the halogen in a given alkylmagnesium halide produces a difference in the rate of reaction. The iodide is more affected by the presence of amine than the bromide and chloride. There is a reversal in the order of reactivity in case of CH₃MgBr and CH₃MgI brought about by triethylamine cosolvent. However, the addition of amine does not change the rate of reaction of a halogen-free solution of diethylmagnesium.

Triethylamine increases the rate of reaction of hexyne with methylmagnesium halides more than with ethylmagnesium halides. Thus the order of reactivity of methyl- and ethylmagnesium bromides (1 molar solution) is reversed if at least 0.1 mole-equivalent of triethylamine is present.

Because of the variation of the temperature during the reaction, it is not possible to determine accurately the rate laws from the individual gas evolution curves. However, casual inspection of the data indicates that the reactions are approximately second order. Thus, it can be seen from Table I

that the relative reactivities are approximately doubled when the concentrations of the alkylmagnesium halide and the hexyne are both doubled, the molarity of amine being constant.

The influence of triethylamine upon the rate of reaction of the Grignard reagent with hexyne cannot be the result of a shift in the Schlenk equilibrium^{6,7} since the relative reaction of halogen-free diethylmagnesium

$$2 \text{ RMgX} \rightleftharpoons \text{R}_2\text{Mg}\cdot\text{MgX}_2 \rightleftharpoons \text{R}_2\text{Mg} + \text{MgX}_2$$

is independent of the amine concentration. This is likely due to the existence of a different mechanism of reaction. However the coordination of the amine with the magnesium atom of reacting species is not an important factor in determining the rate of reaction.

PITTSBURGH, PA.

(7) J. H. Wotiz, C. A. Hollingsworth, and R. E. Dessy, *J. Org. Chem.*, **21**, 1063 (1956).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, DUKE UNIVERSITY]

Conjugate Addition Condensations of Diphenylmethane Involving Methylene Hydrogen by Potassium Amide. Cyclizations of Products by Polyphosphoric Acid¹

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Potassium diphenylmethide, prepared from diphenylmethane and potassium amide, was condensed through conjugate addition with ethyl cinnamate, and the resulting ester was cyclized by means of polyphosphoric acid to form a cyclic ketone. Potassium diphenylmethide also underwent conjugate addition with benzalacetophenone and α -phenylcinnamonitrile but these products failed to be cyclized by polyphosphoric acid. Potassium diphenylmethide underwent with ethoxymethylenemalonic ester conjugate addition accompanied by elimination to form an ester that yielded an aromatic product on cyclization.

Diphenylmethane has previously been shown to enter into several types of carbon-carbon condensations through the metalation of its α -hydrogen by means of sodium or potassium amide in liquid ammonia. Thus, this hydrocarbon has been alkylated,² acylated,³ carbethoxylated,³ carbonated,³ and condensed with the carbonyl group of ketones or aldehydes.⁴ An example of the alkylation that has been realized quantitatively is represented by Equation 1.²

$$(C_6H_5)_2CH_2 \xrightarrow[liq. NH_3]{NaNH_2} (C_6H_5)_2CHNa \xrightarrow[C_6H_5]{C_6H_5} (C_6H_5)_2CHCH_2C_6H_5 \quad (1)$$

In the present investigation, diphenylmethane was found to undergo through its potassium or sodium derivative still another type of condensation, involving conjugate addition with α,β -unsaturated carbonyl compounds or nitriles. This type of condensation is of special interest since certain of the products obtained were cyclized by means of polyphosphoric acid. These reactions will be considered on the basis of the α,β -unsaturated compound empolyed.

Reaction with ethyl cinnamate. Potassium diphenylmethide, prepared from molecular equivalents of diphenylmethane and potassium amide in liquid ammonia containing some ether, underwent conjugate addition with an equivalent of ethyl cinnamate in this medium to form ester I, which was saponified to give acid II in 84% overall yield (Equation 2).

