was evaporated on the steam-bath and the residual precipitate was dissolved in ethylene glycol and treated with sodium in ethylene glycol as above. Addition of ethylcyclohexane as "pusher" and distillation through a Podbielniak column afforded the following cuts: fraction 1, b.p. 94–97°, 0.23 g., n^{25}_{D} 1.4120, picrate m.p. 120–140°; fraction 2, b.p. 97–99°, 1.70 g., n^{25}_{D} 1.4129, picrate m.p. 79–79.5°; fraction 3, b.p. 99–110°, 0.30 g., n^{25}_{D} 1.4139.

Using the above procedure, but substituting cyclohexane for benzene as solvent, yielded the amine in 95% yield.

Kinetic Methods.—To about 49 ml. of a solution of dimethylamine in benzene, in a 50-ml. volumetric flask, was added a certain weight of α-methylallyl chloride. The volume was brought up to the mark with benzene and thorough mixing was achieved by vigorous shaking. Equal aliquots (5.00 ml.) were placed in ampoules, which were cooled in a Dry Ice-bath and sealed and placed in a constant temperature bath. Zero time was taken as the time of immersion. The ampoules were removed at intervals and the contents titrated for ionic halogen using the modified Volhard method.[8] The initial concentration of dimethylamine in the rate runs was determined by titrating the amine solution with standard hydrochloric acid. In an alternate method, the ampoules were broken under 50 ml. of ice-cold water and the amines titrated with dilute hydrochloric acid, using methyl red as indicator.

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LOS ANGELES 24, CALIF.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF CALIFORNIA AT LOS ANGELES]

Allylic Rearrangements. XXXVII. The Ultraviolet Absorption Spectra of Cinnamylmagnesium Bromide and Dicinnamylmagnesium[1]

BY ROBERT H. DEWOLFE, DAVID L. HAGMANN[2] AND WILLIAM G. YOUNG[3]

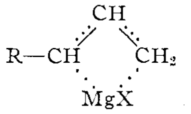
RECEIVED APRIL 18, 1957

The ultraviolet absorption spectra of the Grignard solution prepared from cinnamyl bromide and of dicinnamylmagnesium have been determined. These spectra are quite similar to those of model compounds having an olefinic linkage conjugated with a benzene ring, and it is concluded that the cinnamyl Grignard reagent is formed without rearrangement. The fact that cinnamyl Grignard reagents give rearranged products in reactions with carbonyl compounds is supporting evidence for the cyclic reaction mechanism proposed by Young and Roberts.

Several structures have been considered for Grignard reagents prepared from primary allylic halides. Different reactions of these reagents can best be explained by assuming that the reagent has the primary (I) or the secondary configuration (II) or that it is a cyclic hybrid of I and II (III) or a mixture of I and II.[4]

$RCH{=}CHCH_2MgX$
I

$RCH(MgX)CH{=}CH_2$
II


III

For example, the butenyl[5] and cinnamyl[6] Grignard reagents react with all but the most sterically hindered carbonyl compounds to give products derived from II, while reaction of cinnamylmagnesium chloride with chloramine gives only the primary amine derived from I ($R = C_6H_5$).[7] Reactions with proton donors and coupling reactions with organic halides usually give mixtures of hydrocarbons indicating that a hybrid structure or a mixture of I and II is involved.[8–10]

Due to the fact that rearrangements can occur both during the preparation and subsequent reactions of allylic Grignard reagents, it is doubtful that their chemical properties can furnish reliable evidence concerning their structure. It is only through examination of some physical property such as absorption spectrum that information regarding the structure of these reagents can be obtained. The Grignard reagent prepared from cinnamyl chloride or bromide lends itself particularly well to a study of configuration based on absorption spectra. In the primary form (I, $R = C_6H_5$), this reagent has a double bond conjugated with the aromatic ring. This type of conjugation is reflected in a large molar extinction coefficient at about 250 mμ.[11] In the secondary form (II, $R = C_6H_5$), the double bond is not conjugated with the ring, and the molar extinction coefficient at 250 mμ should be much smaller.

