# REACTION OF N-HETEROAROMATIC CATIONS
WITH ALKALI-METAL AMIDES

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The action of potassium amide on quaternary N-methylimidazolium, N-methyl(aralkyl, aryl)-
benzimidazolium, N-methylnapthimidazolium, N-methylperimidinium, and acridinium salts in
liquid ammonia was studied. In most cases, because of the difficulties involved in aromatization
of the adducts of the N-alkyl salts of the heterocycles with the amide ion, they tend to undergo
various side transformations, the chief of which is hydrolysis to carbinol pseudobases. However,
the fundamental possibility of amination and imination of N-heteroaromatic cations by means of
metal amides was shown in the case of N-methoxybenzimidazolium and N-alkylacridinium salts.

In a study of the Chichibabin reaction one of us advanced the hypothesis [1] that the nitrogen heterocycle
is sorbed on the sodium amide surface in the first step of the process due to forces of ion−dipole interaction
(weak coordination) between the Na^+ ion and the pyridine nitrogen atom. A partial positive charge is induced
on the nitrogen atom in the resulting complex (I), and this should facilitate the subsequent amination.
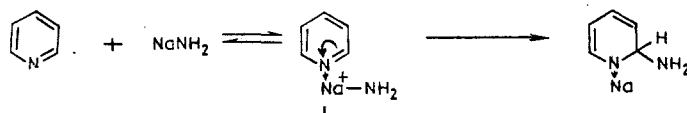
This hypothesis made it possible to explain a large number of experimental observations, particularly
the nonaminability of compounds with reduced ($pK_a < 4$) basicity. During the logical development of this idea,
a question arises as to how quaternary salts of nitrogen heterocycles would behave under the conditions of the
Chichibabin reaction. The present research is devoted to the study of this question.
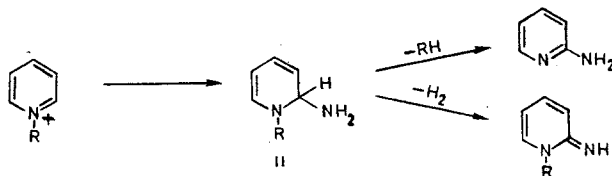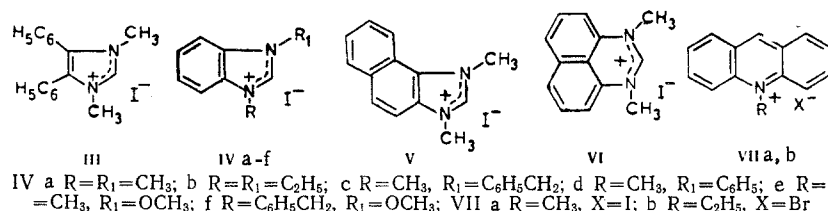

The action of metal amides on N-heteroaromatic cations has not been previously investigated. It might
be expected that the corresponding reaction should proceed under considerably milder conditions than those in
the Chichibabin reaction. In the case of the formation of adduct II in the first step, its aromatization could
lead either to an amine (by splitting out of RH) or to an imine (by splitting out of H_2). The latter variant is the
up-to-now unknown direct imination of nitrogen heterocycles. In addition, one also could not exclude the possi-
bility of any other difficult-to-predict transformations.

We studied the action of potassium amide on the following methiodides of five- and six-membered N-het-
eroaromatic systems:

III   IV a‑f   V   VI   VII a, b

IV a R=R$_1$=CH$_3$; b R=R$_1$=C$_2$H$_5$; c R=CH$_3$, R$_1$=C$_6$H$_5$CH$_2$; d R=CH$_3$, R$_1$=C$_6$H$_5$; e R=
=CH$_3$, R$_1$=OCH$_3$; f R=C$_6$H$_5$CH$_2$, R$_1$=OCH$_3$; VII a R=CH$_3$, X=I; b R=C$_2$H$_5$, X=Br

The reaction was carried out in liquid ammonia, inasmuch as the reagents are insoluble in other solvents. The amount of potassium amide used was one to three moles per mole of quaternary salt. It was found that the direction of the reaction depends on the amount of potassium amide (see Table 1).

