

ucts.<sup>22</sup> 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.<sup>23</sup>

(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.

Young and Roberts<sup>24</sup> 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.

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

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[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]

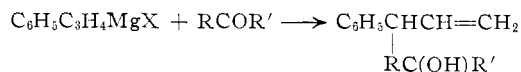
## Allylic Rearrangements. XXXVIII. The Reactions of Cinnamyl Grignard Reagents and Alkali Metal Derivatives of Allylbenzene with Acetophenone<sup>1</sup>

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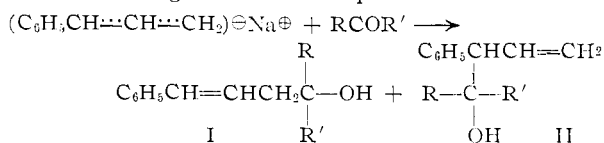
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Cinnamylmagnesium bromide and cinnamylmagnesium chloride react with acetophenone to give 2,3-diphenyl-4-penten-2-ol in high yields. Phenylallylsodium and phenylallylpotassium, on the other hand, react with acetophenone in liquid ammonia solutions to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

Previous work<sup>4</sup> has shown that Grignard reagents prepared from cinnamyl halides react with most carbonyl compounds to give  $\alpha$ -phenylallylcarbinols



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



Ia and IIa, R = C<sub>6</sub>H<sub>5</sub>; R' = CH<sub>3</sub>

Ib and IIb, R = R' = CH<sub>3</sub>

Ic and IIc, R = R' = C<sub>6</sub>H<sub>5</sub>

Carbonylation of phenylallylsodium gave a mixture of acids containing about 90% C<sub>6</sub>H<sub>5</sub>CH(CO<sub>2</sub>H)-CH=CH<sub>2</sub> and 10% C<sub>6</sub>H<sub>5</sub>CH=CHCH<sub>2</sub>CO<sub>2</sub>H, 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.

(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).

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<sub>17</sub>H<sub>18</sub>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.<sup>7</sup> 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 m $\mu$  is much too low for a compound having a styrene chromophore.<sup>8</sup> On the other hand, with the exception of one carefully purified sample, the maximum extinction coefficients of the reaction products were higher at 250 m $\mu$  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

(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).

not established. Even if the only contaminant were Ia, the values of  $E_{\max}$  indicate that less than 10% of this isomer was present in the crude products. The infrared spectrum of this compound, with bands at 920, 1000 and 1450  $\text{cm}^{-1}$ , is consistent with structure IIa, which has a terminal vinyl group.<sup>9</sup> Since IIa has two asymmetric carbon atoms, the reaction products may have been mixtures of diastereoisomers. However, the diastereoisomers would be expected to have very similar physical (and particularly optical) properties.

Phenylallylsodium and phenylallylpotassium, on the other hand, appear to react with acetophenone in liquid ammonia solutions to form predominantly or exclusively Ia, the product of addition at the primary carbon atom of the allylic system. The physical properties of the carbinol obtained from these reactions are in agreement with structure Ia. Its ultraviolet absorption spectrum has a large maximum extinction coefficient (20,000) at 250  $\text{m}\mu$ , excellent evidence for the presence of a styrene chromophore,<sup>8</sup> and its molecular refractivity shows an exaltation of 1.43, further evidence for a structure having a double bond conjugated with an aromatic ring. Dehydration of this carbinol yielded two solid hydrocarbons whose ultraviolet absorption spectra are those to be expected for 1,4-diphenyl-1,3-pentadiene and 1,4-diphenyl-1,4-pentadiene, the most likely dehydration products of Ia.