Experimental

Materials.—Anhydrous Baker and Adams or Mallinckrodt ether was used. For preparing cinnamyl Grignard solutions it was distilled into the reaction flask from an ether solution of n-butylmagnesium bromide. For a spectrophotometric solvent, it was dried over sodium ribbon and then stored over a generous quantity of fresh sodium ribbon in a bottle with a foil-lined screw cap.

Commercial dioxane was purified by the method of Fieser[12] and redistilled from over molten sodium shortly before use.

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[1] Presented at the Regional Meeting of the American Chemical Society, Los Angeles, Calif., May 8, 1954. Taken in part from the Ph.D. thesis of David L. Hagmann, 1950.

[2] Standard Oil Co. Fellow in Chemistry, 1946–1950.

[3] To whom inquiries concerning this paper should be addressed.

[4] (a) W. G. Young and J. D. Roberts, THIS JOURNAL, **68**, 1472 (1946); (b) R. H. DeWolfe and W. G. Young, *Chem. Revs.*, **56**, 872 (1956).

[5] See K. W. Wilson, J. D. Roberts and W. G. Young, THIS JOURNAL, **72**, 218 (1950), and earlier papers by these authors.

[6] (a) H. Gilman and S. A. Harris, *ibid.*, **49**, 1825 (1927); **53**, 3541 (1931); (b) O. Kuin-Houo, *Ann. chim.*, [11] **13**, 175 (1940); (c) R. H. DeWolfe, D. E. Johnson, R. I. Wagner and W. G. Young, THIS JOURNAL, **79**, 4798 (1957).

[7] G. H. Coleman and R. A. Forrester, *ibid.*, **58**, 27 (1936).

[8] K. W. Wilson, J. D. Roberts and W. G. Young, *ibid.*, **72**, 215 (1950).

[9] (a) W. G. Young, G. Ballou and K. Nozaki, *ibid.*, **61**, 12 (1939); (b) W. G. Young, J. D. Roberts and H. Wax, *ibid.*, **67**, 841 (1945); (c) H. Koch, *J. Chem. Soc.*, 1111 (1948).

[10] For other references to the literature on reactions of allylic Grignard reagents, see ref. 4b.

[11] (a) T. W. Campbell, S. Linden, S. Godshalk and W. G. Young, THIS JOURNAL, **69**, 880 (1947); (b) H. P. Koch, *J. Chem. Soc.*, 1123 (1948).

[12] L. F. Fieser, "Experiments in Organic Chemistry," D. C. Heath and Co., New York, N. Y., 1941, p. 368.

Eastman Kodak Co. White Label cinnamyl alcohol was used as received. Cinnamyl bromide was prepared from cinnamyl alcohol and 48% hydrobromic acid by the procedure of Claisen and Tietze.[13] The reaction product, a heavy yellow oil which solidified on cooling, was extracted with ethyl ether, the ether solution shaken with 10% sodium bicarbonate, washed with water and dried over calcium chloride. After removal of the ether, the halide was distilled at reduced pressure, b.p. 112–114° at 2 mm., and redistilled through a 40-cm. Vigreux column at 0.002 mm. shortly before use, the middle fraction being saved. This was a very faintly yellow liquid which solidified upon cooling to room temperature. It was stored in a stoppered container over Dry Ice.

Propenylbenzene.—Allylbenzene, $n^{20}\text{D}$ 1.5119, was isomerized by the action of alkali in *n*-butyl alcohol solution.[14] Fractional distillation through a Podbielniak column yielded a product, $n^{25}\text{D}$ 1.5467, b.p. 175–176°. The 2,4-dinitrobenzenesulfinyl chloride derivative was prepared, m.p. 91.5–92.0°.

Anal. Calcd. for $C_{15}H_{13}SN_2ClO_4$: C, 51.06; H, 3.71. Found: C, 51.36; H, 3.87.

