mixture had warmed to 0° it was acidified with dilute hydrochloric acid. The aqueous layer was extracted with benzene, and the benzene solution combined with the organic layer. The acidic product was taken up in 2 N sodium hydroxide solution and precipitated with hydrochloric acid. The 2'-methoxy-2-biphenylcarboxylic acid, after one recrystallization from benzene, formed light tan crystals, m.p. 149.5–150.5° (reported[7] m.p. 152–153°). A mixed melting point with an authentic sample showed no depression. The

infrared spectrum has peaks ascribable to a 2,2'-disubstituted biphenyl in which the substituents are different (740 and 760 cm.$^{-1}$), a methoxyl group (1023, 1126 and 1253 cm.$^{-1}$), skeletal vibrations of a conjugated aromatic system (1500, 1590 and 1598 cm.$^{-1}$), an aromatic acid (1687 cm.$^{-1}$) and the hydroxyl group of a carboxylic acid (broad band at 2520–2660 cm.$^{-1}$).

URBANA, ILL.

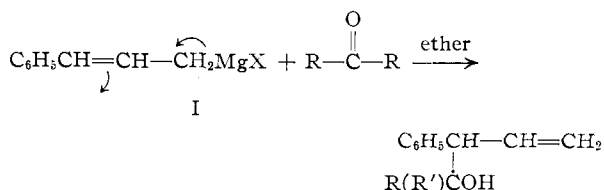
Allylic Rearrangements. XLIV. Reactions of Cinnamylmagnesium Bromide in Liquid Ammonia[1]

BY WILLIAM G. YOUNG AND WILLIAM P. NORRIS

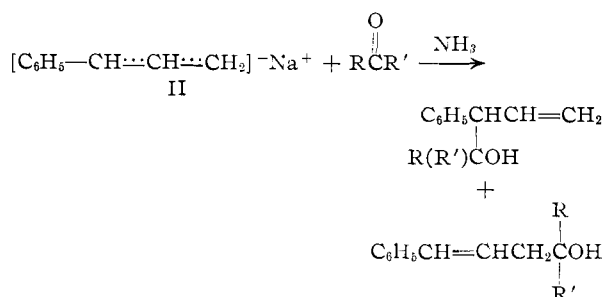Cinnamylmagnesium bromide forms highly colored precipitates in liquid ammonia below −50°. The color of the precipitate is attributed to the phenylallyl carbanion which was formed by solvation of the carbon–magnesium bond by the ammonia. Treatment of the colored precipitate with oxygen yields cinnamaldehyde.

Cinnamylmagnesium halide in ethyl ether reacts with all but the most hindered carbonyl compounds to give α-phenylallylcarbinols. On the other hand,

$$C_6H_5CH=CH-CH_2MgX + R-\overset{O}{\overset{||}{C}}-R \xrightarrow{\text{ether}}$$

I

$$\underset{R(R')\overset{|}{C}OH}{C_6H_5CH-CH=CH_2}$$

phenylallylsodium in liquid ammonia reacts with carbonyl reagents to give a mixture of both the α- and γ-phenylallylcarbinols.[2]

$$[C_6H_5-CH \text{---} CH \text{---} CH_2]^-Na^+ + R\overset{O}{\overset{||}{C}}R' \xrightarrow{NH_3}$$

II

$$\underset{R(R')\overset{|}{C}OH}{C_6H_5CHCH=CH_2}$$

$$+$$

$$\underset{\underset{R'}{|}}{\overset{R}{\underset{|}{C_6H_5CH=CHCH_2\overset{|}{C}OH}}}$$

Cinnamylmagnesium halide in ether is a covalent organometallic compound which exists predominantly or entirely in the primary configuration I.[3] The cyclic mechanism III proposed by Young and Roberts[4] to explain the nature of the products from addition reactions of carbonyl compounds and bu-

$$\underset{\underset{O}{\overset{\diagdown}{\diagup}} \; III}{\underset{RR'C \qquad MgX}{R-CH \underset{||}{\diagup} \overset{CH}{\diagdown} CH_2}}$$
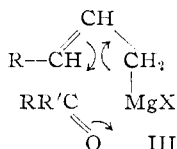
tenyl Grignard would explain how the primary cinnamyl Grignard reagent gives almost exclusively secondary addition products with carbonyl compounds.