1-Methyl-4,5-diphenylimidazole, 1-alkylbenzimidazole, and 1-methyl-naphth[1,2-d]imidazole methiodides react with 3 moles of potassium amide to give the corresponding imidazolones in 45-80% yields. This reaction trend was observed by Takamizawa and co-workers [2], who studied the action of potassium dimsyl on methiodide IVa in dimethyl sulfoxide (DMSO), although the yield of 1,3-dimethylbenzimidazolone in their experiment did not exceed 23%. These investigators expressed the assumption that the formation of 1,3-dimethylbenzimidazolone is the result of autooxidation of ylid-carbene VIII, which is formed by deprotonation of the benzimidazolium cation:


VIIIa   VIII b
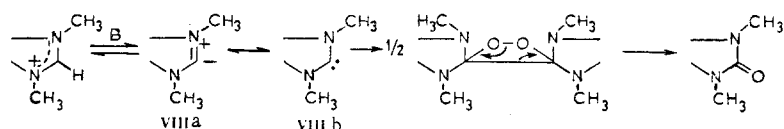
In our case the formation of 1,3-dimethylbenzimidazolone proceeds in a different manner, inasmuch as completely different products are formed by the action of 1 mole of potassium amide on salt IV: N,N'-dialkyl(aralkyl)-N-formyl-o-phenylenediamine (XII) in the case of IVb, c, d, and carbinol pseudobase XI in the case of IVa. It is clear that the amount of potassium amide should not, in principle, affect the transformations described in the preceding scheme. These observations make the following mechanism for the reaction of salts IV with potassium amide more likely:

X   XI   XII   XIII   XIV
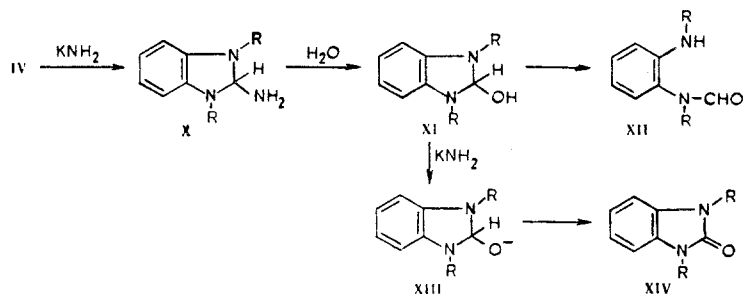
The product of addition of the amide ion to the C=N bond of the benzimidazolium cation (X) evidently is formed initially. Under the influence of the moisture condensed during evaporation of the ammonia, X, being a derivative of the extremely unstable triaminomethane, is readily hydrolyzed to carbinol XI. When R=CH$_3$, the latter is relatively stable and can be isolated, whereas when R=C$_2$H$_5$ and other groups it immediately is converted to the open pseudobase XII. Whereas the formation of a carbinol of the XI type in the benzimidazole series during the action of strong bases on quaternary salts was previously only postulated, 1,3-dimethyl-2-benzimidazolinol is the first example of a compound of this type. Carbinol XI was obtained as colorless cyrstals with mp 119°C. On storage in the crystalline form or in solution it is converted to N,N'-dimethyl-N-formyl-o-phenylenediamine with mp 75° (particularly rapidly in solution). The PMR spectrum can therefore be recorded only for a mixture of these two compounds. The PMR spectrum of a CDCl$_3$ solution of the product contains the singlet of an H$_2$ proton at δ 4.85 ppm, which is absent in the spectrum of the acyclic form of the pseudobase, and a singlet (8.08 ppm) of the proton of a formyl group.

When excess KNH$_2$ is present in the reaction mixture, carbinol XI is converted to O-anion XIII, which is readily oxidized to 1,3-dimethylbenzimidazolone (compare this with the action of alkali on 1,3-dimethyl-5-nitrobenzimidazolium salts [3]). In other words, our proposed scheme explains why benzimidazolones are formed only when excess potassium amide is present.

Theoretically speaking, the formation of benzimidazolones can be also conceived of as occurring through saponification of imine XV, which is formed by oxidation of adduct X:
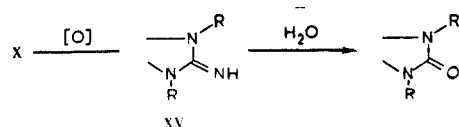
However, we established that imine XV is not affected by KNH_2 in liquid ammonia. It might have been expected that adduct X would be oxidized to imine XV if active manganese dioxide were added to the mixture immediately after mixing the solution of potassium amide in liquid ammonia and quaternary salt IV. Nevertheless, in this experiment we isolated only 1,3-dimethylbenzimidazolone (25% yiel 1) formed as a result of oxidation of carbinol XI, and N,N'-dimethyl-N-formyl-o-phenylenediamine (55%). The open form of the pseudobase can be readily converted to the corresponding imidazolone when a benzene solution of it containing active manganese dioxide is allowed to stand. The ease of this transformation is evidently due to ring–chain tautomerism between the acyclic and carbinol forms of the pseudobase [4].

