1,3-Bis[2-(1-[3-dimethylaminopropyl]-3-methylindol-2-yl)-ethyl]-1,1,3,3-tetramethyldisiloxane (1c).—A freshly prepared solution of 15.07 g of IVa (0.07 mol) in 100 ml of dimethylformamide was stirred under nitrogen and treated with 3.7 g of sodium hydride in mineral oil (51.5%). Stirring was continued for 1 hr. γ-Dimethylaminopropyl chloride (8.9 g) was added dropwise, and the suspension was heated at 60° and stirred for 24 hr. The reaction mixture was poured into 2 l. of water and extracted with ether. The ethereal solution was extracted with 5% hydrochloric acid and the acid extract was made basic, extracted again with ether, and dried over sodium sulfate. The ether was removed and the residue was distilled giving 13.2 g of the product, bp 240–250° (0.04 mm).

Anal. Calcd for $C_{36}H_{68}ON_4Si_2$: C, 69.85; H, 9.44; N, 9.05; Si, 9.07; mol wt, 619. Found: C, 69.96; H, 9.40; N, 9.32; Si, 9.35; mol wt, 582.

The dihydrochloride was prepared with alcoholic hydrogen chloride in acetonitrile; ether was added until the solution clouded. Drying *in vacuo* at 110° gave a product that melted at 170–171°.

Anal. Calcd for $C_{36}H_{60}OCl_2N_4Si_2$: C, 62.48; H, 8.74; Cl, 10.25; N, 8.10; Si, 8.12. Found: C, 62.24; H, 8.95; Cl, 9.91; N, 8.18; Si, 7.82.

The dimethiodide, prepared in refluxing ethanol (MeOH–EtAc), had mp 145–147°.

Anal. Calcd for $C_{38}H_{64}ON_4I_2Si_2$: C, 50.55; H, 7.11; I, 28.11. Found: C, 50.43; H, 7.11; I, 27.97.

Conversion of 2 to 1b.—N-Methyl-3,3-dimethyl-3-silatetrahydrocarbazole (2) (0.5 g, 0.00218 mol) was refluxed with 6 ml of glacial acetic acid and 1 ml of water for 3 hr. When cooled to room temperature and starting to crystallize, the mixture was diluted with 2 ml of methanol and refrigerated. Later it was filtered, washed with 5 ml of methanol containing 1 ml of water, and dried giving 0.34 g (65%) of 1b, mp 108°. One recrystallization from methanol gave material having mp 109–110°. A mixture melting point with a sample described above showed no depression, and the two materials had identical spectra.

When the same experiment was performed employing glacial acetic acid or glacial acetic acid containing only 1% water, the resulting products appeared to be mixtures, since they were of indefinite melting point (125–135°) and more highly colored.

Registry No.—1a, 24571-87-7; 1b, 24571-88-8; 1c, 24571-89-9; 1c·2HCl, 24571-90-2; 1c·2MeI, 24571-51-5; 2, 24571-52-6.
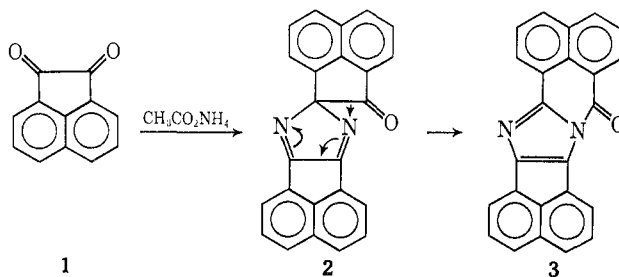

## Reactions of Acenaphthenequinone and Ammonium Acetate in the Presence of Aryl Aldehydes

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1,2 diketones and ammonium acetate in acetic acid react with arylaldehydes to form 2,4,5-trisubstituted imidazoles[1] (reaction 1) and with ketones to form 2,2,4,5-tetrasubstituted 2H-isoimidazoles[2] (reaction 2). However, with acenaphthenequinone, 1, and salicylaldehyde, under the conditions of reaction 1, the major product is a red solid to which the imidazole structure 3 has been assigned. Product 3 is not derived from the aldehyde (*i.e.*, by reaction 1), but instead is the result of a reaction in which 1 acts both as a diketone and as a

(1) (a) D. Davidson, M. Weiss, and M. Jelling, *J. Org. Chem.*, **2**, 319 (1937); (b) for a review see K. Hofmann, "Imidazole and Its Derivatives," Interscience Publishers, Inc., New York, N. Y., 1953, p 33.

