88% yield; b. p. 97–8° (13 mm.), $n^{20}\text{D}$ 1.4450–2. The treatment of the ester with the Grignard reagent was carried out in diethyl ether at 34° and in di-*n*-butyl ether at 142°. The lower temperature gave almost quantitative recovery of unreacted ester. At 142° there were obtained a 70.3% recovery of unchanged ester and a 13% yield of methyl-*t*-butylneopentylacetic acid formed by the splitting of the ester.

Reaction of *t*-Butylacetyl Chloride with Isobutylmagnesium Bromide.—The reaction of 0.5 mole of the acid chloride with 1.45 moles of the Grignard reagent gave isobutyl neopentyl ketone, 15.7 g., 0.102 mole, 20.1%, b. p. 65.5° (15 mm.), $n^{20}\text{D}$ 1.4127–91; isobutylneopentylcarbinol, 38.6 g., 0.244 mole, 48.9%, b. p. 75° (15 mm.), $n^{20}\text{D}$ 1.4237–79, α-naphthylurethan m. p. and mixed m. p. 100–100.5°; diisobutylneopentylcarbinol, 14.7 g., 0.069 mole, 13.8%, b. p. 68.5° (3 mm.), $n^{20}\text{D}$ 1.4395–1.4410, d_{20} 0.8317, mol. ref. calcd., 67.96; found, 68.0.

Reaction of Methyl *t*-Butylacetate with Isobutylmagnesium Bromide.—To isobutylmagnesium bromide prepared from 1.7 gram atoms of magnesium and 1.83 moles of isobutyl bromide was added 65 g., 0.5 mole, of the ester. Fractionation gave isobutyl neopentyl ketone, 32.1 g., 0.16 mole, 32%, b. p. 66.4° (15 mm.), $n^{20}\text{D}$ 1.4120–98; isobutylneopentylcarbinol, 15.2 g., 0.046 mole, 9.2%, b. p. 43–44° (3 mm.), $n^{20}\text{D}$ 1.4232–82, *α-naphthylurethan* m. p. and mixed m. p. 99–101°; diisobutylneopentylcarbinol, 27.0 g., 0.17 mole, 34.2%, b. p. 69.5° (2 mm.), $n^{20}\text{D}$ 1.4375–1.4411, d_{20} 0.8313, mol. ref. calcd., 67.96; found, 68.0.

Anal. Calcd. for $C_{21}H_{29}O_2N$: N, 4.26. Found: N, 4.25.

Summary

1. A comparison of the reactions of trimethylacetyl chloride and methyl trimethylacetate and of *t*-butylacetyl chloride and methyl *t*-butylacetate with ethyl, *n*-propyl, isopropyl, *n*-butyl and isobutyl Grignard reagents has been made. The esters were found to give distinctly less reduction products than the corresponding acid chlorides.

2. The fact that no primary alcohol was found in the reaction of the esters with Grignard reagents indicates that aldehydes are not intermediates in this reaction.

3. The methyl ester of methyl-*t*-butylneopentylacetic acid did not react with methyl Grignard reagent at 34° or at 142°.

4. Isopropylneopentylcarbinol and isopropyl-*t*-amylcarbinol have been prepared.

STATE COLLEGE, PENNSYLVANIA

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

Grignard Reactions. XVIII.[1] Reactions of Benzylmagnesium Chloride

BY FRANK C. WHITMORE AND T. K. SLOAT[2]

The type of rearrangement given by the benzyl Grignard reagent is well known. The first case reported was the reaction of formaldehyde with benzylmagnesium chloride to give *o*-tolylcarbinol instead of the expected benzylcarbinol.[3] The action of a variety of substances with benzylmagnesium chloride has been reported. Not all reactants give rearranged products with this Grignard reagent. The products of rearrangement are usually *o*-tolyl derivatives. In some cases the *p*-tolyl derivative has been reported.[4] Excellent investigations and reviews of the reactions of benzylmagnesium chloride have been made by Gilman and Kirby[5] and by Austin and Johnson.[6] More recently Coleman and Forrester[7] have investigated the action of benzylmagnesium chloride with monochloramine. No rearranged products were found in this case.

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[1] XVII, Whitmore and Forster, THIS JOURNAL, **64**, 2966 (1942).

[2] Present address: Research Division, Westinghouse Electric and Manufacturing Co., East Pittsburgh, Pa.

[3] Tiffeneau and Delange, *Compt. rend.*, **137**, 573 (1903).

[4] Gilman and Kirby, THIS JOURNAL, **51**, 3475 (1929).

[5] Gilman and Kirby, *ibid.*, **54**, 345 (1932).

[6] Austin and Johnson, *ibid.*, **54**, 647 (1932).

[7] Coleman and Forrester, *ibid.*, **58**, 27 (1936).

The present study was undertaken with the hope that repetition of some of the reactions of benzylmagnesium chloride, on a larger scale and with the fractionating equipment now available, might give some rearranged products with reactants which previously had shown no rearrangement. *The results of previous investigators were confirmed without exception.* Our experiments with benzylmagnesium chloride gave only the normal products with acetonitrile, acetamide, acetaldehyde, carbon dioxide, oxygen, ethyl acetate, benzyl chloride and water. The reaction of the benzyl Grignard reagent with acetyl chloride gave the rearranged product, methyl *o*-tolyl ketone. Temperature was shown to have little effect on the yield of ketone, this being 18% at 0° and 16.5% at 25°.

