[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF NOTRE DAME]

Reactions of Acetylenic Primary Amines[1]

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In order to investigate possible uses of acetylenic primary amines in organic syntheses, some assorted reactions of 3-amino-3-methyl-1-pentyne have been studied in detail. It undergoes transformations typical of the amino group, the ethynyl hydrogen and the carbon–carbon triple bond. Alkylation, acylation, hydrogenation and addition to carbonyl compounds proceeded in the expected manner; yields were good in nearly all cases.

Discussion

In the preceding paper[1] it was reported that ammonolysis of ethynylcarbinyl chlorides of the type $R(R')C(Cl){-}C{\equiv}CH$ gives the corresponding primary amines. Since these compounds have not been available previously, it was considered of interest to study their reactions. For this purpose 3-amino-3-methyl-1-pentyne (I) was prepared in quantity and reactions typical of the amino group, the ethynyl hydrogen and the carbon–carbon triple bond were explored.

Treatment of I with acetic anhydride, benzoyl chloride and with cyanic acid gave the expected acetyl (II), benzoyl (III) and urea (IV) derivatives, respectively. Reaction with ethyl *p*-toluenesulfonate resulted in N-alkylation (V) and repetition of the procedure gave the diethylamino compound (VI). Low pressure hydrogenation of VI proceeded with extensive hydrogenolysis, giving chiefly diethylamine and 3-methylpentane and only a very small yield of 3-diethylamino-3-methylpentane. These results are in accord with the previous experience of Jones.[3] In our case the identification of both hydrogenolysis products provides convincing evidence that none of the transformations involved in the over-all synthesis[1] results in rearrangement.

Low pressure hydrogenation of I gave the expected saturated amine (VIII). Semi-reduction with sodium in liquid ammonia[4] yielded the intermediate allylic amine (IX), and catalytic hydrogenation of the latter gave VIII as expected. The two samples of VIII gave the same benzoyl derivative (X); the melting point was not depressed on mixing.

The reaction of carbon disulfide in ethyl alcohol with I, using the procedure of Batty and Weedon,[5] produced the thiazolidine-2-thione (VII) in good yield. It was also observed that VII was formed rapidly by mere mixing of I with carbon disulfide, the reaction being quite exothermic.

Addition of I to sodamide in liquid ammonia gave the sodium acetylide, evidenced by the fact that subsequent treatment with alkyl bromides produced the C-alkyl derivatives, XI and XII.[6] No N-alkylation was observed under these conditions. Hydrogenation of XI with Raney nickel in alcohol gave the saturated amine (XIII). As in the case of I, XI and carbon disulfide gave the thiazolidine-2-thione (XIV).

When the sodium acetylide of I in liquid ammonia was treated with aldehydes or ketones, acetylenic aminoalcohols were formed, *e.g.*, XV and XVI. A few acetylenic tertiary amines have been treated in the same way by Croxall and Dawson.[7] XV and XVI, derived from acetone and benzophenone, respectively, were easily recovered as crystalline solids. A similar reaction with benzaldehyde gave an oil, perhaps due to the formation of diastereoisomers. When a solution of the oil in benzene and light petroleum ether was left in the refrigerator for several weeks, a low yield of crystalline product formed. This material was then recrystallized without difficulty and gave the correct analysis. The aminoalcohols could be hydrogenated at low pressure over Raney nickel to give the saturated products (*e.g.*, XVII) and could be converted to thiazolidine-2-thiones (XVIII and XIX) by treatment with carbon disulfide.

Conversion of I to the aminoketone by hydration of the triple bond was attempted by the method of Rose and Weedon[8] and various modifications were tried. Addition of an aqueous solution of the amine sulfate to 50% sulfuric acid containing a small amount of mercuric sulfate gave a few grams of an unidentified crystalline product, but the results could not be duplicated. However, when the amino group was acylated as in III, the hydration was easily accomplished in aqueous alcohol containing catalytic amounts of sulfuric acid and mercuric sulfate. 3-Benzoylamino-3-methyl-2-pentanone (XX) was easily made in this way.

