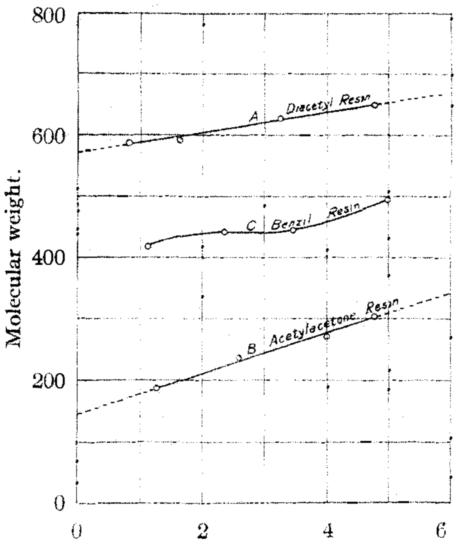

Fig. 1.—Molecular weight–concentration curves.

point at which the benzene started to freeze. Figure 1 shows results obtained with three different resins. Meanwhile Staudinger and co-workers[15] reported similar difficulties with polymers, and offer an explanation for this observed increase in molecular weight with an increase in concentration.

Summary

Acetonylacetone and hydrazine hydrate react to yield 3,6-dimethylpyridazine, the azine-hydrazone of Gray, and an insoluble crystalline polyazine.

The 12-membered ring of Gray could not be isolated under any conditions.

Benzil dihydrazone reacts with benzil, diacetyl, and acetylacetone to yield resins.

The 4-membered ring, formed by the decomposition of benzil monohydrazone, of Curtius could not be isolated.

Acetylacetone and hydrazine hydrate yield 3,5-dimethylpyrazole without polymeric by-product.

Cryoscopic molecular weight determinations of polyazines with benzene as solvent yield values that appear to increase with concentration of polymer.

AUSTIN, TEXAS RECEIVED JUNE 4, 1938

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[15] Staudinger and co-workers, *Ber.*, **68** 2313 (1935).

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

The Reducing Action of Primary Grignard Reagents

BY FRANK C. WHITMORE, A. H. POPKIN, J. S. WHITAKER, K. F. MATTIL AND J. D. ZECH

The reducing action of *t*-butylmagnesium chloride on trimethylacetyl, isobutyryl, *n*-butyryl[1] and *t*-butylacetyl[2] chlorides has been reported already. Similar studies have now been made to find the effect of branching, in both the Grignard reagent and the carbonyl compound, on the yields of the reduction products.

n-Butylmagnesium bromide and trimethylacetyl chloride produced neopentyl alcohol in 27% yield together with a 69% yield of *n*-butyl-*t*-butylcarbinol representing a total yield of 96% of the reduction products. In the case of *t*-butylmagnesium chloride, the yield of neopentyl alcohol was 95% with a 1% yield of di-*t*-butylcarbinol.

Several other reactions of the Grignard reagent were studied next with emphasis on the by-product obtained. Excess *n*-butylmagnesium bromide gave the usual products with acetyl chloride, ethyl acetate, acetaldehyde and 2-hexanone and, in addition, the by-products indicated

$$\begin{array}{rl} CH_3COCl & \longrightarrow 8\%\ CH_3CH_2OH \\ & \searrow 13\%\ CH_3CHOHC_4H_9 \\ CH_3CO_2C_2H_5 & \longrightarrow 3\%\ CH_3CHOHC_4H_9 \\ CH_3CHO & \longrightarrow 18\%\ CH_3CH_2OH \\ CH_3COC_4H_9 & \longrightarrow 9\%\ CH_3CHOHC_4H_9 \end{array}$$

The preparation of a series of tertiary carbinols for subsequent dehydration studies involved the addition of methylneopentyl ketone to some primary Grignard compounds. With ethylmagnesium bromide, evidence of a trace of methylneopentylcarbinol was obtained but its identity was not established positively. This reduction product was identified when higher Grignard reagents were used. The yields of methylneopentylcarbinol were 5.5% using *n*-propylmagnesium bromide, 5.7% using *n*-butylmagnesium bromide

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

[2] Whitmore and Heyd, *ibid.*, **60**, 2030 (1938).

and 3.4% using *n*-amylmagnesium bromide. The conditions of concentration and temperature during the addition of ketone in the preparations of the neopentylcarbinols were approximately identical.

