coöperation in obtaining Raman spectra, to Dr. John O. Edwards for stimulating discussion, and to the National Science Foundation and the National Cancer Institute of the National Institutes of Health (Grant C-3975) for financial support.

WALTHAM 54, MASS.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, DUKE UNIVERSITY]

Benzylation and Related Alkylations of α-Dimethylaminophenylacetonitrile by Means of Alkali Amides. Dehydrocyanation of Products to Form Enamines[1]

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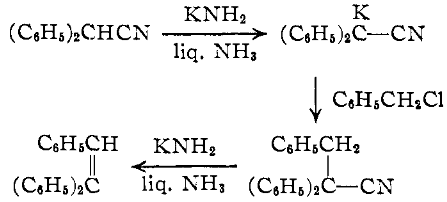
α-Dimethylaminophenylacetonitrile was benzhydrylated, benzhydrylated and α-phenylethylated with the appropriate halide by means of sodium amide or potassium amide in liquid ammonia. The resulting alkylation products were dehydrocyanated thermally or by means of potassium amide in liquid ammonia to form the corresponding enamines. Several types of reactions involving the latter products were effected.

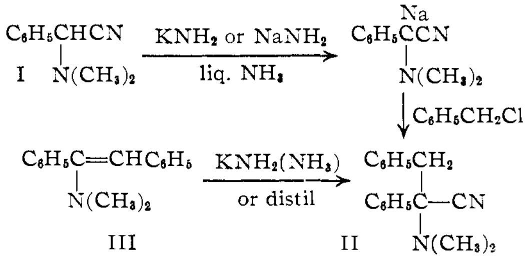
It has recently[3] been shown that diphenylacetonitrile can be benzylated, benzhydrylated and α-phenylethylated with the appropriate halides by means of potassium amide in liquid ammonia, and that the resulting alkylation products undergo dehydrocyanation on further treatment with this reagent. For example, the benzylation was realized in 96% yield, and the subsequent dehydrocyanation in 94% yield (Scheme A).

SCHEME A



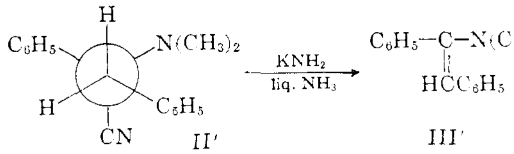
It has now been found that α-dimethylaminophenylacetonitrile (I) can be alkylated similarly with these halides, and that the alkylation products can be dehydrocyanated by further treatment with the alkali amide in liquid ammonia or even by heat alone. Thus, the benzylation of I gave alkylation product II in 91% yield, and the dehydrocyanation of this alkylation product formed enamine III in yields of 84–92% (Scheme B).

SCHEME B



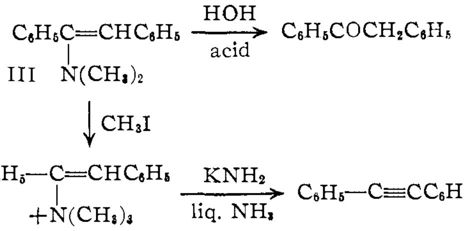
In contrast to the benzylation product of diphenylacetonitrile (see Scheme A), benzylation product II underwent dehydrocyanation[4] under the usual recrystallization conditions and during an attempted distillation *in vacuo*. However, the aminonitrile II was recrystallized satisfactorily from ether at low temperature.

The dehydrocyanation of benzylation product II by means of potassium amide in liquid ammonia produced an 84% yield of enamine III as a solid melting at 29–30°, but a liquid enamine was obtained in 92% yield when the dehydrocyanation was effected by an attempted distillation of II (see Scheme B). Apparently the former conditions formed largely a single geometrical isomer of the enamine whereas the latter conditions produced either the other isomer or a mixture of the two possible geometrical isomers of III.[5] It is suggested that the reaction with potassium amide involved the *trans* β-elimination of hydrogen cyanide from conformation II′ to give the geometrical isomer III′.



