[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF IOWA STATE COLLEGE]

THE FORMATION OF 1,4-DIPHENYLHEXADIENE-1,5 IN THE REACTION BETWEEN CINNAMYL CHLORIDE AND MAGNESIUM

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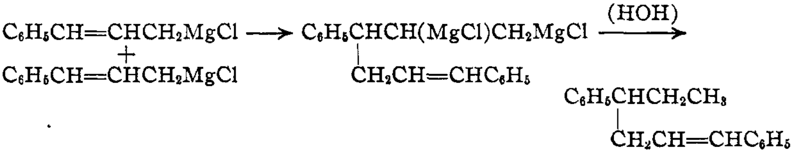
Introduction

Two hydrocarbons have been isolated in the unusual reaction between cinnamyl chloride and magnesium.[1] One of these has been identified definitely as the solid dicinnamyl, $C_6H_5CH{=}CHCH_2CH_2CH{=}CHC_6H_5$. The other hydrocarbon, a liquid, has been designated as 1,4-diphenylhexene-1 and is said to owe its origin to the following reactions

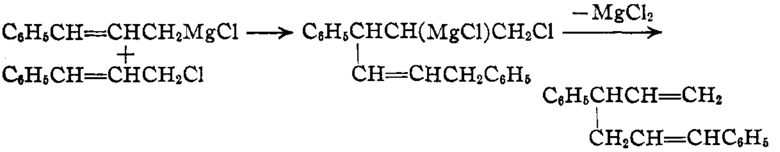


$$\begin{array}{l} C_6H_5CH{=}CHCH_2MgCl \\ \quad + \\ C_6H_5CH{=}CHCH_2MgCl \end{array} \longrightarrow \begin{array}{l} C_6H_5CHCH(MgCl)CH_2MgCl \\ \quad | \\ CH_2CH{=}CHC_6H_5 \end{array} \xrightarrow{(HOH)} \begin{array}{l} C_6H_5CHCH_2CH_3 \\ \quad | \\ CH_2CH{=}CHC_6H_5 \end{array} \qquad (I)$$

(A)

That is, Compound (A) is formed as a consequence of the addition of one molecule of the so-called cinnamylmagnesium chloride to the ethylenic linkage of another molecule of this Grignard reagent. The evidence in support of (A) turns on its ultimate analysis and its oxidation to phenylsuccinic and benzoic acids.

It has also been suggested[2] that the liquid hydrocarbon might be a diolefin formed as follows



$$\begin{array}{l} C_6H_5CH{=}CHCH_2MgCl \\ \quad + \\ C_6H_5CH{=}CHCH_2Cl \end{array} \longrightarrow \begin{array}{l} C_6H_5CHCH(MgCl)CH_2Cl \\ \quad | \\ CH{=}CHCH_2C_6H_5 \end{array} \xrightarrow{-MgCl_2} \begin{array}{l} C_6H_5CHCH{=}CH_2 \\ \quad | \\ CH_2CH{=}CHC_6H_5 \end{array} \qquad (II)$$

(B)

In this mechanism, one molecule of the RMgCl compound adds to the ethylenic linkage of a molecule of cinnamyl chloride to give a new Grignard reagent which then loses magnesium chloride.

Each of these mechanisms suffers from the disadvantage that it postulates addition of a Grignard reagent to an ethylenic linkage. No such addition has been established, and present evidence is overwhelmingly against it.[3] We have shown that the liquid hydrocarbon is Compound

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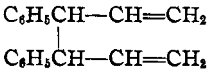
[1] Rupe and Bürgin, *Ber.*, **43**, 172 (1910).

[2] V. Braun and Köhler, *ibid.*, **51**, 79 (1918).

[3] A recent article with leading references on the non-addition of RMgX compounds to an ethylenic linkage is Gilman and Harris, *Rec. trav. chim.*, **49**, 762 (1930). It should be stated that the postulation of such addition was made at a time when there appeared

(B), 1,4-diphenylhexadiene-1,5. This was demonstrated: first, by ultimate analysis, the values for carbon and hydrogen agreeing better for Compound (B) than for (A); second, by catalytic reduction whereby exactly two moles of hydrogen were taken up; third, by ozonization that gave formaldehyde and benzaldehyde, which together with the phenylsuccinic acid obtained previously[1] by permanganate oxidation, definitely supports (B) and makes (A) altogether unlikely because it would hardly be expected to give any formaldehyde, and phenylsuccinic acid is rather to be expected with (B) than (A); and, fourth, by definitely establishing the identity of the reduction product with an authentic specimen of 1,4-diphenylhexane.

