

5. Nitrous acid and O-methylhydroxylamine were found to react to give nitrous oxide and methyl alcohol. The mechanism of the reaction has been discussed.

6. The action of hypochlorous acid on O,N-dialkylhydroxylamines has been found to give either an O-alkyl-ald- or ketoxime depending on the structure of the substituted hydroxylamine.

7. Diethyl ketone *p*-nitrophenylhydrazone and the ester of diethylcarbinol with 3,5-dinitrobenzoic acid have been prepared in order to identify the products of hydrolysis of O-methyldiethylketoxime and O-methyl-N-amyl-3-nitrosohydroxylamine, respectively.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF IOWA STATE COLLEGE]

## ALLYLIC REARRANGEMENT IN THE REACTION BETWEEN CINNAMYL CHLORIDE AND MAGNESIUM

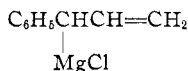
BY HENRY GILMAN AND STANTON A. HARRIS

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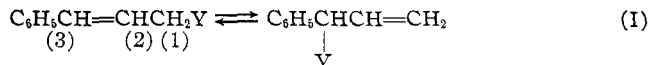
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### Introduction

If ozone is a reliable reagent for the determination of the constitution of unsaturated compounds, then there is no doubt concerning the structure of cinnamyl bromide and chloride,  $C_6H_5CH=CHCH_2Cl$ .<sup>1</sup> In its reaction with magnesium and ether, cinnamyl chloride might be expected to give cinnamylmagnesium chloride,  $C_6H_5CH=CHCH_2MgCl$ . However, the products obtained from the so-called cinnamylmagnesium chloride appear to be derived from an  $RMgCl$  compound having the formula



This transformation is another illustration of the following general interchange



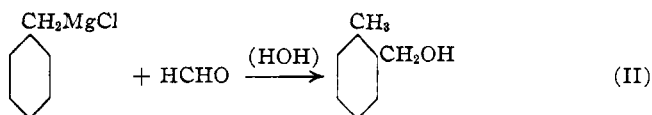
modifications of which have been variously designated as an allylic rearrangement, three-carbon anionotropic system, mobile anion tautomerism, "synionie," etc.<sup>2</sup> The mechanism or mechanisms proposed for the rearrangement of systems like that indicated in Reaction I are various, and at present there is no general agreement. Actually, the transforma-

<sup>1</sup> Burton and Ingold, *J. Chem. Soc.*, 904 (1928). See also, Verley, *Bull. soc. chim.*, 43, 854 (1928), and Doeuvre, *ibid.*, 45, 140 (1929).

<sup>2</sup> Some recent references are Hurd and Cohen, *THIS JOURNAL*, 53, 1917 (1931); Prévost, *Bull. soc. chim.*, 49, 261 (1931); Prévost and Daujat, *ibid.*, 47, 588 (1930); Kirrmann, *ibid.*, 47, 834 (1930); Meisenheimer and Link, *Ann.*, 479, 211 (1930); Burton, *J. Chem. Soc.*, 455 (1929); Burton and Ingold, *ibid.*, 904 (1928).

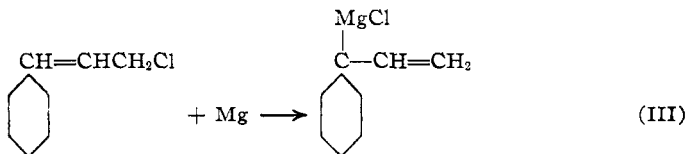
tions have been explained in a way that does not admit of rearrangement, as commonly applied, of either the initial or ultimate products.<sup>3</sup>

This transformation is novel to organomagnesium halides, primarily because of the hitherto<sup>4</sup> uncommon difficulty of preparing such Grignard reagents in satisfactory yields. Another type of rearrangement, involving nuclear introduction of a substituent, is simply illustrated in the following reaction