The transformations discussed above are diagrammed in the accompanying Chart I. Further work is in progress.

Experimental[9,10]

3-Amino-3-methyl-1-pentyne (I) was prepared as previously described.[1] The preparation was usually carried out with five moles of the chloride, yields in the ammonolysis step ranging from 50 to 55%. The acetyl and benzoyl derivatives (II and III) were described in the earlier paper.[1]

3-Ureido-3-methyl-1-pentyne (IV).—One-half mole (48.5 g.) of 3-amino-3-methyl-1-pentyne (I) was treated in the cold with dilute (1:9) hydrochloric acid to a faintly acid reaction to universal indicator paper. A solution of 44.5 g. (0.55 mole) of potassium cyanate in 200 ml. of water was then added in one portion, and the mixture was heated on

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[1] Paper LIX on substituted acetylenes; previous paper, THIS JOURNAL, 75, 1653 (1953).

[2] Eli Lilly Company Fellow, 1951–1953. This paper and the preceding one are abstracted from the Ph.D. dissertation of Eugene G. Teach, University of Notre Dame, 1953.

[3] E. R. H. Jones, R. N. Lacey and P. Smith, *J. Chem. Soc.*, 940 (1946).

[4] K. N. Campbell and L. T. Eby, THIS JOURNAL, 63, 216, 2683 (1941).

[5] J. W. Batty and B. C. L. Weedon, *J. Chem. Soc.*, 786 (1949).

[6] R. F. Parcell and C. B. Pollard, THIS JOURNAL, 72, 2385, 3312 (1950).

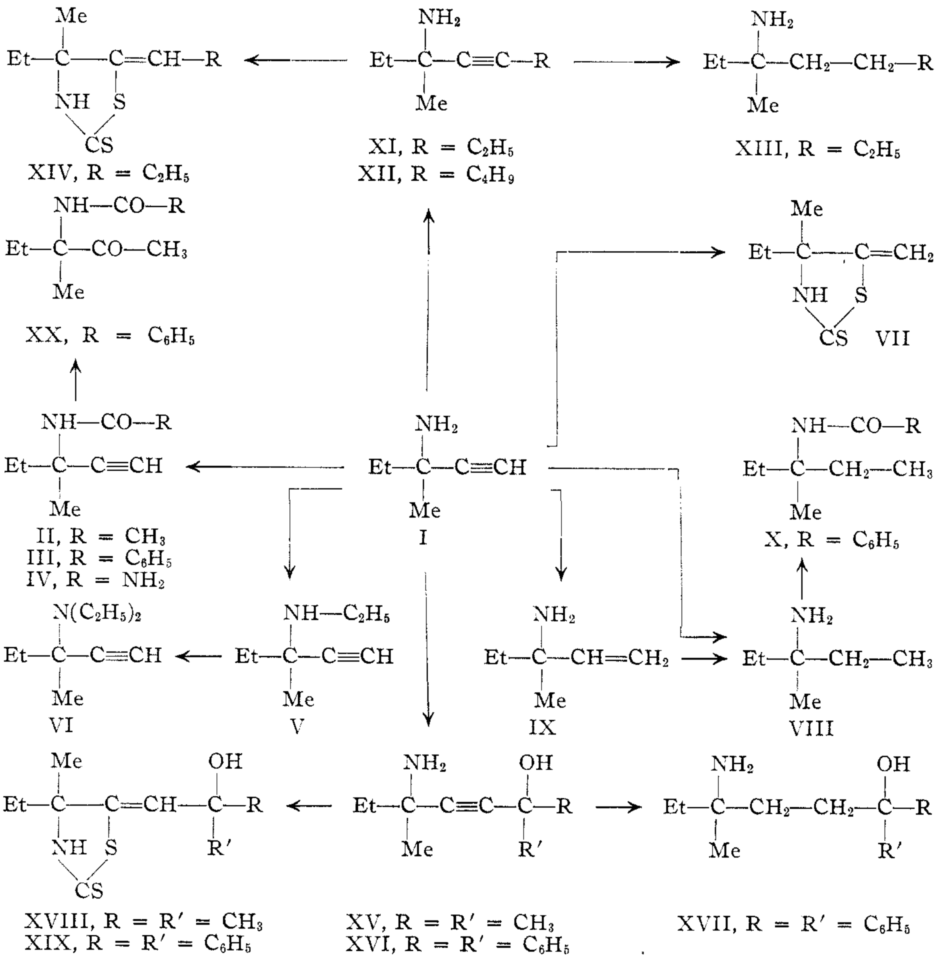
[7] W. J. Croxall and J. W. Dawson, U. S. Patent 2,584,429 (1952).