The enamine structure III was established by an acid-catalyzed hydrolysis of the dimethylamino group to form desoxybenzoin and by methylation followed by β-elimination of the resulting unstable methiodide (Scheme C).

SCHEME C



The type of acid-catalyzed hydrolysis indicated in Scheme C had previously been observed with

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(1) Supported in part by a grant from Merck, Sharpe and Dohme, Rahway, N. J.

(2) Deceased, Eastman Kodak Co. Fellow, 1955–1956.

(3) C. R. Hauser and W. R. Brasen, THIS JOURNAL, **78**, 494 (1956).

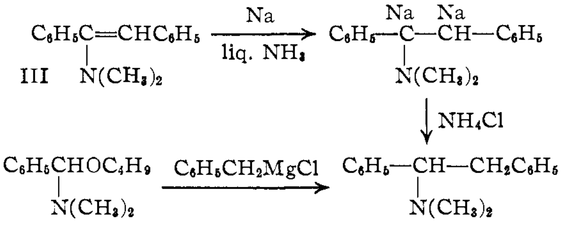
(4) This greater ease of dehydrocyanation of II might be due to the participation of the free pair of electrons on the amino group in the elimination of the cyanide group (along with a β-hydrogen) or to another molecule of II functioning as an amino base facilitating the removal of the β-proton.

(5) Because of the free pair of electrons on the nitrogen, a relatively low energy barrier between the two geometrical isomers might be expected. The isolation of such a pair has been reported by J. J. Conn and A. Taurins, *Can. J. Chem.*, **31**, 1211 (1953).

certain other enamines,[6] while the base-catalyzed β-eliminations of ordinary quaternary ammonium ions having β-hydrogens are well known.

The enamine structure III was confirmed by reduction of the carbon–carbon double bond with sodium in liquid ammonia to form 1,2-diphenyl-N,N-dimethylethylamine, which was independently synthesized from the appropriate α-amino ether and benzylmagnesium chloride[7] (Scheme D).

SCHEME D

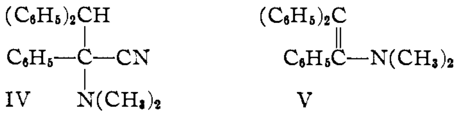


$$\underset{N(CH_3)_2}{C_6H_5C}{=}CHC_6H_5 \ (III) \xrightarrow[\text{liq. NH}_3]{\text{Na}} C_6H_5{-}\overset{Na}{\underset{N(CH_3)_2}{C}}{-}\overset{Na}{CH}{-}C_6H_5 \xrightarrow{NH_4Cl} C_6H_5{-}\underset{N(CH_3)_2}{CH}{-}CH_2C_6H_5$$

$$\underset{N(CH_3)_2}{C_6H_5CHOC_4H_9} \xrightarrow{C_6H_5CH_2MgCl} C_6H_5{-}\underset{N(CH_3)_2}{CH}{-}CH_2C_6H_5$$

Although enamines have previously been hydrogenated catalytically,[6,8] this appears to be the first example of a reduction by means of sodium in liquid ammonia.

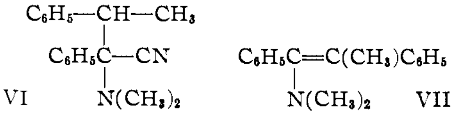
Similar to the benzylation shown in Scheme B, the benzhydrylation of α-dimethylaminophenylacetonitrile (I) was effected with benzhydryl chloride to give presumably alkylation product IV, which slowly eliminated hydrogen cyanide even at room temperature. Attempted recrystallizations were unsatisfactory. The crude alkylation product was dehydrocyanated by heating it in appropriate solvents to form enamine V in an over-all yield of 78%.



