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

The Yields of Some Aliphatic Tertiary Grignard Reagents and the Limits of their Usefulness as Synthetic Reagents

BY FRANK C. WHITMORE AND D. E. BADERTSCHER[1]

Researches on rearrangements being conducted in this Laboratory required a variety of compounds containing the grouping $R_3CC(OH)R'_2$.[2] in which R represents various alkyl groups and R′ represents alkyl or hydrogen. The preparation of these substances by means of the Grignard reaction presented two uncertainties, (1) the decreased yield of Grignard reagents of higher molecular weight especially from tertiary halides which lose halogen acid readily and (2) the limited yields of the desired products obtainable from highly branched Grignard reagents.[3] To obtain information on these points was the purpose of this research.

The literature contains little information on tertiary aliphatic Grignard reagents higher than tertiary amyl. Preliminary studies showed that tertiary chlorides give higher yields of Grignard reagents than the corresponding bromides and iodides. In the present work the following chlorides have been investigated: tertiary butyl, tertiary amyl, dimethyl-*n*-butylcarbinyl, dimethyl-*n*-amylcarbinyl, methyldiethylcarbinyl, methylethyl-*n*-propylcarbinyl, methylethyl-*n*-butylcarbinyl, and triethylcarbinyl. Yields of Grignard reagents from these chlorides varied from 60% for dimethyl-*n*-amyl- and triethylcarbinyl chlorides to 83% for tertiary butyl chloride. All yields were determined by titration of aliquot samples of the clear Grignard solution according to Gilman.[4]

More magnesium chloride was formed during the preparation of the Grignard reagent from the higher tertiary halides. The large amount of olefin which was usually isolated from the reaction mixtures in such cases indicated the withdrawal of hydrogen chloride from the chloride by the magnesium.

The results indicate that the higher tertiary Grignard reagents are not suitable for syntheses which involve the addition of the Grignard reagent to the carbonyl group of a ketone or ester. They can be used to some extent, however, when an active halogen is present, as in the case of ethyl chlorocarbonate and (to a certain extent) acetyl chloride. The reaction with carbon dioxide and with formaldehyde in most cases proceeds normally, although the yields of the desired acid or primary alcohol are not as high as in the case of the lower chlorides.

The reaction between tertiary-butylmagnesium chloride and ethyl

---

[1] Submitted in partial fulfilment of the requirements for the Ph.D. degree.

[2] (a) Whitmore, THIS JOURNAL, **54**, 3274 (1932); (b) Whitmore and Woodburn, *ibid.*, **55**, 361 (1933); (c) Whitmore and Williams, *ibid.*, **55**, 406 (1933).

[3] Conant and Blatt, *ibid.*, **51**, 1227 (1929).

[4] Gilman, *ibid.*, **45**, 150 (1923).

carbonate was investigated. The reaction proceeds only to the first step, *i. e.*, to the ethyl ester of trimethylacetic acid. This is to be expected since Conant and Blatt[3] have reported that there is little or no reaction between ethyl trimethylacetate and tertiary-butylmagnesium chloride. Tertiary-amylmagnesium chloride did not react at all with ethyl carbonate in ethyl ether. With higher boiling solvents (benzene and toluene) a very small amount of the ethyl ester of dimethylethylacetic acid was isolated.

The reaction with ethyl chlorocarbonate, however, is more general. Both tertiary-butyl- and tertiary-amylmagnesium chlorides yield with this reagent the ethyl ester of the trisubstituted acetic acid. This reagent also reacts with the higher tertiary Grignard reagents. Dimethyl-*n*-butylcarbinylmagnesium chloride yielded the ethyl ester of dimethyl-*n*-butylacetic acid.

The reaction between acetyl chloride and the tertiary Grignard reagents was investigated. In each case the ether solution of Grignard reagent was added to an excess of acetyl chloride in ether. From tertiary-butylmagnesium chloride and acetyl chloride was obtained pinacolone in yields large enough to compete with the older process for making this ketone. Tertiary-amylmagnesium chloride and acetyl chloride yielded methyl tertiary-amyl ketone but in lower yield. With methyldiethylcarbinylmagnesium chloride and dimethyl-*n*-butylcarbinylmagnesium chloride the yields of the corresponding ketones were still lower.