⁽¹⁾ Supported by the Office of Ordnance Research, U. S. Army

⁽²⁾ C. R. Hauser and P. J. Hamrick, Jr., J. Am. Chem. Soc., 79, 3142 (1957).

⁽³⁾ R. S. Yost and C. R. Hauser, J. Am. Chem. Soc., 69, 2325 (1947).

⁽⁴⁾ P. J. Hamrick, Jr., and C. R. Hauser, unpublished results.

$$(C_{6}H_{5})_{2}CH_{2} \xrightarrow[liq. NH_{8}]{} (C_{6}H_{5})_{2}CHK \xrightarrow{1. C_{6}H_{5}CHCCOC_{2}H_{5}} \xrightarrow{1. KOH} \xrightarrow{2. HCl} C_{6}H_{5}CHCH_{2}COOC_{2}H_{5} \xrightarrow{2. HCl} C_{6}H_{5}CHCH_{2}COOH (2)$$

$$(C_{6}H_{5})_{2}CH \xrightarrow{I} II$$

Under similar conditions, sodium diphenylmethide produced a lower yield of ester I. These conjugate additions, especially that with sodium diphenylmethide, might have been accompanied by some 1,2 addition leading to the formation of ketone III but neither this ketone nor condensation products with the alkali diphenylmethide were isolated. A small amount of a solid besides ester I was obtained with sodium diphenylmethide, but it was not identified.

Bergmann⁵ has observed that sodium diphenylmethide, prepared from benzhydrylmethyl ether and metallic sodium underwent mainly conjugate addition with methyl or ethyl cinnamate (Equation 3) although some 1,2-addition also appeared to take place. No yields were reported.

$$(C_{6}H_{5})_{2}CH - OCH_{3} \xrightarrow[\text{ether}]{Na} \xrightarrow[\text{ether}]{C_{6}H_{5}} CHNa \xrightarrow[\text{ether}]{C_{6}H_{5}CH = CHCOOC_{2}H_{5}} I \quad (3)$$

The present method starting with diphenylmethane (Equation 2) is more convenient than that of Bergmann since not only is this hydrocarbon more available than benzhydrylmethyl ether, but the cleavage of this ether by sodium has been somewhat tedious.⁶

The mechanism for the conjugate addition presumably involves the attack of the diphenylmethide ion at the β -carbon of ethyl cinnamate to form anion IV from which ester I is obtained on acidification (Equation 4).

$$C_{\delta}H_{\delta}CH = CH - C = O \xrightarrow{(C_{\delta}H_{\delta})_{2}CH} \xrightarrow{\text{liq. NH}_{\delta}} CC_{2}H_{\delta}$$

$$C_{\delta}H_{\delta}CH - CH = C - O \xrightarrow{HCl} I \quad (4)$$

$$(C_{\delta}H_{\delta})_{2}CH \qquad OC_{2}H_{\delta}$$

$$IV \text{ (one resonance form)}$$

Although the related Michael type of condensation of malonic ester or other active methylene carbonyl compound with ethyl cinnamate is known to require only a catalytic amount of base such as ethoxide ion,⁷ the conjugate addition of diphenyl-

methane with this ester was not realized satisfactorily when a catalytic amount of potassium amide was employed. Thus, whereas an equivalent of potassium amide gave within 15 minutes an 84% yield of acid II (after hydrolysis of ester I), twenty mole percent of this base produced during five hours only a 24% yield of acid II through ester I. Since the conversion of diphenylmethane to potassium diphenylmethide by potassium amide is essentially complete,8 twenty mole percent of this hydrocarbon was first converted to potassium diphenylmethide which underwent conjugate addition with the corresponding amount of ethyl cinnamate to form anion IV (Equation 4). However, the ionization of the remaining diphenylmethane by anion IV, which would presumably be required for further conjugate addition to occur, evidently proceeded very slowly under the conditions employed. This may be ascribed to an unfavorable acid-base reaction, the equilibrium of which is probably far on the side of unchanged diphenylmethane and anion IV (Equation 5). It is to be noted that whereas the conjugate addition stops at anion IV when an equivalent of potassium amide is employed, this anion is converted to the neutral