An attempt to isolate neopentyl alcohol from the action of *n*-butylmagnesium bromide on ethyl trimethylacetate was not successful. The only reduction product isolated was *n*-butyl-*t*-butylcarbinol, present in 40% yield. This verified the observation of Leroide.[3] As had been observed previously,[4] the addition of ethyl trimethylacetate to *t*-butylmagnesium chloride in ether produced no reaction, the recovery of the ester being quantitative. There was indication, however, of a reaction at elevated temperatures and studies are now in progress employing di-*n*-butyl ether and benzene as solvents. Because of the unusual stability of ethyl trimethylacetate toward the tertiary Grignard reagent and its reactivity toward *n*-butylmagnesium bromide, an investigation is being made of its behavior toward isopropylmagnesium bromide.

There is the possibility that 2-hexanol might appear as a result of acetaldehyde formation due to peroxidation of the ether.[5,6] Careful studies indicate that this is not the source of the 2-hexanol in the present experiments.

Experimental

Description of Apparatus.—A description of the columns employed is given because of the importance of fractionation in this work. The fractionating columns were of the total condensation, variable take-off type[7] containing single turn, 4-mm. glass helices as packing.[8] The dimensions are reported as length of packing space and internal diameter of the column: Column I, 62 × 0.9 cm.; II, 90 × 1.5 cm.; III, 110 × 1.5 cm.; IV, 68 × 1.5 cm.; V, 58 × 1.1 cm.; VI, 46 × 0.9 cm.; VII, 77 × 1.4 cm.; VIII, 48 × 0.9 cm.; IX, 27 × 0.5 cm.; X, 47 × 0.9 cm.; XI, 64 × 1.2 cm.; XII, indented, 110 × 1.4 cm.

Reaction of *n*-Butylmagnesium Bromide with Trimethylacetyl Chloride.—Trimethylacetyl chloride, b. p. 58° (150 mm.), n^{20}D 1.4126, was prepared in 87% yield from thionyl chloride (Eastman Kodak "practical") and trimethylacetic acid, b. p. 158° (725 mm.), m. p. 34°. *n*-Butylmagnesium bromide was obtained by treating 97 g. (4 moles) of magnesium with 548 g. (4 moles) of *n*-butyl bromide, b. p. 99–100° (724 mm.), n^{20}D 1.4400, and 1400 cc. of anhydrous ether. The undiluted acid chloride was added during one hour. The Grignard complex was decomposed with ice, extracted with ether and the ether removed, b. p. 34° (726 mm.), using column IV. The residue was then placed under column VI and fractions 1–5 were collected, 26.2 g., b. p. 42–105° (726 mm.), n^{20}D 1.3693–1.3718. Fractions 6–12, 24.1 g., b. p. 110–111.5°, were solid at room temperature. Of these, fractions 7 and 12 yielded phenylurethans melting at 112–113° which did not depress the m. p. when mixed with the known phenylurethan of neopentyl alcohol. The yield of neopentyl alcohol based on acid chloride was 27%. Fractions 13 and 14, 2.7 g., 36–71° (16 mm.), n^{20}D 1.4042–1.4190, were the intermediate fractions between the two reduction products. Fractions 15–25, 99.8 g., b. p. 71° (15 mm.), n^{20}D 1.4319–1.4321, gave a phenylurethan melting at 64.5–65.5° which gave no depression on mixing with an authentic sample of the same derivative of *n*-butyl-*t*-butylcarbinol. The yield of the secondary carbinol as reduction product was 69%. A residue of 4.5 g., n^{20}D 1.4329, was pure *n*-butyl-*t*-butylcarbinol, the weight representing the operating hold-up in column VI. A careful search gave no trace of 2-hexanol. It had been suggested that the secondary alcohol might be a product of acetaldehyde formation from peroxide in the ether.