Interesting results were obtained in the reaction of potassium amide in liquid ammonia with N-methoxybenzimidazolium salts. In this case the only reaction product (in 90% yield) is the corresponding 1-substituted 2-aminobenzimidazole:

R = CH₃, C₆H₅CH₂
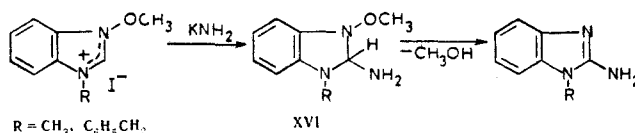
There is no doubt that the reaction proceeeds through the intermediate formation of adduct XVI, the stabilization of which leads to the corresponding amine with splitting out of a CH_3OH molecule. It should be emphasized that 1-substituted benzimidazoles themselves are not aminated by potassium amide under these conditions.

Although 1,3-dimethylperimidinium salt VI does contain a six-membered heteroring, it occupies an intermediate position between azole and azine salts with respect to its properties. A mixture consisting of 40% 1,3-dimethylperimidone XIX and 35% 1,3-dimethyl-2,3-dihydroperimidine XX is obtained by treatment of VI with 1 mole of KNH_2. Similar results were obtained in the reaction of a 10% aqueous KOH solution with salt VI [5]. On the basis of this, we feel that the reaction proceeds through a step involving the formation of carbinol XVIII, which undergoes redox disproportionation:
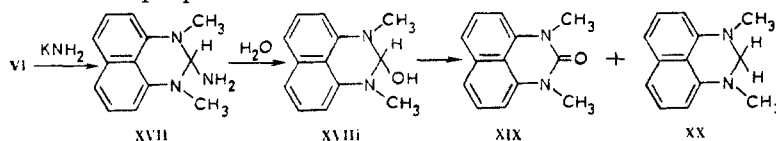
Dihydro derivative XX is not formed in the reaction of VI with 3 moles of KNH_2. The principal reaction products in this case are perimidone XIX (20-45%) and, somewhat unexpectedly, N,N'-dimethyl-1,8-naphthalenediamine (up to 46%). The formation of the latter can be explained in the following way. Carbinol XVIII, in the presence of excess KNH_2, is converted to the O-anion, which, on the one hand, is oxidized to perimidone XIX, and, on the other, gives the open form of the pseudobase (this is apparently an equilibrium process that is shifted to favor cyclic form XXI). Under the influence of excess potassium amide the acyclic pseudobase loses a formyl group to give XXIII.
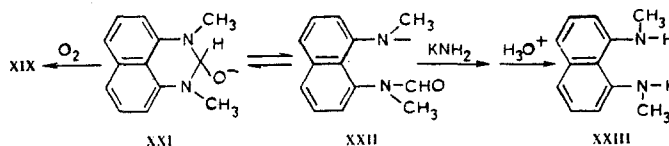
N-Alkylacridone XXVI and N-alkylacridan XXVII are formed in a ratio of ~1:1 (overall yield 70-80%) in the reaction of 1 mole of KNH_2 with acridine alkylhalides (VIIa,b). However, the addition of ferric nitrate to the reaction mixture of salt VIIa and KNH_2 leads to the formation of 10-methyl-9-aminoacridinium nitrate (XXVIII) in addition to XXVI and XXVII. Nitrate XXVII is converted to the known 10-methyl-9-acridone imine [6] on treatment with alkali.

