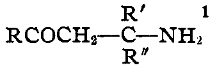
[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, THE UNIVERSITY OF TEXAS]

Keto-carbinamines, $RCOCH_2—\overset{R'}{\underset{R''}{C}}—NH_2$[1]



$$RCOCH_2—\overset{R'}{\underset{R''}{C}}—NH_2$$

BY CHESSIE E. REHBERG[2] WITH HENRY R. HENZE

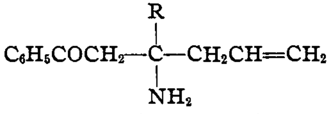
It has been reported recently[3] that allylmagnesium bromide has the unique ability to react with certain alkoxynitriles[4] in the molecular ratio of 2:1, and subsequently, upon hydrolysis of the adduct, to yield carbinamines of the type $R(allyl)_2C—NH_2$. Furthermore, it has been demonstrated that allylmagnesium bromide will react with the addition product formed by interaction of a nitrile and an alkylmagnesium halide to form carbinamines of the type $RR'(allyl)C—NH_2$. Finally, both types readily undergo catalytic reduction, the allyl group being converted into *n*-propyl.

Since this reaction constitutes a method for obtaining a type of amine for which, heretofore, there has been no general method of synthesis, it was desirable to determine its applicability to other types of substituted nitriles.

With the two-fold purpose of attempting to extend the reaction to nitriles containing the carbonyl group and of preparing a series of keto-amines, which were desired for further use in synthesis in this Laboratory, it was decided to determine whether carbinamines could be obtained thus from benzoylacetonitrile.[5] In this connection it was noted that, in a study of relative reactivities of various groups in competitive reaction toward phenylmagnesium bromide, Entemann and Johnson[6] found the carbonyl group in benzophenone to be much more reactive than the nitrile group in benzonitrile. However, Mavrodin[7] has noted that benzoylacetonitrile reacts in the enol form with 2.5 equivalents of ethylmagnesium bromide forming one-third of the anticipated diketone with recovery of two-thirds of the keto-nitrile.

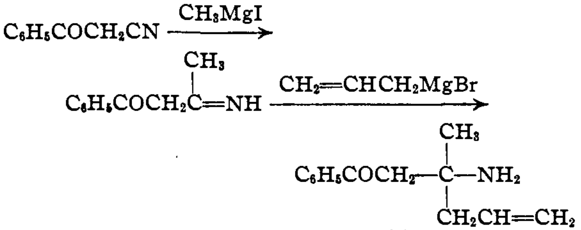
In the course of our study, we have duplicated Mavrodin's work except that ice-cold ammonium chloride solution was used to hydrolyze the adduct with the result that keto-ketimines rather than diketones were obtained. These ketimines were easily hydrolyzed to the corresponding diketones by the action of dilute aqueous solutions of alkali or acid. But when 3 or more equivalents of Grignard reagent was used, no benzoacetonitrile was recovered. Allylmagnesium bromide is definitely more reactive than are the alkyl reagents; however, the product obtained by use of an excess of the allyl reagent was a viscous oil which could not be distilled, was not basic, and readily polymerized to a tar.

In hope of obtaining products with a lesser tendency to polymerize, it was decided to attempt the preparation of carbinamines of the type



$$C_6H_5COCH_2—\overset{R}{\underset{NH_2}{C}}—CH_2CH{=}CH_2$$

by interaction of allylmagnesium bromide and the keto-ketimines obtainable through reaction of alkylmagnesium halides with benzoylacetonitrile. Accordingly, the simplest member of this series of keto-ketimines was prepared by treating benzoylacetonitrile with an excess of methylmagnesium iodide.[8] The ketimine, after recrystallization, was treated in ether solution with an excess of allylmagnesium bromide. The product obtained by hydrolysis of the addition product was the desired allylmethylphenacylcarbinamine (I).



$$C_6H_5COCH_2CN \xrightarrow{CH_3MgI} C_6H_5COCH_2\overset{CH_3}{C}{=}NH \xrightarrow{CH_2{=}CHCH_2MgBr} C_6H_5COCH_2—\overset{CH_3}{\underset{CH_2CH=CH_2}{C}}—NH_2$$

(I)

The ketocarbinamine (I) was found to be unstable at room temperature in that it slowly evolved ammonia. Attempts to distill it at a pressure of 3 mm. led to practically quantitative loss of ammonia from the carbinamine, evolution be-

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[1] Presented before the Division of Organic Chemistry at the 101st meeting of the American Chemical Society at St. Louis, Mo., April 8–10, 1941.