In our experiments the benzylmagnesium chloride was added to an excess of the reactant unless otherwise specified. The order of addition of the Grignard reagent had a decided effect on the yield of rearranged product. In the reaction of acetyl chloride with benzylmagnesium chloride, the yield of methyl *o*-tolyl ketone was 18% when the Grignard reagent was added to the acid chloride while addition of the acetyl chloride to the Grignard reagent gave only 3% of this ketone. This is in agreement with the work of Schmidlin and Garcia-Banùs[8] who reported similar results with aromatic aldehydes.

Several mechanisms have been proposed for the *o*-tolyl rearrangement.[5,6,9] In an attempt to investigate further the mechanism of this rearrangement, acetyl chloride, toluene and anhydrous magnesium chloride were mixed in diethyl ether and refluxed for several hours. No reaction took place. This type of process is similar to that investigated by Tzukervanik and Sidorova.[10] Furthermore, dry toluene was added to ethylmagnesium chloride and then a large excess of acetyl chloride was added. As in the first of these test reactions, no methyl benzyl ketone or methyl *o*-tolyl ketone could be found.

We thank R. S. George of this Laboratory for his help.

Experimental

The benzylmagnesium chloride used in this work was prepared in the usual manner.[11] Titration showed the yields to be over 90%. All fractionations were done with the usual type of column[12] having 12–18 theoretical plates. The reactions of benzylmagnesium chloride with the compounds investigated were all run according to conventional procedures. In many cases only the fractions in the boiling point ranges of the possible rearranged products were thoroughly investigated. The reaction of acetamide with the benzyl Grignard reagent illustrates the procedure used.

To 59 g., 1 mole, of acetamide was added 3 moles of benzylmagnesium chloride. The reaction products were worked up in the usual way. Fractionation gave 55.3 g. or 41.3% of ketone fraction; b. p. 122–125° (50 mm.). The ketone was characterized by its 2,4-dinitrophenylhydrazone; m. p. 152–153°; a mixed m. p. with derivative of authentic methyl benzyl ketone gave no depression.

The experimental part of the study can best be summarized in table form.

TABLE I

Compound	% Normal primary[a] addition	% Primary[a] rearranged product	Order of addition.[b] Direct—reagent added to soln. of benzylmagnesium chloride
Acetamide	41.3	None	Reverse, excess Grignard reagent
Acetaldehyde	65.6	None	Reverse, excess acetaldehyde
Acetonitrile	15.8[c]	None	Reverse
Carbon dioxide	62.7	None	Direct
Oxygen	69.4	None	Direct
Water	95.3	None	Direct
Benzyl chloride	67.6	None	Reverse
Ethyl acetate	2.7[d]	None	Reverse
Acetyl chloride	Trace	18	Reverse, excess acid chloride
	Trace	16.5	Reverse, ditto[e]
	...	3	Direct, excess acid chloride

[a] These figures represent only the products given by the first step of the Grignard reaction. The high boiling tertiary alcohol fractions were not investigated. [b] Unless specified the Grignard reagent and the reactant were present in equal molecular proportions, and the reaction was run at 0°. [c] About 70% of toluene was also obtained. [d] Yield of high boiling alcohol was about 90%. [e] The reaction temperature was 25°.

Acetyl Chloride, Toluene and Magnesium Chloride.—A mixture of 0.75 mole of toluene and 0.75 mole of magnesium chloride in anhydrous ether was stirred for sixteen hours. To this was added 1.5 moles of acetyl chloride, and the mixture was then refluxed for four days. Fractionation gave no methyl *o*-tolyl ketone or methyl benzyl ketone.

Ethylmagnesium Chloride, Toluene and Acetyl Chloride.—To 1 mole of ethylmagnesium chloride in ether and 1 mole of toluene was added 3 moles of acetyl chloride, and the mixture was refluxed for two days. Fractionation gave no methyl *o*-tolyl ketone or methyl benzyl ketone.

Summary

1. Acetaldehyde, acetonitrile, acetamide and water have been shown to give only normal products with benzylmagnesium chloride.

2. Repetition of the reactions of carbon di-

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[8] Schmidlin and Garcia-Banùs, *Ber.*, **45**, 3193 (1912).

[9] Johnson, THIS JOURNAL, **55**, 3029 (1933).

[10] Tzukervanik and Sidorova, *J. Gen. Chem. Russ.*, **8**, 1512 (1938); *ibid.*, **8**, 1899 (1938).

[11] Greenwood, Whitmore and Crooks, THIS JOURNAL, **60**, 2028 (1938).

[12] Whitmore and Lux, *ibid.*, **54**, 3451 (1932).

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.

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

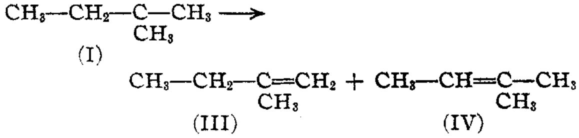
The Dehydration of Alcohols. XIX.[1-4] *t*-Amyl Alcohol and the Related Dimethylneopentylcarbinol

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 Glasebrook[8] 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 Glasebrook[8] 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.



$$\underset{\text{(I)}}{CH_3{-}CH_2{-}\overset{OH}{\underset{CH_3}{C}}{-}CH_3} \longrightarrow \underset{\text{(III)}}{CH_3{-}CH_2{-}\underset{CH_3}{C}{=}CH_2} + \underset{\text{(IV)}}{CH_3{-}CH{=}\underset{CH_3}{C}{-}CH_3}$$

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[1] Whitmore and Karnatz, Diethylcarbincarbinol (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).

[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.