Four of the higher tertiary Grignard reagents were treated with formaldehyde to give homologs of neopentyl alcohol. The study of these alcohols, especially their dehydration with rearrangement, is being continued.

Experimental

Description of Distillation Apparatus.—The fractionating columns used in the various distillations will be referred to by number:[5] Column I, total reflux type, asbestos insulated, packed with 5 × 5 mm. glass rings, 68 × 1.8 cm.; Column II, same but 35 × 2.1 cm.; Column IV, total reflux type, electrically heated jacket, indented, 63 × 1.1 cm. The dimensions, in Columns I and II, are those of the packed sections, and in Column IV, of the indented section.

Preparation of the Tertiary Halides.—The tertiary carbinols (with the exception of the butyl and amyl alcohols[6]) were prepared as indicated in Table I.

The chlorides of these carbinols were prepared by saturating the carbinols with dry hydrogen chloride at 10–15°. The upper (halide) layer was washed once with a cold saturated aqueous solution of potassium carbonate, and dried over anhydrous potassium carbonate for at least twenty-four hours. The halide was then distilled under reduced pressure in the presence of 2 g. of anhydrous potassium carbonate to combine with any liberated acid. The tertiary carbinols and halides were fractionated through Column II.

Preparation of the Tertiary Grignard Reagents.—The main difficulty encountered in preparing the higher tertiary Grignard reagents was that of inducing the reaction to start. The usual expedients were followed.

---

(5) *Cf.* Whitmore and Lux, THIS JOURNAL, **54**, 3451 (1932).

(6) These were supplied by the Hydrocarbon Products Company of New York and the Sharples Solvents Corp. of Philadelphia, respectively.

TABLE I

PREPARATION AND PROPERTIES OF THE TERTIARY CARBINOLS AND CHLORIDES

	Tertiary carbinol	Preparation Carbonyl compd.	 Grignard	Yield,[a] %
1	$CH_3(C_2H_5)_2COH$	$CH_3COC_2H_5$	C_2H_5MgBr	
2	$CH_3(C_2H_5)(n\text{-}C_3H_7)COH$	$CH_3COC_2H_5$	C_3H_7MgBr	65.6 82.3[g]
3	$CH_3(C_2H_5)(n\text{-}C_4H_9)COH$	$CH_3COC_2H_5$	C_4H_9MgBr	70.6
4	$(CH_3)_2(n\text{-}C_4H_9)COH$	CH_3COCH_3	C_4H_9MgBr	64.6 70.5[g]
5	$(CH_3)_2(n\text{-}C_5H_{11})COH$	CH_3COCH_3	$C_5H_{11}MgBr$	63
6	$(C_2H_5)_3COH$	$(C_2H_5)_2CO_3$	C_2H_5MgBr	74

	B. p. range	n_D^{20}	Tertiary chloride B. p. range, °C.	 Yield,[e] %	 n_D^{20}
1	[d]		68–69/160[d]	59[f]	1.4208
2	56/20 to 52/16	1.4231	62–63/52	90	1.4250
3	64–65/16[b]	1.4283	64–65/27[b]	92	1.4314
4	65/35 to 63/29[b]	1.4179[b]	69–72/90[b]	75	1.4202[b]
5	65–66/15[c]	1.4235	49.5–51/15[c]	81	1.4250
6	72–73/52	1.4294	64–65/52	88	1.4329

[a] These are yields of products of the boiling range indicated. They are calculated on the halide used. [b] *Cf.* Ref. 2(b). [c] *Cf.* Ref. 2(c). [d] Favorski and Zalessky-Kibardine give for the carbinol b. p. 121° (755 mm.) and for the chloride b. p. 111° (761 mm.) and 85° (280 mm.), *Bull. soc. chim.*, [4] **37,** 1230 (1925). [e] Yields of products of indicated boiling range, calculated on the carbinol used. [f] Calculated on the ethyl bromide used in making the carbinol. [g] Calculated on the Grignard reagent.

