[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF IOWA STATE COLLEGE]

THE REACTION BETWEEN CITRONELLAL AND SOME ORGANOMAGNESIUM HALIDES

BY HENRY GILMAN AND W. F. SCHULZ

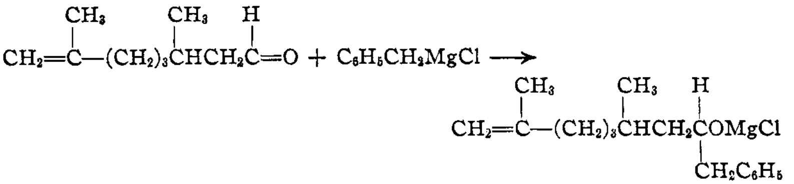
RECEIVED APRIL 28, 1930 PUBLISHED SEPTEMBER 5, 1930

Introduction

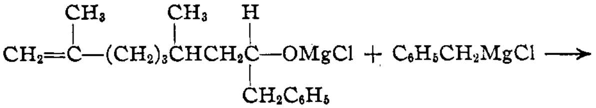
A very good case has been made for the non-addition, under usual experimental conditions, of organomagnesium halides to an ethylenic linkage.[1] There is, however, an apparent addition to such a linkage in compounds having the olefinic bond conjugated with another, and a different double bond, such as the carbonyl group in benzalacetophenone, $C_6H_5CH{=}CH{-}COC_6H_5$. Kohler and co-workers have demonstrated in an unequivocal manner that such conjugated systems can undergo 1,4-addition with the Grignard reagent. The enolic compound obtained subsequent to hydrolysis of the 1,4-addition intermediate then rearranges to give as an ultimate product a compound which might have been interpreted (and was interpreted incorrectly by earlier investigators) as involving direct addition to the ethylenic linkage.

The author of a recent book on organomagnesium halides,[2] in emphasizing the probability of direct addition to an ethylenic linkage, directs attention to a study by Rupe[3] on the purported addition of benzylmagnesium chloride to the ethylenic linkage in citronellal and makes the pointed observation that in this compound "1,4-addition is absolutely excluded."

The following reactions illustrate Rupe's interpretation of the mechanism of reaction.



$$CH_2{=}\overset{\overset{CH_3}{|}}{C}{-}(CH_2)_3\overset{\overset{CH_3}{|}}{C}HCH_2\overset{\overset{H}{|}}{C}{=}O + C_6H_5CH_2MgCl \longrightarrow CH_2{=}\overset{\overset{CH_3}{|}}{C}{-}(CH_2)_3\overset{\overset{CH_3}{|}}{C}HCH_2\underset{\underset{CH_2C_6H_5}{|}}{\overset{\overset{H}{|}}{C}}OMgCl \quad (I)$$



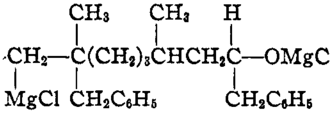
$$CH_2{=}\overset{\overset{CH_3}{|}}{C}{-}(CH_2)_3\overset{\overset{CH_3}{|}}{C}HCH_2\underset{\underset{CH_2C_6H_5}{|}}{\overset{\overset{H}{|}}{C}}{-}OMgCl + C_6H_5CH_2MgCl \longrightarrow$$

---

[1] Gilman and Harris, *Rec. trav. chim.*, **49**, June, (1930). References to earlier studies may be traced from this article.

[2] Courtot, "Le Magnésium en Chimie Organique," published in 1926 by the author at Nancy (see pages 317 and 324).

[3] Rupe, *Ann.*, **402**, 161 (1914). The present controversy on the constitution of citronellal does not affect the discussion in our paper because neither the double bond in the methylene form nor the double bond in the isopropylidene form is conjugated with the carbonyl group.

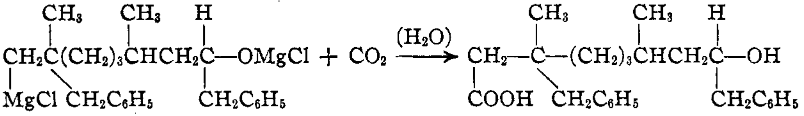


$$\underset{\text{MgCl}}{\text{CH}_2}\text{—}\overset{\text{CH}_3}{\underset{\text{CH}_2\text{C}_6\text{H}_5}{\text{C}}}(\text{CH}_2)_3\overset{\text{CH}_3}{\text{C}}\text{HCH}_2\overset{\text{H}}{\underset{\text{CH}_2\text{C}_6\text{H}_5}{\text{C}}}\text{—OMgCl} \quad \text{(II)}$$

(A)

It appeared highly improbable from our earlier studies[1] that addition had occurred as postulated by Rupe in Reaction II. The results of this study show that there has been no addition to the ethylenic linkage. This has been established by indirect methods.

