The above mixtures of amines were analyzed for amines IX and X by vapor phase chromatography, using the independently synthesized amines (see above, below) to prepare mixtures of known proportions.

Benzylethylmethylamine (X).—This amine, b.p. 92–94.5° at 7 mm., was prepared in 62% yield from benzylmethylamine and ethyl iodide by essentially the method described above for preparation of amine IX.

Anal. Calcd. for $C_{10}H_{15}N$: C, 80.48; H, 10.13; N, 9.39. Found: C, 80.48: H, 10.08; N, 9.36.

Beckmann Rearrangement of Michler's Ketone Oxime in the Presence of Cyanide[1]

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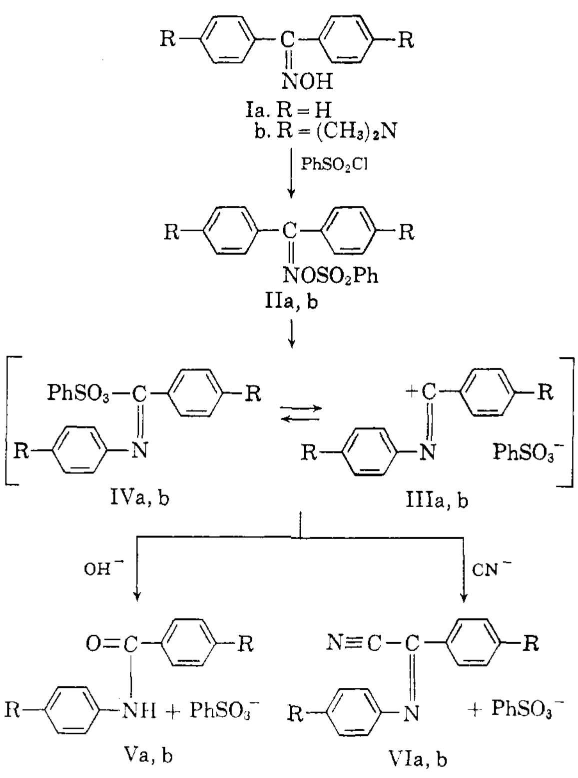
The Beckmann rearrangement of Michler's ketone oxime in the presence of cyanide ion yields α-(4-dimethylaminophenyl imino)-4-dimethylaminophenylacetonitrile. The phenyl groups are assigned *trans* positions on the basis of current theories on the mechanism of the Beckmann rearrangement.

The Beckmann rearrangement of oximes has been the subject of many investigations. One of the most significant contributions to the understanding of the reaction was made by Kuhara and co-workers.[5] They proposed that the rearrangement of benzophenone oxime by benzenesulfonyl chloride proceeds through an unstable iminosulfonate intermediate (IIIa, or IVa) which readily hydrolyzes to *N*-phenylbenzamide (Va) and benzenesulfonic acid (Chart I). Later, Oxley and Short[6] showed spectrophotometrically that the oily ester obtained from *N*-phenylbenzimino chloride and silver benzenesulfonate closely resembled Kuhara's unstable oil. They also added convincing evidence for Kuhara's iminosulfonate intermediate by forming substituted amidines through the Beckmann rearrangement of oximes in the presence of amines. In the work reported here, iminonitriles were obtained through the Beckmann transformation of benzophenone oximes in the presence of cyanide ion. The course of this Beckmann rearrangement also is best explained through Kuhara's iminosulfonate ester intermediate.

Chart I. Course of Beckmann Rearrangement



The ease with which 4,4′-bis(dimethylamino)- and 4,4′-bis(diethylamino)benzophenone oximes undergo the Beckmann rearrangement was indicated in a previous communication.[7] Subsequently, it was found that when Michler's ketone oxime, 4,4′-bis(dimethylamino)benzophenone oxime, was rearranged in the presence of potassium cyanide, a stable, red crystalline substance was formed instead of the colorless anilide. Elemental analyses of the red product established its empirical formula as $(C_9H_{10}N_2)_x$. Its infrared spectrum showed absorption in the triple bond region at 4.54 μ, suggestive of a highly stretched $-C\equiv N$ group. However, the absence of absorption at 6 μ, along with the presence of a broad band underlying the 6.55 μ aromatic band, strongly indicated that if any imino function, $>C=N-$, were present it would have to be conjugated. Also, the spectrum established the presence of *para*-substituted aromatic

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[5] M. Kuhara, K. Matsumiya, and N. Matsunami, *Mem. Coll. Kyoto*, **1**, 25, 105 (1914); *cf.*, A. H. Blatt, *Chem. Revs.*, **12**, 215 (1933).