(2) M. Weiss, *J. Amer. Chem. Soc.*, **74**, 5193 (1952).

monoketone. For reasons described below, the product does not appear to be the 2H-isoimidazole 2 which would normally be the product of reaction 2 but is 3, a rearrangement product of 2.

$$RCOCOR\ +\ R'CHO \xrightarrow{CH_3CO_2NH_4} \quad (1)$$

$$RCOCOR\ +\ R'COR' \xrightarrow{CH_3CO_2NH_4} \quad (2)$$
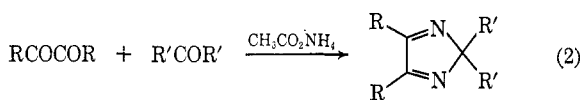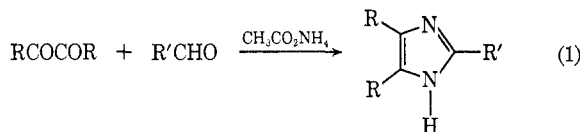
The infrared spectrum of 3 is identical with the spectrum of a compound which was isolated from the reaction of 1 with ammonia previously[3-7] and had been assigned structure 2.[6,7] Structure 2, however, seems less likely than 3 for several reasons. First, the ability of the reaction product to withstand temperatures as high as 400° without decomposition or rearrangement is not characteristic of isoimidazoles,[8] but is typical of imidazoles.[9] Second, the infrared spectrum of the product displays a sharp absorption band at 1500 cm^{-1} which has been found to be characteristic of arylimidazoles[10] and is also present in fused-ring imidazoles such as benzimidazole.[11] The characteristic absorption of simple 2H-isoimidazoles at 1550 cm^{-1} [10] is not present in the product. These spectral data are consistent with the structure containing the imidazole ring. Third, the deep red color of the product (λ_{max} in ethanol mμ 480) requires extensive conjugation which is present in structure 3 but not in 2 where the conjugation is interrupted by the sp^3 center in the 2 position of the isoimidazole ring. Objection to structure 2 on the basis of the color has been made by Schönberg and Singer.[5]

The composition of 3 is consistent with the elemental analysis and the high resolution mass spectrum (the most abundant peak is the parent ion at *m/e* 344.0943; calcd for $C_{24}H_{12}ON_2$, 344.0950). In addition to the

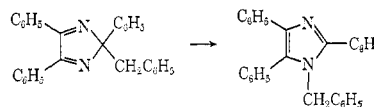(3) C. Graebe and E. Gfeller, *Justus Liebigs Ann. Chem.*, **276**, 1 (1893).

(4) A. Schönberg and F. Nedzati, *Ber.*, **54**, 238 (1921).

(5) A. Schönberg and E. Singer, *Chem. Ber.*, **98**, 3436 (1965).

(6) O. Tsuge and M. Tashiro, *Bull. Chem. Soc. Jap.*, **36**, 970 (1963).

(7) O. Tsuge and M. Tashiro, *ibid.*, **39**, 2477 (1966).

(8) 2-Benzyl-2,4,5-triphenyl-2H-isoimidazole rearranges to N-benzyl-

lophine at 250° in the melt and at *ca.* 118° in acetic acid.[2] Furthermore, 2-benzoyl-2,4,5-triphenyl-2H-isoimidazole appears to rearrange to N-benzoyllophine during an intermediate step in the formation of lophine from benzil and ammonium acetate in acetic acid at *ca.* 118°.[2]
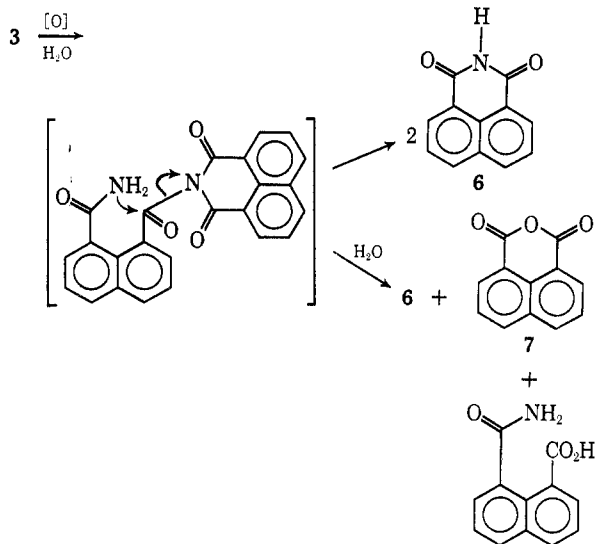
(9) See ref 1b, pp 45–46.

(10) D. M. White and J. Sonnenberg, *J. Org. Chem.*, **29**, 1926 (1964).