In this reaction there are obtained not only the normal and expected  $\beta$ -phenylethyl alcohol,  $\text{C}_6\text{H}_5\text{CH}_2\text{CH}_2\text{OH}$ , but also *o*-tolylcarbinol. This nuclear substitution, which is restricted to a limited number of reactants among which are formaldehyde, benzaldehyde and ethyl chlorocarbonate, is shown by  $\text{RMgX}$  compounds having an aryl nucleus attached to the carbon holding the  $-\text{MgX}$  group. The types so far investigated are related to benzylmagnesium halide and are: benzohydrylmagnesium chloride,  $(\text{C}_6\text{H}_5)_2\text{CHMgCl}$ ,<sup>5</sup> triphenylmethylmagnesium chloride,  $(\text{C}_6\text{H}_5)_3\text{CMgCl}$ ,<sup>6</sup> and  $\alpha$ -naphthylmagnesium chloride;  $\alpha$ - $\text{C}_{10}\text{H}_7\text{CH}_2\text{MgCl}$ .<sup>7</sup>

With such systems as benzylmagnesium chloride, there is a modified allylic type in the sense that the group (here  $-\text{MgCl}$ ) is attached to a carbon atom which in turn is connected with an olefinic or olefinic-like group. In accordance with such a three-carbon system, a correlation is understandable with an allylic rearrangement where an element or group on carbon atom (1) suffers rearrangement or replacement to give a product with the element or group on carbon atom (3). On such a basis some have expected the (cinnamyl chloride + magnesium + reactant) reactions to undergo a sort of double allylic rearrangement, as follows



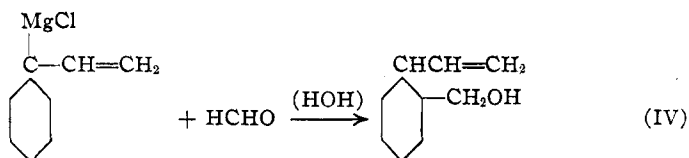
<sup>3</sup> Meisenheimer and Link, *Ann.*, **479**, 211 (1930); Meisenheimer, *ibid.*, **456**, 126 (1927).

<sup>4</sup> It is possible to prepare the so-called cinnamylmagnesium chloride in 87% yield by the use of special conditions described by Gilman and Harris, *Rec. trav. chim.*, **50** (1931). See, also, Gilman and McGlumphy, *Bull. soc. chim.*, **43**, 1322 (1928), for the direct preparation of the related allylmagnesium bromide in excellent yields.

<sup>5</sup> Unpublished observations.

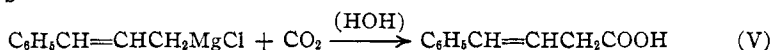
<sup>6</sup> Schmidlin and Garcia-Banús, *Ber.*, **45**, 3193 (1912); Garcia-Banús, *Anales soc. españ. fis. quím.*, **26**, 372 (1928); [*C. A.* **23**, 2178 (1929)].

<sup>7</sup> Gilman and Kirby, *THIS JOURNAL*, **51**, 3475 (1929).

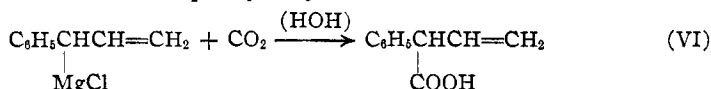


However, the product obtained from formaldehyde and the Grignard reagent from cinnamyl chloride did not give on oxidation any phthalic acid, which is an expected and realized oxidation product of the reaction mixture from benzylmagnesium chloride and formaldehyde.