$$C_6H_5{-}\overset{(C_6H_5)_2CH}{\underset{N(CH_3)_2}{C}}{-}CN \quad (IV) \qquad C_6H_5\overset{(C_6H_5)_2C}{\overset{\|}{C}}{-}N(CH_3)_2 \quad (V)$$

The enamine structure V was established by the acid-catalyzed type of hydrolysis mentioned above to form benzhydryl phenyl ketone in 75% yield. The structure V was confirmed by reduction of the double bond by means of sodium in liquid ammonia to give 1,2,2-triphenyl-N,N-dimethylethylamine (89%), which was synthesized independently from the appropriate α-amino ether and Grignard reagent.[7] These reactions are analogous to those employed with the enamine III in Scheme D.

Also similar to the benzylation shown in Scheme B, the α-phenylethylation of α-dimethylaminophenylacetonitrile (I) was effected with α-phenylethyl chloride to form VI (90%), which was dehydrocyanated to give enamine VII.



$$C_6H_5\overset{C_6H_5{-}CH{-}CH_3}{\underset{N(CH_3)_2}{C}}{-}CN \quad (VI) \qquad \underset{N(CH_3)_2}{C_6H_5C}{=}C(CH_3)C_6H_5 \quad (VII)$$

Apparently this alkylation proceeded stereospecifically to form largely one of the two possible diastereoisomers, since the product, obtained in 90% yield, melted rather sharply (106–107°). Recently[9] the somewhat analogous α-phenylethylation of phenylacetonitrile and of phenylacetic acid were reported to produce largely the *erythro* isomer of the alkylation product, though the stereospecific nature of the reaction was established only in the latter case.

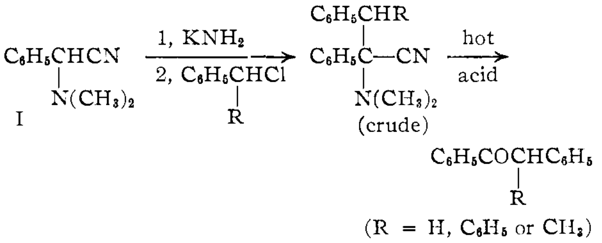
The α-phenylethylation product VI underwent dehydrocyanation to give a solid with potassium amide in liquid ammonia but a liquid on attempted distillation. Even the solid enamine product evidently consisted of a mixture of the two possible geometrical isomers of VII since it melted over a range.[10] Several careful recrystallizations[11] yielded two fairly sharp melting solids which apparently were the geometrical isomers of enamine VII. However, since a satisfactory analysis for the enamine was obtained with only one of the solids, the isolation of the second isomer cannot be considered as accomplished.[5,12]

The enamine structure for VII was established by the acid-catalyzed hydrolysis to form α-methyldesoxybenzoin.

The three enamines mentioned above, III, V and VII, gave strong infrared absorption bands at 1580–1600 cm.$^{-1}$ indicating the presence of the double bond conjugated with an aromatic ring.[13]

Enamine V yielded a picrate, but attempts to prepare the picrates of enamines III and VII resulted in the formation of the picrate of dimethylamine.

It should be mentioned that, not only the enamines III, V and VII, but also the α-aminonitriles II, IV and VI from which they were prepared, were converted in good yields to the corresponding ketones by means of hot acid. The enamines were presumably intermediates, although this was not established. The yields of the ketones given in the Experimental were based on the α-aminonitrile I since the crude alkylation products II, IV and VI were employed.[14]



$$\underset{N(CH_3)_2}{C_6H_5CHCN} \ (I) \xrightarrow[2,\ C_6H_5\underset{R}{CH}Cl]{1,\ KNH_2} C_6H_5\overset{C_6H_5CHR}{\underset{N(CH_3)_2}{C}}{-}CN \ \text{(crude)} \xrightarrow[\text{acid}]{\text{hot}} C_6H_5CO\underset{R}{CH}C_6H_5$$

(R = H, C$_6$H$_5$ or CH$_3$)

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[6] C. Mannich and H. Davidsen, *Ber.*, **69B**, 2106 (1936); C. Mannich, K. Handke and K. Roth, *ibid.*, **69B**, 2112 (1936).