Reaction of *n*-Butylmagnesium Bromide with Acetyl Chloride.—*n*-Butylmagnesium bromide was prepared from 685 g. (5 moles) of *n*-butyl bromide, b. p. 99° (732 mm.), 1450 cc. of dry ether and 122 g. (5 moles) of magnesium. Acetyl chloride ("practical" Eastman Kodak Co. product) was purified by distillation, b. p. 52° (737 mm.), from dry dimethylaniline. The addition of 157 g. (2 moles) of the undiluted acetyl chloride to the above Grignard reagent, concentrated by boiling off one liter of ether, was completed in one hour and twenty minutes. The complex was decomposed with ice, extracted with ether and the ether removed through column IV. The reaction mixture was fractionated through column VI to give: 1, 4.9 g., b. p. 34–64° (736 mm.), n^{20}D 1.3579; 2–3, 8.9 g., 64–78°, 1.3672–1.3800; 4, 3.2 g., 78–86°, 1.3944; 5, 8.8 g., 79–115° (727 mm.), 1.4011; 6–8, 13.0 g., 115–116.5°, 1.4022–1.4032; 9–10, 10.2 g., 120–134°, 1.4047–1.4118; 11–13, 22.5 g., 134–139.5°, 1.4152–1.4169; 14, 8.6 g., 139.5–145°, 15–20, 53.5 g., 35–74° (14 mm.), 1.4181–1.4278; 21–23, 51.9 g., 85–101° (12 mm.), 1.4351–1.4362; residue 8.2 g.

Fraction 1 was largely ether; 2 and 3 represented an 8% yield of ethyl alcohol as identified through the α-naphthylurethan, m. p. and mixed m. p. with an authentic sample, 78.5–79°. Fractions 4 and 5 contained water layers. Fractions 6–8 were identified as *n*-butyl alcohol by the α-naphthylurethan, m. p. and mixed m. p. with an authentic derivative, 70–71°. Fractions 9 and 10 gave no test for 2-hexanone on treatment with 2,4-dinitrophenylhydrazine. They probably consisted of 2-hexanol and *n*-butyl alcohol. Fractions 11–13 were identified as 2-hexanol by oxidation of a sample to the corresponding ketone with an aqueous acid dichromate solution and the formation of the 2,4-dinitrophenylhydrazone, m. p. and mixed m. p., 106–107°. Fractions 14 and 15 were probably mixtures of 2-hexanol with the decenes formed by the dehydration of some of the methyl-di-*n*-butylcarbinol during the fractionation.

Fractions 16–20 proved to be mainly olefins from the dehydration of methyl-di-*n*-butylcarbinol. They approached the values b. p. 97° (84 mm.) and n^{20}D 1.4295.

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[3] Leroide, *Ann. chim.*, [9] **16**, 354 (1921).

[4] Conant and Blatt, THIS JOURNAL, **51**, 1227 (1929).

[5] Clover, *ibid.*, **44**, 1107 (1922).

[6] Pierotti and Stewart, *ibid.*, **59**, 1773 (1937).

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

[8] Wilson, Parker and Laughlin, *ibid.*, **55**, 2795 (1933).

Fractions 21–23 were methyl-di-*n*-butylcarbinol, the constants of a known sample of which were b. p. 100° (24 mm.), n^{20}_{D} 1.4349.

Reaction of *n*-Butylmagnesium Bromide with Ethyl Acetate.—Ethyl acetate was purified by treatment of commercial ethyl acetate (Eastman Kodak Co.) with phosphorus pentoxide and fractionation through column V, b. p. 74° (737 mm.), n^{20}_{D} 1.3722. *n*-Butylmagnesium bromide was prepared using 1465 g. (10.6 moles) of *n*-butyl bromide, 258 g. (10.6 moles) of magnesium and 1750 cc. of dry ether. The addition of the ethyl acetate, 440 g. (5 moles), in 700 cc. of dry ether was completed in ten hours. The products were isolated as usual and fractionated through column IV to give: 1, 17.3 g., 35–55° (737 mm.), n^{20}_{D} 1.3592; 2–4, 88.0 g., 75–76°, 1.3731–1.3688; 5, 8.7 g., 37° (24 mm.), 1.4037; 6, 16.3 g., 58° (24 mm.), 1.4160; 7, 32.8 g., 62.5–100° (24 mm.), 1.4304; 8–17, 513.4 g., 100° (24 mm.), 1.4348–1.4351.