When the Grignard reagent from cinnamyl chloride is carbonated, no phenylisocrotonic acid is obtained, although this might have been expected if the reaction proceeded normally with cinnamylmagnesium chloride as follows



Instead, the initial acid is phenylvinylacetic acid



and this  $\beta,\gamma$ -unsaturated acid rearranges under a variety of conditions to the higher melting, isomeric  $\alpha,\beta$ -unsaturated acid, methylatropic acid,  $\text{C}_6\text{H}_5\text{C}=\text{CHCH}_3$ . The Grignard reagent with phenyl isocyanate gives the

anilide of phenylvinylacetic acid. Derivatives from carbon dioxide and isocyanates have been used very extensively for the characterization of  $\text{RMgX}$  compounds. The Experimental Part contains a description of some other reactions.

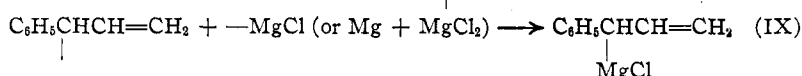
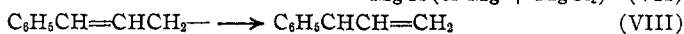
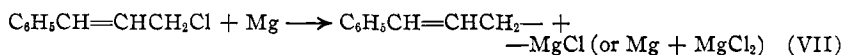
In general, it appears that  $\alpha$ -phenylallyl types,  $\text{C}_6\text{H}_5\text{CHCH}=\text{CH}_2$ , are formed from the cinnamyl chloride Grignard reagent and all reactants, or, in any event, from a greater variety of reactants than give rise to the nuclear substitutions observed with benzylmagnesium chloride types. This is hardly incontrovertible evidence in all cases for an  $\alpha$ -phenylallylmagnesium chloride structure,  $\text{C}_6\text{H}_5\text{CHCH}=\text{CH}_2$ . We might have in-

itially a cinnamylmagnesium chloride,  $\text{C}_6\text{H}_5\text{CH}=\text{CHCH}_2\text{MgCl}$ , some of whose reaction products might, under the experimental conditions, rearrange to  $\alpha$ -phenylallyl derivatives. One way of throwing some light on this question would be to reduce catalytically the Grignard reagent and then carbonate the product. If no rearrangement occurred under such mild conditions, and this may appear to be an unwarranted assumption<sup>8</sup>

<sup>8</sup> However, catalytic reduction is known not to involve the  $-\text{MgX}$  grouping in  $\text{RMgX}$  compounds, with the exception of the dissociated triphenylmethylmagnesium chloride.

in view of the general tendency for rearrangement, then  $\alpha$ -phenylbutyric acid would result if the  $\text{RMgX}$  compound were  $\alpha$ -phenylallylmagnesium chloride, and  $\gamma$ -phenylbutyric acid would be the product if the Grignard reagent were cinnamylmagnesium chloride. Unfortunately, however, it is at present impossible to reduce catalytically the olefinic linkage in unsaturated  $\text{RMgX}$  compounds like the one under consideration and styrylmagnesium bromide,  $\text{C}_6\text{H}_5\text{CH}=\text{CHMgBr}$ .

A current interpretation<sup>9</sup> involving the prior formation of free radicals in the preparation of  $\text{RMgX}$  compounds may account for the products obtained from cinnamyl chloride and magnesium



Reaction (VIII) will probably not maintain with all allyl types, inasmuch as the nature of the radical (with a free valence on carbon (1) or (3)) will be influenced, among other factors, by the so-called negativity of the attached group. With a group like phenyl, the free valence is largely (if not exclusively) on carbon (3); with a very weakly negative group, the free valence would probably be on carbon (1) and so give rise to "normal" products; and with groups of intermediate polarity a mixture of the two free radicals, and therefore of the two  $\text{RMgX}$  compounds, might be expected.<sup>2,9</sup> Such an interpretation is in harmony with other reactions like the ease of preparing cinnamyl halides, and the difficulty of obtaining the isomeric  $\text{C}_6\text{H}_5\text{CH(X)CH}=\text{CH}_2$  compounds.