[2] From the Ph.D. dissertation of Chessie E. Rehberg, June, 1941.

[3] Allen and Henze, THIS JOURNAL, **61**, 1790 (1939).

[4] Unpublished data obtained by Allen and Henze prove that alkyl, alkenyl and aralkyl nitriles react in the same manner.

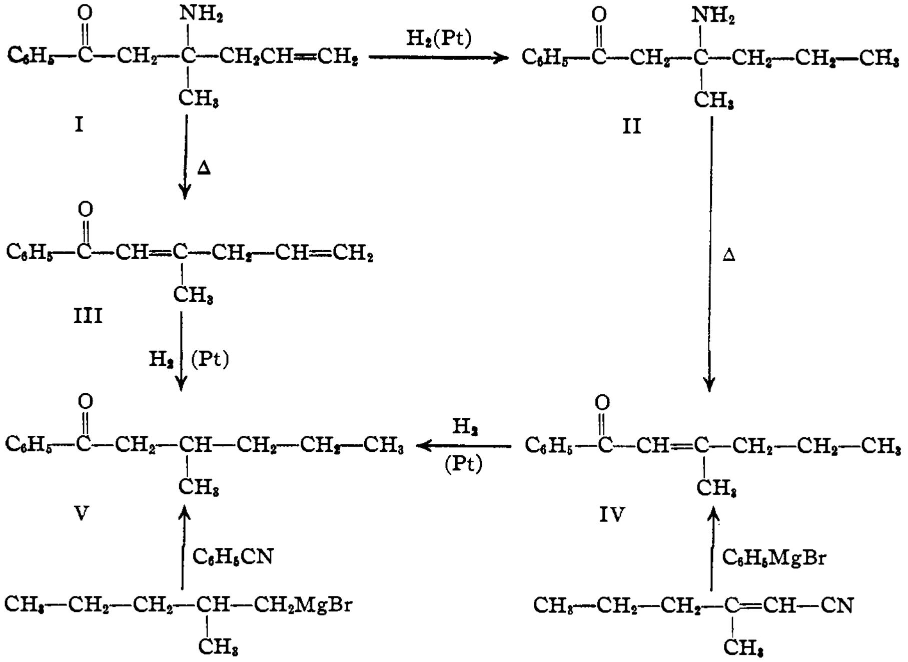
[5] Dorsch and McElvain, THIS JOURNAL, **54**, 2960 (1932).

[6] Entemann and Johnson, *ibid.*, **55**, 2900 (1933).

[7] Mavrodin, *Bul. Soc. Chim. România*, **15**, 99 (1933).

[8] It was found to be more convenient to prepare these keto-ketimines by the method of Beyer and Claisen, *Ber.*, **20**, 2178 (1887). Yields and physical constants checked those reported, but metallic sodium was found to be a more convenient condensing agent than sodium ethylate.

CHART I



coming quite rapid at 50–60°. Solutions of I in dilute hydrochloric acid could be kept almost unchanged at room temperature, separation of a nitrogen-free ketone III being noticeable only after several days. By contrast a sample of the keto-carbinamine after standing at room temperature for twenty-four hours was found to have decomposed to an extent of 50%. Attempts to prepare crystalline derivatives of I led only to oils or tars.

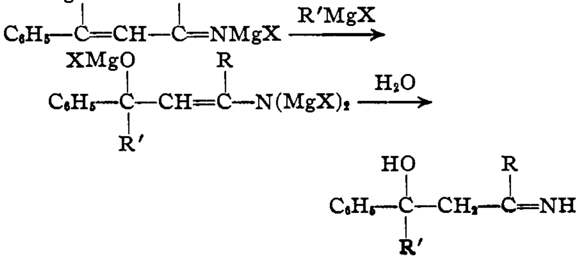
In the hope of stabilizing I, it was hydrogenated with the Adams platinum catalyst. The methylphenacylpropylcarbinamine (II) thus obtained, however, evolved ammonia just as did I, although somewhat less rapidly. Attempts to distill II likewise led to complete loss of nitrogen. The distillate consisted of a nitrogen-free, unsaturated ketone (IV). However, a crystalline picrate of II was obtained.