The procedure in preparing the Grignard reagents is, with one or two minor exceptions, that found bv A. R. Lux of this Laboratory to give good yields of tertiary-butylmagnesium chloride.[7] As has been noted by Gilman and his co-workers,[8] it is essential that the halide–ether solution be added to the reaction mixture slowly. Any considerable deviation from the procedure described, such as varying the amount of ether used, etc., results in an appreciably lower yield of Grignard reagent. Vigorous and thorough agitation of the reaction mixture is essential. It is not necessary to use an excess of magnesium.

A typical procedure as used is given herewith. The procedure described is for a four-mole run, the same proportionate amounts of materials being used for smaller or larger runs.

In a 3-liter 3-necked round-bottomed flask fitted with an efficient stirrer, reflux condenser and dropping funnel are placed first a few small crystals of iodine and then 98 g. (4 moles) of fresh magnesium turnings. The bottom of the flask is heated with a small flame until the iodine commences to vaporize and is then allowed to cool while the halide is being weighed out. Thirty cc. of a mixture of four moles of the tertiary halide and 500 cc. of dry diethyl ether is added directly to the dry magnesium. After reaction has started and progressed for a few minutes, 200 cc. of dry ether is added directly to the reaction mixture. Four hundred and seventy-five cc. of the above halide–ether solution is placed in the dropping funnel and added with stirring at a rate *not faster* than one drop every second. It is advisable to add the halide–ether even more slowly

---

(7) For example, a nine-mole preparation of trimethylacetic acid resulted in a 75% yield of pure acid, based on the tertiary-butyl chloride used.

(8) Gilman and co-workers, THIS JOURNAL, **50,** 425 (1928).

in the case of the higher tertiary halides. The remainder of the halide–ether solution is diluted with 300 cc. of dry ether and added at the same rate with stirring after the first portion is added. The mixture is allowed to reflux during the halide–ether addition, no external cooling being applied. It is unnecessary to heat the mixture after the halide–ether solution has been added. Stirring is continued for an hour. Before titrating for yield the flask containing the Grignard reagent solution is stoppered and left overnight to allow suspended material to settle completely.

In several cases (noted in Table II) reaction did not start upon addition of the first 30 or 40 cc. of halide–ether solution. When this was the case, the addition of a few drops of a more reactive halide, such as ethyl- or *n*-butyl bromide, usually started the reaction.

TABLE II

PREPARATION AND YIELDS OF GRIGNARD REAGENTS OF TERTIARY CHLORIDES

Halide	Moles	Halide–ether addition, hrs.	Yield	Notes
$(CH_3)_3CCl$	3	Note *d*	80	*a*
$(CH_3)_2(C_2H_5)CCl$	3	Note *d*	73.6	*b*
$(CH_3)_2(n\text{-}C_4H_9)CCl$	1.5	7.0	74.4	*a*
	1.5	9.5	79.0	*a*
$(CH_3)_2(n\text{-}C_5H_{11})CCl$	1.5	14	59.9	*g*
$CH_3(C_2H_5)_2CCl$	1.5	Note *d*	70.4[e]	*b*
$CH_3(C_2H_5)(n\text{-}C_3H_7)CCl$	1.5	7.7	67.4	*b*
	3.3	24	75.8	*b*
	4.5	52	77.7	*c*
	5.0	90	75.8	*a*
$CH_3(C_2H_5)(n\text{-}C_4H_9)CCl$	4	77	70.0	*c*
$(C_2H_5)_3CCl$	1.4	6.0	58.3	*f*

[a] Reactions started almost immediately. [b] Reactions started within fifteen minutes. [c] Necessary to add 1 cc. of *n*-butyl bromide and additional iodine to start the reaction. [d] "Not over 1 drop per sec." [e] In this Laboratory, H. S. Rothrock and K. C. Laughlin have obtained yields of the Grignard reagent of 65 and 72%, respectively. Faworski and Zalessky-Kibardine obtained a 34% yield. [f] Necessary to add 1 cc. of ethyl bromide to start reaction. [g] Necessary to add a few drops of methyl iodide and more iodine to start the reaction.

In preparing those Grignard reagents in which the olefin which is formed is not a gas it is advisable to connect the outlet of the apparatus to a sulfuric acid trap to exclude atmospheric moisture.