Fractions 1–5 contained ether, ethyl alcohol and unreacted ethyl acetate. Fraction 6 was identified as 2-hexanol (3% yield) by oxidation to the ketone and preparation of a 2,4-dinitrophenylhydrazone, m. p. and mixed m. p., 106–107°. Treatment of fraction 6 with 2,4-dinitrophenylhydrazine before oxidation gave no evidence of the presence of 2-hexanone. Fraction 7 contained methyl-di-*n*-butylcarbinol with some 2-hexanol as impurity. Fractions 8–17 represented a 64% yield of the tertiary carbinol which gave a 90% yield of decenes, b. p. 69° (27 mm.), n^{20}_{D} 1.4294, when refluxed with anhydrous copper sulfate.

Reaction of *n*-Butylmagnesium Bromide with Acetaldehyde.—*n*-Butylmagnesium bromide was made from 685 g. (5 moles) of *n*-butyl bromide, 121.5 g. (5 moles) of magnesium and one liter of dry ether. After boiling off 400 cc. of ether, 88 g. (2 moles) of acetaldehyde, b. p. 22–23° at 720 mm. (purified by distillation of 500 g. of a technical grade Eastman Kodak Co. product to which had been added 4 g. of hydroquinone), was added. The addition complex was decomposed with ice and an excess of sulfuric acid. The layers were separated and the aqueous layer extracted again with ether. The final water layer was distilled through column IV. After the dissolved ether had been collected at 34°, a fraction, 15.4 g., b. p. 75–90°, which yielded an α-naphthylurethan, m. p. and mixed m. p., 78.5–79°, corresponding to that for ethyl alcohol, was obtained. A second fraction 90–99°, on drying, also gave an α-naphthylurethan corresponding to ethyl alcohol. The weight of fractions 1 and 2 after drying was 21.4 g., or approximately 18% yield.

The ether was removed from the ethereal extracts of the reaction products through column IV and the products were fractionated through column V to give: 1, 8.4 g., 42–75° (727 mm.), n^{20}_{D} 1.3622; 2–4, 11.9 g., 75–134°, 1.3940–1.4100; 5–6, 66.4 g., 136°, 1.4144–1.4147; residue 28 g. Fraction 1 contained a small amount of ethyl alcohol as identified by its α-naphthylurethan. Fractions 5 and 6 contained the normal product, 2-hexanol.

Reaction of *n*-Butylmagnesium Bromide with 2-Hexanone.—Dehydrogenation of 3 kg. of Eastman "Technical" 2-hexanol yielded crude 2-hexanone which was fractionated through column II into 67 fractions of approximately 40 g. each. The best fractions were combined and refractionated through column V. Addition of 200 g. (2 moles) of purified 2-hexanone, b. p. 125° (732 mm.), n^{20}_{D} 1.4010 to 4.5 moles of filtered *n*-butylmagnesium bromide in 2 liters of ether was completed in one hour with the liberation of 0.15 mole of olefin. The reaction mixture was decomposed with ice, the ether layer decanted, and the aqueous layer steam distilled. The aqueous layer of the distillate was extracted with ether and the total ethereal solutions combined for removal of ether through column XII. The residual products were then fractionated through column I to give: 1–12, 33.1 g., 45° (125 mm.) –80° (98 mm.), n^{20}_{D} 1.4051–1.4079; 13–16, 18.1 g., 80° (87 mm.) –82° (24 mm.), n^{20}_{D} 1.4138–1.4186; 17–33, 343 g., 95° (20 mm.) –78° (3 mm.), 1.4331–1.4358.