The evidence based on reduction to 1,4-diphenylhexane obviously supports both (A) and (B). It has been presented, however, in order to exclude a third possible compound, namely, 3,4-diphenylhexadiene-1,5.



$$\begin{array}{l} C_6H_5CH-CH=CH_2 \\ \quad\;\;| \\ C_6H_5CH-CH=CH_2 \end{array} \qquad (C)$$

Actually, Compound (C) has been suggested[4] tentatively as a structure for the oil obtained in related reactions between cinnamyl bromide and ethylmagnesium bromide and phenylmagnesium bromide, respectively. Were it not for the facts that Compound (C) does not agree with the reduction and oxidation products of the liquid hydrocarbon, it might be considered a possibility for the following reasons.

First, it appears altogether probable that the first step involved in a reaction between an RX compound and magnesium in ether is the formation of a free radical which can undergo several reactions, among which are coupling to give an R·R compound, rearrangement to a different free radical and disproportionation.[5] Second, the R·R compound can be formed as follows, also through the intermediate free radicals.[5]

$$2\,RX + 2R'MgX \longrightarrow R{\cdot}R + R'{\cdot}R' + MgX_2 \qquad (III)$$

$$RX + RMgX \longrightarrow R{\cdot}R + MgX_2 \qquad (IV)$$

Third, the reaction between cinnamyl chloride and magnesium gives a

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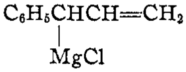
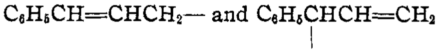
to be some basis for such reaction, and that Professor Rupe is now of the opinion that a Grignard reagent does not add to an ethylenic linkage. See, in this connection, Gilman and Schulz, THIS JOURNAL, **53**, 2799 (1931).

[4] Prévost and Danjat, *Bull. soc. chim.*, **47**, 588 (1930). See, also, Kirrmann, *ibid.*, **47**, 834 (1930). V. Braun and Köhler, *Ber.*, **51**, 83 (1918), earlier studied the reaction between cinnamyl bromide and ethyl- and phenylmagnesium halides.

In a paper by Prévost, *Bull. soc. chim.* **49**, 1372 (1931) [*C. A.* **26**, 1574 (1932)], which became available after our manuscript was submitted for publication, it has been shown that the second hydrocarbon is 1,4-diphenylhexadiene-1,5.

[5] A recent article with leading references is Gilman and Zoellner, THIS JOURNAL, **52**, 3984 (1930).

Grignard reagent which reacts[6] with a wide variety of compounds as though its formula were  $\underset{\text{MgCl}}{C_6H_5\overset{}{C}HCH{=}CH_2}$ and not $C_6H_5CH{=}CHCH_2MgCl$. For these reasons, the two radicals expected in a reaction between cinnamyl chloride and magnesium are



$$C_6H_5CH{=}CHCH_2\text{—} \text{ and } C_6H_5\underset{|}{C}HCH{=}CH_2$$

The union of two of the former (cinnamyl) radicals would give dicinnamyl; the union of two of the latter (α-phenylallyl) radicals would give Compound (C), 3,4-diphenylhexadiene-1,5; and the union of one of each of these radicals would give Compound (B), 1,4-diphenylhexadiene-1,5.

We thus see that there is no basis of expectation, on theoretical grounds, for Compound (A), 1,4-diphenylhexene-1. Compound (C) may be contained in the oily mixture of hydrocarbons which has so far definitely yielded dicinnamyl and 1,4-diphenylhexadiene-1,5 (B). The proportions of R·R compounds in such reactions varies with experimental conditions and with the nature of halogen in the RX compound. For example, with cinnamyl bromide and magnesium the chief hydrocarbon is dicinnamyl[2] and not, as with cinnamyl chloride, 1,4-diphenylhexadiene-1,5.

Experimental Part

Preparation of Hydrocarbon Mixture.—In a typical experiment, 60.8 g. (0.4 mole) of cinnamyl chloride (melting at 7–8°) dissolved in 100 cc. of ether, was added to 5 g. (0.205 atom) of magnesium, the reaction being first started with a small quantity of ether. At the end of the reaction, there was a slight positive color test[7] showing the presence of a small quantity of Grignard reagent.[8] This was destroyed by the addition of 2 cc. of cinnamyl chloride. The solution was then hydrolyzed, and the ether layer dried over calcium chloride and then distilled. On the first distillation, a total yield of 34.9 g. or 74.5% of hydrocarbons was obtained, boiling over the range 165–180° (3–4 mm.). The last portion of the distillate crystallized in the receiver, and was identified as dicinnamyl. After five fractionations, 20 g. or a 42.9% yield of hydrocarbon, distilling at 157–160° (2 mm.), was obtained: n_D^{20} 1.5890; d_{20}^{20} 0.9919. The higher fraction yielded 4.1 g. or 8.75% of dicinnamyl. An intermediate fraction was not investigated.