(11) K. J. Morgan, *J. Chem. Soc.*, 2343 (1961).

parent ion prominent peaks were noted for ions with compositions of $C_{23}H_{11}N_2$, $C_{22}H_{12}N$, and $C_{22}H_{10}N$. The peaks correspond to loss of CO and H, CO and CN, and CO and HCN, respectively, and are consistent with structure **3**. The mass spectrum of an impure sample of **3** also contains peaks at 328.0985 and at 164 which are probably the parent ion and a doubly charged ion of small amounts of an impurity, acenaphthazine, **4**.[12]
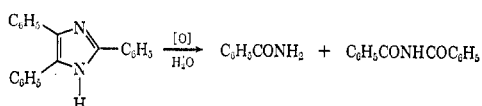

4   5
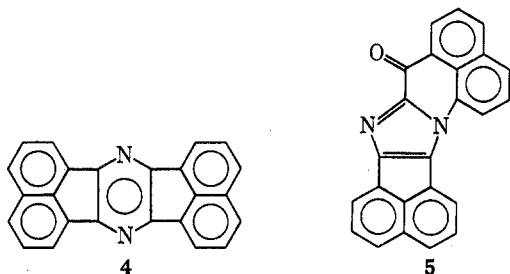
An isomer of **3**, structure **5**, is also consistent with the mass spectrum but seems unlikely since its formation would involve aryl migration instead of aroyl migration during rearrangement of the intermediate isoimidazole.[13] Further support for structure **3** was obtained by oxidative hydrolysis with sodium dichromate. Naphthalimide (**6**) was isolated in 65% yield along with a smaller amount of naphthalic anhydride, **7** (24%), and a trace of material which appears to be the monoamide of naphthalic acid. The formation of these products can be rationalized from structure **3** by the oxidation of the double bond common to the imidazole and acenaphthene rings and by hydrolysis of the imino group.[14]

An intramolecular displacement reaction in the intermediate would produce two molecules of naphthalimide while hydrolysis would produce the other degradation products also.

The competition between **1** and the aldehyde to function as the monocarbonyl component of the reaction is indicated by the yield of **3** in the absence of aldehyde and when several aldehydes with various substituents were present. With salicylaldehyde, a relatively unreactive aldehyde **3** was formed in 70% yield which is only slightly lower than when the aldehyde was absent (87%). With benzaldehyde, the yield was 33% and with the reactive aldehyde *p*-nitrobenzaldehyde only a trace of **3** was detected. The other products which were formed when the aldehydes were present were brown solids which were not isolated in pure form with the exception of the product from *p*-nitrobenzaldehyde. In this case, 2-(*p*-nitrophenyl)-acenaphthimidazole (**8**) was isolated.

8
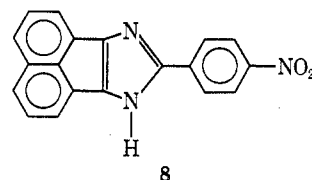
Phenanthraquinone (**9**) does not undergo a reaction analogous to the formation of **3**. When heated with ammonium acetate in acetic acid, the diimine **10** was produced. When aryl aldehyde was present, the

9   10
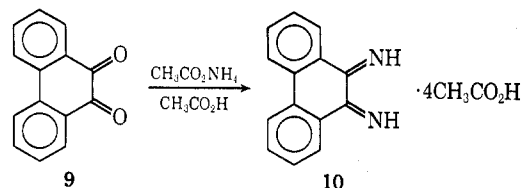
2-arylphenanthrimidazoles were formed in high yield even with compounds such as salicylaldehyde.[15]

Experimental Section[16]

7H-Acenaphth[1',2':4,5]imidazo[1,2-b]benz[d,e]isoquinolinone, 3.—Acenaphthenequinone (**1**, 1.9 g, 0.05 mol), 40 g of ammonium acetate, and 100 ml of acetic acid were heated at reflux for 2.5 hr. The mixture was cooled to 25° and a dark solid was removed by filtration. The solid was washed with acetic acid and then with ethanol and dried at 120° and 10 mm for 20 hr. The deep red-violet product weighed 7.5 g, 87% yield, mp 360–365°. Sublimation at 290° and 0.01 mm produced two zones of sublimate, a trace of a more volatile yellow solid **5**, and deep red crystals of **3**, mp 388–390°. The infrared spectrum showed characteristic bands at 3040 w (CH stretch), 1695 s (carbonyl), 1535 m, 1500 w (imidazole), 1470 ms, 1335 ms, 1280 s, 910 m, 818 ms, 764 s cm⁻¹ (3 adjacent aryl H's). The mass spectrum showed peaks at *m/e* 344.0943 (relative abundance 100), 315.0930 (7), 290.0969 (4), 289 (2), 288.0800 (4), 172 (12), 166 (2), 158 (2), 138 (8). Impure samples of **3** also displayed peaks at 328.0985 and 164. Compound **3** was readily soluble in trifluoroacetic acid and hot dipolar aprotic solvents such as hexamthyltriphosphoramide, but was only slightly soluble in less polar solvents such as chloroform and ethanol.