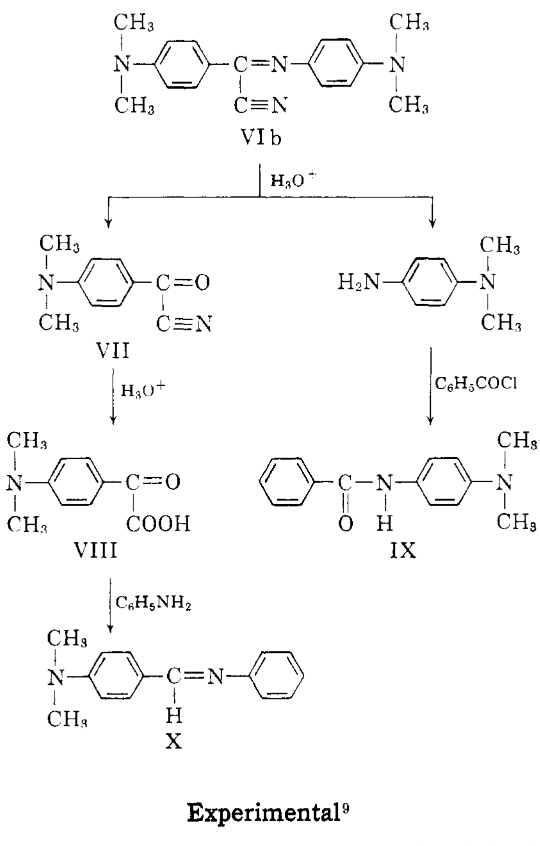
[6] P. Oxley and W. F. Short, *J. Chem. Soc.*, 1514 (1948).

[7] R. D. Morin, J. S. Warner, and R. H. Poirier, *J. Org. Chem.*, **21**, 616 (1956).

rings. On the basis of the analytical and spectral evidence, plus the observations of Oxley and Short[6] on the formation of amidines through the Beckmann rearrangement, the red product was tentatively assigned the iminonitrile structure VIb.

Initial proof of structure VIb was obtained by hydrolytic degradation as summarized in Chart II. Finally, unequivocal proof of structure was completed by synthesis through the condensation of 4-dimethylaminophenylacetonitrile with *N*,*N*-dimethyl-*p*-nitrosoaniline. *trans*-Assignment of the phenyl groups in VIb was prompted by current mechanistic theories on the Beckmann rearrangement.[8] According to these theories the hydrocarbon radical *trans* to the oxime hydroxyl migrates intramolecularly to the oxime nitrogen as the OH is released through a protonated or ester form. The carbonium cation (III) thus produced can subsequently react solvolytically with nucleophilic reagents, such as cyanide ion in the case under consideration.

CHART II. ACID HYDROLYSIS OF VIb



Experimental[9]

α - (4 - Dimethylaminophenylimino) - 4 - dimethylaminophenylacetonitrile (VIb). By Beckmann Rearrangement of Michler's Ketone Oxime. Procedure A.—A solution of 11.3 g. (0.04 mole) of Michler's ketone oxime,[7] m.p. 216–217°, in 240 ml. of acetone was mixed with a solution of 10.4 g. (0.16 mole) of potassium cyanide and 9.2 g. (0.16 mole) of potassium hydroxide in 40 ml. of water and treated dropwise with 14.0 g. (0.08 mole) of benzenesulfonyl chloride while maintaining the reaction mixture at 0–5°. When all of the benzenesulfonyl chloride had been added (about 45 min.), the mixture was stirred in the cold for 30 min., and at room temperature for 2 hr. It was again cooled to 0–5° and diluted by dropwise addition of 250 ml. of water. The red powdery precipitate that separated was removed by filtration and dried in air; yield, 10.65 g. An additional 0.45 g. was obtained by further dilution of the filtrate. Recrystallization of the combined crops from about 200 ml. of benzene and 50 ml. of ethyl alcohol gave 8.6 g. (74%) of red prisms, m.p. 212–213.5°, and another 1.5 g. (13%) of red crystals, m.p. 211–212°, by concentration of the mother liquor.

Anal. Calcd. for $C_{18}H_{20}N_4$: C, 74.0; H, 6.85; N, 19.15. Found: C, 74.6; H, 7.0; N, 18.8.

Procedure B.—A mixture of 5.65 g. (0.02 mole) of Michler's ketone oxime, 5.2 g. (0.08 mole) of potassium cyanide, 75 ml. of ethyl alcohol, and 50 ml. of benzene at room temperature was treated dropwise with a solution of 5.6 g. (0.04 mole) of benzoyl chloride in 5 ml. of benzene. The mixture was warmed to 50–55°, stirrred at that temperature for 1 hr., and then cooled. The red crystals that separated were removed by filtration, washed with ethyl alcohol and water, and finally dried in air. The filtrate and ethyl alcohol washings were combined and concentrated to yield additional material that was orange-red. The two crops of crystals weighed 5.9 g., m.p. 188–212°. After two recrystallizations, once from benzene plus a little ethyl alcohol, and finally from benzene, there was obtained 3.2 g. (55%) of red prisms that melted sharply at 213–214° and was identical with the compound cited above. Concentration of the mother liquors furnished an additional 0.75 g. (13%) of red crystals, m.p. 212–213°.