The interrelationship of the amines and ketones prepared in the present investigation may be presented best in diagrammatic form (Chart I). By this means, too, it is possible to indicate the manner in which the structures of these products have been elucidated.

The ease with which these carbinamines lose ammonia may be explained by analogy to the behavior of carbinols of similar structure. The ease of dehydration of (a) tertiary carbinols and (b) carbinols in which the hydroxyl group is beta to a carbonyl is well known. The keto-amines under consideration are both tertiary carbinamines and β-keto-carbinamines and, by analogy to the loss of water from carbinols of comparable structure, might be expected to lose ammonia quite readily.

By the same method as was used in the preparation of I, its next higher homolog, allylethylphenacylcarbinamine (VI), was prepared. It, likewise, was found to be unstable at room temperature, ammonia being evolved slowly, yielding an unsaturated ketone (VIII). Its other chemical and physical properties were very similar to those of its lower homolog. Also, VI was hydrogenated to form a saturated amine, ethylphenacylpropylcarbinamine (VII), which upon distillation yielded an unsaturated ketone, (IX), too.

Structure of the Reaction Products.—Since it was conceivable that reaction of allylmagnesium bromide involved 1–4 addition to the keto-carbinimines, thus producing hydroxy-imines rather than the desired keto-carbinamines



$$C_6H_5-\overset{XMgO}{C}=CH-\overset{R}{C}=NMgX \xrightarrow{R'MgX} C_6H_5-\underset{R'}{\overset{XMgO}{C}}-CH=\overset{R}{C}-N(MgX)_2 \xrightarrow{H_2O} C_6H_5-\underset{R'}{\overset{HO}{C}}-CH_2-\overset{R}{C}=NH$$

it was necessary to determine the position of the allyl radical, R′, in the product. Also, since it was known that loss of ammonia from the amines produced unsaturation, it was desirable to establish the position of the double bond thus produced. To achieve these two objectives required the elucidation of the structure of each ketone derived from an amine by loss of ammonia. The loss of ammonia in II was tentatively visualized as taking place in such a way that a double bond, conjugated with the carbonyl group, was produced (see Chart I). Support for this formulation was obtained from molecular refraction data. Hydrogenation of both unsaturated ketones, III and IV, produced the same saturated ketone (V).

Synthesis of V by another route was accomplished by treating benzonitrile with the Grignard reagent prepared from 1-bromo-2-methylpentane. The ketone thus obtained was identical with that from the keto-carbinamine.

Two independent syntheses of V left no doubt about the structure of the keto-carbinamines but gave no indication as to the position of the double bond formed when the latter evolved ammonia. Ozonolysis of IV having produced indicative but not decisive results, resort to synthesis by means of the Grignard reaction was again indicated, the reagents used being phenylmagnesium bromide and β-methyl-β-propylacrylonitrile.[9] The ketone thus obtained was identical with that (IV) formed from II by loss of ammonia.

Experimental

Interaction of Benzoylacetonitrile[10] with Alkylmagnesium Halides.—Grignard reagents were prepared in the usual manner and added to an anhydrous ether solution of benzoylacetonitrile. After twelve to eighteen hours the adduct was hydrolyzed by pouring onto a mixture of cracked ice and ammonium chloride. The ether solution was separated, filtered, dried and fractionated. Using 0.5 and 1 mole of *n*-propyl bromide per mole of nitrile, 90 and 83%, respectively, of the nitrile was recovered. Using 2.5 moles, 50% of the nitrile was recovered and 10% of a dimer formed. Using 3 moles, no nitrile was recovered, but 60% of a dimer and 20% of an imine were obtained. Using 3 moles of ethyl bromide and 3 moles of methyl bromide, no nitrile was recovered, but 12% of dimer and 25% of imine, and 52% of imine and some tar, respectively, were found. Using 1 mole and 2.5 moles of allyl bromide, 40 and 0% of nitrile, respectively, were recovered together with a viscous, red oil.

The **dimer**, m. p. 166°, was practically insoluble in ether, but soluble in alcohol, acetone and hot hydrochloric acid.