$$(C_{6}H_{5})_{2}CH_{2} + C_{6}H_{5}CH - CH = C - O - \longrightarrow (C_{6}H_{5})_{2}CH \quad OC_{2}H_{5}$$

$$IV$$

$$(C_{6}H_{5})_{2}\overline{C}H + C_{6}H_{5}CHCH_{2}C = O \quad (5)$$

$$(C_{6}H_{5})_{2}CH \quad OC_{2}H_{5}$$

ester I when a catalytic amount of the base is successful.⁷

The conjugate addition represented by equation 2 is of interest not only as a convenient method of synthesis of ester I and acid II, but also because this ester or acid underwent cyclization with polyphosphoric acid, involving the loss of ethanol or water to form a ketone that analyzed for tetralone V or hydrindone VI. The presence of the ketone group was indicated by conversion of a sample of the product to the corresponding 2,4-dinitrophenylhydrazone. The over-all yield of the ketone from diphenylmethane through ester I was about 50%.

$$C_{6}H_{5}$$

$$C_{6}H_{5}$$

$$V$$

$$CH(C_{6}H_{5})_{2}$$

$$O$$

$$VI$$

This acid-catalyzed cyclization of ester I or acid II seems likely to have produced tetralone V rather than hydrindone VI, since the related Friedel-

⁽⁵⁾ E. Bergmann and O. Blum-Bergmann, J. Chem. Soc., 727 (1938).

⁽⁶⁾ E. Bergmann, J. Chem. Soc., 412 (1936).

⁽⁷⁾ See E. E. Royals, Advanced Organic Chemistry, Prentice-Hall, Inc., New York, N. Y., 1954, pp. 791, 792.

⁽⁸⁾ This conclusion is based on the earlier observation (ref. 2) that diphenylmethane undergoes essentially complete metalation with sodium amide in liquid ammonia.

Crafts type cyclizations of similar acid chlorides have been shown to yield six membered rings in preference to five. For example, acid chloride VII has given tetralone VIII rather than the possible hydrindone IX. 10

$$\begin{array}{c|c} O=C-Cl & O \\ CH_2 \\ CHC_6H_5 & \\ VII & VIII & IX \end{array}$$

Moreover, ether-ester X has been cyclized by polyphosphoric acid to form the ether-ketone XI which was aromatized by hydrogen fluoride to give naphthol XII.¹¹

Since the present product, presumably tetralone V, was readily isolated as a sharp melting solid, it evidently consisted largely of only one of the two possible diastereoisomers.

Reactions with benzalacetophenone and α -phenyl-cinnamonitrile. Under the conditions employed with ethyl cinnamate, potassium diphenylmethide reacted with benzalacetophenone to form a compound that analyzed for either the conjugate addition product or the 1,2-addition product, XIII or XIV, respectively.

That the product was ketone XIII and not the isomeric carbinol XIV was shown by its infrared absorption spectrum which gave a strong band for the carbonyl group but none for the hydroxyl group. Moreover, the product was stable toward acid as might be expected for ketone XIII but not for carbinol XIV which should readily undergo dehydration.

Similarly potassium diphenylmethide reacted with α -phenylcinnammonitrile to form a compound that analyzed for either the conjugate addition product or the 1,2-addition product, XV and XVI respectively.

(9) See W. S. Johnson, Org. Reactions, II, 116 (1944).

(10) J. v. Braun and G. Manz, Ann., 468, 258 (1929).
(11) C. R. Hauser and M. T. Tetenbaum, J. Org. Chem., 23, 233 (1958).

That the product was nitrile XV and not the isomeric imine XVI was indicated by its infrared absorption spectrum which showed a definite (although weak) band for the nitrile group but none for the imine group.