A search of the literature revealed that neither Ia nor IIa has been reported previously. Lora-Tomayo and co-workers,<sup>10</sup> in an effort to prove the identity of a compound assumed (probably correctly) to be cinnamyl bromide, treated their bromide with magnesium in ether, added acetophenone to the resulting solution and isolated a solid substance from the reaction mixture which they reported to have the correct elementary composition for the carbinol  $\text{C}_{17}\text{H}_{15}\text{O}$ . This product apparently was not Ia or IIa. In view of the fact that the procedure these workers used would be expected to lead to extensive coupling of cinnamyl bromide and that their product had the same melting point as dicinnamyl, it seemed likely that their solid was the hydrocarbon, dicinnamyl. Their experiment was repeated as closely as possible from the procedure given in their paper, and the solid product which was obtained was found to have the correct elementary analysis and melting point for dicinnamyl. It is therefore almost certain that the product of Lora-Tomayo, *et al.*, was indeed dicinnamyl and not the carbinol they reported it to be.

The yields of addition product were much lower in reactions of the organo-alkali metal compounds than in the Grignard reactions. The yield of carbinol was about 60% in the reaction of phenylallylsodium with acetophenone and only about 20% in the case of phenylallylpotassium. In a single experiment with phenylallyllithium, no carbinol was isolated from the reaction mixture. These low yields probably are due to enolization of the ketone in the strongly basic reaction medium. The fact

that the intense color of the organometallic compounds disappeared upon addition of an excess of acetophenone makes it seem unlikely that low yields are due to incomplete reaction of the organometallic compound. The isolation of allylbenzene and propenylbenzene from the reaction mixtures is therefore probably due to enolization of the ketone rather than protonation of unreacted phenylallyl carbanion during workup of the reaction mixtures. The limited evidence available indicates that phenylallyllithium and phenylallylpotassium cause more extensive enolization of acetophenone than does phenylallylsodium, but a final decision on this point should be delayed pending further study of these reagents. Campbell and Young<sup>6</sup> obtained a 75% yield of addition product in the reaction of phenylallylsodium with benzophenone. The relatively high yield of carbinol obtained from this hindered, but unenolizable, ketone lends credence to the assumption that the low yields obtained with acetophenone were due to enolization of the methyl ketone.

### Experimental

**Materials.**—Eastman Kodak Co. White Label cinnamyl alcohol was used as received. Eastman technical grade acetophenone was distilled through a 100-cm. vacuum-jacketed glass helix-packed column, the portion boiling at 100.5–101° at 30.6 mm. being saved. Cinnamyl chloride was redistilled from anhydrous potassium carbonate through a Vigreux column. The fraction boiling at 65° at 0.1 mm.,  $n_D^{25}$  1.5819, was stored at 0° until used. Cinnamyl bromide was prepared from cinnamyl alcohol and 48% hydrobromic acid by the procedure of Claisen and Tietze.<sup>11</sup> The crude product was distilled at reduced pressure through a Vigreux column, and the center cut stored over Dry Ice until used. Allylbenzene was prepared from phenylmagnesium bromide and allyl bromide.<sup>12</sup> Reagent grade ethyl ether was distilled from an ether solution of *n*-butylmagnesium bromide shortly before use in the Grignard reactions.

**Cinnamylmagnesium Bromide.**—Cinnamylmagnesium bromide was prepared by slowly adding an ether solution of cinnamyl bromide to a slurry of finely divided magnesium in anhydrous ether. The reaction was carried out using the creased flask and high-speed stirring assembly described by Morton and Redman.<sup>13</sup> In a typical run, 72 g. (3 moles) of magnesium turnings and 1500 ml. of anhydrous ether were placed in a 3-liter 3-necked Morton stirring flask equipped with a high-speed stirring assembly and two condensers. The air in the flask was displaced with dry nitrogen, and the stirrer was operated at top speed (10,000 r.p.m.) for about 15 minutes to powder the magnesium. One-tenth mole (19.7 g.) of cinnamyl bromide dissolved in 200 ml. of dry ether was added to the reaction flask over a 1 hr. period by means of a dropping funnel connected to one of the condensers, with the stirrer operated at about half speed. The heat of the reaction plus the heat produced by stirring cause the ether to reflux vigorously. The Grignard reaction is self-initiating under these conditions and is complete soon after the last of the cinnamyl bromide solution has been added. The yield of Grignard reagent, as calculated from the basic magnesium-bromide ion ratio, determined according to Gilman,<sup>14</sup> is between 90 and 95%.