This olefin is considered to be the *trans* isomer.[15]

1-Phenylbutene-1.—Reaction of *n*-propylmagnesium bromide with benzaldehyde, followed by dehydration of the resulting carbinol by heating with 6 *N* sulfuric acid at reflux temperature, yielded the desired olefin. The product was distilled through a 37-plate column at 377:1 reflux ratio, b.p. 195.0–196.5° at 760.3 mm., $n^{25}\text{D}$ 1.5382.

Anal. Calcd. for $C_{10}H_{12}$: C, 90.85; H, 9.15. Found: C, 90.83; H, 8.92.

The 2,4-dinitrobenzenesulfinyl chloride derivative was prepared, m.p. 144.4–4.8°.

Anal. Calcd. for $C_{16}H_{15}SN_2ClO_4$: C, 52.38; H, 4.12. Found: C, 52.26; H, 4.32.

This olefin is considered to be the *trans* isomer.[16]

Nitrogen.—Commercial nitrogen was freed of oxygen and moisture by passage through two wash bottles of Fieser solution (reference 12, p. 348), one of lead acetate solution, one of concentrated sulfuric acid and finally through a cold-trap immersed in a Dry Ice–acetone mixture.

Cinnamylmagnesium Bromide.—Ethyl ether solutions of cinnamylmagnesium bromide were prepared in a 1-liter creased Morton stirring flask to which was sealed a sidearm and a Dry Ice reflux condenser. The reaction flask was fitted with a high-speed stirring assembly similar to that described by Morton and Redman.[17] The procedure used in carrying out a typical run was as follows: the clean, oven-dried reaction flask was connected with the stirrer, and 20 g. of ether-rinsed, oven-dried magnesium turnings was introduced through the sidearm. A clean, dry, pressure-equalized dropping funnel was placed in the sidearm, and a vacuum pump was connected to the mouth of the funnel. The outlet of the reflux condenser was stoppered, and the system was evacuated to 0.5 mm. and held there for several minutes. The vacuum pump was then sealed off from the system, after which dry, oxygen-free nitrogen was bled into the flask until the internal pressure reached that of the atmosphere. The system was kept under a slight positive pressure of nitrogen from this point on. The condenser was filled with Dry Ice, and about 500 ml. of ether was distilled into the reaction flask from a flask containing ether and *n*-butylmagnesium bromide. After operating the stirrer at full speed (10,000 r.p.m.) for about 10 minutes to break up the magnesium turnings, the desired amount of cinnamyl bromide (from 3 to 6 g.), dissolved in 100 ml. of dry ether, was added to the suspension of magnesium in ether (stirred at about 6000 r.p.m.) over a 2.5-hr. period by means of the dropping funnel. After all of the cinnamyl bromide solution had been added, stirring was discontinued, and about 30 minutes was allowed for the finely divided magnesium to settle to the bottom of the flask. Samples of the clear, colorless solution for spectroscopic measurements were collected in long-necked evacuated sealed tubes (prepared from test-tubes) by breaking the tips from the necks of the tubes beneath the surface of the Grignard solution with the stirrer blade. The sample tubes were resealed immediately after being filled.

The preparation of cinnamylmagnesium bromide is accompanied by considerable coupling of the halide if it is not added under conditions of high dilution to a large excess of magnesium. The high-speed stirring technique described here gives yields of 90–95% if the final concentration of cinnamylmagnesium bromide does not exceed about 0.05 molar.

The cinnamyl Grignard solutions used in this study were in the concentration range 0.02 to 0.05 molar. Yields of Grignard reagent were calculated from the basic magnesium–bromide ion ratio, determined according to Gilman and co-workers.[18]

Dicinnamylmagnesium.—Peroxide-free, freshly distilled dioxane was added to cinnamylmagnesium bromide in ether in excess sufficient to precipitate essentially all of the magnesium bromide.[19] The resulting solution of dicinnamylmagnesium was analyzed for basic magnesium by the procedure of Gilman.[18] Samples for spectrophotometric study were collected in sealed tubes as already described.