Fractions 1–12 were refractionated through column VI to give: 34–36, 10.1 g., 105–111° (739 mm.), n^{20}_{D} 1.4060–1.4008; 37–41, 19.3 g., 116–118°, 1.4017–1.4030; residue, 5 g. Fractions 37–41 were unreacted 2-hexanone, 2,4-dinitrophenylhydrazone, m. p. and mixed m. p., 106–107°.

Fractions 13–16 were refractionated through column IX to give: 42–44, 3.1 g., 131–133.5° (739 mm.), 1.4068–1.4150; 45–50, 7.8 g., 135–136°, 1.4160–1.4162; residue, 0.9 g.

Fractions 42–50 and the residue of that fractionation were identified as 2-hexanol by oxidation with an acid dichromate solution and formation of a 2,4-dinitrophenylhydrazone for 2-hexanone, m. p. and mixed m. p., 106–107°. A portion of fraction 48, 1.7 g., gave no test for 2-hexanone with 2,4-dinitrophenylhydrazine prior to oxidation.

Reaction of *n*-Butylmagnesium Bromide with Ethyl Trimethylacetate.—Ethyl trimethylacetate, b. p. 116.5° (735 mm.), n^{20}_{D} 1.3912 was prepared by the action of ethyl alcohol on trimethylacetyl chloride. *n*-Butylmagnesium bromide was prepared using 97 g. (4 moles) of magnesium, 548 g. (4 moles) of *n*-butyl bromide and 1600 cc. of ether. On completion of Grignard formation, 400 cc. of ether was distilled off and 130 g. (1 mole) of undiluted ethyl trimethylacetate was added to the concentrated Grignard solution during one-half hour. The complex was decomposed with ice, extracted with ether and after removal of the ether through column IV the products were fractionated through column VI to give: 1–2, 4.3 g., 32–110° (741 mm.); 3–4, 4.2 g., 111–116°; 5–6, 7.9 g., 43–63° (11 mm.), n^{20}_{D} 1.4150–1.4208; 7, 7.2 g., 64.5° (11 mm.), 1.4250; 8–13, 57.5 g., 65.5–67° (11 mm.), 1.4295–1.4310; 14–22, 99.6 g., 105.5–107° (11 mm.), 1.4488.

Fractions 3–4 were identified as *n*-butyl alcohol by the α-naphthylurethan, m. p. and mixed m. p., 70–71°. Fractions 8–13 represented a 40% yield of *n*-butyl-*t*-butylcarbinol which gave a phenylurethan melting at 65–66°. Fractions 14–22 were di-*n*-butyl-*t*-butylcarbinol in 50% yield. Based on a density determination of a representative fraction, d^{20}_{4} 0.8498, the molecular refraction was found to be 63.16; calcd. 63.76.

Fractions 5–6 were investigated for 2-hexanol as a possible product of peroxide and aldehyde formation in the ether but no α-naphthylurethan was obtained, nor did oxidation with acid dichromate solution yield any evidence of 2-hexanone. Fraction 7 was impure di-*n*-butyl-*t*-butylcarbinol.

Addition of Methyl Neopentyl Ketone to Ethylmagnesium Bromide.—The methyl neopentyl ketone[9] used in this and subsequent reactions had a b. p. range of 122–124° (725–730 mm.) and n^{20}D 1.4035–1.4040. The Grignard reagent was prepared from 121 g. (5 moles) of magnesium, 545 g. (5 moles) of ethyl bromide (Eastman Kodak Co. "practical"), and 1 liter of ether. The addition of 353 g. (3.1 moles) of ketone was completed in four hours. The complex was decomposed with ice, the mixture extracted with ether, and the ether removed through column XII. The products were fractionated through column XI at reduced pressure to minimize dehydration of the tertiary carbinol. A salt–ice trap and a solid carbon dioxide–acetone trap were used in series to condense the low boiling material evolved as gases when the pressure was lowered: 1, 5.2 g., 40–48° (176 mm.); 2, 3.8 g., 42° (93 mm.); 3, 2.9 g., 35° (18 mm.), n^{20}D 1.4284; 4, 6.8 g., 66° (18 mm.), 1.4315; 5–18, 359 g., 44° (4 mm.), 1.4335–1.4375. The trap condensed 29.1 g. of liquid which, on fractionation through column X, gave 26.5 g. of ether and a residue, 19, of 1.9 g. The 23.2 g. collected in the salt–ice trap gave a residue, 20, of 2.1 g. after the ether had been removed through column X. Fraction 4, above, on distilling through column X, gave 21, 3 g., 115° (739 mm.), 1.4240 which was combined with fractions 3, 19 and 20 to give on distillation through a semi-micro fractionating column (43.5 × 0.6 cm.): 22, 1.1 g., 90–115° (744 mm.), 1.4160; 23, 1.0 g., 130–145°, 1.4288; residue, 6 drops. Since no derivative could be made for 23 using α-naphthyl isocyanate, no methylneopentylcarbinol was found.