**Reaction of Cinnamylmagnesium Bromide with Acetophenone.**—The Grignard reagent described above was concentrated to a volume of 500 ml. and forced by means of nitrogen pressure through a glass tube into a one-liter nitrogen filled flask. Acetophenone (12 g., 0.1 mole) dissolved in 50 ml. of ether was added dropwise during 5 minutes to the stirred Grignard reagent. Saturated aqueous ammo-

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

(12) T. W. Campbell and W. G. Young, *THIS JOURNAL*, **59**, 688 (1947).

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

(14) H. Gilman, P. D. Wilkinson, W. P. Fishel and C. H. Meyers, *THIS JOURNAL*, **45**, 150 (1923).

(9) L. J. Bellamy, "The Infrared Spectra of Complex Molecules," John Wiley and Sons, Inc., New York, N. Y., p. 31.

(10) M. Lora-Tomayo, F. Martin-Panizo and R. P. Ossorio, *J. Chem. Soc.*, 1418 (1950).

nium chloride (300 ml.) was added with stirring to the reaction mixture, and the aqueous layer then separated and extracted with two portions of ether, which were added to the original ether layer. The ether solution was dried over anhydrous calcium sulfate for 12 hr. and filtered. Evaporation of the ether, followed by reducing the pressure to 0.3 mm. for 1 hr. at 35–40°, yielded 25 ml. of viscous, straw-colored liquid. The crude product was freed of volatile impurities by heating it at 90° and 0.005 mm.; about 5 g. of colorless distillate having the odor of acetophenone was collected. The non-volatile residue was placed in a Hickman molecular still and distilled at 95–100° and 0.007 mm. Three fractions, having volumes of 4, 12 and 4 ml., were collected. Fractions 1 and 2 were nearly colorless and fluoresced only slightly under ultraviolet light. Fraction 3 had a definite yellowish color and fluoresced a brilliant blue-white. Fraction 3 probably contained coupling products of cinnamyl bromide or dehydration products of the expected carbinol and was not examined further.

*Anal.* Calcd. for  $C_{17}H_{18}O$ : C, 85.67; H, 7.61; mol. wt., 238.0. Found for Fraction 1: C, 85.43; H, 7.45. Fraction 2: C, 85.48; H, 7.75. 0.0638 g. of the carbinol lowered the melting point of 0.6583 g. of camphor by 18.0°; mol. wt. (Rast method), 214.

The infrared absorption spectra of fractions 1 and 2 were nearly identical and showed the following bands: 3540(s), 3020(s), 1960(w), 1820(w), 1600(m), 1490(m), 1450(s), 1340(s), 1200(w), 1080(m), 1000(m) and 920(s)  $cm^{-1}$ . The ultraviolet absorption spectra of fractions 1 and 2 in methanol solution exhibited a maximum at 250  $m\mu$  and a minimum at 230  $m\mu$ . The value of  $E_{max}$  was 2,700 for fraction 1 and 1,780 for fraction 2. The refractive indices, densities and molecular refractivities of these fractions were

Fraction	$n_D^{25}$	$d_{25}^{25}$	$[R_D]_D$ (found)	$[R_D]_D$ (calcd.)
1	1.5741	1.051	74.73	74.62
2	1.5762	1.051	74.96	74.62

Eight ml. of fraction 2 was poured into an 0.8 × 60 cm. column packed with alumina, and air pressure was then applied at the top of the column. Several successive fractions of from 0.3 to 0.5 ml. were collected at the bottom of the column and their refractive indices determined. The values of  $n_D^{25}$  for the seven fractions collected were: 1.5739, 1.5734, 1.5738, 1.5734, 1.5739, 1.5739 and 1.5740. The ultraviolet absorption spectrum of the third fraction in methanol solution was determined:  $\lambda_{min}$ , 235  $m\mu$ ,  $\lambda_{max}$ , 250  $m\mu$ ,  $E_{max}$ , 1,930.