Procedure C.—A mixture of 1.33 g. (3.4 mmoles) of the benzoate of Michler's ketone oxime[7] and 35 ml. of ethyl alcohol saturated with potassium cyanide was refluxed for 2 hr. during which time it became orange-red. Upon pouring the reaction mixture into water there precipitated an orange-red solid, which after two crystallizations from benzene–ethyl alcohol yielded 0.52 g. (55%) of red crystals, m.p. 211–212°. This product did not depress the melting point of the product obtained from the reaction of Ib with benzoyl chloride and potassium cyanide.

By Reaction of 4-Dimethylaminophenylacetonitrile with *N*,*N*-Dimethyl-*p*-nitrosoaniline.—A solution of 0.8 g. (5 mmoles) of 4-dimethylaminophenylacetonitrile,[10] 0.75 g. (5 mmoles) of *N*,*N*-dimethyl-*p*-nitrosoaniline and 10 drops of 5 *N* aqueous sodium hydroxide in 15 ml. of ethyl alcohol was heated on a steam bath for 1 hr. The reaction mixture changed color from green to brown to brick red, and a large a mount of red solid separated. After cooling in ice water, the mixture was filtered and the solid was collected and washed with a little ethyl alcohol. The crude product weighed 1.45 g., m.p. 208.5–210°, and, after one crystallization from benzene–ethyl alcohol yielded 0.7 g. (48%) of red crystals, m.p. 212–213.5°. This product, too, proved to be identical to the red product formed by the Beckmann rearrangement of Ib in the presence of cyanide ion.

Characterization of VIb through Acid Hydrolysis. 4-Dimethylaminobenzoyl Cyanide (VII).—Addition of 1.45 g. (5 mmoles) of VIb to 10 ml. of concd. hydrochloric acid at room temperature first formed a red solution, which, within a few seconds faded to yellow. As soon as the red color had disappeared, the solution was diluted with 30 ml. of water, whereupon 0.70 g. (81%) of bright yellow crystals, m.p. 170–171°, were precipitated. Recrystallization from ethyl alcohol gave 0.5 g. (58%) of bright yellow flakes, m.p. 172–173°.

Anal. Calcd. for $C_{10}H_{10}N_2O$: C, 69.0; H, 5.75; N, 16.1. Found: C, 68.7; H, 5.7; N, 16.7.

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[8] "Structure and Mechanism in Organic Chemistry," by C. K. Ingold, Cornell University Press, Ithaca, N. Y., 1953, p. 510.

[9] All melting points are uncorrected.

[10] Obtained as tan crystals, m.p. 57–58°, in 12% yield from 4-aminophenylacetonitrile and methyl sulfate; J. von Braun and G. Blessing, *Ber.*, **56**, 2153 (1923), give m.p. 55–56°.

4-Dimethylaminobenzoyl Formic Acid (VIII).—In another hydrolysis of VIb, the acid solution was allowed to stand at room temperature overnight. The mixture was made alkaline with 5 *N* sodium hydroxide solution and the *N*,*N*-dimethyl-*p*-phenylenediamine that separated was removed by extraction with ether–benzene. The aqueous phase then was cooled in ice water and acidified to *p*H 2 by means of dilute hydrochloric acid to obtain 0.5 g. of greenish yellow crystals, that melted with liberation of gas and darkening at 173–175°. Recrystallization from ethyl alcohol gave 0.4 g. (42%) of greenish yellow needles, and raised the melting-decomposition point to 175–176°. The pure keto acid[11] is finally obtained in golden yellow needles, m.p. 180° dec. from ethanol.

Anal. Calcd. for $C_{10}H_{11}NO_3$: C, 62.2; H, 5.7; N, 7.3. Found: C, 62.8; H, 6.0; N, 7.5.

4-Dimethylaminobenzalaniline (X).—Further proof of 4-dimethylaminobenzoylformic acid as one of the degradation products from the hydrolysis VIb was obtained by decarboxylation of its anil according to a method described by Bouveault.[12] Thus, 0.95 g. (0.05 mole) of the keto acid and 2.0 g. (0.02 mole) of freshly distilled aniline were boiled for 10 min. Excess aniline was then distilled under reduced pressure, leaving a yellow oily residue that solidified upon cooling. Two crystallizations from ethyl alcohol gave 0.4 g. of micro, yellow crystals, m.p. 98.5–99.5°. This substance did not depress the melting point of an authentic specimen of the anil (m.p. 98–99°) derived from 4-dimethylaminobenzaldehyde.