### Experimental Part

**Carbonation of Grignard Reagent.**—The carbonation of the  $\text{RMgCl}$  compound which is now obtainable in high yields<sup>4</sup> gave a liquid acid which when dissolved in a small quantity of petroleum ether (b. p. 40–60°) and cooled to –10° deposited a heavy mass of crystals melting at 23–24° on recrystallization. As mentioned previously,<sup>10</sup> this low melting acid (now known as phenylvinylacetic acid) is converted by heat to methylatropic acid,<sup>11</sup> which melts at 135–136°. The conversion can also be effected by warming with acids or alkalis. Ozonization, by the method of Doeuvre,<sup>1</sup> of the acid

<sup>9</sup> Gilman and Zoellner, *THIS JOURNAL*, **52**, 3984 (1930). Earlier references are contained in this article. The authors are grateful to Dr. C. D. Hurd for suggestions concerned with the intermediate free radicals.

<sup>10</sup> Gilman and Harris, *ibid.*, **49**, 1825 (1927).

<sup>11</sup> In one experiment involving this transformation, there was obtained, in addition to the methylatropic acid, a small quantity of an acid melting at 77–78°. This acid has the neutralization equivalent of methylatropic acid and may be stereoisomeric with it. By the method of mixed melting points it was shown not to be phenylisocrotonic or  $\alpha$ -methylcinnamic acid, which have melting points near it.

melting at 23–24° gave formaldehyde; and catalytic reduction with Adams' catalyst gave  $\alpha$ -phenylbutyric acid.

The identity of the  $\alpha$ -phenylbutyric acid was confirmed by a mixed melting point determination made with an authentic specimen synthesized by the carbonation of  $\alpha$ -phenyl-*n*-propylmagnesium bromide,  $\text{C}_6\text{H}_5\text{CH}(\text{MgBr})\text{CH}_2\text{CH}_3$ . This  $\text{RMgBr}$  compound<sup>12</sup> was prepared in an 83% yield (by acid titration) using an excess of magnesium.

**Reaction with Phenyl Isocyanate.**—An ether solution of the Grignard reagent when treated in a customary manner with phenyl isocyanate gave the anilide of phenylvinylacetic acid, melting at 97–98° after successive crystallizations from benzene, alcohol, chloroform and finally benzene.

*Anal.* Calcd. for  $\text{C}_{16}\text{H}_{15}\text{ON}$ : C, 81.01; H, 6.33. Found: C, 80.68 and 80.86; H, 6.36 and 6.40.

The anilide,  $\text{C}_6\text{H}_5\text{CH}(\text{CONHC}_6\text{H}_5)\text{CH}=\text{CH}_2$ , showed no depression in a mixed melting point determination with the anilide prepared from phenylvinylacetic acid, thionyl chloride and aniline.

In the preparation of the anilide from phenylvinylacetic acid, a very small quantity of an anilide was obtained which melted at 192° (193° in a sealed capillary tube). This anilide was shown to be identical with that obtained from methylatropic acid by the thionyl chloride and aniline method. The formation of this small quantity of the anilide of methylatropic acid is undoubtedly due to a partial conversion, under the experimental conditions, of the labile phenylvinylacetic acid to the stable methylatropic acid.

The anilide of phenylisocrotonic acid,  $\text{C}_6\text{H}_5\text{CH}=\text{CHCH}_2\text{COOH}$ , melts at 89°, and a mixed melting point determination with this anilide and that from phenylvinylacetic acid showed a marked depression.

**Reaction with Ethyl Chlorocarbonate.**—The reaction product of the  $\text{RMgCl}$  compound and ethyl chlorocarbonate was hydrolyzed by heating with 20% hydrochloric acid or by shaking for two days with alkali. Practically pure methylatropic acid was obtained, as might have been expected because of the conversion of phenylvinylacetic acid to methylatropic acid by the action of heat, acids and alkalies. In another preparation from ethyl chlorocarbonate, the reaction product was oxidized with permanganate and a special search failed to reveal any phthalic or terephthalic acid. These acids should form if nuclear substitution occurred, after the type of reaction known to take place between benzylmagnesium chloride and ethyl chlorocarbonate. The product of the reaction from the  $\text{RMgCl}$  compound and formaldehyde was likewise oxidized with potassium permanganate, and benzoic acid but no phthalic or terephthalic acid was obtained.

