acid chloride used while the secondary carbinol isolated accounted for 71% of the acid chloride.

All melting points are uncorrected.

Summary

1. The reaction of *t*-butylmagnesium chloride with a large excess of pivalyl chloride at −10° gives a 32% yield of hexamethylacetone and an 8% yield of neopentyl alcohol as its pivalic ester.

2. The reaction of a large excess of *t*-butylmagnesium chloride at about 40° with pivalyl, isobutyryl and *n*-butyryl chlorides results, respectively, in a 1.5, 63 and 71% yield of addition and in a 94, 20 and 9% yield of reduction of the acid chloride to primary alcohol.

STATE COLLEGE, PENNA. RECEIVED JUNE 4, 1938

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

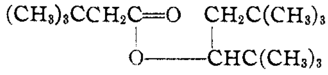
The Action of *t*-Butylmagnesium Chloride on *t*-Butylacetyl Chloride

BY FRANK C. WHITMORE AND J. W. HEYD

The preparation of *t*-butylneopentylcarbinol in quantity for use in a dehydration study involved the reaction of *t*-butylmagnesium chloride with *t*-butylacetyl chloride. An investigation of the reduction products has proved interesting when compared with the action of the same Grignard compound on trimethylacetyl chloride.[1] The addition of the acid chloride to *t*-butylmagnesium chloride produced *t*-butylneopentylcarbinol in 71% yield together with a 1% yield of neopentylcarbinol. Investigation of the products of this reaction boiling above the secondary carbinol indicates a 5% yield of *t*-butylneopentylcarbinyl *t*-butylacetate as the product of the esterification of the secondary alcohol complex with unreacted acid chloride. However, addition of *t*-butylacetyl chloride to a suitable excess of *t*-butylmagnesium chloride permitted all of the secondary carbinol to be recovered without esterification, thus raising the yield to 76%.

Addition of a slight excess of a filtered solution of *t*-butylmagnesium chloride to an ethereal solution of *t*-butylacetyl chloride, produced *t*-butylneopentyl ketone in 51% yield. In this case all of the secondary carbinol formed as reduction product underwent esterification in the presence of excess acid chloride to yield 17% of pure *t*-butylneopentylcarbinyl *t*-butylacetate. Attempts to saponify this ester by refluxing with alcoholic potassium hydroxide for seventy-one hours or by heating for fifty-six hours in a sealed tube at 90–100° were not successful. However, an authentic sample of the ester obtained from the reaction of *t*-butylneopentylcarbinol and *t*-butylacetyl chloride checked in physical constants with the reduction product and proved equally stable toward saponification under similar conditions.[2]

No reduction was obtained when *t*-butyl neopentyl ketone was treated with a solution of aluminum isopropylate in isopropyl alcohol. This inertness and the inability to form a semicarbazone or an oxime[3] are related to the steric arrangement about the carbonyl group of this ketone. The inertness of the ester is dependent on similar steric conditions.



$$\begin{array}{ll}(CH_3)_3CCH_2C{=}O & CH_2C(CH_3)_3\\ \qquad\qquad\quad\ | & \ | \\ \qquad\qquad\quad\ O\text{———} & CHC(CH_3)_3\end{array}$$

Experimental

Addition of *t*-Butylacetyl Chloride to *t*-Butylmagnesium Chloride.—A solution of 5.4 moles of *t*-butylmagnesium chloride in 2400 cc. of dry ether was prepared by the action of *t*-butyl chloride, b. p. 50° (732 mm.), n^{20}_D 1.3850, on magnesium. *t*-Butylacetyl chloride, b. p. 79° (150 mm.), n^{20}_D 1.4212, was prepared in 86% yield from *t*-butylacetic acid and thionyl chloride.[4] Addition of 336 g. (2.5 moles) of the acid chloride in a liter of ether to the Grignard solution (5.4 moles) was completed in three days and then the thick reaction mixture was refluxed for four days. The complex was decomposed with ice, the products extracted with ether and the solvent removed with an efficient column.[5] Fractionation of the products yielded: Fractions 1–3, 72.9 g., b. p. 34–81° (735 mm.), n^{20}_D 1.3520–1.3880; 4–5, 34.0 g., 81–167°, 1.4081–1.4220; 6–9, 282.3 g., 167–173°, solid; 10–11, 47.9 g., 122–208° (50–45 mm.), 1.4363–1.4450; solid residue, 15.4 g. Fractions 6–9 represent a 71% yield of *t*-butylneopentylcarbinol. A portion of the solid, by a series of fractional crystallizations, gave a pure sample of carbinol, m. p. 49.4° (corr.).

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

[2] Since the completion of this paper, J. S. Whitaker of this Laboratory has succeeded in partially saponifying this ester and identifying *t*-butylacetic acid as the acid fragment.

[3] Bouveault and Locquin, *Bull. soc. chim.*, [3] **35**, 642 (1906).

[4] Homeyer, Whitmore and Wallingford, THIS JOURNAL, **55**, 4209 (1933).

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

A similar run using 2.25 moles of acid chloride was also completed and the material from both reactions boiling above the secondary carbinol was refractionated to give 8 fractions, 61.1 g., b. p. 90° (5 mm.), n^{20}D 1.4392–1.4359. Refractionation of these gave 8 fractions, 39.7 g., b. p. 90° (5 mm.), n^{20}D 1.4367–1.4339, which represented a 5% yield of *t*-butylneopentylcarbinyl *t*-butylacetate. The refractive index gradually approached the correct index for the synthetic ester, n^{20}D 1.4320. The boiling point was correct for the ester. The mol. wt. found from the depression of the f. p. of benzene is 250; calcd. 256.