Phenylallylsodium is a solid salt-like colored compound in inert solvents such as alkanes and ether and the electrophilic character of the sodium ion is quite important in coupling reactions with allylic halides, for instance.[5] In liquid ammonia, a polar solvent of relatively high dielectric constant, the ion pairs are dissociated and the sodium ions solvated so that the carbanion II reacts more or less independently. The amount of reaction at the α- or γ-positions depends on steric requirements of the two reactants and the relative reactivities of the α- and γ-positions.

Cinnamylmagnesium halide in ether reacts with aqueous acid to give a hydrocarbon product consisting of 75% allylbenzene and 25% propenylbenzene[6a,b] and when phenylallylsodium in pentane is added to excess methanol the hydrocarbon product is 74% allylbenzene and 26% propenylbenzene, essentially the same ratio.[5] If the phenylallylsodium is dissolved in liquid ammonia and treated with a proton donor the hydrocarbon mixture contains 85% propenylbenzene and 15% allylbenzene.

All reported reactions of cinnamylmagnesium halides have been carried out in ether or dioxane solutions, both solvents of low dielectric constant. The work reported here was carried out to see what effect ammonia, a high dielectric constant solvent, would have on the reactions of cinnamylmagnesium bromide.

When a concentrated ether solution of cinnamylmagnesium bromide was forced through a small capillary into well-stirred liquid ammonia at −76° a bright orange insoluble precipitate formed. This colored precipitate was stable for several hours at −76°. If the liquid ammonia mixture warmed up to −60° the orange precipitate changed to blue. At about −50° the blue color usually disappeared

(1) Presented at the 133rd Meeting of the American Chemical Society, April 13, 1958, in San Francisco, Calif.

(2) R. H. DeWolfe, D. E. Johnson, R. I. Wagner and W. G. Young, THIS JOURNAL, 79, 4798 (1957).

(3) R. H. DeWolfe, D. L. Hagmann and W. G. Young, ibid., 79, 4795 (1957).

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

(5) R. Y. Mixer and W. G. Young, ibid., 78, 3379 (1956).

(6) (a) W. G. Young, G. Ballou and K. Nozaki, ibid., 61, 12 (1939); (b) T. W. Campbell and W. G. Young, ibid., 69, 688 (1947).

to leave a white precipitate. The blue precipitate was also formed when an ether solution of cinnamyl-magnesium bromide at −40° was treated with one equivalent of liquid ammonia. When an equimolar amount of magnesium bromide dietherate was added to a liquid ammonia solution of phenylallyl-sodium at −70° an orange precipitate was formed, presumably the same as the orange precipitate above.

The colored precipitates in liquid ammonia were treated with a number of reagents to see if any organometallic character remained. Those which resulted only in protonolysis were carbon dioxide and acetaldehyde. Acetonitrile had a stabilizing effect on the colored precipitates. With acetonitrile in the liquid ammonia, warming the system to −34° caused the orange precipitate to turn a blue-green color. Cooling the system to −75° again caused the orange color to reappear. However, after 16 hours even at −75° the precipitate had turned white and liberated allyl- and propenylbenzene. The reagents were either too unreactive, as with acetonitrile which was recovered unchanged, or they reacted with the ammonia to give materials with acidic hydrogens, as was the case with carbon dioxide and acetaldehyde. The hydrocarbon product recovered from these reactions had essentially the same composition as the hydrocarbon obtained from the protonolysis of phenylallylsodium in liquid ammonia.[5] Excess liquid ammonia itself above −50° reacts with cinnamylmagnesium bromide to give hydrocarbon with the same composition as above.