Fraction 22 gave no indication of the presence of *s*-butyl alcohol as a by-product of peroxide and aldehyde formation in the ether. Fractions 5–18 represented methylethylneopentylcarbinol.[10]

Addition of Methyl Neopentyl Ketone to *n*-Propylmagnesium Bromide.—*n*-Propylmagnesium bromide was prepared from 553 g. (4.5 moles) of *n*-propyl bromide, b. p. 70–71° (735 mm.), n^{20}D 1.4344, 109 g. (4.5 moles) of magnesium and one liter of ether. The addition of 342 g. (3 moles) of methyl neopentyl ketone was completed in three hours. The complex was decomposed with ice, extracted with ether which was then removed through column XII, and the products fractionated through column V to give: 1, 27.1 g., 37–87° (728 mm.), n^{20}D 1.3850; 2, 5.2 g., 20.5° (13 mm.). Dehydration of the tertiary carbinol made fractionation difficult. The remainder was dried with anhydrous potassium carbonate, then fractionated through column XI using a salt–ice trap and a solid carbon dioxide–acetone trap in series to give: 3–7, 101.8 g., 35–56° (14 mm.), 1.4232–1.4260; 8–13, 42.6 g., 62–73° (14 mm.), 1.4280–1.4352; 14–20, 74.1 g., 74–75° (14 mm.), 1.4367–1.4371; 21–23, 32.8 g., 85–97° (14 mm.), 1.4528–1.4590; residue, 26 g.; trap, 2.9 g.

Fractions 8–13, fractions 32–39 and the residue of the refractionation (below) represented 106 g. (0.76 mole) of olefin.

Fractions 14–20 contained 77 g. (0.49 mole) of methyl-*n*-propylneopentylcarbinol.

Fractions 1, 2, 3–7 and the contents of the traps were dried over anhydrous sodium sulfate, and fractionated through column X to give at 741 mm. pressure: 24–28, 33.5 g., 35–132°, 1.3630–1.4130; 29–31, 16.6 g., 132–140°, 1.4170–1.4218; 32–39, 39.4 g., 142–150°, 1.4237–1.4260; residue 25 g. Fractions 29–31, gave the 3,5-dinitrobenzoate of methylneopentylcarbinol, m. p. and mixed m. p., 95°. This was confirmed by the α-naphthylurethan, m. p. 86–87°, which likewise did not depress in m. p. when mixed with the α-naphthylurethan of methylneopentylcarbinol.

Fractions 24–29 were refractionated through column X, in an attempt to isolate possible 2-pentanol. Fractions 40–44, 17.2 g., 35–116° (738 mm.), 1.3655–1.3920; 45–47, 1.8 g., 116–126°, 1.4006–1.4050; 48–52, 15.4 g., 126–145°, 1.4090–1.4245; residue 4.1 g. were obtained. Fractions 45–47 gave no 2-pentanol. The rapid absorption of bromine with liberation of hydrogen bromide in fractions 44–52 indicated the presence of unchanged methylneopentyl ketone.

Based on boiling point and refractive index curves, the total yield of methylneopentylcarbinol was 5.5%.