[7] C. R. Hauser and A. T. Stewart, Jr., THIS JOURNAL, **77**, 1098 (1955).

[8] U. S. Patent 2,110,199; *C. A.*, **32**, 3418^6 (1938).

[9] C. R. Hauser, D. Lednicer and W. R. Brasen, THIS JOURNAL, **80**, 4345 (1958).

[10] On the assumption that the diastereoisomer of VI was pure, its reaction with potassium amide was evidently accompanied by some racemization. This could have occurred if the β-hydrogen were ionized to form a transient intermediate carbanion, the formation of which appeared to be indicated by the production of color during the reaction.

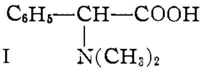
[11] In one attempt at recrystallization there was obtained a liquid enamine product similar to that resulting from the distillation of VI.

[12] If the two geometrical isomers were isolated their structures might be determined through the *cis* addition of hydrogen, since the configurations of the diastereoisomers of the resulting saturated amines are known; see D. J. Cram, THIS JOURNAL, **78**, 790 (1956).

[13] L. J. Bellamy, "The Infra-red Spectra of Complex Molecules," second edition, John Wiley and Sons, Inc., New York, N. Y., 1958, p. 72.

[14] This method is suitable for the preparation of α-methyldesoxybenzoin (see Experimental) and it shows promise of being useful for the synthesis of ring-substituted desoxybenzoins from appropriately substituted α-aminonitriles and halides.

Actually these conversions of alkylation products II, IV and VI to ketones were realized in connection with attempts to effect the hydrolysis of the cyanide group to form the corresponding α-amino acids. Although the amino acids were not isolated from the substituted α-aminonitriles,[15] the α-amino acid VIII was obtained in 89% yield by acid-catalyzed hydrolysis of I.



$$\underset{\textstyle \mathrm{N(CH_3)_2}}{\mathrm{C_6H_5{-}\overset{}{CH}{-}COOH}}$$

VIII

Experimental[16]

α-N,N-Dimethylaminophenylacetonitrile (I).—To a stirred solution of 624 g. (6 moles) of sodium bisulfite in 1.5 l. of water was added 636 g. (6 moles) of benzaldehyde (Eastman Kodak Co. white label product used without further purification) followed by 270 g. (6 moles) of anhydrous dimethylamine in 500 ml. of 50% aqueous methanol solution. The resulting mixture was cooled in an ice-bath, and 294 g. (6 moles) of solid sodium cyanide was added during 20 minutes. The ice-bath was removed, and the mixture was stirred at room temperature for 4 hours. The layers were separated, and the aqueous layer was extracted with ether. The ethereal extract was combined with the original organic layer and the ethereal solution dried over anhydrous magnesium sulfate. After filtering, the solvent was removed. The residue was distilled to give 912 g. (95%) of I, b.p. 78–79° at 1.1 mm., $n^{25}\mathrm{D}$ 1.5120; reported b.p. 85–87° at 1 mm., $n^{25}\mathrm{D}$ 1.5128[17] and b.p. 97–98° at 5 mm., $n^{25}\mathrm{D}$ 1.5120.[18]

Benzylation of I.—To a stirred suspension of 0.5 mole of sodium amide[19] in 500 ml. of liquid ammonia was added 80.6 g. (0.5 mole) of α-dimethylaminophenylacetonitrile (I) in an equal volume of dry ether. The resulting green solution was stirred for 5 minutes, and 63.3 g. (0.5 mole) of benzyl chloride in an equal volume of ether was then added during 15 minutes. The green color disappeared as the last of the halide was added. The mixture was stirred, and the ammonia was removed on the steam-bath as an equal volume of ether was being added. The resulting ethereal suspension was filtered, and most of the solvent was removed from the filtrate under reduced pressure at room temperature or below. The remaining solution was cooled to −78° in a Dry Ice-acetone-bath. Scratching induced crystallization. Two more crops were collected on a funnel giving a total of 114 g. (91%) of α-dimethylamino-α,β-diphenylpropionitrile (II) as a white solid with a faint yellow tinge, melting at 43–44°. A sample was dissolved in dry ether and cooled slowly to −78° to give large rock-like crystals, melting at 40–41°.