[8] J. D. Rose and B. C. L. Weedon, *J. Chem. Soc.*, 782 (1949).

[9] All melting points reported are uncorrected.

[10] Fractional distillations were carried out with an electrically heated glass helix packed column, packed section 1.4 × 45 cm.

CHART I



the steam-bath for 4 hours. Overnight crystallization gave 67.3 g. (96% yield), m.p. 101–103°. The product was twice crystallized from ethanol, m.p. 103–105°.

Anal. Calcd. for $C_7H_{12}N_2O$: N, 19.99. Found: N, 19.50.

3-Ethylamino-3-methyl-1-pentyne (V).—One mole (97 g.) of amine (I) was added slowly to one mole (200 g.) of ethyl *p*-toluenesulfonate in a one-liter round-bottom flask fitted with a reflux condenser. The mixture was heated by an oil-bath to 110° when an exothermic reaction occurred. The bath was lowered and the reaction mixture allowed to stand 4 hours. Heating was then resumed at 120–130° for 2 hours and the product was allowed to cool overnight. The amine was released with 75 g. of sodium hydroxide dissolved in 300 ml. of water, taken up in ether and the aqueous layer was extracted twice with 100-ml. portions of ether. The combined ethereal solution was dried superficially over anhydrous magnesium sulfate, then with anhydrous potassium carbonate. Distillation[10] gave 59.5 g. of product, b.p. 74–82° at 120 mm., $n^{25}\text{D}$ 1.4390–1.4310. Redistillation afforded 42 g. (35% yield), b.p. 77–78° at 120 mm., $n^{25}\text{D}$ 1.4318, d^{25} 0.802. A copious white precipitate formed when a few drops were added to ammoniacal silver nitrate solution, confirming the presence of the ethynyl group.

Anal. Calcd. for $C_8H_{15}N$: N, 11.19. Found: N, 11.18.

3-Diethylamino-3-methyl-1-pentyne (VI).—Ninety-seven grams (1.0 mole) of 3-amino-3-methyl-1-pentyne (I) was added to 250 ml. of benzene containing 200 g. (1.0 mole) of ethyl *p*-toluenesulfonate. The solution was refluxed for 2 hours and then allowed to cool (crystallization). Fifty grams of sodium hydroxide dissolved in 400 ml. of water was added with vigorous agitation. The benzene layer was separated and the aqueous layer extracted with 50 ml. of benzene. The combined benzene solution was dried with anhydrous potassium carbonate, filtered and a second 200-g. portion of ethyl *p*-toluenesulfonate was added. The solution was refluxed for 6 hours and then cooled overnight. The amine was released with 50 g. of sodium hydroxide in 400 ml. of water, and the benzene layer dried and distilled; yield 63.5 g., b.p. 99–103.5° at 120 mm., $n^{25}\text{D}$ 1.4362–1.4397. Redistillation gave 56.5 g. (37% yield), b.p. 103–105° at 120 mm., $n^{25}\text{D}$ 1.4397, d^{25} 0.812. The ammoniacal silver nitrate test was strongly positive.

Anal. Calcd. for $C_{10}H_{19}N$: N, 9.14. Found: N, 8.86.