Absorption Spectra.—Absorption spectra were determined in anhydrous ether solution using a Beckman model DU quartz photoelectric spectrophotometer. A special procedure was used in preparing solutions of cinnamylmagnesium bromide and dicinnamylmagnesium for spectrophotometric study, since it was necessary rigidly to exclude oxygen and water vapor from these solutions. The simplest and most successful way found for doing this was as follows: The silica absorption cell was oven dried at 120°; while hot, it was fitted with a rubber sleeve made from a 6-cm. length of rubber tubing. The upper end of the sleeve was loosely stoppered, and a glass tube connected to a source of dry, oxygen-free nitrogen was passed through an opening in the sleeve into the absorption cell. The cell was flushed with dry nitrogen for several minutes. The passage of nitrogen into the sleeve was continued, and the cell was chilled by dipping its lower portion briefly into a Dry Ice–acetone bath (to minimize evaporation of ether). Three ml. of anhydrous ether was then measured into the cell by means of a pipet which had been rinsed several times with dry ether. A sealed sample of the organomagnesium solution was opened and a clean, dry microburet immediately filled with the solution. The desired volume of solution (0.01 to 0.03 ml.) was then measured from the microburet directly into the ether in the absorption cell, with the tip of the microburet immersed well beneath the surface of the ether. A dry, ether-rinsed cork stopper was then inserted through the sleeve into the mouth of the cell and firmly seated. Cork stoppers were used since they give a tighter seal than glass stoppers and were found not to measurably contaminate the ether solutions. This procedure consistently gave clear solutions with reproducible absorption spectra. If even a small amount of air was allowed to come in contact with the contents of the cell, a turbid solution resulted.

Carbonation of Dicinnamylmagnesium.—Cinnamylmagnesium bromide (0.053 mole) was prepared in the usual manner, and 0.12 mole of purified dioxane was added with stirring. When the dioxanate precipitate had settled, the clear supernatant solution of dicinnamylmagnesium was siphoned under nitrogen pressure onto crushed solid carbon dioxide with vigorous stirring of the reaction mixture. The dioxanate precipitate together with a small amount of the supernatant solution was siphoned and washed onto a second batch of powdered Dry Ice. The acidic products from the two reactions (total yield, 51%) were worked up separately by dissolving them in aqueous alkali, heating to the boiling point to isomerize phenylvinylacetic acid to methylatropic acid, acidifying with dilute sulfuric acid and then collecting the crystalline products and drying them for analysis. The acids were analyzed spectrophotometrically by measuring their extinction coefficients in the range 274–292 mμ. The sole acidic product of both reactions was methylatropic acid, as determined by comparing spectra of the unknown substance with those of pure β-benzalpro-

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(13) L. Claisen and E. Tietze, *Ber.*, **58**, 279 (1925).

(14) M. Tiffeneau, *Compt. rend.*, **139**, 481 (1904).

(15) R. Y. Mixer, R. F. Heck, S. Winstein and W. G. Young, THIS JOURNAL, **75**, 4094 (1953).

(16) D. J. Cram, *ibid.*, **71**, 3881 (1949).

(17) A. A. Morton and L. M. Redman, *Ind. Eng. Chem.*, **40**, 1190 (1948).

(18) (a) H. Gilman, P. D. Wilkinson, W. P. Fishel and C. H. Meyers, THIS JOURNAL, **45**, 150 (1923); (b) H. Gilman, E. A. Zoellner and J. B. Dickey, *ibid.*, **51**, 1579 (1929).

(19) W. Schlenk and W. Schlenk, Jr., *Ber.*, **62**, 920 (1929).

pionic acid (m.p. 85–86°) and methylatropic acid (m.p. 138°).

Discussion

The ultraviolet absorption spectra of the cinnamyl Grignard solution and dicinnamylmagnesium are qualitatively and quantitatively quite similar to spectra of model compounds having a double bond conjugated with a benzene ring (Fig. 1). The maximum extinction coefficient of dicinnamylmagnesium at 250 mμ is almost as large as the extinction coefficients of the model compounds (Table I). The maximum extinction coefficient per mole of cinnamyl groups was consistently 15–20% lower for the Grignard solutions than for dicinnamylmagnesium prepared from them. This lower extinction coefficient could be due to the presence of cinnamylmagnesium bromide in the Grignard solution, provided that this species has a lower extinction coefficient than dicinnamylmagnesium.