Anal. Calcd. for $C_{17}H_{18}N_2$: C, 81.56; H, 7.25; N, 11.19. Found: C, 81.38; H, 7.19; N, 11.21.

Thermal Dehydrocyanation of II.—Attempted distillation of the purified α-dimethylamino-α,β-diphenylpropionitrile (II) resulted in dehydrocyanation to form α-dimethylaminostilbene (III), which distilled.

In one experiment the benzylation of I was carried out on the 0.2-mole scale, and the crude alkylation product II, obtained as a residual oil on evaporating all of the solvent from the ethereal solution of the product (see above), was heated under reduced pressure employing an efficient Dry Ice trap and a sodium hydroxide trap to remove the hydrogen cyanide evolved. There was obtained 41.0 g. (92% over-all yield) of the enamine III as a viscous yellow oil, b.p. 132–135° at 1.4 mm., $n^{25}\mathrm{D}$ 1.6250. A sample was redistilled for analysis, b.p. 109° at 0.3 mm.

Anal. Calcd. for $C_{16}H_{17}N$: C, 86.05; H, 7.67; N, 6.27. Found: C, 86.18; H, 7.63; N, 6.33.

Dehydrocyanation of II with Potassium Amide.—To a stirred solution of potassium amide (0.1 mole) in 500 ml. of liquid ammonia[20] was added 25 g. (0.1 mole) of α-dimethylamine-α,β-diphenylpropionitrile (II). The resulting purple-brown suspension was stirred until the ammonia had evaporated. Ether was added, and the last traces of ammonia were removed by gently warming the mixture on the steam-bath. Water was added, and the two layers were separated. The ethereal layer was combined with the ethereal extract of the aqueous layer. The combined ethereal solution was dried over anhydrous magnesium sulfate and filtered. The solvent was removed under reduced pressure to give a yellow oil which was dissolved in methanol at room temperature. After filtering, the solution was cooled to −78° to precipitate 18.6 g. (84%) of α-dimethylaminostilbene (III), m.p. 28–29°. A sample was recrystallized by dissolving it in hexane and cooling to −78°, m.p. 30°.

Anal. Calcd. for $C_{16}H_{17}N$: C, 86.05; H, 7.67; N, 6.27. Found: C, 85.97; H, 7.67; N, 6.10.

Hydrolysis of Enamine III.—α-Dimethylaminostilbene (III) was hydrolyzed in good yield with acid to form desoxybenzoin by the procedure used for the hydrolysis of α-dimethylaminotriphenylethylene (V), described below. The identity of the desoxybenzoin was confirmed by its melting point and mixed melting point with an authentic sample.

Methylation of Enamine III and β-Elimination.—Excess methyl iodide was added to the enamine III in acetonitrile. Dry ether was added to precipitate the quaternary salt, which soon decomposed even in a desiccator. The freshly prepared salt (25 g., 0.0685 mole) was added to 0.2 mole of sodium amide in 400 ml. of liquid ammonia. After stirring for 2 hours, solid ammonium chloride was added, and the ammonia removed on the steam-bath as ether was being added. Water was added and the layers separated. The ethereal layer was washed with water, dilute hydrochloric acid and then water. After drying the ethereal solution over magnesium sulfate, the solvent was removed leaving an oil, which crystallized on cooling. Recrystallization from methanol–water gave 6.2 (51%) of diphenylacetylene (tolane), m.p. 59–60°, picrate m.p. 111–112°; reported m.p. for tolane 60–62°,[21] picrate 111–112°.[22]