If addition had taken place in accordance with Reaction II, then a new Grignard reagent should result. This organomagnesium chloride having the terminal group —CH_2MgCl would be expected to react essentially like other compounds having the —CMgX group, and on carbonation, for example, should give the corresponding carboxylic acid.



$$\underset{\text{MgCl}}{\text{CH}_2}\overset{\text{CH}_3}{\underset{\text{CH}_2\text{C}_6\text{H}_5}{\text{C}}}(\text{CH}_2)_3\overset{\text{CH}_3}{\text{C}}\text{HCH}_2\overset{\text{H}}{\underset{\text{CH}_2\text{C}_6\text{H}_5}{\text{C}}}\text{—OMgCl} + \text{CO}_2 \xrightarrow{(\text{H}_2\text{O})} \underset{\text{COOH}}{\text{CH}_2}\text{—}\overset{\text{CH}_3}{\underset{\text{CH}_2\text{C}_6\text{H}_5}{\text{C}}}\text{—}(\text{CH}_2)_3\overset{\text{CH}_3}{\text{C}}\text{HCH}_2\overset{\text{H}}{\underset{\text{CH}_2\text{C}_6\text{H}_5}{\text{C}}}\text{—OH} \quad \text{(III)}$$

(B)

The absence of this carboxylic acid was established in a reaction involving citronellal and three equivalents of benzylmagnesium chloride. This excess of Grignard reagent left one equivalent of benzylmagnesium chloride over and above that required by Reactions I and II. On carbonating the entire reaction mixture, the excess of benzylmagnesium chloride should be converted to the corresponding phenylacetic acid, $C_6H_5CH_2COOH$. If Reaction II took place, then subsequent to carbonation, hydrolysis and extraction with alkali a mixture of acid (B) (from Reaction III) and phenylacetic acid should result. The only acid obtained, however, was pure phenylacetic acid. The purity of the acid was established by determinations of melting point, mixed melting point and neutralization equivalent. We also showed, in like manner, that phenylmagnesium bromide and *n*-butylmagnesium bromide did not add to the ethylenic linkage, although it should be stated that of the Grignard reagents studied by Rupe only benzylmagnesium chloride was said to have added to the ethylenic linkage.[4]

Objections can be raised against this indirect proof. First, addition may have occurred at the ethylenic linkage, prior to addition to the carbonyl group, and the aldehydo-Grignard reagent formed in this manner might then have undergone intramolecular reaction to give a cyclic secondary alcohol. This is altogether unreasonable when one considers that aldehydes react almost instantly with Grignard reagents,[5] and that there is

---

[4] Rupe (Ref. 3, footnote on p. 161) has remarked that "benzylmagnesium chloride has a great tendency to 1,2-addition to a double bond." No such tendency was noted in a comprehensive study by Gilman and McGlumphy, *Rec. trav. chim.*, **47**, 418 (1928).

[5] Gilman, Heck and St. John, *ibid.*, **49**, 212 (1930). Obviously aldehydes with high

not, up to the present time, any case of even a slow addition of RMgX compounds to a non-conjugated ethylenic linkage.[6] Second, the acid (B) might actually have been formed in accordance with Reactions II and III and yet not revealed itself in the alkali extraction because of intramolecular esterification to give a ten-membered lactone. This also is highly unlikely *per se*, and particularly under our experimental conditions, because the lactone even though formed quantitatively should have been hydrolyzed in part, at least, by the alkali treatment to give the acid (B). This acid might subsequently have been converted to lactone, in part. Either or both of these products should have revealed themselves as impurities in the phenylacetic acid, but the high purity of this acid belied admixture, in any significant quantity, of contaminating lactone or acid.

Experimental Part

A solution of 23.1 g. (0.15 mole) of citronellal in 50 cc. of ether was added dropwise to a well-stirred solution containing 0.45 mole of benzylmagnesium chloride in 250 cc. of ether. Stirring and gentle refluxing were continued for fifteen minutes after addition of the aldehyde. The reaction mixture was then carbonated in a customary manner,[7] poured into iced dilute sulfuric acid, and the ether layer separated, washed with water and extracted with 10% sodium hydroxide. The alkaline extract was washed with ether, acidified with hydrochloric acid, and the precipitate so obtained filtered, washed with a minimum of water and dried in the air. Its melting point and mixed melting point with phenylacetic acid were identical with that of phenylacetic acid. The neutralization equivalent was 137.1, and the calculated value for phenylacetic acid is 136.1.

The reaction undoubtedly proceeded in accordance with that carried out by Rupe[3] because we also obtained the oil described by him (the product from hydrolysis of compound (A) in Reaction II) and its boiling point (244°/9 mm.) agreed with that determined by him. We have not investigated the constitution of this compound.

In a corresponding experiment with phenylmagnesium bromide the benzoic acid obtained melted at the correct melting point for this acid and showed no depression in a mixed melting point determination with an authentic specimen. The neutralization equivalent was 121.2, and the calculated equivalent for benzoic acid is 122.

The *n*-valeric acid obtained from a similar reaction between citronellal and an excess of *n*-butylmagnesium bromide had the following constants: b. p. 186°; d_{20}^{20} 0.9362; n_{α}^{20}, 1.404; and its neutralization equivalent was 108.8 (calcd. 102.1).

Summary

Contrary to the interpretations of others, benzylmagnesium chloride does not add to the ethylenic linkage in citronellal.

AMES, IOWA

---

steric hindrance about the carbonyl group will react more slowly than aldehydes without such steric hindrance.

[6] An interesting case of 1,4-addition to a conjugated system that is part aliphatic and part aromatic has been described recently by Gilman, Kirby and Kinney, THIS JOURNAL, **51**, 2252 (1929). There is a somewhat remote possibility that even though there is no formal conjugated system in citronellal, there still might be addition to a conjugated system resulting from the spatial contiguity of the aldehyde and ethylenic groups.

[7] Gilman and Parker, *ibid.*, **46**, 2816 (1924).