However, it is not safe to assign an extinction coefficient to the species cinnamylmagnesium bromide, for at least two reasons. First, it is not known whether a Grignard solution is an equilibrium mixture of RMgX, R_2Mg and MgX_2; whether it consists of $R_2Mg \cdot MgX_2$, R_2Mg and MgX_2; or whether even more complicated systems are involved.[20] Second, even if it is assumed that R_2Mg and RMgX are the only organomagnesium compounds present in the Grignard solution, there is no reliable means of estimating their relative abundance. It was found that the yield of dicinnamylmagnesium obtainable from a cinnamyl Grignard solution varies with the amount of dioxane used in precipitating the halogen-containing component of the solution and possibly also with the rate of addition of dioxane and time of standing of the solution over the dioxanate precipitate. For example, in one experiment where 0.6-, 1.0- and 10-ml. portions of dioxane were added to identical 100-ml. samples of 0.052 *M* cinnamyl Grignard solution, the yields of dicinnamylmagnesium were 79, 72.5 and 68.5% of the theoretical value.

TABLE I

MAXIMUM EXTINCTION COEFFICIENTS OF CERTAIN COMPOUNDS IN ETHER SOLUTION

Compound	ϵ_{max}	λ, mμ
$C_6H_5CH_2CH{=}CH_2$	240[a]	259
$C_6H_5CHCH{=}CH_2$ | $C_6H_5CHCH{=}CH_2$	370[b]	260
$C_6H_5CH{=}CHCH_3$	17,850	250
$C_6H_5CH{=}CHCH_2CH_3$	16,300	251
$(C_6H_5CH{=}CHCH_2)_2$	33,000[b]	255
$C_6H_5CH{=}CHCH_2OH$	12,000	252
$(C_6H_5CH{=}CHCH_2)_2Mg$	20,000	252

[a] 95% ethanol solution (ref. 11a). [b] Cyclohexane solution (ref. 11b).

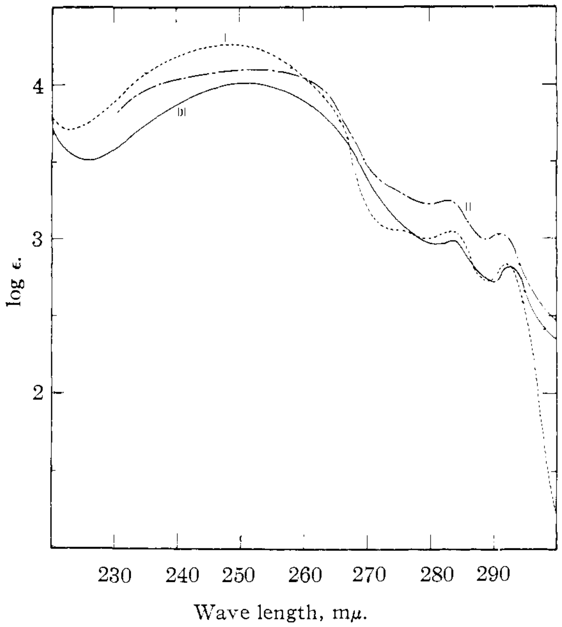
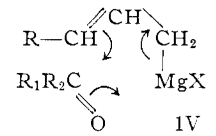


Fig. 1.—Ultraviolet absorption spectra: I, *trans*-propenylbenzene; II, cinnamyl alcohol; III, dicinnamylmagnesium.

Cinnamyl Grignard reagents have been observed to react with a variety of carbonyl compounds to give only products derived from II (R = C_6H_5).[6] It was found that dicinnamylmagnesium also reacts with carbon dioxide to give only the product of addition at the secondary carbon atom of the allylic system, phenylvinylacetic acid. Since this investigation indicates that the cinnamyl radicals in the Grignard solution are predominantly or entirely of the primary configuration, it seems likely that carbonyl addition reactions involving this reagent occur by a mechanism which gives secondary products from the primary form of the reagent. Such a mechanism is the cyclic process IV which was proposed by Young and Roberts[21] to explain the high yields and nature of the products obtained in carbonyl addition reactions of the butenyl Grignard reagent.