Anal. Calcd for $C_{24}H_{12}ON_2$: C, 83.7; H, 3.51; N, 8.1. Found: C, 83.7; H, 3.7; N, 8.0.

The procedure above was followed except that salicylaldehyde (5.3 g, 0.05 m) was also added at the start of the reaction. Compound **3** was isolated as red crystals, mp 388–390° (after sublimation and recrystallization from chloroform–ethanol),

(12) Acenaphthazine has been identified as a side product from **1** and ammonia.[7]

(13) The greater tendency for aroyl migration rather than aryl migration is indicated by the lower stability of 2-benzoyl-2,4,5-triphenyl-2H-isoimidazole (where the benzoyl group appears to migrate preferentially)[2,8] compared with 2,2,4,5-tetraphenyl-2H-isoimidazole which melts without decomposition near 200° and survives synthesis conditions in acetic acid at reflux.[2]

(14) Chromium oxide oxidation of lophine produces analogous products:

E. Fischer and H. Truschke, *Ber.*, **13**, 1706 (1880).

(15) E. A. Steck and A. R. Day, *J. Amer. Chem. Soc.*, **65**, 452 (1943).

(16) Infrared spectra were obtained with potassium bromide pellets. Melting points are uncorrected.

yield 6.0 g (70%). Similarly, with benzaldehyde (5.3 g, 0.05 mol) instead of salicylaldehyde: **3** was formed: mp 365–370°; after sublimation, mp 388–390°, yield 2.8 g (33%).

2-(p-Nitrophenyl)acenaphthimidazole, 8.—Acenaphthene-quinone (**1**, 9.1 g, 0.05 mol), p-nitrobenzaldehyde (7.56 g, 0.05 mol), 40 g of ammonium acetate, and 100 ml of acetic acid were heated at reflux 2 hr. The mixture was cooled to 25° and filtered to remove a solid which was washed with acetic acid, dried at 120° and 10 mm, and weighed 11.4 g. Extraction of the solid with 1000 ml of boiling ethanol dissolved 6.0 g. A second ethanol extraction dissolved in additional 2.5 g. The residue, 2.9 g, contained <1 g of **3** by thin layer chromatography, infrared analysis, and sublimation. The combined ethanol extracts were cooled to 5° and crystals formed. Filtration, washing with ethanol, and drying afforded **8**, 6.2 g, mp 300–305° (between 215 and 295° phase changes occur which have the appearance of partial melting and then resolidification). Recrystallization from ethanol and sublimation at 240° and 0.01 mm produced pure yellow-orange crystals of **8**, mp 310–312°. The infrared spectrum showed bands at 3000–2600 m (broad NH), 1587 ms, 1500 s (nitro, imidazole), 1470 s, 1330 s (nitro), 1310 s, 850 m (2 adjacent Ar H's), 812 m, 760 (acenaphthene H's) cm^{-1}.

Anal. Calcd for $C_{19}H_{11}N_3O_2$: C, 72.8; H, 3.54; N, 13.4. Found: C, 72.9; H, 3.45; N, 13.3.

A second crop of impure **8**, 1.0 g, was isolated from concentration of the ethanol extracts.

Oxidation of 3.—The procedure was similar to the one of Tsuge and Tashiro.[5] To a suspension of **3** (0.50 g, 1.45 mmol) in 15 ml of acetic acid was added 1.5 g of sodium dichromate. The mixture was heated at reflux (116°) for 1 hr. The dark red solution was poured into 50 ml of water, and the precipitate was filtered off and washed with water. The solid was triturated with 70 ml of 10% sodium carbonate solution for 1 hr. The solid that remained was collected on a filter, washed with water, and dried; wt 0.43 g; analysis indicated a mixture of 70% naphthalimide and 30% naphthalic anhydride. Acidification of the sodium carbonate solution afforded 0.04 g of crystals after drying, mp 294–302°. Anaysis indicated these to be 85% naphthalimide and 15% naphthalic anhydride. Ether extraction of the filtrate removed 0.07 g of a material which had an infrared and mass spectrum consistent with approximately one-third naphthalimide and two-thirds of the monoamide of naphthalic acid. Analyses of the three fractions were carried out by infrared and nmr. The spectra were compared with spectra of mixtures of naphthalimide and naphthalic anhydride of known composition. In addition, each fraction was sublimed to separate the more volatile anhydride from the imide. No melting point depressions were noted when each zone of the sublimate was mixed with the appropriate known compound. Mass spectra of the fractions were identical with mass spectra of the known compounds. The overall yields of the two major components were naphthalimide, 0.35 g (65%), and naphthalic anhydride, 0.13 g (24%).