Ethyl Carbonate and Tertiary-butylmagnesium Chloride.—To 3.8 moles of tertiary-butylmagnesium chloride in 1500 cc. of ether was added, with stirring, 450 g. (3.8 moles) of ethyl carbonate (b. p. 125° (734 mm.)). The reaction was mild. The mixture was refluxed on the water-bath during the addition. As reaction progressed a pasty solid separated and the mixture became quite viscous, making stirring difficult. Stirring was continued for two hours after the addition was complete. The mixture was decomposed on ice and enough dilute sulfuric acid was added to dissolve the precipitate. The layers were separated and the aqueous layer extracted three times with 100-cc. of ether. The ether solutions were dried overnight with 75 g. of anhydrous potassium carbonate.

The ether was distilled off through a small packed partial condensation column and the residue was distilled through Column I with a high reflux ratio to give the following fractions with the weights and boiling points (740 mm.) indicated: (1) 16.5, 77–80°; (2) 10.0, 80–83°; (3) 75, 83–117°; (4) 280.0, 117–118.5°, n^{20}_D 1.3888; (5) 125.0, 118.5–126°.

Fraction (4) represented a 56% yield of ethyl trimethylacetate based on the Grignard reagent used. Its saponification products were identified by means of solid derivatives.

Ethyl Carbonate Tertiary-amylmagnesium Chloride.—A reaction carried out in the same way as with the tertiary-butylmagnesium chloride yielded only unchanged ethyl carbonate.

In another experiment, after the Grignard reagent had been prepared, benzene was added and the ether was distilled off through a small column. The calculated amount of ethyl carbonate was added. The reaction mixture was maintained at 60–70° for several hours. Upon working up in the usual way only a trace of the ethyl ester of dimethylethylacetic acid was obtained. Another reaction carried out in the same way except that toluene was used in place of benzene also gave only a trace of the ester. A total of 20 g. of the ester was obtained in the last two reactions from a total of 1.66 moles of tertiary-amylmagnesium chloride. The ester boiled at 140–141°. It was identified by saponification.

Ethyl Chlorocarbonate and Tertiary-butylmagnesium Chloride.—To 2.2 moles of tertiary-butylmagnesium chloride in 900 cc. of ether solution was added 244.2 g. (2.25 moles) of ethyl chlorocarbonate, b. p. 91–92.5° (741 mm.), in 500 cc. of ether at a rate of 2 to 3 drops per sec., with stirring. The mixture was allowed to reflux from the heat of reaction. A gray precipitate separated rapidly, soon making stirring difficult. At the end of the reaction the mixture was almost solid. This did not break up when 200 cc of ether was added and the mixture stirred vigorously. The mixture stood overnight and was then decomposed on ice. Most of the solid dissolved. Ammonium chloride was added to dissolve the small amount of gelatinous precipitate. The mixture was worked up in the usual way except that the crude product was refluxed and stirred with sodium bicarbonate solution to remove unreacted chlorocarbonate. The product was then dried over 15 g. of anhydrous sodium sulfate and fractionated at 737 mm. through Column I to give the following fractions: (1) 9.5 g., 112–115°; (2) 9.0 g., 115–116°; (3) 18.0 g. 116–117°; (4) 135.0 g., 117°, n^{20}_{D} 1.3890; (5) 15.5 g. of residue. Fractions 2–4 were identified as ethyl trimethylacetate, yield 56% based on the Grignard reagent. This yield could undoubtedly be increased by using a larger volume of ether so as to permit more efficient stirring.

Ethyl Chlorocarbonate and Tertiary-amylmagnesium Chloride.—To 1.97 moles of tertiary-amylmagnesium chloride in a total volume of 1020 cc. was added with stirring and refluxing (water-bath), at a rate of 1 to 2 drops per second, 212 grams (1.97 moles) of ethyl chlorocarbonate. After the addition, the reaction mixture was refluxed and stirred for five hours. A gray precipitate gradually separated. The water-bath was removed and the mixture stirred overnight. In the morning the mixture was almost solid. It was refluxed with stirring for four hours longer and then treated as usual. The product was fractionated at 735 mm. through Column I, giving (1) 51.2 g., 128–140°; (2) 116.9 g., 140–141°; and a residue of 36.9 g. Fraction 2 was identified as ethyl dimethylethylacetate, yield 46% based on the Grignard reagent.