Reduction of Enamine III with Sodium in Liquid Ammonia.—To 500 ml. of liquid ammonia was added 33.5 g. (0.15 mole) of α-dimethylaminostilbene (III) followed by 13.8 g. (0.6 g. atom) of metallic sodium, added in small pieces over a period of about 20 minutes. The solution was stirred for 2 hours, and then excess ammonium chloride was added cautiously, followed by wet ether. The dark color of the solution was discharged by the ammonium chloride. The ammonia was replaced by ether. Water was added and the layers were separated. The ether layer was washed with water, and the aqueous washings were extracted with ether. The combined ethereal solutions were dried over anhydrous magnesium sulfate. After filtering, the solvent was removed, and the residue was distilled giving 29.3 g. (87%) of 1,2-diphenyl-N,N-dimethylethylamine, b.p. 125–127° at 2.5 mm., $n^{25}\mathrm{D}$ 1.5569; reported b.p. 142° at 1.0 mm., $n^{25}\mathrm{D}$ 1.5569. The picrate, recrystallized from methanol, melted at 156–157°; reported m.p. 159–160°[7] and 156–157°.[23] A mixed melting point of the picrate with an authentic sample (see Scheme D) showed no depression.

Benzhydrylation of I and Dehydrocyanation of Alkylation Product.—The benzhydrylation of α-dimethylaminophenylacetonitrile (I) was effected on the 0.2-mole scale essentially as described above for the benzylation. The liquid ammonia was replaced by ether. After filtering, the solvent was removed to give a colored solid. Attempts to recrystallize this benzhydrylation product as described for the benzylation product II were unsatisfactory because of the ease with which it evolved hydrogen cyanide. A hot benzene solution of the crude product was treated with Norite, and filtered. The solvent was removed by boiling

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[15] An attempt to effect hydrolysis of the cyanide group of VI by means of concentrated sulfuric acid at room temperature (6 hr.) was unsuccessful. On pouring the solution onto crushed ice, 85% of VI was recovered.

[16] Analyses were performed by Galbraith Microanalytical Laboratories, Knoxville, Tenn. Melting points were determined on a Fisher–Johns apparatus and are uncorrected. Boiling points are uncorrected. Infrared spectra were produced on a Perkin–Elmer model 21 instrument.

[17] L. H. Goodson and H. Christopher, THIS JOURNAL, **72**, 358 (1950).

[18] W. C. Chambers, Ph.D. Thesis, Duke University, 1956.

[19] See C. R. Hauser, F. W. Swamer and J. T. Adams, "Organic Reactions," Vol. VIII, John Wiley and Sons, Inc., New York, N. Y., 1954, p. 122.

[20] See C. R. Hauser and T. M. Harris, THIS JOURNAL, **81**, 1160 (1959).

[21] A. Schwanert, *Ann.*, **148**, 330 (1868).

[22] G. Bruni and E. Tornani, *Gazz. chim. ital.*, **35**, 307 (1905).

[23] T. Thompson and T. S. Stevens, *J. Chem. Soc.*, 1932 (1932).

under the hood (hydrogen cyanide evolved), and the residual oil again heated in benzene solution until the solvent had evaporated. The resulting residue was heated in hot methanol solution for a short time and the solution was allowed to cool slowly (finally in the refrigerator). The precipitated bright yellow solid was collected on a funnel and air-dried to give 46.5 g. (79% over-all yield) of α-dimethylaminotriphenylethylene (V), m.p. 122–123°. A sample recrystallized from methanol melted at 124.5–125.5°.

Anal. Calcd. for $C_{22}H_{21}N$: C, 88.25; H , 7.07; N, 4.68. Found: C, 87.93; H, 6.81; N, 4.80.

The picrate of X, recrystallized from methanol, melted at 167–168°.

