[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF MICHIGAN]

THE FORMATION OF TRIPHENYLMETHYL IN THE ETHYL ACETO-ACETATE SYNTHESIS

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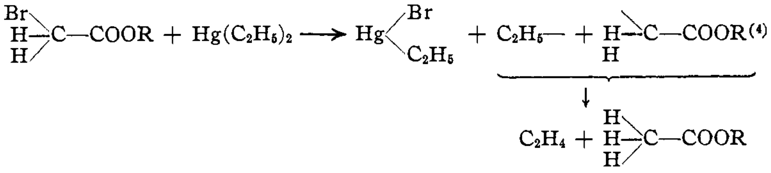
A number of years ago Allen and Kölliker[1] reported that triphenylbromomethane reacts with the mono-sodium derivative of ethyl aceto-acetate with the formation of a di-triphenylmethyl substitution product of ethyl aceto-acetate; it was claimed that the latter, upon hydrolysis, yielded the ethyl ether of triphenylcarbinol, an observation which could hardly be correct.

Recently we had occasion to investigate this reaction and found that triphenylbromomethane reacts with one equivalent of the mono-sodium derivative of ethyl aceto-acetate, suspended in ether, with the formation of an orange solution; upon contact with air this color disappears. We have shown that the color of the solution is due to the presence of triphenylmethyl, and this radical in the form of its peroxide was isolated and identified. The mono-triphenylmethyl substitution product of ethyl aceto-acetate was also formed as a reaction product, and upon hydrolysis yielded β,β,β-triphenylpropionic acid.

The formation of triphenylmethyl in this connection leads us to believe that in many other types of reactions too—reactions of organic halogen compounds with metals or metallic organic compounds, the reducing action of certain Grignard reagents on aldehydes or ketones—the formation of unsaturated hydrocarbons may probably be attributed to the initial formation of alkylmethyls which are then spontaneously oxidized through loss of hydrogen.

$$2\ C_2H_5\boxed{Na + Hg} \longrightarrow 2\ C_2H_5^- \longrightarrow C_2H_4 + C_2H_6\,^{(2)}$$

$$C_2H_5\boxed{Br + Br{-}Mg}{-}C_2H_5 \longrightarrow C_2H_4 + C_2H_6\,^{(3)}$$



At any rate, such a behavior of aliphatic trivalent carbon radicals, together with their ability to undergo polymerization and addition reactions, would be consistent with their nature as far as we are able to predict this from a study of trivalent carbon in the triarylmethyls.

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[1] Allen and Kölliker, *Ann.*, **227**, 107 (1885).

[2] Buckton, *Ann.*, **112**, 220 (1859). Schorigin, *Ber.*, **43**, 1931 (1910).

[3] Späth, *Monatsh.*, **34**, 1976 (1913).

[4] Sell and Lippman, *J. prakt. Chem.*, **99**, 431 (1866).

Reaction between Triphenylbromomethane and the Sodium Derivative of Ethyl Aceto-acetate.—Sixty cc. of absolute ether and 8.1 g. of freshly distilled ethyl aceto-acetate were poured into a flask fitted with a reflux condenser and a soda-lime tube; 1.4 g. (1 equivalent) of sodium, in the form of thin slabs, was then added. When the evolution of hydrogen had become very slow the protective crust was removed from the surface of the metal by means of a stirring rod. After all of the sodium had reacted the flask was filled with dry nitrogen. A solution of 20.2 g. (1 equivalent) of triphenylbromomethane in 70 cc. of warm benzene was then added to the mixture. Reaction began almost immediately, heat was evolved and the solvent gradually became a deep orange. The mixture was shaken frequently and after 24 hours as much as possible of the clear liquid was removed from the sodium bromide with the aid of a pipet and allowed to flow into an evaporating dish. The sodium bromide residue was washed with ether a number of times and then filtered. The amount of sodium bromide formed (5.9 g.; calcd., 6.0 g.) showed that the materials had reacted practically quantitatively. In a short time the orange-red color of the solution in the evaporating dish had changed to a pale yellow. After the solvent had evaporated an oily product remained. The latter (22 g.), from which we were not able to obtain a crystalline product, was dissolved in 50 cc. of alcohol and after the addition of 11 g. of sodium hydroxide, dissolved in a small amount of water, was heated for three hours on a steam-bath. The alcohol was removed, the residue diluted with water and cooled with ice. The resulting crystalline, alkali-insoluble material (1.5 g.) was filtered. The filtrate was extracted with ether several times to remove suspended matter and the aqueous layer then separated. Air was blown into the latter to remove dissolved ether, and the clear alkaline solution cooled with ice and acidified with hydrochloric acid. The gummy precipitate which formed was placed in a beaker under a small amount of glacial acetic acid. After some time the material, most of which had become granular, was placed on a porous plate; yield, 7 g. After recrystallization from a mixture of water and acetic acid and finally from glacial acetic acid the material melted at 177–178°. This melting point is given by Henderson[5] for β,β,β-triphenylpropionic acid; he prepared this substance from sodium malonic ester and triphenylbromomethane with subsequent hydrolysis of the resulting product.

The crystalline, alkali-insoluble material mentioned above was treated with 15 cc. of hot acetic acid and quickly filtered. The crystalline residue was dried and then recrystallized twice from xylene. The latter operation must be carried out quickly since triphenylmethyl peroxide decomposes in boiling xylene.[6] The material melted at 185–186° and the melting point was not lowered when the substance was mixed with peroxide prepared from triphenylchloromethane, silver and air.

Summary

Triphenylbromomethane reacts with the monosodium derivative of ethyl aceto-acetate with the formation of triphenylmethyl. In addition, there was obtained β,β,β-triphenylpropionic acid, formed by subsequent hydrolysis of the mono-triphenylmethyl substitution product of ethyl aceto-acetate.

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[5] Henderson, *J. Chem. Soc.*, **51,** 226 (1887).

[6] Wieland, *Ber.*, **44,** 2550 (1911).