Ethyl Chlorocarbonate and Dimethyl-*n*-butylcarbinylmagnesium Chloride.—Six hundred cc. of a filtered ether solution of 0.99 mole of dimethyl-*n*-butylcarbinylmagnesium chloride was added during two hours to 116 g. (1.07 mol) of ethyl chlorocarbonate in 200 cc. of dry ether. The reaction was vigorous and accompanied by the formation of a white precipitate. The mixture was allowed to reflux. The mixture stood overnight and was then worked up in the usual way. The product was fractionated through Column II at 735 mm. for the first three fractions and at 16 mm. for the last three to give: (1) 17.2 g., 86–90°; (2) 27.9 g., 90–94°; (3) 3.9 g., 94–106°; (4) 16.6 g., 106° (735 mm.) to 66.5° (16 mm.); (5) 47.1 g., 66.5–70.0° (16 mm.), n^{20}_{D} 1.4148; (6) 7.7 g., 70–105.5° (mainly 103–105.5° (16 mm.)), n^{20}_{D} 1.4225. Fraction 5 was identified as ethyl dimethyl-*n*-butylacetate. This was converted to dimethyl-*n*-butylacetamide, m. p. and mixed m. p. 92.8-93.8°. Fractions 1 and 2 decolorized bromine solution.

Acetyl Chloride and Tertiary-butylmagnesium Chloride.[9]—Nine hundred cc. of a filtered solution of 2.26 moles of tertiary-butylmagnesium chloride was added to 236 g. (3 moles) of redistilled acetyl chloride in 600 cc. of dry ether during six hours with stirring. The reaction was vigorous. A white to buff precipitate formed. The mixture was allowed to reflux from its own heat of reaction. A stream of gas which decolorized bromine was evolved slowly. After standing twelve hours the mixture was worked up as usual. The product was fractionated at 740 mm. through Column I to give: (1) 13.6 g., 62–94°; (2) 11.5 g., 94-101°; (3) 8.2 g., 101–103°; (4) 92.3 g., 103–106°; (5) 23.0 g., 106–132°; (6) 11.4 g., 132–133° dec.; (7) 20 g. of black tarry residue. Fraction 4 was identified as pinacolone by m. p. and mixed m. p. determinations on its semicarbazone and 2,4-dinitrophenylhydrazone.[10] These points were 154–154.5° and 125.5–126°, respectively. The yield of pinacolone was 40.7% based on the Grignard reagent. Other runs have given somewhat higher yields. K. C. Laughlin of this Laboratory has obtained a 54% yield by this method.

Acetyl Chloride and Tertiary-amylmagnesium Chloride.—Two reactions were carried out, one in which the temperature of the reaction mixture was maintained at or below 0°, and one at the temperature of boiling ether.

Reaction at 0°.—To 172.7 g. (2.2 moles) of acetyl chloride dissolved in 400 cc. of dry ether was added with stirring 900 cc. of tertiary-amylmagnesium chloride solution containing 1.97 moles of Grignard reagent. The flask containing the acetyl chloride solution was immersed in a salt–ice freezing mixture. At one time the temperature of the mixture rose to +3°, but most of the time it was at −3° or below. A cream-colored precipitate formed. The mixture was stirred for half an hour at −2° after all the Grignard reagent was added and for another half hour with the cooling mixture removed. It was then decomposed on ice and treated as usual. The product was fractionated at 730 mm. through Column II to give: (1) 6.0 g., 68-120°; (2) 7.3 g., 120–125°, $n^{20}_{\rm D}$ 1.4038; (3) 25.7 g., 125–130°, 1.4066; (4) 24.7 g., 130–135°, 1.4100; (5) 16.1 g., 135–140°; 57.6 g. of residue. The desired methyl tertiary-amyl ketone was undoubtedly in the material boiling at 125–140° but no constant boiling point was obtained.

Reaction in Refluxing Ether.—To 196 g. (2.5 moles) of acetyl chloride dissolved in 600 cc. of dry ether was added with stirring during six and one-half hours 900 cc. of tertiary-amylmagnesium chloride solution containing 1.99 moles of Grignard reagent. The reaction was quite vigorous and the ether refluxed steadily. After 300 cc. of Grignard solution had been added, 50 g. (0.6 mole) of acetyl chloride was added to ensure an excess of chloride in the reaction mixture. A white precipitate formed. The reaction mixture stood overnight in the laboratory and was then filtered by suction. The filtrate and precipitate were worked up separately.