IV

The results of this investigation also bear on the possible ionic character of Grignard reagents. If the cinnamyl Grignard reagent were appreciably dissociated into cinnamyl carbanions, its absorption spectrum should exhibit a large bathochromic and hyperchromic effect, due to enhanced resonance of the carbanion compared to the non-ionic cinnamyl group. If there were any appreciable tendency for the cinnamyl Grignard reagent to ionize, the dilute solutions required for spectroscopic measurements (about 10^{-4} molar) would particularly favor dissociation; actually, the spectra of these solutions closely resembled those of the model compounds. When an ion pair of relatively free cinnamyl ion is produced, as in the preparation of phenylallyl sodium in petroleum ether or liquid ammonia, reaction with carbon dioxide gives a mixture of primary and secondary addition prod-

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(20) For references on the constitution of Grignard reagents, see M. S. Kharasch and O. Reinmuth, "Grignard Reactions of Organic Substances," Prentice-Hall, Inc., New York, N. Y., 1954, pp. 99 ff.

(21) W. G. Young and J. D. Roberts, THIS JOURNAL, **68**, 649 (1946).

ucts.[22] Only the secondary product (phenylvinylacetic acid) is obtained from cinnamylmagnesium bromide or chloride or dicinnamylmagnesium. Since the cinnamyl Grignard reagent is much more favorably constituted than a saturated Grignard reagent with regard to stabilization of a free carbanion by resonance, it may be concluded that normal Grignard reagents do not contain appreciable concentrations of carbanions.[23]

Young and Roberts[24] concluded after a thorough study of the reactions of the butenyl Grignard reagent that it is probably crotylmagnesium bromide, even though it gives rearranged addition products with unhindered carbonyl compounds. This investigation supports their conclusion; it is hoped that a study of the infrared spectrum of the butenyl reagent will provide a final proof of its configuration.

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(22) (a) T. W. Campbell and W. G. Young, THIS JOURNAL, **69**, 3066 (1947); (b) D. L. Hagmann, Ph.D. Thesis, U.C.L.A., 1950.

(23) Young and Roberts (ref. 4) list other reasons for doubting that ionic dissociation of Grignard reagents occurs.

(24) W. G. Young and J. D. Roberts, THIS JOURNAL, **67**, 319 (1945).

LOS ANGELES 24, CALIF.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF CALIFORNIA AT LOS ANGELES AND THE DEPARTMENT OF PHYSICAL SCIENCES, SANTA BARBARA COLLEGE OF THE UNIVERSITY OF CALIFORNIA]

Allylic Rearrangements. XXXVIII. The Reactions of Cinnamyl Grignard Reagents and Alkali Metal Derivatives of Allylbenzene with Acetophenone[1]

BY ROBERT H. DEWOLFE, DUANE E. JOHNSON,[2] ROSS I. WAGNER AND WILLIAM G. YOUNG[3]

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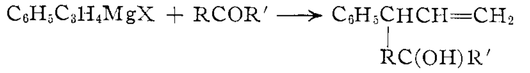
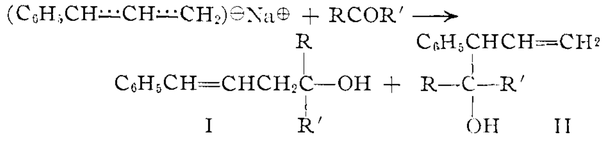
Cinnamylmagnesium bromide and cinnamylmagnesium chloride react with acetophenone to give 2,3-diphenyl-4-penten-2-ol in high yields. Phenylallylsodium and phenylallylpotassium, on the other hand, react with acetophenone in liquid ammonia solutions to form 2,5-diphenyl-4-penten-2-ol.