Oxygen did react with the colored precipitate and a 15% yield of cinnamaldehyde was isolated from the reaction product. Oxygen reacts with alkyl-magnesium halides at −75° in ether to give good yields of alkyl hydroperoxide.[7] The cinnamaldehyde probably was formed from cinnamyl hydroperoxide under the slightly acid conditions used in working up the product. None of the isomeric phenyl vinyl ketone was isolated. However, it

$$C_6H_5CH=CHCHO\overset{+}{O}H_2 \longrightarrow$$
$$C_6H_5CH=CHCH_2O^+ + H_2O \longrightarrow$$
$$C_6H_5CH=CHCHO + H_3O^+$$
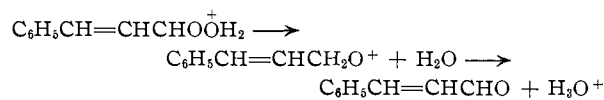
could have been present in small quantities and gone undetected or it may have been polymerized and lost. The reaction with oxygen established the organometallic character of the color precipitates.
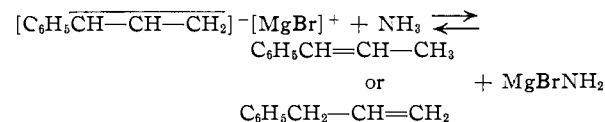
The intense color of the precipitate and the composition of the allylbenzene–propenylbenzene fractions indicate that the carbon–magnesium bond in cinnamylmagnesium bromide in liquid ammonia is ionized. Phenylallylsodium dissolved in liquid ammonia has a deep red color due to the free phenylallyl carbanion. In pentane, where the unsolvated phenylallyl ion is held in close association with the sodium ion in the crystal lattice, the color is an olive-green.[5] The orange color of the precipitate of cinnamylmagnesium bromide in liquid ammonia may indicate that the carbanion is not as free as the carbanion of phenylallylsodium in liquid ammonia but neither is it held in such a tight ion pair as-

(7) C. Walling and S. A. Buckler, THIS JOURNAL, **75**, 4372 (1953).

sociation as with phenylallylsodium in pentane. The blue color of the precipitate observed at −60° and above may represent a lower degree of solvation (ammoniation) with a consequent higher degree of ion pair association between the carbanion and the magnesium ion.

The instability of cinnamylmagnesium bromide in liquid ammonia is directly attributable to the magnesium ion. Phenylallylsodium, which contains the same carbanion II, is entirely stable at −34° in liquid ammonia, but when anhydrous magnesium bromide dietherate is added at −75° an orange precipitate forms which liberates allyl- and propenylbenzene upon warming to −34°.

One explanation might be that coördination of ammonia with the doubly charged magnesium ion imparts enough positive character to the amino nitrogen to make the hydrogens sufficiently acidic to react with the carbanions, the process being rapid above −50°.

Another possibility is that magnesium amide or magnesium amide bromide is much less soluble than the cinnamylmagnesium bromide–ammonia complex resulting in the complete precipitation of the magnesium as the amide or amide bromide with the consequent liberation of the hydrocarbons. The

$$[C_6H_5\overline{CH=CH-CH_2}]^-[MgBr]^+ + NH_3 \rightleftharpoons$$
$$C_6H_5CH=CH-CH_3$$
$$\text{or} \qquad + MgBrNH_2$$
$$C_6H_5CH_2-CH=CH_2$$

rate of solution of the cinnamylmagnesium bromide ammonia complex would, of course, increase with temperature and account for the more rapid destruction of the complex at the higher temperatures.

These experiments show that cinnamylmagnesium bromide can exist in liquid ammonia at low temperature although it has changed from the covalent organometallic it was in ether to an ionic solid.

Experimental

Preparation of Cinnamylmagnesium Bromide Using the High Speed Stirring Technique.—Three moles (72 g.) of magnesium turnings was placed in a 3-liter 3-necked, creased flask (Morton high-speed stirring type), fitted with two condensers and containing about 1500 ml. of anhydrous ether. The magnesium turnings were broken up by operating the high-speed stainless steel stirrer at full power for a few minutes. The stirrer was powered by a one-fourth h.p., 10,000 r.p.m., Bodine Electric Co. motor, type NSE-34. Cinnamyl bromide (19.7 g., 0.10 mole) dissolved in about 300 ml. of anhydrous ether was added over a one-hour period through a condenser to the flask containing the stirred magnesium and ether. The stirring motor was operated at about 80 volts during addition of the bromide. A nitrogen atmosphere under a slight positive pressure was maintained at all times in the apparatus. The heat of stirring plus the heat of reaction caused the ether to reflux vigorously. One aliquot of the Grignard solution was added to excess standard hydrochloric acid and back titrated to the methyl orange end-point with standard sodium hydroxide. Another aliquot was analyzed for bromide ion by the Volhard method. The yield of cinnamylmagnesium bromide calculated from this information was 94%.