The filtrate was poured on ice. There was no turbidity. The ether layer was separated and the aqueous portion extracted twice with small amounts of ether. The combined ether solutions were stirred for ten minutes with about one-fourth their volume of saturated aqueous potassium carbonate solution. The solution was light yellow in color. It was dried over 50 g. of anhydrous potassium carbonate for two hours and the ether was removed through a small partial condensation column. The product was fractionated at 738 mm. through Column II to give: (1) 5.5 g., 46–99°; (2) 5.0 g., 99–110°; (3) 19.9 g., 110–125°; (4) 9.4 g., 125–128°; (5) 12.0 g., 128–133°.

The precipitate was decomposed with ice in the usual way. The product was dried as usual and was fractionated at 737 mm. through Column II to give: (1) 3.5 g., 120–125°, $n^{20}_{\rm D}$ 1.4074; (2) 20.5 g., 125–129°, 1.4086; (3) 34.2 g., 129–132°, 1.4100; (4) 21.5 g., 132–137°, 1.4122; (5) 19.5 g., 137–160°; (6) 15 g., black tarry residue.

Purification of the Methyl Tertiary-amyl Ketone.—The 125–140° fractions from the

---

(9) Whitmore and Badertscher, THIS JOURNAL, **54**, 825 (1932).

(10) Allen, *ibid.*, **52**, 2958 (1930).

three preceding fractionations were combined and steam distilled from aqueous potassium carbonate solution in order to remove the last traces of acetyl chloride. The ketone was salted out of the distillate with sodium chloride and separated. It was dried overnight with sodium sulfate at 0°. It was then fractionated at 721 mm. through Column I, giving 68.3 g. of product boiling at 129–131°. The semicarbazone melted at 138.5–139°. Wischnegradski[11] gives the boiling range of this ketone as 131.5–132.5° and Meerwein[12] reports the melting point of the semicarbazone as 136–138°.

A small sample of the ketone was oxidized with chromic acid. The amide of the high-boiling oxidation product (b. p. range 145–185°) was prepared. This was compared with the amide prepared from a known sample of ethyldimethylacetic acid; known and unknown and mixed m. p. 102.7–103.2°. Haller and Bauer[13] give the melting point of this amide as 103–104°.

Acetyl Chloride and Methyldiethylcarbinylmagnesium Chloride.—A one mole run carried out in the usual way gave a product which on fractionation at 749 mm. through Column I gave the following: (1) 10.8 g., 36–63°; (2) 20.0 g., 63–65°, n^{20}_{D} 1.3870; (3) 17.8 g., 66–70°, 1.3989; (4) 17.8 g., 70–151°; (5) 21.9 g., 151–156°, 1.4206. Fraction 5 represented an 18% yield of 3-methyl-3-ethylpentanone-2 semicarbazone, m. p. 168.5–169°. Nybergh gives the boiling point of this ketone as 153.5° and the melting point of its semicarbazone as 168°.[14] Fraction 2 decolorized bromine.

Acetyl Chloride and Dimethyl-*n*-butylcarbinylmagnesium Chloride.—A one mole run was carried out in the usual way. The reaction was very vigorous. The dried product, fractionated at 743 mm. and at 20 mm., gave the following fractions: (1) 41 g., 35–41°; (2) 19.4 g., 41–81°; (3) 13.5 g., 81–90°, n^{20}_{D} 1.3900; (4) 28.6 g., 90–91°, 1.3950; (5) 26.2 g., 91–93° dec., 1.3986; (6) 13.1 g., 68–70.5° (20 mm.), 1.4206; (7) 8.9 g., 71–74° (20 mm.), 1.4218. Fractions 3–5 decolorized bromine. Fraction 6 represented a 9% yield of 3,3-dimethylheptanone-2, semicarbazone, m. p. 129–130°. Leers gives the boiling point of this ketone as 169.5° (735 mm.) and the melting point of its semicarbazone as 130°.[15]

Reactions of Tertiary Grignard Reagents with Formaldehyde.—The following tertiary Grignard reagents were treated with gaseous formaldehyde: dimethyl-*n*-amylcarbinyl-, methylethyl-*n*-propylcarbinyl-, methylethyl-*n*-butylcarbinyl- and triethylcarbinylmagnesium chloride.[16]

2,2-Dimethylheptanol-1 (from dimethyl-*n*-amylcarbinylmagnesium chloride and formaldehyde)—b. p. 88–89° (15 mm.), n^{20}_{D} 1.4339; yield, 40.7%, based on Grignard reagent.