Anal. Calcd. for $C_{16}H_{14}N_2O_2$: mol. wt., 290.3; C, 74.47; H, 4.86; N, 9.65. Found: mol. wt. (Rast), 279; C, 74.34; H, 4.96; N, 9.64.

Obtained by action of *n*-propylmagnesium bromide, the **imine**, m. p. 93–94°, was moderately soluble in ether, quite soluble in alcohol, acetone and acids, but insoluble in water and basic solutions.

Anal. Calcd. for $C_{12}H_{15}NO$: C, 76.16; H, 7.99; N, 7.40. Found: C, 76.10; H, 8.11; N, 7.35.

Interaction of Benzoylacetonitrile with Allylmagnesium Bromide.—Addition of an ether solution containing allylmagnesium bromide[11] to one containing an equivalent of benzoylacetonitrile resulted in the formation of a white granular precipitate. The mixture was poured onto cracked ice and ammonium chloride; a heavy white precipitate insoluble in ether resulted and was removed by filtration. After recrystallization from alcohol, the solid melted at 79–80° and when mixed with benzoylacetonitrile (m. p. 80–81°), the mixture melted at 79–80°; 40% of the nitrile was recovered. From the ether solution was obtained a viscous red oil which was insoluble in acid and decomposed upon attempted distillation under 5 mm. pressure.

When two and one-half equivalents of allylmagnesium bromide was added to one equivalent of benzoylacetonitrile, a white precipitate formed but redissolved, then a gummy yellow precipitate separated. Upon hydrolysis no solid remained undissolved and from the ether solution only a viscous oil was obtained.

Preparation of Allylmethylphenacylcarbinamine (I).—To the Grignard reagent prepared from 48.4 g. of allyl iodide was added an ether suspension of 16.1 g. of methylphenacylketimine;[12] reaction produced a moderate evolution of heat and complete solution of the ketimine. After standing for twelve hours, the reaction mixture was poured onto 300 g. of crushed ice and 50 g. of ammonium chloride. Two clear layers resulted, no insoluble solid being formed. The ether layer was reduced in volume to 200 cc. and extracted twice with dilute hydrochloric acid. The acid extract was made alkaline with sodium hydroxide and the oil which separated was taken up in ether. The latter was dried over anhydrous sodium sulfate and evaporated under diminished pressure. The yield of allylmethylphenacylcarbinamine thus obtained was 17.3 g. (85% of the theoretical); $n^{20}\text{D}$ 1.5135; $d^{20}{}_4$ 0.9814; $M\text{R}\Sigma$ 62.20; $M\text{R}$ found 62.28.

This carbinamine was a yellow, oily liquid with an ammoniacal odor, soluble in alcohol, acetone, ether and acids, but insoluble in water and alkalies. At room temperature it slowly evolved ammonia; at higher temperatures, am-

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(9) This nitrile was prepared by the method of Gardner and Haworth, *J. Chem. Soc.*, **95**, 1963 (1909).

(10) The procedure of Dorsch and McElvain, ref. 5, was found to be very satisfactory, and 60% yields of benzoylacetonitrile were obtained; m. p. 80–81°.

(11) Gilman and McGlumphy, *Bull. soc. chim.*, **43**, 1322 (1928).

(12) Acetophenone and ethyl acetate were condensed by means of sodium, following the procedure of Claisen [*Ann.*, **291**, 51 (1896)] to form methyl phenacyl ketone; m. p. 60–61°. The diketone was dissolved in absolute alcohol, the solution was saturated at 0° with ammonia, placed in a steel bomb and the latter placed in an oven at 110° for twelve hours. Upon cooling and opening the bomb, most of the product was obtained as a crystalline mass. The latter was recrystallized from hot alcohol; m. p. 143–144° (cor.); yield 90–95%; Beyer and Claisen [*Ber.*, **20**, 2181 (1887)] report m. p. 143°. This method for preparation of the ketimine is superior to that involving the interaction of benzoylacetonitrile and methylmagnesium iodide.

monia was lost much more rapidly; at 0° the amine was sufficiently stable to be kept for several days without excessive decomposition. However, solutions of the carbinamine in acid solution were kept for two months without evidence of decomposition. Attempts to distill the amine at 3 mm. pressure resulted in complete loss of nitrogen in the form of ammonia. Attempts to form a picrate, benzoate, oxalate, tartrate, acetate and chloroplatinate produced gummy or oily materials.