Attempts to hydrolyze the nitrile group of XV with concentrated sulfuric acid or with aqueous or alcoholic potassium hydroxide were unsuccessful. Had the product been imine XVI, it might be expected to have undergone hydrolysis under these conditions to form the corresponding ketone, but the original compound was recovered.

In contrast to ester I from the conjugate addition with ethyl cinnamate, ketone XIII and nitrile XV failed to undergo cyclization with polyphosphoric at 125–130°, or even at 200° (in the case of ketone XIII), the starting compounds being recovered

Reaction with ethoxymethylenemalonic ester. Besides the ordinary α,β -unsaturated carbonyl compounds employed in the experiments described above, ethoxymethylenemalonic ester (XVII) was used with potassium diphenylmethide after the liquid ammonia had been replaced by ether. The reaction that resulted evidently involved conjugate addition accompanied by elimination of ethoxide ion to form ester XVIII, which possesses sufficient unsaturation to produce an aromatic ring on cyclization. Such a cyclization was realized with the corresponding carboxylic acid XIX by means of polyphosphoric acid (PPA) to given naphthol-acid XX in an overall yield of 47% from diphenylmethane or ester XVII. These reactions are represented in Scheme A.

Scheme A

$${}^{\circ}_{2}H_{6}O-CH=C-C-OC_{2}H_{5}\xrightarrow{(C_{6}H_{6})_{5}CHK}\xrightarrow{ether}$$

$$COOC_{2}H_{5}\xrightarrow{(C_{6}H_{6})_{2}CH-C=C-OC_{2}H_{5}}$$

$$C_{2}H_{5}O-CH-C=C-OC_{2}H_{5}$$

$$(C_{6}H_{8})_{2}CH\xrightarrow{COOC_{2}H_{5}}$$

$$C=COOH$$

$$CCOOH$$

$$CCOOH$$

$$H_{6}C_{6}$$

$$C=CH\xrightarrow{(C_{6}H_{5})_{2}CH}\xrightarrow{(C_{6}H_{5})_{2}CH}\xrightarrow{COOC_{2}H_{5}}$$

$$XIX$$

$$XVIII$$

$$COOH$$

XX

XXI

These reactions furnish a convenient method for the synthesis of naphthol-acid XX which appears not to have been described previously. The structure of this product was established as XX by decarboxylation to form the corresponding naphthol XXI which is a known compound (see Scheme A).

EXPERIMENTAL¹²

Conjugate addition with ethyl cinnamate to form ester I and acid II. To a stirred solution of 0.2 mole of potassium amide in 300 ml. of anhydrous liquid ammonia³ was added 33.6 g. (0.2 mole) of diphenylmethane in an equal volume of anhydrous ether, and the resulting dark orange solution of potassium diphenylmethide was stirred for 15 min. A solution of 35.2 g. (0.2 mole) of ethyl cinnamate in an equal volume of anhydrous ether was added with stirring. The color was discharged and a heavy white precipitate formed. The ammonia was evaporated on the steam bath as an equal volume of anhydrous ether was added, and the resulting ether suspension was refluxed for 15 min. Excess iced hydrochloric acid was added, and the two layers were separated. The aqueous layer was extracted three times with ether, and the ether extracts combined with the ether layer. The ethereal solution was dried over Drierite, and the solvent removed. The oily residue was cooled in the refrigerator for three days to give 66 g. of ethyl 3,4,4-triphenylbutyrate (I) as a white, amorphous solid which resisted satisfactory recrystallization.

A sample (10 g.) of ester I was saponified with aqueous potassium hydroxide, and the resulting mixture acidified with iced hydrochloric acid. The precipitate was collected on a funnel, and recrystallized from 50% acetic acid to give 8 g. (84% based on diphenylmethane) of 3,4,4-triphenylbutyric acid (II) m.p. 174–177°. After another recrystallization this acid melted at 178–179° (reported m.p. 178°).

When the conjugate addition reaction was repeated on a 0.1 molar scale employing sodium amide¹³ instead of potassium amide, there were obtained 23 g. of ester I, 1 g. of an unidentified solid, m.p. 148–149°, and 6 g. of a recovered mixture of diphenylmethane and ethyl cinnamate.

