from the dye itself, since the order of magnitude of the concentration of formaldehyde is extremely small, without exception, and can be controlled at will by varying the experimental conditions, particularly of hydrogen-ion concentration.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF IOWA STATE COLLEGE]

THE REACTION BETWEEN CINNAMYL CHLORIDE, MAGNESIUM AND CARBON DIOXIDE

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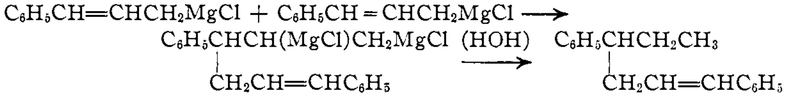
RECEIVED APRIL 16, 1927 PUBLISHED JULY 5, 1927

Introduction

In several quantitative studies, it has been proved that a few typical organomagnesium halides do not add to a wide variety of ethylenic and acetylenic hydrocarbons. Gilman and Crawford[1] used ethylmagnesium iodide with 11 ethylenic hydrocarbons; Gilman and Shumaker[2] used ethylmagnesium bromide and iodide with four acetylenic compounds; and Gilman and Peterson[3] used ethylmagnesium bromide, phenylmagnesium bromide, butoxymagnesium iodide, *p*-tolylmercaptomagnesium iodide, methylaniline-magnesium bromide and ethylzinc iodide with 18 variously substituted ethylenic compounds.

A recent book[4] and review[5] of the chemistry of organomagnesium halides direct attention to the work of Rupe and Bürgin[6] who have presumably proved that cinnamylmagnesium chloride (and bromide) adds to the ethylenic linkage of the cinnamyl group. They postulate the following reactions.



$$C_6H_5CH{=}CHCH_2MgCl + C_6H_5CH{=}CHCH_2MgCl \longrightarrow \underset{\displaystyle CH_2CH{=}CHC_6H_5}{C_6H_5CHCH(MgCl)CH_2MgCl} \xrightarrow{(HOH)} \underset{\displaystyle CH_2CH{=}CHC_6H_5}{C_6H_5CHCH_2CH_3}$$

(1)

In support of the hydrocarbon (1,4-diphenyl-hexene-1) obtained by the addition of one molecule of cinnamylmagnesium chloride to the ethylenic linkage of another like molecule, they obtained phenylsuccinic and benzoic acids among the products of oxidation of their hydrocarbon. They were unsuccessful in their attempts to effect a reaction between the cinnamylmagnesium chloride (or bromide) and aldehydes or ketones.

The hydrocarbon which they obtained in limited amounts after eight

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[1] Gilman and Crawford, THIS JOURNAL, **45**, 554 (1923).

[2] Gilman and Shumaker, *ibid.*, **47**, 514 (1925).

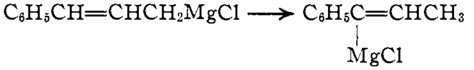
[3] Gilman and Peterson, *ibid.*, **48**, 423 (1926).

[4] Courtot, "Le Magnesium en Chimie organique," pp. 54, 318. Published by the author at Nancy, **1926**.

[5] Grignard, *Bull. soc. chim.*, **39**, 1285 (1926).

[6] Rupe and Bürgin, *Ber.*, **43**, 172 (1910).

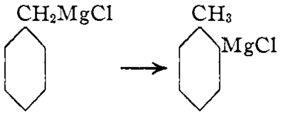
fractional distillations has not as yet been identified by us. However, their mechanism of reaction is probably incorrect. A Grignard reagent is formed when cinnamyl chloride reacts with magnesium in ether. This RMgX compound is not the cinnamylmagnesium chloride which they postulate in the explanation of the ethylenic hydrocarbon. Instead, it is an RMgX compound formed by the rearrangement of the cinnamylmagnesium chloride.



$$C_6H_5CH{=}CHCH_2MgCl \longrightarrow \underset{\displaystyle MgCl}{C_6H_5\overset{}{C}}{=}CHCH_3 \qquad (2)$$

Evidence for the correctness of the RMgX compound formed by rearrangement is the production of methyl atropic acid, $C_6H_5C({=}CHCH_3)$-COOH, when cinnamyl chloride and carbon dioxide are added to magnesium under ether.

Rearrangements of this type have previously been noted by others with related Grignard reagents. For example, benzylmagnesium chloride[7] with formaldehyde gives *o*-tolylcarbinol and not *β*-phenylethyl alcohol. Here we have a comparable rearrangement, where the —MgCl group may be assumed to have gone from an alpha to a gamma carbon atom.



(3)

So far as known, carbon dioxide has not given such rearrangement reactions with benzylmagnesium chloride and triphenylmethylmagnesium chloride. The reagents that generally induce such rearrangement are formaldehyde and benzaldehyde. Some unpublished work with J. E. Kirby on the mechanism of these rearrangements shows that ethyl chlorocarbonate gives the *ortho* product of rearrangement with benzylmagnesium chloride (namely, ethyl *o*-toluate), and that *α*-naphthylmethylmagnesium chloride gives abnormal products with both formaldehyde and ethyl chlorocarbonate.

Experimental Part

The cinnamyl chloride was prepared in 78% yield according to Rupe and Bürgin.[6] It was used in preference to the bromide, because such chlorides give a higher yield of RMgX compound than do the corresponding bromides.[8] One-half of the magnesium they used was activated

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[7] Schmidlin and Garcia-Banùs, *Ber.*, **45**, 3193 (1912). In this article mention is also made of the rearrangement of triphenylmethylmagnesium chloride. References are given to the earlier work on both benzylmagnesium chloride and triphenylmethylmagnesium chloride.