Anal. Calcd. for $C_{28}H_{24}N_4O_7$: C, 63.63; H, 4.58; N, 10.60. Found: C, 63.58: H, 4.64; N, 10.72.

Hydrolysis of Enamine V.—To 300 ml. of 6 *M* hydrochloric acid was added 29.9 g. (0.1 mole) of α-dimethylaminotriphenylethylene (V), and the solution warmed on a steam-bath for 0.5 hour. The resulting suspension was cooled, and the white solid was collected on a funnel to give, after recrystallization from ethanol, 20.5 g. (75%) of benzhydryl phenyl ketone, m.p. 135–136°, reported[24] m.p. 137°.

Reduction of Enamine V with Sodium in Liquid Ammonia.—Reduction of α-dimethylaminotriphenylethylene (V) was carried out on the 0.1-mole scale essentially as described above for enamine III. After removal of the ether, the grayish-white solid was dissolved in hot methanol, treated with Norite, filtered and air-dried to give 26.9 g. (89%) of 1,2,2-triphenyl-N,N-dimethylethylamine, m.p. 126.5–127.5°, picrate m.p. 223–224° dec. The reported melting point of the amine is 126.5–127.5°, and that of the picrate m.p. 223–224° dec.[7] Mixed melting points of both the amine and its picrate with authentic samples were not depressed.

α-Phenylethylation of I.—This reaction was carried out on the 0.1-mole scale essentially as described for the benzylation. The solvent was removed under reduced pressure from the ethereal solution of the reaction product to give a yellow solid which was dissolved in dry methanol and a small amount of acetone. After treatment with Norite and filtering, the solution was cooled in a refrigerator to give 21.5 g. of α-dimethylamino-α,β-diphenylbutyronitrile (VI), m.p. 106–107°. The filtrate was cooled to −78°, and the resulting precipitate recrystallized to give an additional 2.5 g. of the product, m.p. 106–107°, total yield 23.7 g. (90%). A sample, recrystallized by dissolving it in ether at room temperature and cooling to −78°, melted at 106.5–107.5°.

Anal. Calcd. for $C_{18}H_{20}N_2$: C, 81.78; H, 7.63; N, 10.26. Found: C, 82.23; H, 7.73; N, 10.47.

Thermal Dehydrocyanation VI.—The α-phenylethylation of I carried out on the 0.2-mole scale and the crude alkylation product was heated under reduced pressure yielding 39.7 g. (84%) of α-methyl-α′-dimethylaminostilbene (VII) as a viscous yellow oil, b.p. 115–118° at 0.65 mm., $n^{25}D$ 1.6005. An analytical sample distilled at 108° at 0.4 mm.

Anal. Calcd. for $C_{17}H_{19}N$: C, 86.03; H, 8.07; N, 5.90. Found: C, 86.19; H, 8.29; N, 5.87.

Attempts to prepare a picrate gave only the picrate of dimethylamine as evidenced by its analysis and melting point.

Dehydrocyanation of VI by Potassium Amide.—To a solution of 0.1 mole of potassium amide in 500 ml. of liquid ammonia was added 26.4 g. (0.1 mole) of α-dimethylamino-α,β-diphenylbutyronitrile (VI) in a small amount of ether to produce a purple color. After stirring for 3 hours under a Dry Ice–acetone condenser, the purple color disappeared. After stirring for 1.5 hours longer, 5.4 g. of ammonium chloride was added and the ammonia replaced by ether. After filtering, the solvent was removed under reduced pressure. The residual solid was dissolved in dry methanol and acetone and the solution cooled in a refrigerator to give 6.9 g. of a solid, m.p. 68–76° after recrystallization from methanol. After further recrystallizations from hexane (cooled to −78°) there was isolated 3.3 g. (14%) of α-methyl-α′-dimethylaminostilbene (VII), m.p. 73–74°.

Anal. Calcd. for $C_{16}H_{17}N$: C, 86.03; H, 8.07; N, 5.80. Found: C, 86.18; H, 7.97; N, 5.75.