Anal. Calcd. for $C_{18}H_{18}$: C, 92.26; H, 7.74. Found: C, 92.08; H, 7.95.

Catalytic Reduction of Liquid Hydrocarbon.—The reduction of 11.7 g. (0.05 mole) of hydrocarbon in 50 cc. of alcohol was effected with 0.15 g. of Adams' catalyst. In ten minutes, 7.6 pounds (0.1 mole) of hydrogen was absorbed, showing the presence of two ethylenic linkages. Like results were obtained with 0.025 mole of the hydrocarbon.

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[6] Gilman and Harris, This Journal, **49**, 1825 (1927); *ibid.*, **53**, 3541 (1931). This latter reference and that of Gilman and Kirby, *ibid.*, **54**, 345 (1932), describe several mechanisms proposed for the allylic rearrangements of Grignard reagents like cinnamylmagnesium chloride. See, also, Austin and Johnson, *ibid.*, **54**, 647 (1932).

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

[8] Cinnamylmagnesium chloride can be prepared in an 87% yield. See Gilman and Harris, *Rec. trav. chim.*, **50**, 1052 (1931).

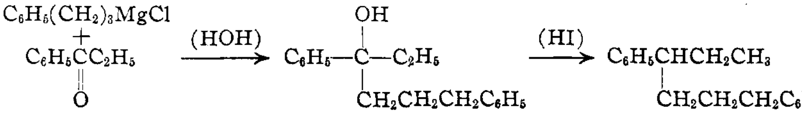
The product, subsequently identified as 1,4-diphenylhexane, boiled at 147–148° (3 mm.); n^{20}_{D} 1.5456; d^{20}_{20} 0.9608.

Anal. Calcd. for $C_{18}H_{22}$: C, 90.75; H, 9.24. Found: C, 90.4; H, 9.16.

Dicinnamyl likewise took up the theoretical quantity of hydrogen.

Ozonization of Liquid Hydrocarbon.—Ozonization, by the procedure of Doeuvre,[9] gave formaldehyde and benzaldehyde. Under the same conditions, dicinnamyl yielded benzaldehyde but no formaldehyde.

Synthesis of 1,4-Diphenylhexane.—The following transformations were used in the preparation of 1,4-diphenylhexane.



$$C_6H_5(CH_2)_3MgCl + C_6H_5\underset{\overset{\|}{O}}{C}C_2H_5 \xrightarrow{(HOH)} C_6H_5-\overset{OH}{\underset{CH_2CH_2CH_2C_6H_5}{C}}-C_2H_5 \xrightarrow{(HI)} C_6H_5\underset{CH_2CH_2CH_2C_6H_5}{C}HCH_2CH_3$$

The γ-phenylpropyl chloride was obtained in an 82% yield by heating an ether solution of 80 g. (0.59 mole) of γ-phenylpropyl alcohol with 75 g. (0.63 mole) of thionyl chloride for one hour. The corresponding Grignard reagent, γ-phenylpropylmagnesium chloride, was obtained in a 98% yield[10] in a 0.5 mole run, the reaction being started with activated magnesium–copper alloy. When treated in a customary manner with propiophenone, the Grignard product yielded 81.5 g. or a 64% yield of 1,4-diphenylhexanol-4; b. p. 177–179°; n^{20}_{D} 1.5508; d^{20}_{20} 1.0284.

Anal. Calcd. for $C_{18}H_{22}O$: C, 85.04; H, 8.66. Found: C, 84.96; H, 8.69.

Twelve and one-half grams of the carbinol was heated in a pressure bottle with 25 cc. of constant boiling hydriodic acid and some red phosphorus for two hours at 140–150°. The synthetic 1,4-diphenylhexane obtained in this manner had the following constants: b. p. 147–149° (3–4 mm.); n^{20}_{D} 1.5460; d^{20}_{20} 9660.

Anal. Calcd. for $C_{18}H_{22}$: C, 90.75; H, 9.24. Found: C, 90.57; H, 9.19.

Summary

The liquid hydrocarbon formed from cinnamyl chloride and magnesium in ether has been shown to be 1,4-diphenylhexadiene-1,5 and not 1,4-diphenylhexene-1, as previously reported. Mechanisms have been proposed for its formation.

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[9] Doeuvre, *Bull. soc. chim.*, **45**, 140 (1929).

[10] By the acid-titration method of Gilman, Wilkinson, Fishel and Meyers, THIS JOURNAL, **45**, 150 (1923). See, also, Gilman, Zoellner and Dickey, *ibid.*, **51**, 1576 (1929).