Hydrogenation of 3-Diethylamino-3-methyl-1-pentyne.—To 100 ml. of methanol was added 31.6 g. (0.21 mole) of 3-diethylamino-3-methyl-1-pentyne and a 3-5-g. portion of Raney nickel. The mixture was shaken with hydrogen at an initial pressure of 60 p.s.i.g. for 7 hours. The catalyst was removed by filtration and the methanol solution treated with 50 ml. of 1:1 hydrochloric acid. An upper layer, presumed to be hydrocarbon, appeared at this stage. The entire mixture was distilled, the first 50 ml. of distillate boiling at 47–48°, obviously an azeotrope. This fraction was treated with ice-water and the hydrocarbon layer was separated, washed with water and dried over calcium chloride; weight 12 g. Distillation of this material gave 10 g., b.p. 64–68°, $n^{25}\text{D}$ 1.3820–1.3870. After redistillation from metallic sodium, the b.p. was 65–68°, $n^{25}\text{D}$ 1.3810–1.3860. Since these values are not good for 3-methylpentane, the infrared spectrum was examined and an olefinic impurity thus detected. After washing with four 5-ml. portions of concentrated sulfuric acid, water, 10% sodium carbonate solution, etc., the b.p. (3.6 g.) was 62–63.5°, $n^{25}\text{D}$ 1.3738–1.3740, in excellent agreement with the literature.[11] The infrared spectrum corresponded exactly for 3-methylpentane.[12]

The original methanolic solution was distilled to near dryness and 30 g. of 50% sodium hydroxide added to the residue. The amine layer was separated and dried with potassium hydroxide pellets. Distillation gave 3.7 g., b.p. 55–56°, $n^{25}\text{D}$ 1.3835, and 4.2 g., b.p. 79–81° at 30 mm., $n^{25}\text{D}$ 1.4343. The lower boiling product was readily identified as diethylamine; the *p*-toluenesulfonamide melted correctly at 59–60°. The higher boiling product, 3-diethylamino-3-methylpentane, was redistilled for analysis, 2.9 g., b.p. 79–80° at 30 mm., $n^{25}\text{D}$ 1.4350.

Anal. Calcd. for $C_{10}H_{23}N$: N, 8.91. Found: N, 9.20.

3-Amino-3-methylpentane (VIII).—Freshly distilled 3-amino-3-methyl-1-pentyne (I) (18.4 g.) was dissolved in 95 ml. of 95% ethanol, and 3-5 g. of Raney nickel was added. The mixture was shaken with hydrogen at an initial pressure of 60 p.s.i.g. for 1 hour and an additional 20.4 g. of I was added (total 0.4 mole). The apparatus was repressurized to 60 p.s.i.g. and the hydrogenation resumed. The catalyst was removed by filtration and the solution acidified with 50

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[11] G. Egloff, "Physical Constants of Hydrocarbons," Vol. I' Reinhold Publ. Corp., N. Y., 1939, p. 37.

[12] D. C. Smith, "Infrared Spectra of Pure Hydrocarbons," NRL Report No. C-3274, Naval Research Laboratory, Washington, D. C., 1948, p. 52.

ml. of concentrated hydrochloric acid. Alcohol and water were then removed by distillation *in vacuo*. The crystalline hydrochloride was dissolved in 25 ml. of water, and 50 ml. of 40% sodium hydroxide was added with cooling. The amine layer was taken up in ether and the solution dried with anhydrous potassium carbonate. Distillation gave 24.4 g. of VIII, b.p. 100–107°, $n^{25}{}_{\mathrm{D}}$ 1.4089–1.4115. Redistillation afforded 20.2 g. (50% yield), b.p. 108–109°, $n^{25}{}_{\mathrm{D}}$ 1.4115, d^{25} 0.759.

Anal. Calcd. for $C_6H_{15}N$: C, 71.21; H, 14.94; N, 13.84. Found: C, 71.04; H, 14.94; N, 13.58.