TABLE 1. Reaction of N-Heteroaromatic Cations with Potassium Amide

Quaternary salt	KNH_2, moles	Reaction product	Yield, %
IVa	3	1,3-Dimethylbenzimidazolone	80
IVa	1	1,3-Dimethyl-2-benzimidazolinol	90
IVb	3	1,3-Diethylbenzimidazolone	45
IVb	1	N,N'-Diethyl-N-formyl-o-phenylenediamine	96
IVc	1	N-Methyl-N'-benzyl-N-formyl-o-phenylenediamine	90
IVd	1	N-Methyl-N'-phenyl-N-formyl-o-phenylenediamine	96
IVd	1	1-Methyl-2-aminobenzimidazole	93
IVf	1	1-Benzyl-2-aminobenzimidazole	90
III	3	1,3-Dimethyl-4,5-diphenylimidazolone	76
V	3	1,3-Dimethylnaphth[1,2-d]imidazolone	75
V	1	N,N'-Dimethyl-N-formyl-1,2-naphthalenediamine	93
IV	3	⎰1,3-Dimethylperimidone	20—45
		⎱N,N'-Dimethyl-1,8-naphthalenediamine	46
IV	1	⎰1,3-Dimethylperimidone	40
		⎱1,3-Dimethyl-2,3-dihydroperimidine	35
VIIa	3	⎧N-Methylacridone	41 / 39*
		⎨N-Methylacridan	41 / 39*
		⎩10-Methyl-9-aminoacridinium nitrate	5 / 9*
VIIa	1	⎧N-Methylacridone	40 / 38† / 28*
		⎨N-Methylacridan	40 / 36† / 26*
		⎩10-Methyl-9-aminoacridinium nitrate	— / 11† / 38*
VIIb	3	⎰N-Ethylacridone	40
		⎱N-Ethylacridan	47
VIIb	1	⎧N-Ethylacridone	32 / 30‡
		⎨N-Ethylacridan	45 / 39‡
		⎩10-Methyl-9-aminoacridinium nitrate	— / 5‡

*In the presence of equimolecular amounts of ferric nitrate (III).

† Catalytic amounts of ferric nitrate (III).

‡ Equimolecular amounts of silver nitrate.

The first step in the reaction evidently consists in the formation of the product of addition of the amide ion (XXIV), which, in the absence of an oxidizing agent, is hydrolyzed completely to carbinol XXV. Carbinol XXV (a substance with bright-green fluorescence) is also the primary reaction product. However, it undergoes disproportionation to give XXVI and XXVII when attempts are made to isolate it in pure form [7]. When ferric nitrate was present, the ferric ions oxidized adduct XXIV to salt XXVIII (under these conditions the NO_3^- ion is not an oxidizing agent, inasmuch as replacement of ferric nitrate by potassium nitrate does not lead to XXVIII).
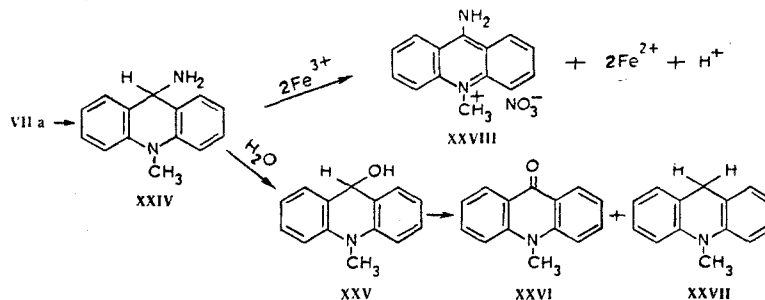
We have not yet been able to completely suppress hydrolysis of XXIV and direct the reaction to favor the formation of salt XXVIII, inasmuch as the oxidation process apparently proceeds slowly. However, it is extremely difficult to protect the mixture from moisture, for it gets into the mixture not only because of the extremely high hygroscopic character of ammonia but also because it is introduced with the ferric nitrate, which exists in the crystal hydrate form. Nevertheless, the minimum yield of XXVIII, which was obtained when 1 mole of ferric nitrate was used, was 38%, which is higher than the yield of 9-aminoacridine

in the amination of acridine [8]. The other oxidizing agents that we investigated [chloranil, $K_3Fe(CN)_6$, $AgNO_3$, Ni_2O_3, $Mn(CH_3COO)_3 \cdot 2H_2O$, and activated MnO_2] do not raise the yield of the imine.

We were unable to obtain 10-ethyl-9-acridone imine under these conditions. We isolated 10-ethyl-9-aminoacridinium nitrate in only one case in the presence of $AgNO_3$, but the yield was very low (5%).

10-Methyl-9-aminoacridinium nitrate (5-9%) and N-methylacridone and N-methylacridan in approximately equal ratios (overall yield 75-80%) are also formed in the reaction of 3 moles of potassium amide with acridine methiodide.

Thus the fundamental possibility of amination and imination of nitrogen heterocycles by means of metal amides in conformity with the above scheme was demonstrated in the case of N-methoxybenzimidazolium (IVe, f) and N-alkylacridinium (VII) salts. In addition, because of the difficulties involved in the aromatization of the adducts of the N-alkyl salts of heterocycles they tend to undergo various side transformations, the chief of which is hydrolysis to carbinol pseudobases. However, in the future we hope to find more convenient solvents and oxidizing agents and achieve conversion of the adducts to imines.