Previous work[4] has shown that Grignard reagents prepared from cinnamyl halides react with most carbonyl compounds to give α-phenylallylcarbinols



$$C_6H_5C_3H_4MgX + RCOR' \longrightarrow \begin{array}{l} C_6H_5CHCH{=}CH_2 \\ \quad\;\;| \\ \quad RC(OH)R' \end{array}$$

The organosodium compound prepared from allylbenzene and sodium amide in liquid ammonia (hereafter called phenylallylsodium[5]), on the other hand, was found[6] to give mixtures of products



$$(C_6H_5CH\overset{\cdots}{-}CH\overset{\cdots}{-}CH_2)^{\ominus}Na^{\oplus} + RCOR' \longrightarrow$$

$$\underset{\text{I}}{C_6H_5CH{=}CHCH_2\begin{array}{c} R \\ | \\ C{-}OH \\ | \\ R' \end{array}} + \underset{\text{II}}{\begin{array}{c} C_6H_5CHCH{=}CH_2 \\ | \\ R{-}C{-}R' \\ | \\ OH \end{array}}$$

Ia and IIa, $R = C_6H_5$; $R' = CH_3$

Ib and IIb, $R = R' = CH_3$

Ic and IIc, $R = R' = C_6H_5$

Carbonation of phenylallylsodium gave a mixture of acids containing about 90% $C_6H_5CH(CO_2H)$-$CH{=}CH_2$ and 10% $C_6H_5CH{=}CHCH_2CO_2H$, while reaction with acetone gave approximately equal amounts of Ib and IIb, and reaction with benzophenone yielded only Ic. It was considered that these mixtures arise due to different rates of reaction at the primary and secondary carbon atoms of the phenylallyl carbanion and that steric effects probably are important in determining product ratios.

The present paper reports the results of a study of the products formed when cinnamylmagnesium chloride, cinnamylmagnesium bromide, phenylallylsodium and phenylallylpotassium are allowed to react with acetophenone.

The reaction of cinnamylmagnesium bromide and cinnamylmagnesium chloride with acetophenone gave excellent yields of a liquid whose elementary composition is that of the expected carbinol, $C_{17}H_{18}O$. The low volatility of this material prevented its purification by fractional distillation, but purification could be effected by low pressure flash distillation to remove volatile impurities, followed by chromatographic separation of coupling and dehydration products and molecular distillation of the carbinol. The physical properties of the carbinol isolated from these reaction mixtures indicate that it is IIa, the expected product of addition at the secondary carbon atom of the allylic Grignard reagent. The molecular refractivity of this compound is in excellent agreement with that calculated for IIa, using Vogel's bond refractions.[7] While the ultraviolet absorption spectrum varied slightly from sample to sample, depending on the method of purification, it was definitely not that to be expected for Ia. The extinction coefficient of this substance in the vicinity of 250 mμ is much too low for a compound having a styrene chromophore.[8] On the other hand, with the exception of one carefully purified sample, the maximum extinction coefficients of the reaction products were higher at 250 mμ than would be expected for IIa. Whether this was due to the presence of small amounts of Ia or whether the samples were contaminated with dehydration products of IIa was

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(1) This work was supported in part by a grant from the National Science Foundation.

(2) Taken in part from the Ph.D. Thesis of Duane E. Johnson.

(3) To whom inquiries concerning this paper should be addressed.

(4) (a) H. Gilman and S. A. Harris, THIS JOURNAL, **49**, 1825 (1927); **53**, 3541 (1931); *Rec. trav. chim.*, **50**, 1052 (1931); (b) O. Kuin-Hono, *Ann. chim.*, [11] **13**, 175 (1940); (c) unpublished work from this Laboratory.

(5) R. Y. Mixer and W. G. Young, THIS JOURNAL, **78**, 3379 (1956).

(6) T. W. Campbell and W. G. Young, *ibid.*, **69**, 3066 (1947).

(7) A. I. Vogel, "Practical Organic Chemistry," Longmans, Green and Co., New York, N. Y., p. 901.

(8) T. W. Campbell, S. Linden, S. Godshalk and W. G. Young, THIS JOURNAL, **69**, 880 (1947).