Anal. Calcd. for $C_9H_{20}O$: C, 74.91; H, 13.98. Found: C, 74.70, 74.74; H, 13.75, 13.85.

2-Methyl-2-ethylpentanol-1 (from methylethyl-*n*-propylcarbinylmagnesium chloride and formaldehyde)—b. p. 75.5–76° (15 mm.), n^{20}_{D} 1.4353; yield, 30%, based on Grignard reagent.

Anal. Calcd. for $C_8H_{18}O$: C, 73.76; H, 13.92. Found: C, 73.76, 73.73; H, 13.70, 13.75.

2-Methyl-2-ethylhexanol-1 (from methylethyl-*n*-butylcarbinylmagnesium chloride and formaldehyde)—b. p. 85.5–86° (11 mm.), n^{20}_{D} 1.4401; yield, 31%, based on Grignard reagent.

---

(11) Wischnegradski, *Ann.*, **178**, 105 (1875).

(12) Meerwein, *ibid.*, **396**, 256 (1913).

(13) Haller and Bauer, *Compt. rend.*, **148**, 129 (1909).

(14) *Ber.*, **55B**, 1960 (1922).

(15) Leers, *Bull. soc. chim.*, [4] **39**, 651 (1926).

(16) *Cf.* Whitmore and Church, THIS JOURNAL, **55**, 1119 (1933).

Anal. Calcd. for $C_9H_{20}O$: C, 74.91; H, 13.98. Found: C, 74.87, 75.06; H, 13.76, 13.91.

2,2-Diethylbutanol-1 (from triethylcarbinylmagnesium chloride and formaldehyde)—b. p. 75–78° (12 mm.), n^{20}_{D} 1.443; yield, 10%, based on Grignard reagent.

Anal. Calcd. for $C_8H_{18}O$: C, 73.76; H, 13.92. Found: C, 73.78, 73.54; H, 13.75, 13.64.

Reaction of Carbon Dioxide with Dimethyl-*n*-butylcarbinylmagnesium Chloride and with Dimethyl-*n*-amylcarbinylmagnesium Chloride.—No attempt was made to obtain the maximum yield of acids since the runs were small, and it has been our experience that the best yields of Grignard reagent are not obtained in small runs. K. C. Laughlin of this Laboratory has obtained a 42% yield of methyldiethylacetic acid in a 3-mole run, based on the methyldiethylcarbinyl chloride used.

Dimethyl-*n*-butylcarbinylmagnesium Chloride and Carbon Dioxide.—A half mole preparation of the Grignard reagent was made as usual. The total time for the halide–ether addition was four hours. Fifty cc. of ether was added and carbon dioxide was passed into the stirred mixture for five hours, pressure being applied by dipping the outlet tube of the apparatus into a 60-mm. column of mercury. The reaction flask was cooled by an ice–salt freezing mixture. The reaction mixture was decomposed by acidifying with 1:1 sulfuric acid. The ether layer was separated and the aqueous layer extracted ten times with 10-cc. portions of ether and the combined ether solutions dried over 30 g. of sodium sulfate in the refrigerator.

Suction (water pump) was applied and the ether removed. The amide was prepared from this crude acid in the usual way by heating a small portion with two or three times its volume of phosphorus trichloride until a pasty yellow solid commenced to precipitate and then decanting the mixture into cold aqueous ammonia. The amide was insoluble in water and was recrystallized by dissolving in ethyl acetate and precipitating with petroleum ether; m. p. of amide, 92.8–93.8° (uncorr.).