When the conjugate addition reaction was carried out in a similar manner employing 0.2 mole each of diphenylmethane and ethyl cinnamate, and only 0.02 mole of potassium amide (refluxed 5 hours in the liquid ammonia-ether mixture), there were obtained 23 g, of ester I, and 33 g, of a mixture of recovered diphenylmethane and ethyl cinnamate. Saponification of an 8 g, sample of ester I gave 2.6 g, of acid II, m.p. 174–177°, which corresponds to a 24% yield of the conjugate addition product based on diphenylmethane.

Cyclization of ester I and acid II. A mixture of 8 g. of crude ester I and excess of polyphosphoric acid¹⁴ was stirred and heated at 125–130° for 30 min. After cooling, ice water was added, and the resulting mixture extracted with ether. The ethereal solution was dried over Drierite, and the solvent removed, to leave 3 g. (50% based on diphenylmethane, of slightly colored cyclic ketone (V or VI), m.p. 157–160). This product was recrystallized twice from ether to give a white powder, m.p. 164.5–165°.

.4nal. Calcd. for $C_{22}H_{18}O$: C, 88.56; H, 6.08. Found: C, 88.72; H. 6.07.

In a similar manner, 3 g. of pure acid II was cyclized to give 1.6 g. (57%) of the cyclic ketone, m.p. $157-160^{\circ}$.

A sample of the cyclic ketone (V or VI) was converted to

the corresponding 2,4-dinitrophenylhydrazone in the usual manner. The derivative melted at 290° after recrystallization from glacial acetic acid.

Anal. Calcd. for C₂₈H₂₂N₄O₄: N, 11.71. Found: N, 11.65. Conjugate addition with benzalacetophenone to form ketone XIII. To a stirred solution of potassium diphenylmethide, prepared from 0.1 mole each of potassium amide and diphenylmethane in 300 ml. of liquid ammonia and about 50 ml. of ether, was added 20.8 g. (0.1 mole) of solid benzalacetophenone. Most of the color was discharged. After stirring for 1 hr., the liquid ammonia was replaced by ether, and the resulting brown ether suspension was refluxed for 15 min. Iced hydrochloric acid was added, and the resulting white precipitate of 2,3,3-triphenylbutyrophenone (XIII) was collected on a funnel. More of this ketone was recovered from the aqueous-ethereal filtrate. The total yield was 30 g. (80%), m.p. 181-183°. After two recrystallizations from a mixture of chloroform and petroleum ether (b.p. 30-60°), the ketone melted at 187–188°

Anal. Calcd. for $C_{28}H_{24}O$: C, 89.32; H, 6.43. Found: C, 89.11: H, 6.40.

An infrared absorption spectrum of this ketone gave a strong band at 5.94μ showing the presence of the carbonyl group. Attempts to convert samples of this compound to the oxime or the 2,4-dinitrophenylhydrazone under the usual conditions were unsuccessful.

Also, this ketone was recovered after treatment with polyphosphoric acid at 125-130° or at 200° for 30 min., or with concentrated sulfuric acid at room temperature for 1 hr.

Reaction with α-phenylcinnamonitrile. To a stirred solution of potassium diphenylmethide, prepared from 0.1 mole each of potassium amide and diphenylmethane in 300 ml. of liquid ammonia and 50 ml. of ether, was added 20.5 g. (0.1 mole) of solid α-phenylcinnamonitrile. The greenish mixture was stirred for 15 min., and the liquid ammonia then replaced by ether. The resulting tan colored ether suspension was refluxed for 15 min., and iced-hydrochloric acid then added. The resulting mixture (which contained much solid) was extracted three times with ether, and the combined ether extracts dried over Drierite. The solvent was removed, leaving 23 g. (62%) of white nitrile XV (or immine XVI) m.p. 210–211°. Two recrystallizations from a mixture of chloroform and ether gave white needles, m.p. 211–211.5° (softening slightly at 175°).