EXPERIMENTAL

The IR spectra of the compounds were recorded with a UR-20 spectrometer. The PMR spectra of $CDCl_3$ solutions were measured with a Tesla BC 487C spectrometer (80 MHz) with hexamethyldisiloxane as the internal standard. The δ values presented in the study were converted with respect to the signal of tetramethylsilane.

Reaction of 1,3-Dimethyl-4,5-diphenylimidazolium Iodide with 3 Moles of Potassium Amide. A 1.88-g (0.005 mole) sample of 1-methyl-4,5-diphenylimidazole methiodide was added to a solution of potassium amide, obtained from 0.6 g (0.015 g-atom) of potassium metal in 50 ml of liquid ammonia, and the mixture was stirred at −70° for 1.5 h. The ammonia was then evaporated to dryness at room temperature, and the solid residue was extracted with hot absolute benzene (70-80 ml). Workup gave 1.0 g (76%) of colorless prisms of 1,3-dimethyl-4,5-diphenylimidazolone with mp 183-184° (from dilute acetic acid) (mp 185° [9]). IR spectrum, cm^{-1} ($CHCl_3$): $\nu_{C=O}$ 1685.

Reaction of 1,3-Dimethylbenzimidazolium Iodide with 3 Moles of Potassium Amide. A 2.74-g (0.01 mole) sample of 1-methylbenzimidazole methiodide was added to a solution of 0.03 mole of KNH_2 in 50 ml of liquid ammonia. After 10-15 min, a gray precipitate formed, and the mixture was then stirred at −70° for 2 h. The ammonia was then evaporated to dryness, and the residue was extracted with 50 ml of absolute benzene. Workup gave 1.3 g (83%) of colorless needles of 1,3-dimethylbenzimidazolone with mp 109° (from heptane) (the same melting point was obtained in [10]). No melting-point depression was observed for a mixture of this product with a genuine sample. IR spectrum, cm^{-1} ($CHCl_3$): $\nu_{C=O}$ 1680.

Reaction of 1,3-Dimethylbenzimidazolium Iodide with 1 Mole of Potassium Amide. A 2.74-g (0.01 mole) sample of methiodide IVa was added to a solution of potassium amide obtained from 0.39 g (0.01 g-atom) of potassium in 60 ml of liquid ammonia. After 20-25 min, the solid material had dissolved completely, and the reaction mixture was then stirred at −70° for 2 h. The mixture was then evaporated to dryness, and the solid residue was extracted with 50 ml of absolute benzene. Evaporation of the benzene solution in air left 1.5 g (90%) of colorless prisms of 1,3-dimethyl-2-benzimidazolinol. The product was quite soluble in alcohol, acetone, benzene, and ether but only slightly soluble in petroleum ether. Found: C 65.8; H 7.1; N 17.4%. $C_9H_{12}N_2O$. Calculated: C 65.3; H 7.3; N 17.1%. The IR spectrum was identical to the spectrum of XII (R = CH_3) obtained by the action of 10% NaOH on methiodide IVa: $\nu_{C=O}$ 1665 cm^{-1} and ν_{NH} 3360 cm^{-1} (mineral oil).

Reaction of 1,3-Dimethylbenzimidazolium Iodide with 1 Mole of Potassium Iodide in the Presence of Active Manganese Dioxide. A 1.37-g (5 mmole) sample of methiodide IVa was added to a solution of potassium amide obtained from 0.2 g (5 mmole) of potassium in 50 ml of liquid ammonia, after which the mixture was stirred at −70° for 2 h. A 1.5-g sample of activated MnO_2 was then added, and the ammonia was evaporated. The dry residue was treated with absolute benzene (50-60 ml), and the benzene extract was evaporated to give 0.7 g of colorless crystals, which were found to be a mixture of 1,3-dimethylbenzimidazolone and N,N'-dimethyl-N-formyl-o-phenylenediamine. The products were separated by chromatography with a column filled with Al_2O_3 (elution with chloroform). The first fraction eluted contained 0.26 g (25%) of colorless needles of 1,3-dimethylbenzimidazolone with mp 108-109° (from octane). No melting-point depression was observed for a mixture of this product with a genuine sample. The second fraction contained

0.45 g (55%) of colorless prisms of N,N'-dimethyl-N-formyl-o-phenylenediamine with mp 74-75° (from petroleum ether). No melting-point depression was observed for a mixture of this product with a genuine sample.