Preparation of Allylethylphenacylcarbinamine (VI).—In a manner entirely analogous to that used for the lower homolog this carbinamine was prepared in 89% yield from interaction of 43.8 g. of ethylphenacylketimine and allylmagnesium bromide; n^{20}_D 1.5200; d^{20}_4 0.9903; $M_R\Sigma$ 66.82; M_R found 66.69; picrate, m. p. 110–111° (cor.).

Anal. Calcd. for $C_{20}H_{22}N_4O_8$: N, 12.55. Found: N, 12.68.

The physical and chemical properties of this carbinamine were very similar to those of its lower homolog, although it was slightly more stable in that it evolved ammonia less rapidly. It too gave a nitrogen-free distillate when distilled at low pressure.

Hydrogenation of Allylmethylphenacylcarbinamine (I).—By hydrogenation in the presence of Adams catalyst, I was converted into methylphenacylpropylcarbinamine (III). With 95% ethyl alcohol as solvent and 0.1 g. of the catalyst, 10.1 g. of the allylcarbinamine (I) was reduced in four hours at room temperature, using hydrogen at approximately two atmospheres pressure. After removal of the catalyst and evaporation of the solvent under diminished pressure, the oily residue was dissolved in 50 cc. of 5% hydrochloric acid. The acid solution was washed with ether and made alkaline; the oil thus caused to separate was taken up in ether and dried over sodium sulfate. After removal of ether, 9 g. (89% yield) of yellow oil remained; n^{20}_D 1.4876; d^{20}_4 0.9669; $M_R\Sigma$ 62.67; M_R found 61.13. This amine was but slightly more stable than the allylcarbinamine from which it was prepared.

Picrate of Methylphenacylpropylcarbinamine.—Prepared by adding a saturated aqueous solution of picric acid to one of the carbinamine in sulfurous acid; crystallized from alcohol, m. p. 93–94°. When heated above this melting point, the picrate evolved a gas at 110–120°, resolidified at 130–140°, remelted at 154–155°, again solidified at 156–160°, and finally melted with decomposition at 180–185°. When recrystallized from benzene, the m. p. was 123–124°; heated above this melting point, the behavior was identical as before. Upon repeated recrystallization from either dilute alcohol or benzene, the material melted at 154–155° (cor.), resolidified at 156–160°, final fusion at 180–185° (dec.).

Anal. Picrate of m. p. 93–94°. Calcd. for $C_{19}H_{22}N_4O_8\cdot {}^1/_2H_2O$: C, 51.47; H, 5.23; N, 12.63. Found: C, 51.60; H, 5.25; N, 12.74.

Anal. Picrate of m. p. 154–155°. Calcd. for $C_{19}H_{22}N_4O_8$: C, 52.49; H, 5.11; N, 12.89. Found: C, 52.35; H, 5.15; N, 12.73.

Hydrogenation of Allylethylphenacylcarbinamine (VI).—From 10.9 g. of this carbinamine, 10 g. (91%) of ethylphenacylpropylcarbinamine (VII) was obtained; n^{20}_D 1.4587; d^{20}_4 0.9191; $M_R\Sigma$ 67.29; M_R found 65.21. This carbinamine loses nitrogen in the form of ammonia slowly at room temperature and completely upon distillation under diminished pressure.

Picrate of Ethylphenacylpropylcarbinamine.—After one crystallization from dilute alcohol, m. p. 93–94°, resolidification at 135–150°, and fusion with decomposition at 180–185°. Recrystallization from benzene raised the melting point to 129–130° (cor.), with resolidification at 135–140°, refusion at 180–185° (dec.).

Anal. Calcd. for $C_{20}H_{24}N_4O_8$: N, 12.49. Found, N, 12.38.

Conversion of Allylmethylphenacylcarbinamine (I) into an Unsaturated Ketone (III).—From distillation at 10 mm. pressure of 20.3 g. of this carbinamine there was obtained 16 g. of distillate boiling at 130–145°. Traces of basic material were removed and the dry, neutral liquid was redistilled; yield 12 g. (64.5%); b. p. 135–137° (10 mm.); n^{20}_D 1.5950; d^{20}_4 1.0169; $M_R\Sigma$ 58.33; M_R found 62.23.