Anal. Calcd. for $C_{15}H_{16}N_2$: C, 80.35; H, 7.15; N, 12.5. Found: C, 80.35; H, 7.24; N, 12.2.

***N*′-Benzoyl-*N*,*N*-dimethyl-*p*-phenylenediamine (IX).**—The acid filtrate obtained upon precipitation of the 4-dimethylaminobenzoyl cyanide was evaporated to dryness by heating on a steam bath under a stream of air until most of the water was driven off, and finally by heating in a vacuum oven at 50°. The 1.1 g. of white salt that remained was dissolved in 2 ml. of water and, with ice cooling, was treated successively with 1 ml. each of benzoyl chloride and 5 *N* sodium hydroxide. The tan benzoyl derivative formed was recrystallized from benzene–ethyl alcohol to give 0.45 g. (37%) of white needles, m.p. 228–229°. These did not depress the melting point of the benzoyl derivative (m.p. 226–228°) of an authentic specimen of *N*,*N*-dimethyl-*p*-phenylenediamine.

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[11] H. Staudinger and H. Stockmann, *Ber.*, **42**, 3485 (1909), prepared it from dimethylaniline and oxalyl chloride or oxalyl monoester chloride, m.p. 187°.

[12] L. Bouveault, *Bull. soc. chim.* **15**, 1020 (1896); **17**, 363 (1897).

Dienone–Phenol Rearrangements of 4-Dichloromethyl- and 4-Trichloromethyl-4-methyl-2,5-cyclohexadien-1-one[1]

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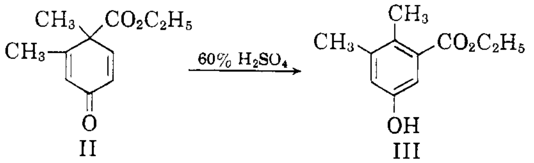
4-Dichloromethyl-4-methyl-2,5-cyclohexadien-1-one and 4-trichloromethyl-4-methyl-2,5-cyclohexadien-1-one undergo the normal dienone–phenol rearrangement in 80% sulfuric acid. The latter compound, in addition to the normal product, gives 10% of a cresotic acid derivative resulting from a 1,3-shift of the trichloromethyl group.

The dienone–phenol rearrangement is generally acknowledged to proceed through migration of a hydrocarbon radical with its pair of bonding electrons.[2] Consistent with this mechanism are indications that the rearrangement may proceed with difficulty or be prevented altogether if the site from which the migrating group must leave is made electron-deficient by the introduction of electron-attracting groups. Thus, 4 - dichloromethyl - 4 - methyl-2,5-cyclohexadien-1-one (I)[3] and its naphthalenic analog, 4-dichloromethyl-4-methyl-1(4*H*)-naphthalenone,[4] fail to rearrange when treated with a catalytic amount of sulfuric acid in acetic anhydride, a medium which serves well for similar unchlorinated compounds.[5]

Results reported in two papers indicate that 2,5-cyclohexadien-1-ones with an electron-withdrawing group in the *gem* position may, in fact, rearrange abnormally.[6] Compound II has been found to give III upon treatment with 60% sulfuric acid,[7]



II III

and Newman and Wood have described a rearrangement of IV in polyphosphoric acid in which the trichloromethyl group undergoes a 1,3-shift.[8] The same authors report that in polyphosphoric acid, V undergoes only the normal rearrangement in addition to complete loss of the trichloromethyl group.[8]

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[1] The author is indebted to the National Science Foundation for support of this work under NSF-G6578.

[2] E. S. Gould, "Mechanism and Structure in Organic Chemistry," Henry Holt and Co., New York, 1959, p. 639.

[3] K. v. Auwers and G. Keil, *Ber.*, **35**, 4207 (1902).

[4] R. C. Fuson and T. G. Miller, *J. Org. Chem.*, **17**, 316 (1952).

[5] R. T. Arnold, J. S. Buckley, and J. Richter, *J. Am. Chem. Soc.*, **69**, 2322 (1947).

[6] Migratory aptitudes in the rearrangement of carbonium ions generally increase as the electron-releasing ability of the group increases, unless steric factors are predominant—see ref. 2, p. 609. The term "abnormal rearrangement" is thus used here to indicate that the poorest electron donor of the *gem*-substituents has migrated.

[7] H. Pleininger and T. Suehiro, *Ber.*, **89**, 2789 (1956).

[8] M. S. Newman and L. L. Wood, Jr., *J. Am. Chem. Soc.*, **81**, 6450 (1959). Although these rearrangements do not give phenolic products, the nature of the starting materials and the reagent used suggest their comparison to the conventional dienone–phenol rearrangement.