3-Amino-3-methyl-1-pentene (IX).—Forty-six grams (2 gram atoms) of sodium was dissolved in 2 liters of liquid ammonia contained in a 3-liter, 3-neck round-bottom flask fitted with a dropping funnel, mechanical stirrer and vent. A solution of 65 g. of 3-amino-3-methyl-1-pentyne (I) (0.67 mole) in 200 ml. of anhydrous ether was added dropwise with stirring during 2 hours. After an additional 2.5 hours stirring, 110 g. of ammonium chloride was added cautiously in small portions. Liquid ammonia (500 ml.) and ether (500 ml.) were added and the mixture was allowed to stand overnight. Then 300 ml. of ether and 500 ml. of water were added with stirring and the ethereal layer separated. The aqueous portion was extracted with 100 ml. of ether and the combined ethereal extracts dried over anhydrous magnesium sulfate. Distillation gave 41 g. of product, b.p. 103–104°, $n^{25}{}_{\mathrm{D}}$ 1.4252–1.4281. Redistillation yielded 29.5 g. (45% yield), b.p. 103–104°, $n^{25}{}_{\mathrm{D}}$ 1.4250–1.4260, d^{25} 0.782.

Anal. Calcd. for $C_6H_{13}N$: N, 14.12. Found: N, 13.79.

Hydrogenation of 3-Amino-3-methyl-1-pentene.—Freshly distilled material (9.9 g.) was hydrogenated in 50 ml. of ethanol with Raney nickel as described above. The product was taken up in benzene, the solution dried with anhydrous magnesium sulfate and treated with 11.6 g. of benzoyl chloride and 5 ml. of pyridine. After working up in the usual way, 15.3 g. of 3-benzoylamino-3-methylpentane (X), m.p. 70–72°, was obtained. The melting point was 73–74° after recrystallization from light petroleum ether. A different sample, made from 3-amino-3-methylpentane (VIII) described above, also melted at 73–74° and the melting point was not depressed by mixing.

Anal. Calcd. for $C_{13}H_{19}NO$: N, 6.82. Found: N, 6.96.

4-Methyl-4-ethyl-5-methylenethiazolidine-2-thione (VII).—3-Amino-3-methyl-1-pentyne (9.7 g.) and carbon disulfide (10 ml.) were dissolved in 50 ml. of ethanol and the solution refluxed for 4 hours. The ethanol and excess carbon disulfide were removed by distillation. The residue solidified on cooling, yielding 17 g. of pale yellow solid. The material was recrystallized from cyclohexane and light petroleum ether, yielding 15 g. of colorless crystals, m.p. 96–98°. A second crystallization from a mixture of benzene and petroleum ether raised the m.p. to 97–98°.

Anal. Calcd. for $C_7H_{11}NS_2$: C, 48.51; H, 6.40; N, 8.08. Found: C, 48.90; H, 6.60; N, 8.02.

3-Amino-3-methyl-4-heptyne (XI).—Sodamide was prepared in the usual way[13] from 16.5 g. of sodium in liquid ammonia, and 70 g. of 3-amino-3-methyl-1-pentyne (0.72 mole) diluted with 100 ml. of anhydrous ether was added dropwise with stirring. When addition was complete, the mixture was stirred for 30 minutes and 120 g. of ethyl bromide, diluted with 100 ml. of anhydrous ether, was added slowly. Addition required 45 minutes and after 30 minutes additional stirring, the mixture was allowed to stand overnight to evaporate most of the ammonia. Chopped ice (150 g.) was added and the ethereal layer was separated. The aqueous layer was extracted once with 50 ml. of ether and the combined ethereal solution was dried over anhydrous potassium carbonate. Distillation yielded 64 g. of product, b.p. 94–98° at 120 mm., $n^{25}{}_{\mathrm{D}}$ 1.4460–1.4435. Redistillation for analysis gave 54 g. (62% yield), b.p. 98–99° at 120 mm., $n^{25}{}_{\mathrm{D}}$ 1.4438, d^{25} 0.812.