Anal. Calcd. for C₂₈H₂₃N: C, 90.05; H, 6.21; N, 3.75. Found: C, 89.92; H, 6.34; N, 3.84.

An infrared absorption spectrum of this product gave a weak band at 4.48 μ indicating the presence of the nitrile group.

This product was recovered when treated with polyphosphoric acid at 125–130° for 30 min., liquid hydrogen fluoride at room temperature, aqueous and alcoholic refluxing potassium hydroxide solution for 5 hr., and concentrated sulfuric acid for 1 hr. on the steam bath.

Reaction with ethoxymethylenemalonic ester and cyclization. A solution of potassium diphenylmethide was prepared from 0.1 mole each of potassium amide and diphenylmethane in 300 ml. of liquid ammonia, and the liquid ammonia was replaced by anhydrous ether. After refluxing for 15 min., 21.6 g. (0.1 mole) of ethoxymethylenemalonic ester in an equal volume of anhydrous ether was added with stirring and the resulting ether suspension refluxed for 1 hr. After hydrolysis with iced hydrochloric acid, the ether layer was separated and combined with three ether extracts of the aqueous layer. The ethereal solution was dried over Drierite, and the solvent removed. The oily residue was distilled in vacuo until 9 g. of a mixture of diphenylmethane and ethoxymethylenemalonic ester were recovered, leaving a residue of ester XVII which was saponified with aqueous potassium hydroxide. The resulting acid XIX, obtained on acidification with hydrochloric acid, was stirred and heated with excess polyphosphoric acid at 120° for 30 min. After cooling, iced hydrochloric acid was added and the precipitate was recrystallized three times from a mixture of chloroform and

⁽¹²⁾ Melting points are uncorrected. Analyses are by Galbraith Microanalytical Laboratories, Knoxville, Tenn.

⁽¹³⁾ C. R. Hauser, F. W. Swamer, and J. T. Adams, Org. Reactions VIII, 122 (1954).

⁽¹⁴⁾ We are indebted to the Victor Chemical Works, Chicago, Ill., for a generous sample of polyphosphoric acid.

ligroin (b.p. $60-90^{\circ}$) to give 12.5 g. (47% overall yield) of 1-hydroxy-4-phenyl-2-naphthoic acid (XX), m.p. $227-228^{\circ}$ dec.

Anal. Calcd. for $C_{17}H_{12}O_3$: C, 77.26; H, 4.58. Found: C, 77.02; H, 4.47.

This compound gave a greenish-blue coloration with aqueous-alcoholic ferric chloride.

Decarboxylation of naphthol-acid XX. An 0.18 g. sample of naphthol-acid XX was heated above its melting point in a covered crucible. The resulting tarry material was recrystal-

lized from a mixture of chloroform and ligroin (b.p. $60-90^{\circ}$) to produce 0.10 g. (67%) of 4-phenyl-1-naphthol (XXI) as a brownish powder, m.p. $139-140^{\circ}$ (lit. value 140°). This compound gave a dark blue coloration with aqueous alcoholic ferric chloride.

DURHAM, N. C.

(15) W. Borsch, S. Kettner, M. Giles, H. Kuhn, and R. Manteuffel, *Ann.*, 526, 21 (1936).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, DUKE UNIVERSITY]

Condensations of Benzhydryl Methyl Ether Involving α -Hydrogen by Potassium Amide. Cyclization of Conjugate Addition Product by Polyphosphoric Acid¹

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The α -hydrogen of benzhydryl methyl ether was metalated by means of potassium amide, and the resulting potassium derivative then condensed with benzyl chloride and ethyl cinnamate. The product from the latter condensation was cyclized by means of polyphosphoric acid to form a methoxytetralone which was subsequently aromatized by means of hydrogen fluoride to give a naphthol. Some other reactions were also effected.