Addition of Methyl Neopentyl Ketone to *n*-Butylmagnesium Bromide.—The addition of methyl neopentyl ketone, 342 g. (3 moles), to 3.17 moles of *n*-butylmagnesium bromide, was completed in two hours. The products were isolated in the usual fashion and fractionated through column XI, using salt–ice and dry ice–acetone traps, to give: 1–7, 44.9 g., 28° (187 mm.) −78° (9 mm.), 1.3900–1.4354; 8–19, 325 g., 78–79° (9 mm.), 1.4400; 20–23, 40.5 g., 125° (6 mm.), 1.4572–1.4590; residue 8.2 g., wt. in traps, 91 g.

Fractions 8–19 represented a 62% yield of methyl-*n*-butylneopentylcarbinol.

The 91 g. collected in the traps left 10.1 g. after removal of ether. This was combined with fractions 1–7 and refractionated at 739 mm. through column X to give: 24–31, 30.6 g., 48–136°, 1.3820–1.4168; 32–33, 7.1 g., 137°, 1.4180–1.4190; 34, 2.4 g., 145°, 1.4225; residue, 3 g.

Fraction 32 gave a quantitative yield of the α-naphthylurethan of methylneopentylcarbinol, m. p. 86–87°, when treated with α-naphthyl isocyanate indicating the presence of methylneopentylcarbinol as reduction product and the absence of 2-hexanol in detectable quantities. The same fraction gave a 3,5-dinitrobenzoate which, on one crystallization, melted at 95–95.5° corresponding to the derivative of methylneopentylcarbinol, again indicating the purity of the fraction. Both derivatives were confirmed by mixed melting points with authentic samples. Boiling point and refractive index curves showed a 5.7% yield of methylneopentylcarbinol as reduction product.

Addition of Methyl Neopentyl Ketone to *n*-Amylmagnesium Bromide.—The addition of 342 g. (3 moles) of the ketone to 3.75 moles of the Grignard reagent was completed in two and one-half hours. The products were isolated in the usual fashion and fractionated through column XI to give: 1–6, 39.4 g., 55° (31 mm.) −48° (16 mm.), 1.4080–1.4150; 7–8, 12.3 g., 48–49° (16 mm.), 1.4215–1.4245; 9–17, 105 g., 79–81° (16 mm.), 1.4340–1.4350; 18–30, 222 g., 92° (8 mm.), 1.4425; 31–32, 16.4 g., 103–109° (6 mm.), 1.4540–1.4587; residue, 43 g. The traps used in this fractionation condensed 41 g. of low boiling material which

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[9] Methyl neopentyl ketone is one of the products of the chromic acid oxidation of diisobutylene. The experimental details of its preparation will be discussed in a later paper.

[10] Previously prepared by K. C. Laughlin of this Laboratory.

contained 9.6 g. after removal of ether through column X. This was combined with fractions 1–6 to give through column X: 33–36, 14.8 g., 35–122° (750 mm.), 1.3542–1.4040; 37–39, 10.3 g., 122–132°, 1.4040–1.4140; 40–41, 6.6 g., 136°, 1.4158–1.4170; residue, 3.5 g.

The residue above, 37–39, and fractions 7–8 were combined and fractionated through column X to give 5.0 g. of methylneopentylcarbinol, $n^{20}\mathrm{D}$ 1.4175–1.4195, which gave an α-naphthylurethan, m. p. and mixed m. p., 86–87°. This was checked with a 3,5-dinitrobenzoate, m. p. and mixed m. p., 95–95.5°. This sample, together with the 6.6 g. of fractions 40–41, represents a 3.4% yield of reduction product. Attempts to find 2-heptanol were unsuccessful. Fractions 9–17 contained dodecenes (0.63 mole) and fractions 18–30 contained methyl-*n*-amylneopentylcarbinol.

Summary

1. The yields of reduction products from the action of *n*-butylmagnesium bromide on acetyl chloride and trimethylacetyl chloride are reported.