Anal. Calcd. for $C_{13}H_{14}O$: C, 83.83; H, 7.57. Found: C, 83.78; H, 7.40.

Conversion of Allylethylphenacylcarbinamine (VI) into an Unsaturated Ketone (VIII).—Distillation of 18 g. of the carbinamine (VI) yielded, after purification and redistillation of the product, 12 g. (72% yield); b. p. 130–132° (3 mm.); n^{20}_D 1.5914; d^{20}_4 1.0120; $M_R\Sigma$ 62.94; M_R found 66.92; 2,4-dinitrophenylhydrazone, m. p. 153–154° (cor.).

Anal. Calcd. for $C_{14}H_{16}O$: C, 83.94; H, 8.05. Found: C, 83.79; H, 8.16.

Conversion of Methylphenacylpropylcarbinamine (II) into an Unsaturated Ketone (IV).—Here, 10.3 g. of II was distilled, the product freed from basic material, dried and redistilled; yield, 7.4 g. (78.5%); b. p. 123–125° (5 mm.); n^{20}_D 1.5410; d^{20}_4 0.9714; $M_R\Sigma$ 58.79; M_R found 60.92; 2,4-dinitrophenylhydrazone, m. p. 140–141° (cor.).

Anal. Calcd. for $C_{13}H_{16}O$: C, 82.94; H, 8.56. Found: C, 82.60; H, 8.72.

Anal. Calcd. for $C_{19}H_{20}N_4O_4$: N, 15.20. Found: N, 15.15.

Conversion of Ethylphenacylpropylcarbinamine (VII) into an Unsaturated Ketone (IX).—By distillation of 22 g. of VII, with subsequent purification and fractionation, there was obtained 16.5 g. (81%) yield; b. p. 130–132° (4 mm.); n^{20}_D 1.5378; d^{20}_4 0.9663; $M_R\Sigma$ 63.41; M_R found 65.47; 2,4-dinitrophenylhydrazone, m. p. 131–133° (cor.).

Anal. Calcd. for $C_{14}H_{18}O$: C, 83.11; H, 8.97. Found: C, 82.95; H, 9.00.

Preparation of β-Methylcaprophenone. (V). A. By Hydrogenation of III.—By reduction in alcohol solution in the presence of the Adams catalyst, 10-g. portions of III were converted in essentially quantitative yield into V; b. p. 105–108° (3 mm.); n^{20}_D 1.5074; d^{20}_4 0.9516; $M_R\Sigma$ 59.26; M_R found 59.56.

Anal. Calcd. for $C_{13}H_{18}O$: C, 82.07; H, 9.53. Found: C, 81.94; H, 9.46.

2,4-Dinitrophenylhydrazone, m. p. 139–141° (cor.).

Anal. for $C_{19}H_{22}N_4O_4$: N, 15.13. Found: N, 14.91.

B. By Hydrogenation of IV.—Using the same conditions as in A above, IV was reduced to form V in quantitative yield; b. p. 105–108° (3 mm.); n^{20}_{D} 1.5042; d^{20}_{4} 0.9502; *M*R found 59.33; 2,4-dinitrophenylhydrazone, m. p. 138–140°.

C. **By Synthesis.**—2-Methylpentanol-1 was converted into the corresponding bromide by heating for three hours at 100° with 10% excess of phosphorus tribromide. A fraction was collected boiling at 42–44° (17 mm.); yield 65%; n^{20}_{D} 1.4495; d^{20}_{4} 1.1624; *M*RΣ 37.67; *M*R found 38.13.[13] An ether solution containing 103 g. (1 mole) of benzonitrile was added to one containing the Grignard reagent prepared from 219 g. (133 mole) of 1-bromo-2-methylpentane. After standing overnight, the adduct was hydrolyzed by slow addition of 400 cc. of 10% hydrochloric acid. An oily layer, insoluble in both ether and hydrochloric acid, separated, but after heating this oil to boiling in contact with the acid layer, it became soluble in ether. After washing the ether extract with alkali and with water, it was dried and fractionated to yield 48 g.; 25% yield; b. p. 106–108° (3 mm.); n^{20}_{D} 1.5067; d^{20}_{4} 0.9524; *M*R found 59.42; 2,4-dinitrophenylhydrazone, m. p. 140–141°.