Examination of the infrared spectrum revealed a doublet peak at 3.00 and 3.08 μ which was assigned to the amino group. The characteristic band at *ca.* 4.75 μ, indicative of terminal acetylenes, was absent. A band at 6.30 μ corresponds to the N–H bending frequency. The silver nitrate test was negative.

Anal. Calcd. for $C_8H_{15}N$: C, 76.74; H, 12.08; N, 11.19. Found: C, 76.72; H, 12.08; N, 11.16.

3-Amino-3-methyl-4-nonyne (XII) was prepared in the same way from 12 g. of sodium converted to sodamide, 47.5 g. of I and 68.5 g. of *n*-butyl bromide. The first distillation gave 53 g., b.p. 85–91° at 25 mm., $n^{25}{}_{\mathrm{D}}$ 1.4490–1.4465. Redistillation yielded 44 g. (59% yield), b.p. 92–93° at 25 mm., $n^{25}{}_{\mathrm{D}}$ 1.4470, d^{25} 0.810. The silver nitrate test for terminal acetylenes was negative.

Anal. Calcd. for $C_{10}H_{19}N$: N, 9.14. Found: N, 8.63.

3-Amino-3-methylheptane (XIII).—Thirty-seven and one-half grams of 3-amino-3-methyl-4-heptyne was hydrogenated with Raney nickel in alcohol as described above. After filtration of the catalyst, the solution was distilled and 35 g. of product recovered, b.p. 92–97° at 120 mm., $n^{25}{}_{\mathrm{D}}$ 1.4235–1.4242; redistillation: 29.5 g. (76% yield), b.p. 96–97° at 120 mm., $n^{25}{}_{\mathrm{D}}$ 1.4233, d^{25} 0.776.

Anal. Calcd. for $C_8H_{15}N$: N, 10.84. Found: N, 10.64.

The 4-Methyl-4-ethyl-5-propylidenethiazolidine-2-thione (XIV).—Five grams of 3-amino-3-methyl-4-heptyne was heated with 5 ml. of carbon disulfide as described above; yield, 7.5 g. of pale yellow solid, m.p. 56–58°. Two recrystallizations from petroleum ether gave colorless crystals, m.p. 59–60°.

Anal. Calcd. for $C_9H_{15}NS_2$: N, 6.96; S, 31.85. Found: N, 6.63; S, 31.89.

2,5-Dimethyl-5-amino-3-heptyne-2-ol (XV).—Metallic sodium (7.6 g.) was converted to the amide in liquid ammonia, and 32.3 g. of 3-amino-3-methyl-1-pentyne diluted with 50 ml. of anhydrous ether was added dropwise with stirring followed by 19.5 g. of acetone. The mixture was stirred for two hours and then left overnight to evaporate the ammonia. Chopped ice and ether were used for hydrolysis. The ethereal extract was dried and the ether evaporated. The residue was twice crystallized from a mixture of carbon tetrachloride and petroleum ether, giving 31 g. (60% yield) of white waxy crystals, m.p. 70–72°.

Anal. Calcd. for $C_9H_{17}NO$: C, 69.63; H, 11.04. Found: C, 69.50; H, 11.12.

1,1-Diphenyl-4-amino-4-methyl-2-hexyne-1-ol (XVI) was made in the same way from 7.6 g. of sodium, 32.3 g. of I and 67 g. of benzophenone. Two crystallizations from a mixture of benzene and petroleum ether gave 75 g. (76% yield), m.p. 108–109°. The hemisulfate was prepared from 5.6 g. of this material by neutralization with exactly the required amount of 95% sulfuric acid in 30 ml. of acetone. It was recrystallized from ethyl alcohol, m.p. 198° (dec.).

Anal. Calcd. for $C_{19}H_{21}NO\cdot{}^1/_2H_2SO_4$: C, 69.48; H, 6.75. Found: C, 68.75; H, 6.94.