**Cinnamylmagnesium Chloride.**—Cinnamylmagnesium chloride was prepared by the general procedure described previously for cinnamylmagnesium bromide. Cinnamyl chloride (0.1 mole, 15.3 g.) in 200 ml. of dry ether was added to a stirred suspension of 75 g. of finely divided magnesium in 1.5 l. of dry ether during a period of 1 hr. Analysis of the resulting Grignard reagent by the method of Gilman<sup>14</sup> indicated a yield of 99.5%. In a subsequent run the quantity of magnesium used was reduced to 50 g. without affecting the yield of Grignard reagent. It is probable that satisfactory yields of cinnamylmagnesium chloride could be obtained by the high-speed stirring technique with still smaller excesses of magnesium.

**Reaction of Cinnamylmagnesium Chloride with Acetophenone.**—This reaction was carried out by the procedure described above for the analogous reaction of cinnamylmagnesium bromide. Evaporation of the ether, followed by evacuation to 0.001 mm. for an hour at room temperature, yielded 20.0 g. of crude product. Distillation of 14.25 g. of this viscous, yellowish liquid in a Hickman molecular still yielded a 2-ml. forerun consisting mostly of acetophenone and three fractions having refractive indices of 1.5621, 1.5718 and 1.5740. The fraction with  $n_D^{25}$  1.5740 yielded the following elementary analysis:

*Anal.* Calcd. for  $C_{17}H_{18}O$ : C, 85.67; H, 7.61. Found: C, 85.36; H, 7.84.

The ultraviolet absorption spectrum of this fraction in anhydrous ether was determined, using a Cary recording spectrophotometer, and is described as in the tabulation.

The remainder of the crude product was dissolved in petroleum ether (Skellysolve B) and added to a 55 × 3.5 cm. chromatographic column wet-packed with Florex 60/100 (Floridin Co., Quincy, Fla.) in petroleum ether. The

$\lambda_{max}$	$E_{max}$	$\lambda_{min}$	$E_{min}$
247	1750	233	1250
258	1430	257	1420
284	200	281	195
294	135	291	127

column was eluted with successive 500-ml. portions of petroleum ether and petroleum ether–benzene mixtures. The residues from the first two fractions of eluate weighed only a few mg. and contained a colorless crystalline solid, probably dicynamyl. The liquid residues from fractions 4–7 were combined and distilled in the Hickman still at 0.001 mm. and 110°. The principal fraction from this distillation was a viscous, faintly yellowish liquid,  $n_D^{25}$  1.5728.

*Anal.* Calcd. for  $C_{17}H_{18}O$ : C, 85.67; H, 7.61. Found: C, 85.52; H, 7.65.

The ultraviolet absorption spectrum of this material in anhydrous ethyl ether solution was determined with a Cary recording spectrophotometer, and is described as

$\lambda_{max}$	$E_{max}$	$\lambda_{min}$	$E_{min}$
239	1200	234	1160
259	525	256	435
265	425	263	390
268	322	267	320
279	145	275	140
287	140	283	130

In a second run, designed to determine the maximum yield of IIa obtainable from cinnamylmagnesium chloride and acetophenone, 15.00 g. of acetophenone in 50 ml. of ether was added to the Grignard reagent prepared in 99.5% yield from 15.00 g. (0.098 mole) of cinnamyl chloride and 50 g. of magnesium in 1500 ml. of ether. The addition reaction was carried out in the presence of the excess magnesium from the preparation of the Grignard reagent. The reaction mixture was allowed to stand overnight, and then worked up as usual. A careful quantitative separation of the organic phase yielded 3.15 g. of unreacted acetophenone (calculated excess, 3.10 g.) and 23.2 g. (0.097 mole) of carbinol. The yield of carbinol was therefore almost 99% of the theoretical.

**Reinvestigation of the "Carbinol" of Lora-Tomayo, Martin-Panizo and Ossorio.**<sup>10</sup>—The experimental procedure by which Lora-Tomayo and co-workers claimed to get a solid carbinol having the formula  $C_{17}H_{18}O$  was repeated as nearly exactly as possible.