The fractions of the two preparations boiling in the range of 79–168° (732 mm.), were combined and refractionated to give 2 fractions, wt. 6.9 g., b. p. 139–143°, n^{20}D 1.4150–1.4179. These were identified as neopentylcarbinol by means of the α-naphthylurethan, m. p. 82–83°, which gave no depression with α-naphthylurethan of known neopentylcarbinol. The yield of this reduction product was thus 1%.

An addition of 0.65 mole of *t*-butylacetyl chloride to 1.5 moles of *t*-butylmagnesium chloride produced the secondary carbinol in 76% yield with no evidence for the formation of *t*-butylneopentylcarbinyl *t*-butylacetate.

Addition of *t*-Butylmagnesium Chloride to *t*-Butylacetyl Chloride.—To a solution of 128 g. (0.95 mole) of *t*-butylacetyl chloride in 1300 cc. of ether was added one mole of *t*-butylmagnesium chloride in a liter of ether over a period of thirty-six hours. The addition complex was decomposed with ice, extracted with ether, and the product fractionated, after removal of solvent, to give: 1, 2, 54.8 g., b. p. 33–110° (728 mm.), n^{20}D 1.3520–1.3640; 3–6, 7.8 g., 110–158°, 1.4042–1.4125; 7–9, 18.9 g., 158–161°, 1.4135–1.4150; 10–12, 75.4 g., 161°, 1.4158–1.4160; 13–14, 15.9 g., 161–164°, 1.4167–1.4175; residue, 39.2 g. Fractions 10–12 represent a 51% yield of *t*-butyl neopentyl ketone, which did not form a semicarbazone or oxime and yielded a 2,4-dinitrophenylhydrazone with great difficulty, m. p. 123.5–124.5°.

The residue of this fractionation was combined with that of a 0.5 mole run to give 6 fractions of pure *t*-butylneopentylcarbinyl *t*-butylacetate, wt. 33 g. (17% yield), b. p. 90° (5 mm.), n^{20}D 1.4320, d^{20}_4 0.8553. Molecular refraction; calcd. 77.74, found 77.73. *Anal.* Calcd. for $C_{16}H_{32}O_2$: C, 75.0; H, 12.5. Found: C, 75.6; H, 12.6.

Treatment of 19.8 g. of the pure ester with 12 g. of potassium hydroxide in 60 cc. of absolute methyl alcohol at reflux temperature for seventy-one hours gave no evidence of saponification. Treatment of 16.7 g. of the ester with 20 g. of potassium hydroxide in 125 cc. of 95% ethyl alcohol in a sealed tube at 90–100° for fifty-six hours likewise gave no evidence of saponification.

Preparation of *t*-Butylneopentylcarbinyl *t*-Butylacetate.—The addition of 53 g. (0.39 mole) of *t*-butylacetyl chloride to 55.3 g. (0.35 mole) of *t*-butylneopentylcarbinol, m. p. 50–51°, gave a slight evolution of heat. The reaction mixture was refluxed for two hours, cooled, washed with 10% sodium carbonate solution, dried with anhydrous potassium carbonate and fractionated to give: 1–5, 22.2 g., b. p. 30–94° (5–7 mm.), n^{20}D 1.4188–1.4260; 6–8, 16.5 g., 93° (7 mm.), 1.4312–1.4316; 9–12, 36.0 g., 93° (7 mm.), 1.4318–1.4320; 13, 5.7 g., 93° (7 mm.), 1.4311; residue, 1.6 g. Fractions 6–13 represent 65% yield of the ester. A density determination on fraction 10, n^{20}D 1.4320, indicated d^{20}_4 0.8549. Treatment of 10 g. of the synthetic ester with 20 g. of potassium hydroxide in 120 cc. of 95% ethyl alcohol gave no indication of saponification after refluxing the mixture for seventy-two hours.

Summary

1. A study has been made of the normal addition and reduction products formed by the addition of *t*-butylacetyl chloride to *t*-butylmagnesium chloride and of those formed by the reverse addition.

2. The synthesis and physical constants of *t*-butylneopentylcarbinyl *t*-butylacetate have been described.

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[CONTRIBUTION FROM THE METCALF CHEMICAL LABORATORY OF BROWN UNIVERSITY]

Photochemical Studies. XXVIII. The Photochemical Decomposition of Ethyl Methyl Ketone by Wave Lengths from 1850–2000 Å.

BY VICTOR R. ELLS AND W. ALBERT NOYES, JR.

Ethyl methyl ketone, in common with other ketones, absorbs in the near ultraviolet, the approximate limits being 2400 and 3200 Å. No discrete structure could be found in this region,[1] although fluorescence may be excited, at least by the 3130 Å. line of mercury. However, recent work[2] on the fluorescence of acetone has raised the question as to whether the ketones or some of their decomposition products are mainly responsible for the emission of fluorescent radiation.

The photochemical decomposition of ethyl methyl ketone in the near ultraviolet has been investigated by Norrish and Appleyard.[3] The products of the reaction were found to be carbon monoxide and approximately equal amounts of ethane, propane and butane, together with small amounts of ethylene and acetaldehyde. In the

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(1) Duncan, Ells and Noyes, THIS JOURNAL, **58**, 1454 (1936).

(2) Matheson and Noyes, *ibid.*, **60**, 1857 (1938).

(3) Norrish and Appleyard, *J. Chem. Soc.*, 874 (1934).