1,1-Diphenyl-4-amino-4-methyl-1-hexanol (XVII).—Fourteen grams of XVI described above was dissolved in 200 ml. of ethanol, and 3 g. of Raney nickel was added. The mixture was shaken under hydrogen under an initial pressure of 60 p.s.i.g. for 12 hours. Filtration of the catalyst and evaporation of the alcohol yielded a solid which was crystallized from aqueous acetone; yield 12.7 g. (89%), m.p. 85–89°. Two recrystallizations from petroleum ether raised the m.p. to 94–95°.

Anal. Calcd. for $C_{19}H_{25}NO$: N, 4.94. Found: N, 4.88.

4-Methyl-4-ethyl-5-(2′-methyl-2′-hydroxypropylidene)-thiazolidine-2-thione (XVIII).—Six grams of 2,5-dimethyl-5-amino-3-heptyne-2-ol (XV) was heated with 5 ml. of carbon disulfide in 30 ml. of ethanol during 4 hours. Distillation of the alcohol and crystallization of the residue from petroleum ether gave 7.6 g. of product, m.p. 168–170°. Two recrystallizations from ethyl alcohol raised the m.p. to 173–174° (dec.).

Anal. Calcd. for $C_{10}H_{17}NOS_2$: C, 51.91; H, 7.41; N, 6.05. Found: C, 52.15; H, 7.59; N, 6.14.

4-Methyl-4-ethyl-5-(2′,2′-diphenyl-2′-hydroxyethylidene)-thiazolidine-2-thione (XIX) was prepared similarly from 9.3 g. of XVI and 5 ml. of carbon disulfide in 50 ml. of ethanol. The product, 9.2 g., m.p. 156–158°, was crystallized twice from a mixture of benzene and petroleum ether; m.p. 163–164° (dec.).

Anal. Calcd. for $C_{20}H_{21}NOS_2$: C, 67.57; H, 5.95; N, 3.94. Found: C, 67.40; H, 5.97; N, 4.10.

3-Benzoylamino-3-methyl-2-pentanone (XX).—A solution of 3-benzoylamino-3-methyl-1-pentyne (III) in alcohol (6.5 g. in 20 ml.) was added slowly to 0.3 g. of mercuric sulfate, 1 ml. of sulfuric acid, 10 ml. of water and 40 ml. of ethanol.

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[13] T. H. Vaughn, R. R. Vogt and J. A. Nieuwland, THIS JOURNAL, **56**, 2120 (1934).

The temperature was maintained at 60–70° throughout the addition and for 30 minutes thereafter. The mixture was cooled, filtered and evaporated to crystallization. The solid was collected and crystallized from aqueous alcohol; yield 2.7 g., m.p. 85–87°. Recrystallization raised the m.p. to 87–88°. The product did not respond to the ammoniacal silver nitrate test.

Anal. Calcd. for $C_{13}H_{17}NO_2$: N, 6.39. Found: N, 5.81.

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NOTRE DAME, INDIANA

[CONTRIBUTION FROM THE WESTERN REGIONAL RESEARCH LABORATORY[1]]

Reaction of Diacetyl and Cyclohexylamine

BY J. F. CARSON

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Diacetyl and anhydrous cyclohexylamine react at 0–25° to yield, as the principal product, the new crystalline 1,4-dicyclohexylimino-2,5-dimethyl-2-hydroxycyclohexene, I. This colorless crystalline compound when dissolved in methano- readily eliminates water under unusually mild conditions to yield the yellow crystalline diimine, N,N'-dicyclohexyl-2,5-dil methyl-1,4-benzoquinonediimine, VI. The diimine has interesting thermochromic properties. Solutions in methanol are yellow at 25° or above and red at 0° or below.