[8] Gilman and McCracken, THIS JOURNAL, **45**, 2462 (1923). Gilman and Kirby, *ibid.*, **48**, 1733 (1926).

according to the method of Baeyer.[9] In our first experiments, the reaction was started with a very small amount of the highly active magnesium-copper alloy of Gilman, Peterson and Schulze.[10] Later, however, it was found that the reaction started comparatively easily by the usual addition of a crystal of iodine, accompanied by moderate heating.

When allowed to proceed at room temperature, the reaction is quite vigorous and a positive color test for Grignard reagent was obtained by the use of Michler's ketone as described by Gilman and Schulze.[11] However, when the reaction mixture is heated prior to removing the small sample for a color test, no Grignard reagent is present. Accordingly, in subsequent runs, the reaction mixture was cooled moderately, and a stream of carbon dioxide was bubbled through the ether simultaneously with the addition of cinnamyl chloride. Because the reaction slowed down too decidedly when the cooling was effected by an ice-water bath, the cooling medium selected was running tap water.

Under these conditions, 3.7 g. or an 11.4% yield of an acid melting at 135–136° was obtained from 30.5 g. or 0.2 mole of cinnamyl chloride. In another 0.2-mole run the volume of ether was increased from 100 cc. to 500 cc., the reaction having been started with several cc. of cinnamyl chloride in 50 cc. of ether before bubbling in carbon dioxide at about 20°. The yield of acid from this run was 8.8 g., or 27.1%.

In this second run the acid was obtained as an oil. Believing that it might be a labile form of phenyl isocrotonic acid, $C_6H_5CH{=}CHCH_2\text{-}COOH$ (the normal reaction product if the RMgX compound was truly the cinnamylmagnesium chloride postulated by Rupe and Bürgin), part of it was boiled gently in a test-tube to get α-naphthol. On cooling, a solid acid was obtained identical (by mixed melting point) with that described above; m. p., 135–136°. This acid was identified as methyl atropic acid by a mixed-melting-point determination with an authentic specimen prepared according to directions of Oglialoro[12] from sodium phenylacetate, paraldehyde and acetic anhydride. Its neutralization equivalent was 161 (calcd., 162). The oil may be a stereoisomer of the 135–136° solid.

In another run, the Grignard reagent was started with iodine and

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[9] Baeyer, *Ber.*, **38**, 2759 (1905).

[10] A preliminary account of this and other means of activation was given in a paper presented at the Philadelphia meeting of the American Chemical Society, September 7, 1926. Mention of the alloy is contained in a recent paper by Hurd and Webb, THIS JOURNAL, **49**, 546 (1927).

Bars or ingots of the 12.75% copper-magnesium alloy may be purchased from the American Magnesium Corporation at Niagara Falls, New York. The powdered alloy of 200 mesh is sold by the Eastman Kodak Co., Rochester, New York.

[11] Gilman and Schulze, *ibid.*, **47**, 2002 (1925).

[12] Oglialoro, *Gazz. chim. ital.*, **15**, 514 (1885). Rupe, *Ann.*, **369**, 322 (1909).

moderate warming in the presence of a carbon dioxide atmosphere. The reaction was allowed to proceed at the boiling point of ether (due to the heat of reaction) and from a 0.2-mole run there was obtained 6.5 g., or a 20% yield of methyl atropic acid. There is then a restricted optimal temperature range, below which the reaction is virtually stopped, and above which the yield of acid drops.

Summary

Methyl atropic acid is obtained when cinnamyl chloride and carbon dioxide are added to magnesium in ether. The formation of this acid probably is due to the rearrangement of cinnamylmagnesium chloride.

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[Contribution from the Chemical Laboratory of the University of Illinois]

SOME BROMINE DERIVATIVES OF PENTANOIC AND HEXANOIC ACIDS

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Received April 16, 1927 Published July 5, 1927

The ω-halogen derivatives of pentanoic and hexanoic acids are of some interest in connection with the preparation of compounds related to ornithine and lysine. Several methods of synthesis are already available but they are not entirely satisfactory in all details.

5-Bromopentanoic acid has been prepared by Cloves[1] by heating 5-phenoxypentanoic acid with concd. hydrobromic acid in a sealed tube at 145°. The 5-phenoxypentanoic acid is best prepared by Gabriel's method[2] from diethyl phenoxypropylmalonate. This ester has been described in several papers[2,3] and the yields are said to be about 55% when γ-chloropropylphenyl ether is condensed with the sodium derivative of malonic ester.

All of these reactions have been reinvestigated and the methods and yields have been improved. Thus, in the preparation of diethyl phenoxypropylmalonate, the use of γ-bromopropylphenyl ether in place of the chloro compound has increased the yield of the ester to about 70–80%. The 5-phenoxypentanoic acid has been reacted with 48% hydrobromic acid without the use of sealed tubes to give better than 60% of the calculated amount of 5-bromopentanoic acid. A more direct preparation of this bromo acid was developed, in which the diethyl phenoxypropylmalonate was treated directly with 48% hydrobromic acid. The yield based on the ester is 65–69%.

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[1] Cloves, *Ann.*, **319**, 367 (1901).

[2] Gabriel, *Ber.*, **25**, 418 (1892).

[3] (a) Funk, *Ber.*, **26**, 2569 (1893). (b) Granger, *Ber.*, **28**, 1199 (1895). (c) Günther, *Ber.*, **31**, 2136 (1898).