**Reaction with Benzophenone.**—In order to determine whether the  $\text{RMgCl}$  compound underwent any dissociation after the known dissociation of triphenylmethylmagnesium chloride<sup>13</sup> and benzohydrylmagnesium chloride,<sup>14</sup> a filtered solution of the Grignard reagent was added to benzophenone. A very faint, transient red color was noticed, but the apparent absence of benzopinacol belies any significant dissociation.

### Summary

The Grignard reagent from cinnamyl chloride reacts chiefly, if not exclusively, as though it has the structure  $\text{C}_6\text{H}_5\text{CH}=\text{CH}_2$  and not  $\text{C}_6\text{H}_5\text{CH}=\text{CHCH}_2\text{MgCl}$ . This type of allylic transformation is comparable with

<sup>12</sup> Grignard and Ono, *Bull. soc. chim.*, **39**, 1589 (1926).

<sup>13</sup> Gilman and Fothergill, *THIS JOURNAL*, **51**, 3149 (1929).

<sup>14</sup> Gilman and Zoellner, *ibid.*, **52**, 3984 (1930) (see Ref. 12 on p. 3986).

that previously noted with  $\text{RMgX}$  compounds like benzylmagnesium chloride which give nuclear disubstituted products with a more restricted class of reactants. A mechanism, based on intermediate free radicals, has been suggested for the cinnamyl transformations.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF HARVARD UNIVERSITY]

## THE CONDENSATION OF BETA-NAPHTHOL WITH PHTHALIC ANHYDRIDE

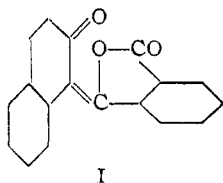
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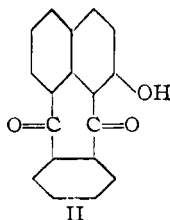
PUBLISHED SEPTEMBER 5, 1931

The appearance of a paper by Rieche and Frühwald<sup>1</sup> on a compound described as "phthaloyl- $\beta$ -naphthol" prompts me to publish at this time results obtained in an investigation of the same subject, even though this work is not yet completed. The results to be presented offer certain obstacles to an acceptance of the structural formula proposed by the German investigators, and my work thus leads to a different conception of the nature of the interesting compound which results in excellent yield from the condensation of the reactants noted.

The present work originated in the discovery by Emma M. Dietz in the Bryn Mawr laboratory that the process described in the patent literature<sup>2</sup> for the condensation of  $\beta$ -naphthol with phthalic anhydride in the presence of aluminum chloride does not lead to the formation of an hydroxy-naphthantraquinone as claimed in the patent, but to a yellow substance,  $\text{C}_{18}\text{H}_{10}\text{O}_3$ , having quite different properties.<sup>3</sup> As a possible structure, she proposed formula I, which was suggested by the structure assigned by Schaarschmidt<sup>4</sup> to a somewhat similar condensation product from  $\alpha$ -anthrol, although the evidence for his structure was very incomplete. In



I



II

continuing her brief study, it was soon found that formula I is ruled out by the fact that the yellow substance has one active hydrogen atom.

<sup>1</sup> Rieche and Frühwald, *Ber.*, **64**, 1603 (1931).

<sup>2</sup> Fr. Bayer and Co., German Patent 298,345 (1916); Friedländer, *Fortschritte der Teerfarbenfabrikation*, **13**, 390 (1923-1924).

<sup>3</sup> Dietz, Dissertation, Bryn Mawr, 1929.

<sup>4</sup> Schaarschmidt, *Ber.*, **49**, 381 (1916).