Magnesium shavings (1.1 g.) were placed in a 250-ml. 3-necked flask fitted with a mechanical stirrer, a condenser and a dropping funnel. After flushing the flask with dry nitrogen, 9.0 g. (0.045 mole) of freshly distilled cinnamyl bromide dissolved in 30 ml. of dry ether was added dropwise to the stirred magnesium shavings during about 30 minutes. The resulting mixture was refluxed for 1.5 hr. and then 5 g. of acetophenone dissolved in 15 ml. of dry ether was added dropwise with stirring. Refluxing was continued for another 2 hr., after which saturated aqueous ammonium chloride was added to the mixture. The ether phase was saved and the aqueous phase was extracted with ether. The combined ether solutions were washed with water and dried over anhydrous sodium sulfate. The solution was filtered and the ether evaporated from the filtrate, following which the residual oil was heated at 100° and 0.008 mm. to remove the unreacted acetophenone. Most of the acetophenone used, ca. 4 g., was recovered. The residue which remained was a yellowish oil which partially crystallized on cooling in an ice-bath. After standing overnight at 0°, the slurry was filtered by suction, giving 0.36 g. of a white crystalline solid, m.p. 73–76°. Two recrystallizations from aqueous ethanol raised the melting point to 79–80°. A sample of the purified product was submitted for analysis.

*Anal.* Calcd. for  $C_{15}H_{16}$ : C, 92.26; H, 7.74. Found: C, 91.75; H, 8.09.

**Reaction of Phenylallyl Sodium with Acetophenone.** Run I.—The sodium derivative of allylbenzene was prepared according to the procedure of Campbell and Young,<sup>12</sup> using 59 g. (0.5 mole) of allylbenzene and 11.5 g. (0.5 mole) of sodium in 1.5 l. of liquid ammonia. Acetophenone (60 g., 0.5 mole) in 150 ml. of anhydrous toluene was added to

the ammonia solution. When the red color of the organo-sodium compound had faded to gray (*ca.* 15 minutes), 30 g. of ammonium chloride was added to the reaction mixture. The liquid ammonia was allowed to evaporate, and 500 ml. of water was added to facilitate separation of the organic material from the ammonium chloride. The mixture was filtered through a Celite pad, the aqueous layer was washed twice with ether and the combined organic layer and ether extracts were dried over anhydrous magnesium sulfate. The ether and most of the toluene were removed by distillation at atmospheric pressure. Reduced-pressure fractional distillation through a vacuum-jacketed center-rod column yielded, in addition to approximately one-third of the acetophenone used, a fraction boiling between 160–170° at 2 mm. Several recrystallizations of this product from methanol, hexane and ether yielded a solid hydrocarbon, *m.p.* 68.5–70°. The ultraviolet absorption spectrum of this compound in cyclohexane solution was determined, using a Beckman model DU spectrophotometer:  $\lambda_{\max}$  250  $\mu$ ,  $E_{\max}$  29,000,  $\lambda_{\min}$  225  $\mu$ ,  $E_{\min}$  12,000.

*Anal.* Calcd. for  $C_{17}H_{16}$ : C, 92.68; H, 7.32; mol. wt., 220. Found: C, 92.99; H, 7.75. The melting point of 0.0744 g. of camphor was lowered 20.0° by 0.0079 g. of the hydrocarbon mol. wt. (Rast method), 213.

The pot residue from the distillation partially crystallized on standing at room temperature. The solid was washed with methanol and after several recrystallizations from methanol and methanol-benzene, melted at 95–96°. The ultraviolet absorption spectrum of this compound in cyclohexane solution exhibited maxima at 230  $\mu$  ( $E_{\max}$ , 13,500) and 305  $\mu$  ( $E_{\max}$ , 28,000) and a minimum at 255  $\mu$  ( $E_{\min}$ , 5,500).

*Anal.* Calcd. for  $C_{17}H_{16}$ : C, 92.68; H, 7.32; mol. wt., 220. Found: C, 92.53; H, 7.99. The melting point of 0.0674 g. of camphor was lowered by 25.1° by 0.0091 g. of the hydrocarbon; mol. wt. (Rast method), 214.