The conditions for optimum yield were never determined and it may be that the addition time might be shortened considerably and concentrations increased without affecting the yield greatly.

Treatment of the Blue Ammoniated Cinnamylmagnesium Bromide Complex with Acetaldehyde.—An ether solution containing 0.042 mole of cinnamyl-magnesium bromide was

concentrated until a thick sirup remained. Anhydrous ammonia gas was passed into the flask containing the Grignard reagent. The flask became hot immediately and the surface of the Grignard solution turned white. The flask and contents were then cooled in a Dry Ice–acetone-bath and liquid ammonia condensed in the flask. The solid residue in the flask turned a dark blue. The blue material was not soluble in the liquid ammonia. Most of the liquid ammonia was force-siphoned off leaving just enough to cover the solid. When 20 ml. of acetaldehyde was added to the reaction mixture, very rapid disappearance of color occurred. The ammonia was evaporated and the residue was treated with water and ether and the ether layer separated. The ether layer was dried, the ether evaporated and the residue distilled at 15 mm. pressure. The first fraction of 3.5 g. had a boiling range of 75 to 105°. The temperature then rose rapidly to 190° and 6 g. of material distilled over in a 10° range.[8] There was 2 g. of residue remaining in the pot. No material distilled over at 122–123°, the boiling point of 2-hydroxy-3-phenylpentene-4.[9] The distillates were combined, dissolved in petroleum ether, b.p. 60–70°, and poured onto an alumina column containing 300 g. of activated alumina. The first 800 ml. of petroleum ether removed 3.5 g. (71% calculated as propenylbenzene) of oil from the column. The oil had b.p. 65–70° at 15 mm. and n^{25}D 1.5283. Two liters more of petroleum ether and one liter of carbon tetrachloride passed through the column and removed 5.5 g. of material which partially solidified upon standing. Subsequent elution of the column with chloroform and then with methanol removed only a small amount of colored sticky material.

The C₉-hydrocarbon fraction was not fractionated on a column and therefore no composition was computed in terms of allyl- and propenylbenzene.

Treatment of the Blue Ammoniated Cinnamylmagnesium Bromide Complex with Acetaldehyde.—One hundred milliliters of an ether solution containing 0.085 mole of cinnamylmagnesium bromide was treated with 200 ml. of dry pentane. This was an attempt to extract all coupled and hydrolysis products. Two liquid phases formed. The two phases were thoroughly mixed by stirring and the pentane layer was separated. Evaporation of the pentane layer gave 2.5 g. of oily material (probably coupled products and hydrolysis products). The remaining ether layer, containing the Grignard solution, was cooled to −70° and 200 ml. of liquid ammonia was distilled from an ammonia solution of sodium onto the very viscous Grignard solution. The dark blue cake which was formed was broken up in the ammonia until a dark blue slurry was formed. Most of the liquid ammonia was force-siphoned off and evaporated leaving only a trace of solid material. This indicates that the blue solid is not soluble in liquid ammonia. The blue mush, wet with liquid ammonia, remaining in the reaction flask was treated with 50 ml. of acetaldehyde. Water and ammonium chloride were added and the mixture was extracted with 200 ml. of ether. The ether phase was washed with 200 ml. of saturated sodium bicarbonate solution and then with 200 ml. of cold water. The ether layer was dried over anhydrous sodium sulfate and then distilled at 15 mm. pressure from a Claisen distilling flask to give a 7-g. (70% yield of C₉-hydrocarbon) fraction, b.p. 64–68°, and a 1-g. fraction, b.p. 155–165°. The 7 g. fraction was distilled at 20 mm. pressure through a wire gauze packed column rated at 30 theoretical plates using a diphenyl ether pusher. The distillation data are given below.