Anal. Calcd. for $C_{19}H_{22}N_4O_4$: N, 15.13. Found: N, 15.15. Melting points of mixtures of 2,4-dinitrophenylhydrazone samples: **A** + **B**, 138–140°; **A** + **C**, 139–140°; **B** + **C**, 138–140°.

Preparation of β-Ethylcaprophenone. A. By hydrogenation of VIII.—B. p. 130–132° (5 mm.); n^{20}_{D} 1.5028; d^{20}_{4} 0.9421; *M*RΣ 63.88; *M*R found 64.09; 2,4-dinitrophenylhydrazone, m. p. 130–131°.

B. By hydrogenation of IX.—B. p. 130–132° (5 mm.); n^{20}_{D} 1.5016; d^{20}_{4} 0.9413; *M*R found 64.01; 2,4-dinitrophenylhydrazone, m. p. 129–131°. Melting point of mixture of 2,4-dinitrophenylhydrazones of samples **A** + **B**, 129–131°.

Synthesis of β-Methyl-β-*n*-propylacrylophenone (IV).—This compound was prepared by reaction of phenylmagnesium bromide with β-methyl-β-*n*-propylacrylonitrile, the latter according to the directions of Gardner and Haworth[14]: b. p. 70–72° (16 mm.); n^{20}_{D} 1.4346; d^{20}_{4} 0.8366; *M*RΣ 33.88; *M*R found 34.02.

Eight grams of β-methyl-β-*n*-propylacrylonitrile was allowed to react with the Grignard reagent formed from 15.7 g. of bromobenzene. After standing overnight, the reaction mixture was hydrolyzed with dilute hydrochloric acid and the product extracted with ether. A small amount of oil, insoluble in both ether and dilute acid, was heated to boiling with the aqueous layer of the hydrolysis mixture, after which the oil was ether-soluble. The ether extract was dried and distilled. A fraction of about 3 cc. was collected within the range 110–140° (5 mm.). On cooling the distillate, some biphenyl crystallized and was separated. The residual liquid was distilled and 1.2 g. (9% yield) of β-methyl-β-*n*-propylacrylophenone was collected at 122–125° (5 mm.); n^{20}_{D} 1.5445; d^{20}_{4} 0.9755; *M*RΣ 58.79; *M*R found 60.98; 2,4-dinitrophenylhydrazone, m. p. 138–140° (cor.). When mixed with a sample of the 2,4-dinitrophenylhydrazone of IV prepared by hydrogenation of II, the mixture melted at 138–140°.

Ozonolysis of β-Methyl-β-*n*-propylacrylonitrile (IV).—Following Whitmore's[15] procedure, 2-g. samples of the ketone (IV) in 30 cc. of petroleum ether (b. p. 25–35°) were ozonized for six to ten hours; the solutions were then dropped slowly into a boiling suspension of zinc dust in water. Examination of the aqueous and petroleum ether layers established the presence of benzoic acid and formic acid, and traces of acetophenone and methyl propyl ketone.

Summary

1. The preparation of carbinamines from nitriles by the use of allylmagnesium bromide has been extended to the preparation of β-keto-carbinamines, of which four examples have been described.

2. These β-keto-carbinamines have been found to be unstable in that they readily decompose with loss of ammonia to form unsaturated ketones. The position of the double bond produced by this decomposition has been shown to be conjugated with the carbonyl group.

3. The unsaturated ketones have been hydrogenated and the resulting ketones characterized. A total of six new ketones has been described.

AUSTIN, TEXAS RECEIVED MAY 19, 1941

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[13] Shonle, Waldo, Keltch and Coles, [THIS JOURNAL, **58**, 586 (1936)] reported b. p. 51–53° (25 mm.); $n^{26.5}_{D}$ 1.4484 for 1-bromo-2-methylpentane.

[14] Gardner and Haworth, ref. 9, reported b. p. 95–96° (30 mm.), but no other data.

[15] Church, Whitmore and McGrew, THIS JOURNAL, **56**, 176 (1934).