**Run II.**—Allylbenzene (29.5 g., 0.25 mole) was added to 0.25 mole of sodium amide in liquid ammonia. Acetophenone (30 g., 0.25 mole) dissolved in 75 ml. of toluene was added to the resulting mixture. Five grams of ammonium chloride and 200 ml. of water were added to the mixture after reaction was complete and the organic layer was separated. The aqueous layer was extracted with two 50-ml. portions of ether and the ether extracts combined with the organic layer. The ether solution was dried over anhydrous magnesium sulfate, following which the ether and toluene were removed by distillation at pressures sufficiently low to prevent the pot temperature from exceeding 30°. Analysis of the crude product for acetophenone with 2,4-dinitrophenylhydrazine reagent indicated that only 65% of the acetophenone used reacted with the phenylallylsodium.

Chromatographic separation of 10.0 ml. of the crude product on a 4 × 20 cm. column of alumina, using petroleum ether as developer and methanol as eluting solvent, resulted in recovery of 6.87 g. of non-volatile organic material. The principal fraction, 3.05 g., was a viscous liquid which gave an elementary analysis consistent with the formula  $C_{17}H_{16}O$ . This fraction was distilled in a Hickman molecular still at 100° and 0.001 mm. About 1.2 ml. of liquid was collected,  $n_D^{25}$  1.5934,  $d_4^{25}$  1.061;  $[R_L]_D$  calcd. for  $C_{17}H_{16}O$ , 74.62; found 76.05 (exaltation, 1.43).

*Anal.* Calcd. for  $C_{17}H_{16}O$ : C, 85.67; H, 7.61; mol. wt., 238.3. Found: C, 85.38; H, 7.60. The melting point of 0.9106 g. of camphor was lowered 15.3° by 0.0834 g. of this compound; mol. wt. (Rast method), 238. The ultraviolet absorption spectrum of this compound in anhydrous ether solution showed the following maxima and minima:

$\lambda_{\max}$	$E_{\max}$	$\lambda_{\min}$	$E_{\min}$
254	18,000	226	3600
284	1,540	282	1480
293	920	290	765

**Attempted Reaction of Phenylallyllithium with Acetophenone.**—Lithium amide was prepared from 2.48 g. (0.358 mole) of lithium and liquid ammonia. Allylbenzene (35 g., 0.30 mole) was added to the lithium amide-ammonia mixture over a period of 1 hr. Fifty grams (0.42 mole) of redistilled acetophenone, diluted with an equal volume of ether, was added to the deep orange suspension of phenylallyllithium. After disappearance of the orange color, 19.5

g. of ammonium chloride was added. After allowing the ammonia to evaporate, the residue was heated lightly to remove remaining ammonia. Water was added and the aqueous phase extracted with three 150-ml. portions of ether. The ether extracts were dried over anhydrous magnesium sulfate and the ether removed through a Vigreux column. The residue was fractionated through an efficient column to give a recovery of 27.5 g. (0.233 mole) of allyl- and propenylbenzene. Chromatography of the pot residue on Florex failed to yield an isolable amount of carbamol.

**Reaction of Phenylallylpotassium with Acetophenone in Liquid Ammonia.**—Potassium (16.5 g., 0.4 mole) was converted into potassium amide in liquid ammonia. Allylbenzene (47.2 g., 0.4 mole) and acetophenone (48.1 g., 0.4 mole) were added successively to the mixture. After addition of 21.2 g. of ammonium chloride, the reaction mixture was worked up as described in previous experiments. A 20% yield of crude Ia was obtained after removal of solvents,  $C_6$ -hydrocarbons and unreacted acetophenone by low pressure flash distillation. A sample of the crude alcohol was purified by chromatography on a 3.5 × 40 cm. column of alumina, using pentane-ether mixtures as developing solvent and ether as the eluting solvent. The purified product was distilled using a Hickman molecular still at 0.002 mm. and 80°. Three fractions of viscous, slightly yellowish liquid were collected, having refractive indices ( $n_D^{25}$ ) of 1.5924, 1.5938 and 1.5939. The middle fraction was analyzed for carbon and hydrogen.