Oxidation of N,N-Dimethyl-N-formyl-o-phenylenediamine with Manganese Dioxide. A suspension of 0.9 g (0.01 mole) of active MnO_2 and 0.17 g (0.001 mole) of N,N'-dimethyl-N-formyl-o-phenylenediamine in 30 ml of benzene was stirred at room temperature for 48 h, after which the MnO_2 was removed by filtration, and the benzene solution was evaporated to dryness to give 0.16 g ($\sim$100%) of colorless needles of 1,3-dimethylbenzimidazolone with mp 110° (from octane). No melting-point depression was observed for a mixture of the product with an authentic sample.

Reaction of 1,3-Diethylbenzimidazolium Bromide with 3 Moles of Potassium Amide. The reaction was carried out as described for 1,3-dimethylbenzimidazolium iodide to give 1,3-diethylbenzimidazolone in 45% yield. The product was purified by sublimation at 90° (10 mm) to give a product with mp 68-69°, in agreement with the melting point reported in [10]. IR spectrum, cm^{-1} ($CHCl_3$): $\nu_{C=O}$ 1675.

Reaction of 1,3-Diethylbenzimidazolium Bromide with 1 Mole of Potassium Amide. Equimolecular amounts of potassium amide and ethylbromide IVb in liquid ammonia were stirred at −70° for 2 h. Thirty minutes after the cooling bath had been removed, the solid material had dissolved completely. N,N'-Diethyl-N-formyl-o-phenylenediamine was isolated as described for 1-methylbenzimidazole methiodide to give 1.85 g (96%) of colorless prisms with mp 72-73° (from petroleum ether). Found: C 68.9; H 8.2; N 14.6%. $C_{11}H_{16}N_2O$. Calculated: C 68.7; H 8.3; N 14.6%. The same substance was obtained by treatment of ethylbromide IVb with 20% aqueous NaOH solution and had mp 72° (from petroleum ether). No melting-point depression was observed for a mixture of the two products. IR spectrum, cm^{-1} (mineral oil): $\nu_{C=O}$ 1670 and ν_{NH} 3365.

Reaction of 1,3-Methylbenzylbenzimidazolium Iodide with 1 Mole of Potassium Amide. This reaction was carried out under similar conditions to give N-methyl-N'-benzyl-N-formyl-o-phenylenediamine as a colorless oil in 90% yield. The picrate was obtained as yellow needles with mp 191-192° (from glacial acetic acid). Found: C 55.0; H 4.0; N 15.6%. $C_{15}H_{16}N_2O \cdot C_6H_3N_3O$. Calculated: C 54.9; H 4.1; N 15.3%. No melting-point depression was observed for a mixture of this product with an authentic sample.

Reaction of 1-Methyl-3-phenylbenzimidazolium Iodide with 1 Mole of Potassium Amide. This reaction was carried out as described for 1-methylbenzimidazolium methiodide to give N-methyl-N'-phenyl-N-formyl-o-phenylenediamine as pinkish prisms with mp 166-167° (from alcohol) in 96% yield. Found: C 73.5; H 6.0; N 12.6%. $C_{14}H_{14}N_2O$. Calculated: C 73.3; H 6.1; N 12.4%. IR spectrum, cm^{-1} ($CHCl_3$): $\nu_{C=O}$ 1680 and ν_{NH} 3320 and 3410.

Reaction of 1,3-Dimethylnaphth[1,2-d]imidazolium Iodide with 3 Moles of Potassium Amide. Methiodide V (4 mmole) was added to a suspension of freshly prepared potassium amide (12 mmole) in 200 ml of technical-grade liquid ammonia, after which the ammonia was allowed to evaporate spontaneously at room temperature. The residue was treated with 100 ml of boiling benzene, and the extract was worked up to give 0.6 g (75%) of 1,3-dimethylnaphth[1,2-d]imidazolone with mp 175-176° (from alcohol). Found: C 73.5; H 5.9; N 13.0%. $C_{13}H_{12}N_2O$. Calculated: C 73.6; H 5.7; N 13.2%. IR spectrum, cm^{-1} (mineral oil): $\nu_{C=O}$ 1690.

Reaction of 1,3-Dimethylnaphth[1,2-d]imidazolium Iodide with 1 Mole of Potassium Amide. This reaction was carried out similarly to give colorless prisms of N,N'-dimethyl-N-formyl-1,2-naphthalenediamine with mp 129-130° (from alcohol) in 93% yield. Found: C 73.1; H 6.8; N 13.4%. $C_{13}H_{14}N_2O$. Calculated: C 72.9; H 6.5; N 13.1%. IR spectrum, cm^{-1} (CCl_4): $\nu_{C=O}$ 1675 and ν_{NH} 3370.