DISTILLATION OF THE C₉-HYDROCARBON FRACTION

Fraction	B.p. range, °C.	Wt., g.	n^{25}D
1	62–71	0.85	1.5338
2	71–72	0.91	1.5435
3	72–72	1.61	1.5463
4	72–72	1.24	1.5472
5	72–72	0.75	1.5472
6	72–72	0.26	1.5470

(8) A rough extrapolation of the boiling point of 1,4-diphenylhexa-1,5-diene, 157–160° (2 mm.) [H. Gilman and S. A. Harris, THIS JOURNAL, **54**, 2072 (1932)], to 15 mm. pressure would give a boiling range for this compound in the vicinity of 190°. This, then, is the coupled product.

(9) On. Kinn-Hono, *Ann. chim.*, **13**, 193 (1940).

The composition of this C₉-hydrocarbon fraction on the basis of refractive index is 96% *cis*- and *trans*-propenylbenzene and 4% allylbenzene.

There was no material isolated which would correspond to an addition product between cinnamyl Grignard and acetaldehyde.[9]

Carbonation of the Blue Ammoniated Cinnamylmagnesium Bromide Complex in Liquid Ammonia.—An ether solution (250 ml.) containing 0.10 mole of cinnamylmagnesium bromide was cooled to Dry Ice–acetone temperature and 100 ml. of anhydrous liquid ammonia was added. The first few drops of liquid ammonia caused an orange precipitate to form. As more liquid ammonia was added the color changed to blue. A magnetic stirring bar was used for stirring but so much solid formed that the stirring rapidly became ineffective. The slurry of blue solid was force-siphoned into a flask containing crushed Dry Ice. The ammonia was allowed to evaporate, the solution was acidified and extracted with ether. The ether layer was then extracted with aqueous sodium hydroxide. The aqueous layer was acidified and extracted with ether. Evaporation of the ether left no organic acid. The neutral fraction gave a 77% yield of C₉-hydrocarbons calculated from the refractive index to be 93% propenylbenzene and 7% allylbenzene.

Addition of One Equivalent of Ammonia to Cinnamylmagnesium Bromide in Ether at −40°.—An ether solution (350 ml.) containing 0.070 mole of cinnamylmagnesium bromide was cooled to −40° and 0.07 mole (1.5 ml. at −70°) of anhydrous liquid ammonia was added to the stirred solution. A blue precipitate formed immediately.

Treatment of the Yellow Ammoniated Cinnamylmagnesium Bromide Complex with Acetonitrile in Liquid Ammonia.—A 100-ml. ether solution, containing 0.078 mole of cinnamylmagnesium bromide, was forced through a capillary (0.05 mm. in diameter) into 400 ml. of stirred anhydrous ammonia at −76°. The Grignard formed a bright orange precipitate as soon as it hit the liquid ammonia. A Dry Ice–acetone-bath was kept around the reaction flask during the Grignard addition. At this point 6.3 ml. (0.15 mole) of acetonitrile, b.p. 80.5–81°, was added to the stirred reaction mixture. No immediate change was observed in the color of the precipitate. However, as the mixture warmed up to −34° the color changed through a green phase to a blue-green color. After 1 hour the precipitate was still a blue-green color. When the ammonia was cooled down again to −76° the precipitate changed back to orange. After standing for 11 more hours most of the time at −76° the yellow precipitate had turned white. Four and two-tenths grams of ammonium chloride was added to the liquid ammonia reaction mixture and the ammonia evaporated. The residue was washed with 400 ml. of ether and filtered. The ether was removed from the filtrate through a 2-ft. Vigreux column. The residue was fractionated through a column rated at 30 theoretical plates. Acetonitrile was recovered chiefly as its water azeotrope.[10] The C₉-hydrocarbon composition on the basis of refractive index analysis was 97% *cis*-and *trans*-propenylbenzene and 3% allylbenzene.