2. Reductions involving *n*-butylmagnesium bromide with ethyl acetate, acetaldehyde and 2-hexanone are also described.

3. The reducing actions of ethyl-, *n*-propyl-, *n*-butyl- and *n*-amyl-magnesium bromides with methyl neopentyl ketone are reported.

4. No evidence was found that ether peroxide was the source of the carbinols.

STATE COLLEGE, PENNA.

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

The Action of Primary Grignard Reagents on *t*-Butylacetyl Chloride

BY FRANK C. WHITMORE, A. H. POPKIN, J. S. WHITAKER, K. F. MATTIL AND J. D. ZECH

The reduction of trimethylacetyl chloride to neopentyl alcohol in 95% yield[1] and *t*-butylacetyl chloride to neopentylcarbinol[2] in 1% yield when treated with *t*-butylmagnesium chloride has been reported. The results of the present investigation agreed with these observations, the action of ethyl-, *n*-propyl-, *n*-butyl- and *n*-amylmagnesium bromides on *t*-butylacetyl chloride giving no evidence for the formation of neopentylcarbinol in detectable quantities. In view of the yields of primary alcohol obtained by the reduction of isobutyryl-, *n*-butyryl-[3] and pivalyl chlorides using *t*-butylmagnesium chloride and of acetyl chloride using *n*-butylmagnesium bromide,[4] it is possible that the primary, secondary or tertiary character of the groups attached to the α-carbon of the acid chloride may have a more pronounced influence on the extent of reduction than has the branching of the chain. This possibility is being studied.

No reduction product was isolated when *t*-butylacetyl chloride was added to ethylmagnesium bromide, but similar addition to *n*-propyl, *n*-butyl and *n*-amylmagnesium bromides produced the corresponding secondary carbinols in 24.4, 20.5 and 19.3% yields. The chief products were the expected tertiary alcohols, although the recognized instability of such higher molecular weight tertiary carbinols was again evidenced in the partial dehydration of di-*n*-propylneopentyl-, di-*n*-butylneopentyl- and the complete dehydration of di-*n*-amylneopentylcarbinols during fractionation at reduced pressure.

Pure *n*-propyl-, *n*-butyl- and *n*-amylneopentylcarbinols were required for identification of the reduction products obtained. The action of aluminum isopropylate in isopropyl alcohol on *n*-propyl, *n*-butyl and *n*-amyl neopentyl ketones produced the desired secondary carbinols in 92, 93 and 89% yields, respectively. The ketones had been prepared in excellent yields by the action of the appropriate Grignard compound on *t*-butylacetamide.[5]

Experimental

Addition of *t*-Butylacetyl Chloride to Ethylmagnesium Bromide.—The Grignard solution was prepared from 545 g. (5 moles) of ethyl bromide, b. p. 36° (730 mm.), $n^{20}\mathrm{D}$ 1.4240, magnesium and 1.5 liter of dry ether. Addition of 182 g. (1.3 moles) of *t*-butylacetyl chloride, b. p. 68° (100 mm.), $n^{20}\mathrm{D}$ 1.4226, prepared in 86% yield from the action of thionyl chloride on the acid, was completed in seventy-five minutes. The complex was decomposed with ice, extracted with ether and the product, on removal of solvent using column XII, was fractionated through column XI,[6] to give: fraction 1, 2.6 g., b. p. 35–78° (740 mm.), $n^{20}\mathrm{D}$ 1.3770–1.4010; 2, 7.7 g., 50° (10 mm.), 1.4370;

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

[2] Whitmore and Heyd, *ibid.*, **60**, 2030 (1938).

[3] Greenwood, Whitmore and Crooks, *ibid.*, **60**, 2028 (1938).

[4] Whitmore, Popkin, Whitaker, Mattil and Zech, *ibid.*, **60**, 2458 (1938).

[5] A detailed description of the synthesis of branched aliphatic ketones from the acid amide and Grignard reagent is in preparation.

[6] The fractionating columns used have already been described, Whitmore, Popkin, Whitaker, Mattil and Zech, THIS JOURNAL, **60** 2458 (1938).