Reaction of 1,3-Dimethylperimidinium Iodide with 3 Moles of Potassium Amide. A 0.01-mole sample of methiodide VI was added to a solution of freshly prepared potassium amide (0.3 mole) in 150 ml of technical-grade liquid ammonia, and the mixture was stirred until the ammonia had evaporated completely. The solid residue was treated with 100 ml of boiling xylene, and the extract was worked up to give 1.75 g of gray-brown cyrstals, which were found to be a mixture of 1,3-dimethylperimidone and N,N'-dimethyl-1-8-naphthalenediamine. The components were separated by treating the mixture with a hot 3% solution of HCl, and the insoluble 1,3-dimethylperimidone [0.43 g (20%)] was removed by filtration to give colorless crystals with mp 209° (from alcohol), in agreement with the melting point reported in [5]. IR spectrum, cm^{-1} (mineral oil): $\nu_{C=O}$ 1675. The hydrochloric acid filtrate was neutralized with ammonia, and the mixture was

worked up to give 0.88 g (46%) of colorless crystals of N,N'-dimethyl-1-8-naphthalenediamine with mp 96-98° (from aqueous alcohol), in agreement with the melting point reported in [11]. IR spectrum, cm^{-1} (CHCl$_3$): νNH 3385.

Reaction of 1,3-Dimethylperimidinium Iodide with 1 Mole of Potassium Amide. A 3.24-g (0.01 mole) sample of methiodide VI was added to a freshly prepared solution of 0.01 mole of potassium amide in 200 ml of liquid ammonia, and the mixture was stirred until the ammonia had evaporated completely. The residue was treated with 100 ml of hot benzene, and the extract was worked up to give 1.6 g of 1,3-dimethyl-perimidone and 1,3-dimethyl-2,3-dihydroperimidine. The components were separated by treatment of the mixture with 30 ml of boiling 3% HCl solution; the insoluble 1,3-dimethylperimidone [0.85 g (40.5%)] was removed by filtration to give colorless crystals with mp 209° (from alcohol). The hydrochloric acid filtrate was neutralized with ammonia, and the precipitated 1,3-dimethyl-2,3-dihydroperimidine [0.7 g (35.5%)] was removed by filtration to give colorless crystals with mp 149-150° (from alcohol). No melting-point depression was observed for a mixture of this product with an authentic sample.

Reaction of N-Methylacridinium Iodide with 1 Mole of Potassium Amide. A 3.2-g (0.01 mole) sample of methiodide VIIa was added to a solution of potassium amide obtained from 0.39 g (0.01 g-atom) of potassium metal in 70 ml of liquid ammonia, after which the mixture was stirred at −70° for 1 h. The ammonia was then evaporated to dryness, and the dry residue was treated with 100 ml of absolute benzene. Workup of the extract yielded 1.9 g of a mixture of substances; the components of the mixture were separated by chromotography on a column filled with Al$_2$O$_3$ (elution with benzene). The first fraction yielded 0.7 g (36%) of colorless plates of N-methylacridan with mp 96-97° (from alcohol), in agreement with the melting point reported in [12]; the second fraction yielded 0.8 g (38%) of yellowish needles of N-methylacridone with mp 203-204° (from benzene), in agreement with the melting point reported in [12]. IR spectrum, cm^{-1} (CHCl$_3$): $\nu_{C=O}$ 1680. A third substance was eluted from the column with acetone, during which it was converted to N-methylacridan and N-methylacridone.

Reaction of N-Methylacridinium Iodide with 1 Mole of Potassium Amide in the Presence of 1 g-eq of Ferric Nitrate. This reaction was carried out similarly except that 2.02 g (1 g-eq) of Fe(NO$_3$)$_3$ · 9H$_2$O was added 5 min after the addition of methiodide VIIa. The ammonia was evaporated, and the dry residue was extracted with 100 ml of benzene. The extract was worked up to give 1.2 g of a mixture of substances, the components of which were separated as described above to give 0.4 g (21%) of N-methylacridan and 0.5 g (24%) of N-methylacridone. The solid residue remaining after treatment with benzene was extracted with 150 ml of boiling absolute alcohol. Workup of the alcohol extract yielded 0.87 g (38%) of 1-methyl-9-amino-acridinium nitrate. Recrystallization from water gave yellow needles with mp 275° (dec.). Found: C 62.2; H 5.0; N 15.4%. C$_{14}$H$_{13}$N$_3$O$_3$. Calculated: C 62.0; H 4.8; N 15.5%. Treatment of the nitrate with 5% NaOH solution gave 0.8 g of light-brown prisms of 10-methyl-9-acridone imine with mp 138° (from aqueous alcohol). No melting-point depression was observed for a mixture of this product with an authentic sample.