Concentration of the above filtrates and further recrystallization at low temperature yielded 9.8 g. of a yellow solid, m.p. 40–42°, the carbon and nitrogen analysis for which were approximately 0.5 and 0.9 below the calculated values for the enamine VII.

In one experiment a hexane solution of the crude dehydrocyanation product (m.p. 62–70°) was allowed to stand at room temperature (about 35°) for several days. On then cooling to −78°, there was precipitated material that melted at room temperature even in a vacuum desiccator.

Hydrolysis of Enamine VII.—α-Methyl-α′-dimethylaminostilbene (VII), obtained as a liquid dislated of VI, was hydrolyzed in good yield to α-methyldesoxybenzoin by the method described above for enamine VI form.

Conversions of Crude Alkylation Products III, IV and VI to Ketones.—α-Dimethylaminophenylacetonitrile (I) was alkylated with benzyl chloride on the 0.2-mole scale as described above, and the ammonia was removed from the reaction mixture. Water (100 ml.) was added and the mixture heated on the steam-bath, with stirring, to remove the ether; 50% sulfuric acid (200 ml.) was added and the mixture stirred and heated at 110° for 4 hours under the hood (hydrogen cyanide evolved) to produce an oily layer on top of the water layer. The mixture was cooled and poured onto ice. The resulting precipitate was recrystallized from methanol (using Norite) to give 35.1 g. (90% based on I) of desoxybenzoin, m.p. 55–56°, which was undepressed on admixture with an authentic sample.

Similarly, α-aminonitrile I was alkylated on the 0.2-mole scale with benzhydryl chloride, and the crude reaction product was heated with acid. After hydrolysis and two recrystallizations from acetone–methanol, there was obtained an 84% yield of benzhydryl phenyl ketone, m.p. 134–135°, reported[22] m.p. 137°.

Similarly α-aminonitrile I was alkylated with α-phenylethyl chloride on the 0.1-mole scale, and the crude reaction product was hydrolyzed with acid. After recrystallization from methanol, 15.0 (72%) of α-methyldesoxybenzoin was obtained as fluffy white needles, m.p. 50–51°, reported[25] m.p. 53°.

Hydrolysis of I to Form α-Dimethylaminophenylacetic Acid (VII).—To 100 ml. of concentrated sulfuric acid was added with stirring 80.0 g. (0.5 mole) of α-dimethylaminophenylacetonitrile (I). The mixture became very hot. After stirring for 3 hours, enough water was added carefully to make an acid concentration of approximately 70%. The resulting mixture was heated to 150° and stirred, for 15 hours. After cooling, the solution was poured onto crushed ice, and concentrated ammonium hydroxide was added until the solution had the *p*H of 7. No product precipitated at this point indicating the absence of any amide. Norite (10 g.) was added to the cold brownish solution which was then filtered. Dilute sulfuric acid was added to *p*H 6. The resulting cloudy solution was concentrated to one-half its volume (about 750 ml.) and cooled in a refrigerator to precipitate 79.4 g. (89%) of α-dimethylaminophenylacetic acid (VIII), m.p. 241–241.5° (after drying at 110°). Recrystallization from ethanol–water raised the melting point to 246–247°, reported m.p. 240–241 and 254–255.5° dec.,[26] and 260–262°.[27]

Anal. Calcd. for $C_{10}H_{12}NO_2$: C, 67.02; H, 7.31; N, 7.82. Found: C, 67.20; H, 7.27; N, 8.22.

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[24] A. Werner, *Ber.*, **39**, 1278 (1906).

[25] V. Meyer and L. Oelkers, *Ber.*, **21**, 1295 (1888).

[26] J. A. King and F. H. McMillan, THIS JOURNAL, **73**, 4451 (1951).

[27] A. Knoop, H. Oesterlin, *Z. physiol. Chem.*, **170**, 186 (1927).