A Novel Catalytic Salt Effect in Base-Initiated Aryne Reactions Conducted in Dimethylamine Solvent[1a]

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We have routinely carried out aryne reactions in dimethylamine[2] using bromo aromatic compounds with

(1) (a) Supported in part by R. A. Welch Grant N-118, Houston, Texas; (b) Robert A. Welch Predoctoral Fellows.
(2) Reactions of this general type were first developed for synthetic purposes by J. F. Bunnett and T. K. Brotherton, *J. Org. Chem.*, **22**, 832 (1957).
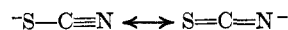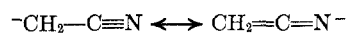
either sodamide or potassium amide as the base and a reaction time of 3 hr to prepare the corresponding N,N-dimethyl aromatic amines in high yields (90–93%). In addition, high yields of aromatic amines can be obtained using chloro aromatic compounds and potassium amide in dimethylamine. Recently, we have observed that the reaction of chlorobenzene and o- or p-chlorotoluene produces the corresponding aromatic amine in low yields (5–7%) if sodamide is used as the base. However, if these reactions are carried out in the presence of the sodium salts of certain nitriles (0.5 equiv per equiv of sodamide), high yields (67–78%) of the appropriate aromatic amines are obtained. In addition, a small amount (8–17%) of the corresponding

$$\text{ArCl} + \text{NaNH}_2 + \text{NaCHRCN} \xrightarrow{\text{HN(CH}_3)_2} \text{ArN(CH}_3)_2 + \text{ArCHRCN}$$
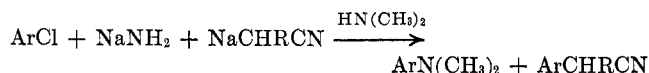
arylated nitriles is produced. Table I summarizes the aforementioned results.

In addition the yields of N,N-dimethylaniline obtained from the action of sodamide on chlorobenzene are increased from 5 (no salt present) to 28, 56, and 56% by the addition of 0.8 equiv/equiv of sodamide of the inorganic salts, sodium nitrite, sodium thiocyanate, and potassium thiocyanate, respectively. Similarly, the yields of N,N-dimethyl-o- and -m-toluidines obtained from the action of sodamide on o-chlorotoluene are increased from 5 to 50, 80, and 80% by the addition of 0.8 equiv of sodium nitrite, sodium thiocyanate, and potassium thiocyanate, respectively. The isomer ratios of the N,N-dimethyltoluidines are in all cases 53:47, *ortho:meta*, respectively. In contrast, no increase in yields is observed by the addition of the salts KCl, KBr, NaCl, NaBr, Na$_2$SO$_4$, NaNO$_3$, KNO$_3$, or KI.

The specific action of only certain salts in increasing the conversion of chloro aromatics argues against a general salt effect. In addition, it appears that the anion portion of the salt is responsible for the catalytic behavior. Interestingly, only those salts which are linear and in which the negative charge is resonance stabilized appear to be effective catalysts. See, for example

$$^-\text{CH}_2{-}\text{C}{\equiv}\text{N} \longleftrightarrow \text{CH}_2{=}\text{C}{=}\text{N}^-$$

$$^-\text{S}{-}\text{C}{\equiv}\text{N} \longleftrightarrow \text{S}{=}\text{C}{=}\text{N}^-$$

Since the rate-determining step of the aryne reaction[3] is the abstraction of a hydrogen atom by a strong base, it appears that the salts are increasing the base strengths of sodamide in liquid dimethylamine. This action could either be the result of the salts (1) increasing the concentration of sodamide in dimethylamine, or (2) effecting a change in the aggregate populations which most likely exist in dimethylamine. Unfortunately, little is known concerning (1) the solubility of sodamide in dimethylamine, (2) the effect of salts on the solubility of sodamide in dimethylamine, and, most importantly, (3) the form in which sodamide exists in dimethylamine. We currently are investigating the mechanistic aspects of these unusual catalytic effects.

(3) J. D. Roberts, D. A. Semenow, H. E. Semenow, and L. A. Carlsmith, *J. Amer. Chem. Soc.*, **78**, 601 (1956).