Temperature Effects on the Yellow Ammoniated Cinnamylmagnesium Bromide Complex.—An ether solution (75 ml.) containing 0.080 mole of cinnamylmagnesium bromide was added under pressure through a 0.05-mm. capillary to 350 ml. of anhydrous liquid ammonia at −75°. The ammonia was well stirred as the Grignard was added. A bright orange precipitate formed and the temperature rose to −65°. When the flask was allowed to warm to −60° the orange color began to disappear and a blue colored precipitate appeared along with an apparent change in the structure of the precipitate. The orange precipitate was of a granular nature whereas the blue precipitate was much finer. When the temperature was reduced to −76° again the color remained blue. The mixture was then allowed to warm up and at about −60° white precipitate became evident. At −50° there was only white precipitate. The reaction mixture was allowed to warm up to −34° and filtered. The filtrate was allowed to evaporate spontaneously and 7.5 g. of oily residue remained. This residue was distilled at atmospheric pressure from a Claisen flask to give 7.0 g. (74%) of material, b.p. 170–177°, n^{25}D 1.5462; composition 95% propenylbenzene, 5% allylbenzene.

Treatment of Phenylallyl sodium in Liquid Ammonia with Magnesium Bromide Dietherate.—A solution of phenylallyl-

(10) L. H. Horsley, "Azeotropic Data," American Chemical Society, Washington, D. C., 1952, p. 6.

sodium (0.10 mole) in liquid ammonia (300 ml.) was prepared according to the directions of Campbell and Young.[3] The dark red solution was cooled to −76° and 33.2 g. (0.10 mole) of magnesium bromide dietherate was added, with stirring, in small portions. The dark red color of the solution disappeared and an orange precipitate appeared when all the magnesium salt had been added. The ammonia was allowed to evaporate, ether was stirred with the residue and filtered off and the ether evaporated to give 10.5 g. of crude product. Distillation at atmospheric pressure from a Claisen distilling flask gave 9.0 g. of material, b.p. 170–177°, n^{25}D 1.5460. This represents a 76% recovery of C_9-hydrocarbon; composition 94% propenylbenzene, 6% allylbenzene.

Treatment of the Orange Ammoniated Cinnamylmagnesium Bromide Complex with Oxygen in Liquid Ammonia.— An ether solution (50 ml.) containing 0.040 mole of cinnamylmagnesium bromide was forced, under pressure, through a 0.5-mm. capillary into 400 ml. of stirred liquid ammonia. The temperature of the liquid ammonia was at −76° initially but rose to −70° after the addition of the Grignard solution. A bright orange precipitate formed the instant the Grignard solution came in contact with the liquid ammonia. Oxygen was bubbled through the reaction mixture for 10 to 15 minutes with no perceptible change occurring. The temperature was allowed to rise to about −60°, oxygen addition continuing, and the yellow color of the precipitate changed to greenish-yellow and then to white in about 5 minutes. The ammonia was then allowed to evaporate. Ether and water (75 ml. of each) were added to the reaction mixture and carbon dioxide was bubbled through the stirred mixture for 2 hours. This would decompose the magnesium salts of all alcohols and hydroperoxides which might be present. An easily filterable magnesium salt residue was formed. The reaction mixture was filtered. The ether layer was distilled to remove the ether and the residue was distilled at 20 mm. to give 1.2 g. of material, b.p. 67–73°. (This corresponds to the boiling range for the C_9-hydrocarbons.) The pressure was then reduced to 1 mm. and 0.8 g. of material distilled over between 70 and 100°. This fraction smelled strongly of cinnamaldehyde and gave a positive carbonyl test with 2,4-dinitrophenylhydrazine. There was 2.3 g. of dark residue remaining in the pot. The crude yield of cinnamaldehyde was 15% and of C_9-hydrocarbon, 25%.

The 2,4-dinitrophenylhydrazone had a melting point of 256–257° and was not depressed when mixed with an authentic sample of the 2,4-dinitrophenylhydrazone of cinnamaldehyde.
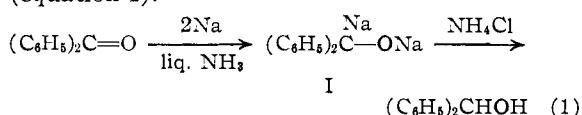
Los Angeles 24, Calif.
China Lake, Calif.