*Anal.* Calcd. for  $C_{17}H_{16}O$ : C, 85.67; H, 7.61. Found: C, 85.78; H, 7.79.

A sample of this alcohol was dehydrated by treatment with acetyl chloride at 100°. A solid hydrocarbon was obtained which melted, after two recrystallizations from ethanol, at 93–95°. The melting point of a mixture of this hydrocarbon with that resulting from the dehydration of the reaction product of phenylallylsodium and acetophenone was 94–95°.

### Discussion of Results

The results of this investigation are in agreement with previous studies of reactions of allylic organometallic compounds with carbonyl compounds. The cinnamyl Grignard reagents react with acetophenone, as with other carbonyl compounds,<sup>4</sup> to yield the product of addition by the secondary carbon atom of the allylic system (IIa). The ultraviolet absorption spectrum of cinnamylmagnesium bromide has a strong absorption peak at 250  $\mu$ , as do the spectra of other compounds containing the cinnamyl group.<sup>15</sup> The absorption spectrum of the Grignard reagent strongly indicates that it is formed from cinnamyl bromide without allylic rearrangement. The formation of addition products in which the cinnamyl group has undergone rearrangement in reactions of this Grignard reagent with carbonyl compounds thus provides support for the cyclic mechanism proposed by Young and Roberts<sup>16</sup> to explain the high yields and structures of the products formed in reactions of the butenyl Grignard reagent with carbonyl compounds.

Formation of Ia in the reaction of phenylallylsodium with acetophenone probably is due to attack by the primary carbon atom of the phenylallyl carbanion on the carbonyl group of the ketone being considerably faster than attack by the secondary carbon atom of the carbanion. This result is easily accounted for in terms of the greater steric hindrance to attack by the secondary carbon atom.<sup>5</sup>

The use of cinnamylmagnesium halides and phenylallylsodium in reactions with ketones having at least one relatively bulky substituent should provide a stereospecific route to phenylallylcar-

(15) R. H. DeWolfe, David L. Hagmann and W. G. Young, *This Journal*, **79**, 4795 (1957).

(16) W. G. Young and J. D. Roberts, *ibid.*, **68**, 649 (1946).

binols. The Grignard reagents would be expected in most cases to yield  $\alpha$ -phenylallyl carbinols (II), while phenylallylsodium in liquid ammonia should

yield products consisting predominantly of  $\gamma$ -phenylallylcarbinols (I).

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[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF NORTHWESTERN UNIVERSITY]

## The Stereochemistry of the 2,3-Dichloro-*p*-dioxanes

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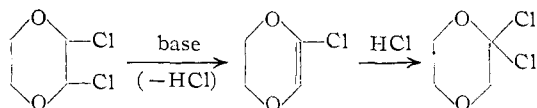
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The preparation of the second isomer of 2,3-dichloro-*p*-dioxane is described. The previously known isomer is shown to be the *trans* form by kinetic resolution with brucine, and the new isomer must therefore be assigned the *cis* configuration. Isomerization experiments show that the *trans* form is the more stable. Addition of chlorine to *p*-dioxene by means of iodobenzene dichloride results in almost exclusive formation of *trans*-2,3-dichloro-*p*-dioxane, whereas molecular chlorine gives a mixture of the *cis* and *trans* isomers, with predominance of the *cis* form. The products from various reactions of *cis*-2,3-dichloro-*p*-dioxane are the same as those from the *trans* isomer; however, there are considerable differences in the rates of the reactions. In 50% aqueous dioxane, the *cis* isomer hydrolyzes fourteen times as fast as the *trans* isomer.

### Discussion

Some years ago, Umhoefer<sup>1</sup> and later Lappin<sup>2</sup> obtained a compound, m.p. 53°, as a product in the photochlorination of dioxane in carbon tetrachloride solution. Molecular weight determination and elementary analysis indicated the formula C<sub>4</sub>H<sub>6</sub>O<sub>2</sub>Cl<sub>2</sub>, and on the basis of incomplete evidence the structure of 2,2-dichloro-*p*-dioxane was tentatively assigned. The investigation was suspended because of the apparent instability of the compound and difficulties in consistently obtaining satisfactory yields.

