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

alpha-Bromo Secondary Alkyl Ketones. II. Reaction of 3-Bromo-3-methyl-2-butanone with Methylmagnesium Iodide[1]

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In the light of the previous work on 3-bromo-3-methyl-2-butanone[2] it seemed that the reaction of the Grignard reagent with this ketone would be of interest.

Tiffeneau[3] found that α-chloroacetophenone reacts with methylmagnesium bromide to yield methyl benzyl ketone. There is not much doubt that this product is the result of a rearrangement of the chlorhydrin formed by primary addition to the carbonyl groups.[4] A similar rearrangement is probably involved when α-chlorocyclohexanone reacts with Grignard reagents to yield alkyl cyclopentyl ketones.[5] The product of normal metathesis, an α-alkylcyclohexanone was also found.

When an α-bromo ketone is hindered the action of the Grignard reagent often results in the replacement of the halogen by hydrogen rather than addition to the carbonyl group.[6] This phenomenon has been exhaustively investigated for aromatic α-halo-ketones by Kohler and Tishler,[7] who discuss the earlier literature on this reaction. Umnowa[8] found that α-bromo-pentamethylacetone was converted to pentamethylacetone by methylmagnesium iodide.

The present work shows that 3-bromo-3-methyl-2-butanone gives only pentamethylethanol, when treated with methylmagnesium iodide. This product can result either by normal addition followed by normal replacement of halogen or by addition with rearrangement followed by addition of a second mole of methylmagnesium iodide to the resulting ketone.

The important fact is that addition to the carbonyl group is not hindered.

Experimental

Pentamethylethanol Hydrate from 3-Bromo-3-methyl-2-butanone.—A Grignard reagent was prepared in the usual manner from 2 moles of methyl iodide in one liter of commercial anhydrous ether. To this solution was added 0.75 mole of the bromo ketone over a period of five hours, the rate being such that only a slight refluxing of the ether occurred. The mixture was finally stirred for ten hours at room temperature. The complex was decomposed by pouring on ice and the ether layer decanted. The solid residue was dissolved in hydrochloric acid and the solution well extracted with ether. After washing with dilute sodium carbonate solution this ether was added to the main batch. The combined extracts were dried over anhydrous potassium carbonate and concentrated to a volume of 100 cc. by fractionation. The residue was distilled from a small flask to yield a mixture of pentamethylethanol and pentamethylethanol hydrate which boiled at 120–125°, 740 mm. This material was all converted to the hydrate by treatment with a small amount of cold water and filtration. The yield was 0.47 mole or 62%, of material melting at 82–83°. A mixed melting point with a sample, m. p. 82–83°, prepared from the product of the reaction of trimethylacetyl chloride and methylmagnesium chloride, was not depressed.

Summary

The action of methylmagnesium iodide on 3-bromo-3-methyl-2-butanone yields pentamethylethanol in 62% yield. The significance of this result is discussed.

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[1] From the doctorate thesis of R. B. Greenburg, The Pennsylvania State College, 1940.

[2] Aston and Greenburg, THIS JOURNAL, **62**, 2590 (1940).

[3] Tiffeneau, *Ann. chim.*, (8), **10**, 367 (1907).

[4] For a discussion of such rearrangements see: Cottle and Powell, THIS JOURNAL, **58**, 2267 (1936).

[5] Bouveault and Chereau, *Compt. rend.*, **142**, 1986 (1906).

[6] Fisher, Oakwood and Fuson, THIS JOURNAL, **52**, 5036 (1930).

[7] Kohler and Tishler, *ibid.*, **54**, 1594 (1932).

[8] Umnowa. *J. Russ. Phys.-Chem. Soc.*, **45**, 881 (1913); *Chem. Zentr.*, **84**, I, 1402 (1913).