Reductive Metalation of Benzophenone and Benzalacetophenone by Alkali Metals in Liquid Ammonia and Some Condensations of the Resulting Dialkali Sålts[1,2]

By Phillip J. Hamrick, Jr., and Charles R. Hauser

Disodiobenzophenone prepared by the reductive metalation of benzophenone with two equivalents of sodium metal in liquid ammonia underwent several types of carbon–carbon condensations including alkylations, addition to the carbonyl group of benzaldehyde and conjugate addition to benzalacetophenone. Similarly, benzalacetophenone was reductively metalated by sodium or potassium in liquid ammonia to form dialkali derivatives. The dipotassio salt produced the corresponding saturated ketone on acidification, and gave the β-benzyl derivative with an equivalent of benzyl chloride. With two equivalents of the halide benzylation occurred at the β- and α-carbon atoms. Also, the dipotassio salt underwent an addition reaction with benzophenone to give the same product that was obtained from the conjugate addition of disodiobenzophenone to benzalacetophenone.

Wooster[3] has shown that benzophenone is reductively metalated by two equivalents of sodium metal in liquid ammonia to form the disodio salt I and that benzhydrol is obtained almost quantitatively on acidification with ammonium chloride (equation 1).

$$(C_6H_5)_2C{=}O \xrightarrow[\text{liq. NH}_3]{2\text{Na}} (C_6H_5)_2C{-}ONa \xrightarrow{\text{NH}_4Cl}$$
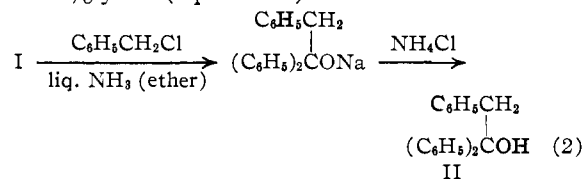$$\text{I}$$
$$(C_6H_5)_2CHOH \quad (1)$$

He also observed that disodio salt I can be alkylated with ethyl bromide to form 1,1-diphenylpropanol-1. The yield was not given, and ethylamine was obtained as a side reaction product.

Schlenk and his co-workers[4] had previously shown that such a reductive metalation of benzophenone and of biphenyl phenyl ketone can be accomplished in ether, and that the resulting disodio salt of the latter ketone can be carbonated to form the corresponding hydroxy-acid. The yield of this acid was not reported.

In the present investigation disodio salt I was found to take part in several carbon–carbon condensations to give good yields of products. More significantly it was shown that benzalacetophenone, which is a vinylog of benzophenone, will form similar dialkali salts and that they will undergo related reactions.

Results with Dialkali Salts of Benzophenone.— Disodiobenzophenone (I) was prepared by means of two equivalents of sodium in liquid ammonia (containing some ether) and benzylated with an equivalent of benzyl chloride to form carbinol II in 76% yield (equation 2).

$$\text{I} \xrightarrow[\text{liq. NH}_3 \text{ (ether)}]{C_6H_5CH_2Cl} (C_6H_5)_2\overset{\overset{\displaystyle C_6H_5CH_2}{|}}{C}ONa \xrightarrow{\text{NH}_4Cl}$$

$$(C_6H_5)_2\overset{\overset{\displaystyle C_6H_5CH_2}{|}}{C}OH \quad (2)$$
$$\text{II}$$

Evidently this preferential alkylation at the carbanion portion of disodio salt I was not accompanied by appreciable O-alkylation.

Similarly, disodio salt I was benzhydrylated with benzhydryl chloride to give carbinol III in 82% yield.

$$(C_6H_5)_2\overset{\overset{\displaystyle (C_6H_5)_2CH}{|}}{C}OH \quad \text{III}$$
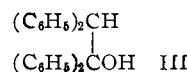
The structure of the latter product was established as III by an independent synthesis from

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

(2) Reported before the Regional Meeting of the American Chemical Society at Durham, N. C., November, 1957.

(3) C. B. Wooster, This Journal, **50**, 1388 (1928).

(4) W. Schlenk, J. Appenrodt, A. Michael and A. Thal, Ber., **47**, 473 (1914).