Reaction of N-Methylacridinium Iodide with 3 Moles of Potassium Amide. A 3.21-g (0.01 mole) sample of methiodide VIIa was added to a solution of potassium amide obtained from 1.17 g (0.03 g-atom) of potassium in 100 ml of liquid ammonia, after which the mixture was stirred at −70° for 1 h, and the ammonia was evaporated to dryness. The residue was extracted with 100 ml of absolute benzene, and the extract was worked up to give 1.8 g of a mixture of substances. The components of the mixture were separated on a column filled with Al$_2$O$_3$ (elution with benzene) to give 0.8 g (41%) of N-methylacridan, 0.85 g (41%) of N-methylacridone, and 0.1 g (5%) of 10-methyl-9-aminoacridinium nitrate.

The following reaction products were formed when the experiment was carried out in the presence of an equimolecular amount of ferric nitrate; N-methylacridan (39%), N-methyl+acridone (39%), and 10-methyl-9-acridone imine (9%).

Reaction of N-Ethylacridinium Bromide with 1 Mole of Potassium Amide. The experiment was carried out as described for methiodide VIIa. After evaporation of the ammonia, the dry residue was treated twice with 100 ml of absolute benzene, and the extract was worked up to give 1.5 g of a mixture of substances, the components of which were separated on a column filled with Al$_2$O$_3$ (elution with benzene) to give 0.5 g (32%) of colorless needles of N-ethylacridan with mp 94-95° (from alcohol) (the product darkened rapidly in air). Found: C 86.5; H 5.9; N 7.9%. C$_{15}$H$_{15}$N. Calculated: C 86.7; H 5.6; N 7.8%. Also isolated was 0.75 g (45%) of yellowish needles of N-ethylacridone with mp 159-160°, in agreement with the melting point reported in [13].

Reaction of N-Ethylacridinium Bromide with 1 Mole of Potassium Amide in the Presence of 1 g-eq of Silver Nitrate. A 2.13-g (7.5 mmole) sample of ethylbromide VIIb was added to a solution of potassium

amide obtained from 0.3 g (7.5 mg-atom) of potassium in 80 ml of liquid ammonia, 10 min after which 1.3 g (7.5 mmole) of $AgNO_3$ was added. The mixture was then stirred at $-70°$ for 1 h, after which the ammonia was evaporated to dryness. The dry residue was extracted with absolute benzene to give 1.5 g of a mixture of substances, the components of which were separated by chromatography on a column filled with Al_2O_3 (elution with benzene) to give 0.45 g (30%) of N-ethylacridan and 0.65 g (39%) of N-ethylacridone. The 10-ethyl-9-aminoacridinium nitrate that was not eluted by benzene was extracted with boiling alcohol from the Al_2O_3 layer to give 0.1 g (5%) of dark-yellow needles with mp 265° (dec., from alcohol). Found: C 63.0; H 5.3; N 14.9%. $C_{15}H_{15}N_3O_3$. Calculated: C 63.2; H 5.3; N 14.7%.

Reaction of 1-Methyl-3-methoxybenzimidazolium Iodide with 1 Mole of Potassium Iodide. A 2.9-g (0.01 mole) sample of methiodide IVe was added to a solution of potassium amide obtained from 0.39 g (0.01 g-atom) of potassium in 100 ml of liquid ammonia, after which the mixture was stirred at $-70°$ for 2 h. The ammonia was then evaporated to dryness, and the solid dark-brown residue was treated with 20 ml of cold water. The aqueous mixture was filtered to give 1.35 g (93%) of colorless prisms of 1-methyl-2-aminobenzimidazole with mp 201-202° (from water), in agreement with the melting point reported in [14].

Reaction of 1-Benzyl-3-methoxybenzimidazolium Iodide with 1 Mole of Potassium Amide. This reaction was carried out similarly. Workup gave light-rose-colored prisms of 1-benzyl-2-aminobenzimidazole with mp 194-195° (from benzene) (in agreement with the melting point reported in [15] in 90% yield.

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