Recently we had need of some 2,2-dichloro-*p*-dioxane and synthesized it in satisfactory yields, using 2,3-dichloro-*p*-dioxane as starting material. The abstraction of hydrogen chloride to give chlorodioxane was achieved by means of dimethylaniline, and gaseous hydrogen chloride was then added to produce the desired 2,2-dichloro-*p*-



dioxane.<sup>3</sup> Its structure was proved by hydrolysis to *p*-dioxanone and reaction with phenylmagnesium bromide to give 2,2-diphenyldioxane.<sup>4</sup> The 2,2-dichloro-*p*-dioxane, a liquid at room temperature, had entirely different properties from the compound prepared by Umhoefer and by Lappin. Since only one isomer of this structure is possible, we decided to reinvestigate the matter.

We repeated the chlorination of dioxane in carbon tetrachloride solution and isolated the 53° compound in about 25% yield. The four possible structural arrangements for a dichlorodioxane can be differentiated by their hydrolysis products as pointed out by Boeseken, Tellegen and Henriquez.<sup>5</sup>

(1) R. R. Umhoefer, Ph.D. Dissertation, Northwestern University, 1948.

(2) G. R. Lappin, Ph.D. Dissertation, Northwestern University, 1946.

(3) Melvin J. Astle and William C. Gergel, U. S. Patent 2,756,240, have described the preparation of chlorodioxane by thermal decomposition of 2,3-dichloro-*p*-dioxane.

(4) James P. Settle, M.S. Thesis, Northwestern University, 1950.

(5) J. Boeseken, F. Tellegen and P. C. Henriquez, *Rec. trav. chim.*, **50**, 909 (1931).

The 2,2-isomer would give rise to hydroxyethoxyacetic acid or its lactone. Both the 2,5- and the 2,6-isomer would yield two moles of glycolaldehyde, whereas only the 2,3-isomer would form one mole of glyoxal and glycol. When the new compound was hydrolyzed, we obtained one mole of glyoxal, determined quantitatively as *p*-nitrophenylosazone, and ethylene glycol, characterized as dibenzoate. The 2,3-structure of the new compound was also shown by its reaction with silver acetate to give a 79% yield of the known diacetate of 2,3-*p*-dioxane-diol, m.p. 104°.<sup>6</sup>

The preparation of the other isomer of 2,3-dichloro-*p*-dioxane, described for the first time by Boeseken, Tellegen and Henriquez,<sup>5</sup> is generally accomplished by chlorinating dioxane at reflux temperature, which varies from 100° at the start of the reaction to about 150°, as higher boiling products accumulate. Fractionation of the reaction product after consumption of the calculated amount of chlorine yields a solid, m.p. 31°, in very good yields. The two isomers of 2,3-dichloro-*p*-dioxane have distinctively different infrared spectra, especially in the region from 8 to 12  $\mu$ . We used the peaks at 10.55  $\mu$  (53° isomer) and at 11.42  $\mu$  (31° isomer) to analyze mixtures of the two compounds. It was found that the chlorination of dioxane in carbon tetrachloride solution at reflux temperature gives rise to a mixture of 35–40% of the 53° isomer and 65–60% of the 31° isomer. The chief function of the carbon tetrachloride is to maintain a moderate reaction temperature, since the same results were obtained when dioxane was chlorinated without solvent at temperatures of about 75°. By taking samples at approximately 25, 35 and 55% completion of the reaction, we found that the ratio of the two isomers did not change during the reaction at 75°. When the reaction mixture was heated above 110°, the 53° isomer was converted gradually into the 31° isomer, the rate of conversion increasing rapidly with temperature. This explains the fact that the 53° isomer was not found in chlorinations of dioxane previously described in the literature, since most of

(6) J. Boeseken, F. Tellegen and P. C. Henriquez, *This Journal*, **55**, 1284 (1933).