Dimethyl-*n*-amylcarbinylmagnesium Chloride and Carbon Dioxide.—A one-third mole preparation of the Grignard reagent was carried out in the usual manner. The mixture was diluted with 100 cc. ether, a salt–ice freezing mixture was placed around the reaction flask and carbon dioxide gas was passed into the flask with stirring, pressure being applied by dipping the outlet tube 80 mm. under the surface of mercury contained in a test-tube. The reaction mixture was decomposed and worked up in the same manner as in the preceding preparation. The ether was taken off through Column IV and the distillation continued until the temperature reached 115° at atmospheric pressure. The distillate consisted of olefins. The remaining olefin was removed by suction and the residue was fractionated at 10 mm. through Column IV to give: (1) 1.3 g., 110–117°; (2) 3.9 g., 117–118°, n^{20}_{D} 1.4335; (3) 4.9 g., 118°, 1.4318; (4) 3.2 g., 118–118.5°, 1.4305. Fractions 2–4 represented a 22% yield of dimethyl-*n*-amylacetic acid. Its amide, prepared in the usual way, melted at 102.5–103.5°.

Summary

1. The yields of eight aliphatic tertiary organomagnesium chlorides have been determined. These range from 60 to 80%.

2. The reaction between tertiary Grignard reagents and ethyl chlorocarbonate gives the ethyl ester of the corresponding substituted acetic acid. This reaction is useful synthetically.

3. Tertiary-butylmagnesium chloride reacts with ethyl carbonate to form ethyl trimethylacetate. Higher tertiary Grignard reagents react little or not at all with ethyl carbonate.

4. Tertiary-butylmagnesium chloride, when added to an excess of acetyl chloride in ether, gives pinacolone in good yields. The yields of the corresponding ketones from higher tertiary Grignard reagents and acetyl chloride are lower.

5. Four homologs of neopentyl alcohol, 2,2-dimethylheptanol-1, 2-methyl-2-ethylpentanol-1, 2-methyl-2-ethylhexanol-1, and 2,2-diethylbutanol-1 have been prepared from the action of formaldehyde with tertiary Grignard reagents.

6. Preliminary studies have been made on the action of carbon dioxide with certain higher tertiary Grignard reagents.

STATE COLLEGE, PENNSYLVANIA RECEIVED AUGUST 24, 1932
PUBLISHED APRIL 6, 1933

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

The Interconversion of Arylmercuric Halides and Diarylmercury Compounds. II[1]

BY R. W. BEATTIE[2] AND FRANK C. WHITMORE

The conversion of simple mercurated organic compounds of the type, RHgX, to the mercuri-bis type, R_2Hg, has long been of interest.[1] In the present work this change has been produced in a large number of aromatic mercury compounds by means of sodium alcoholates and alcoholic potassium hydroxide[3] and by means of a long known but neglected reagent for this purpose, namely, sodium cyanide.[4] These studies have been conducted with the chloronaphthylmercuric chlorides prepared from a series of new chloronaphthalene sulfinic acids obtained from the chloronaphthalene sulfonyl chlorides made available in this Laboratory in another research.[5] The diarylmercury compounds were converted to the arylmercuric bromides and iodides by treatment with mercuric bromide and iodide.

Experimental

A. Mercury Compounds of the Chloronaphthalenes

The Chloronaphthalene Sulfinic Acids.—Of the various ways of converting sulfonyl chlorides to sulfinic acids,[6] the sodium sulfite method was adopted for the present work. In place of the sodium bicarbonate usually recommended an equivalent amount of dilute sodium hydroxide solution was used. The preparation of 1-chloronaphthalene-6-sulfinic acid may be taken as typical.

A solution of 400 cc. of water, 25.2 g. (0.2 mole) of sodium sulfite, 80 cc. of 20% sodium hydroxide solution (0.4 mole) was heated to boiling in a 1-liter beaker equipped

---

(1) Whitmore and Sobatzki, THIS JOURNAL, **55**, 1128 (1933).

(2) Submitted in partial fulfilment of the requirements for the Ph.D. degree.

(3) Whitmore, Hanson and Carnahan, THIS JOURNAL, **51**, 894 (1929).

(4) Buckton, *Ann.*, **108**, 105 (1858).

(5) Beattie and Whitmore, THIS JOURNAL, **55**, 1546 (1933).

(6) "Organic Syntheses," **2**, 90 (1922).