It is well known that one of the methylene hydrogens of diphenylmethane can be metalated readily by means of sodium amide or potassium amide in liquid ammonia, and that the resulting alkali diphenylmethide can serve as the carbanion component in several useful types of carboncarbon condensations. One of these types of reaction involves alkylation, certain of which have been effected quantitatively (Equation 1).²

$$(C_6H_5)_2CH_2 \xrightarrow[liq. NH_2]{NaNH_2} (C_6H_5)_2CHNa \xrightarrow[C_6H_6)_2CHCH_2C_6H_5]$$

$$(C_6H_6)_2CHCH_2C_6H_5$$

$$(C_6H_6)_2CHCH_2C_6H_5$$

$$(C_6H_6)_2CHCH_2C_6H_5$$

Another type of condensation involves conjugate addition such as that with ethyl cinnamate, which has been realized in good yield (Equation 2).³

$$(C_6H_5)_2CH_2 \xrightarrow[liq. NH_5]{KNH_2} (C_6H_5)_2CHK \xrightarrow{1. C_6H_6CH = CHCOOC_2H_5}$$

$$C_6H_5CHCH_2COOC_2H_5 \qquad (2)$$

$$(C_6H_5)_2CH$$

It has now been found that the α -hydrogen of benzhydryl methyl ether (I) can be metalated similarly with potassium amide, and that the resulting potassium derivative can enter into the two analogous condensations with benzyl chloride and ethyl cinnamate to form ether II and ether-ester III in yields of 63% and 62%, respectively (Equations 3a and 3b).

$$(C_{6}H_{5})_{2}CH \longrightarrow CCH_{3} \xrightarrow{KNH_{2}} I$$

$$I$$

$$CH_{2}C_{6}H_{5}$$

$$(C_{6}H_{5})_{2}C \longrightarrow CCH_{3} \xrightarrow{C_{6}H_{6}CH_{2}Cl} (C_{6}H_{5})_{2}C \longrightarrow CCH_{3} (3a)$$

$$1. C_{6}H_{6}CH = CHCOOC_{2}H_{5} \longrightarrow C_{6}H_{6}CHCH_{2}COOC_{2}H_{5} (3b)$$

$$2. HCl$$

$$(C_{6}H_{5})_{2}C \longrightarrow CCH_{3}$$

$$III$$

The conjugate addition with ethyl cinnamate (Equation 3b) might have been accompanied by some 1,2 addition to form α,β -unsaturated ketone IV, but neither this product nor products that might have arisen from its further reaction with the potassium derivative of benzhydryl methyl ether were isolated.

$$\begin{array}{c} \text{C}_6\text{H}_5\text{CH} \!\!=\!\!\! \text{CH} \!\!-\!\!\! \text{C} \!\!=\!\!\! \text{O} \\ \text{(C}_6\text{H}_5)_2\text{C} \!\!-\!\!\! \text{OCH}_3 \\ \text{IV} \end{array}$$

The reactions represented by equations 3a and 3b, in which the ether group remains intact, are to be distinguished from those reported by Bergmann⁴ who cleaved benzhydryl methyl ether (I) by means of metallic sodium, and then employed the resulting sodium diphenylmethide in corresponding condensations. Such a cleavage, followed by alkylation, is illustrated by equation 4, the end result of which is analogous to that represented in Equation 1.

$$(C_6H_5)_2CH - OCH_3 \xrightarrow{\text{Na}} \text{ether}$$

$$(C_6H_5)_2CHNa \xrightarrow{\text{RX}} (C_6H_5)_2CHR \quad (4)$$

⁽¹⁾ Supported by the Office of Ordnance Research, U. S. Army.

⁽²⁾ C. R. Hauser and P. J. Hamrick, Jr., J. Am. Chem. Soc., 79, 3142 (1957).

⁽³⁾ M. T. Tetenbaum and C. R. Hauser, J. Org. Chem., 23, 229 (1958).

⁽⁴⁾ E. Bergmann, J. Chem. Soc., 412 (1936); E. Bergmann and O. Blum-Bergmann, J. Chem. Soc., 727 (1938).