In connection with investigations on the non-enzymatic browning of vegetables, the reactions of some simple α-hydroxy-carbonyl and dicarbonyl compounds with primary aliphatic amines have been investigated.[2] In particular, the reactions of diacetyl have been examined, since diacetyl has been reported as a degradation product[3] resulting from the reaction of sugars and amino acids. Dicarbonyl compounds may also be of significance inasmuch as they effect the Strecker degradation of α-amino acids.[4] Reaction of diacetyl with methylamine, ethylamine or *n*-butylamine in aqueous solution at *p*H 7.0 (buffered with phosphate) at 25° slowly deposits intensely colored blue or purple precipitates which on longer standing gradually turn brown. Difficulties in the isolation of pure constituents from these reactions led to investigations under anhydrous conditions. These reactions, however interesting, have not yielded a satisfactory explanation of reactions in aqueous systems.

Reaction of diacetyl with a number of primary aliphatic amines yielded only brown resins or oils except in the case of cyclohexylamine. Reaction of diacetyl with excess anhydrous cyclohexylamine at 0–25° yielded the new compound I and traces of diacetyldicyclohexylimine II. The new dicyclohexyliminodimethylcyclohexenol derivative I is a colorless crystalline compound, very unstable in polar solvents at 25° but moderately stable in hydrocarbons. The compound is isolated and purified by recrystallizing from hexane at −20° or lower, the diacetyldicyclohexylimine II accumulating in the mother liquors. Although yields of the crude product are good, losses in recrystallization result in low yields (25–33%) of pure product.

Evidence for the structure of the new compound is obtained from elemental analysis, catalytic hydrogenation with the absorption of three moles of hydrogen, and particularly from the facile decomposition of the compound to a N,N'-dicyclohexylquinonediimine VI. In the ultraviolet, the compound has a maximum at 257 mμ (isoöctane). Infrared spectrum shows strong absorption at 6.12 and 6.20 μ and weak absorption at 6.28 μ in the region of C=C or C=N stretching. Strong absorption at 2.98 μ indicates that the oxygen atom is present as a hydroxyl group. One may speculate that the reaction proceeds first by an aldol condensation of two molecules of monocyclohexylimine III to yield IV followed by an internal aldolization accompanied by loss of the elements of water to yield I. Diacetyl in the presence of strong aqueous alkali is reported to condense in a similar manner to yield 2,5-dimethyl-1,4-benzoquinone.[5]

The new compound I undergoes an interesting solvolysis in methanol to the yellow crystalline N,N'-dicyclohexyl-2,5-dimethyl-1,4-benzoquinonediimine (VI) by loss of the *t*-hydroxyl group. The decomposition proceeds in good yield in methanol at 25° over a three-day period or in a few minutes in boiling methanol. The reaction also takes place in ethanol or isopropyl alcohol but more slowly. In the presence of chloroform, pyridine or acetic acid, compound I decomposes to give brown resinous material.

The structure of N,N'-dicyclohexyl-2,5-dimethyl-1,4-benzoquinonediimine (VI) was established by elemental analysis and by acid hydrolysis to cyclohexylamine and *p*-xylo-*p*-quinone. On hydrogenation in the presence of platinum oxide, VI absorbs one mole of hydrogen giving the crystalline aromatic diamine, N,N'-dicyclohexyl-2,5-dimethyl-*p*-phenylenediamine—supporting evidence of a qui-

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(1) Bureau of Agricultural and Industrial Chemistry, Agricultural Research Administration, U. S. Department of Agriculture. Presented at 123rd National Meeting of American Chemical Society, Los Angeles, March, 1953. Article not copyrighted.

(2) J. F. Carson, THIS JOURNAL, **75**, 4337 (1953).

(3) Report of Non-Enzymatic Browning Conference, Quartermaster Food and Container Institute for the Armed Forces, Feb. 1, 1952, published by Research and Development Associates, Food and Container Institute, Inc., Aug., 1952, pp. 31–34.

(4) A. Schönberg, R. Moubasher and A. M. Mostafa, *J. Chem. Soc.*, 176 (1948).

(5) H. von Pechmann and E. Wedekind, *Ber.*, **28**, 1846 (1895).