N-ANIONS OF HETEROAROMATIC AMINES

III.* METHYLATION OF N-ANIONS OF HETEROAROMATIC AMINES IN LIQUID AMMONIA. CONVENIENT METHOD FOR THE PREPARATION OF DIMETHYLAMINO DERIVATIVES OF HETEROCYCLIC COMPOUNDS

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UDC 547.822.7+547.833.5+
547.781.5:542.95

The methylation of N-anions of heteroaromatic amines with methyl iodide in liquid ammonia in most cases gives good yields of the corresponding dimethylamino derivatives. The reaction is of preparative value.

The introduction of a dimethylamino group is an important synthetic method in the chemistry of heterocyclic compounds. It is usually carried out by replacing a halogen atom or a sulfo group by a $N(CH_3)_2$ group by heating the appropriate derivatives with dimethylamine. However, this method has a number of disadvantages: the necessity of using sealed ampuls, the time required, and often the laborious synthesis of the starting materials. In many cases, when the halogen or sulfo group is of low activity, it is not applicable at all. In connection with the availability of heteroaromatic amines, it seems most rational to use them as starting materials for the synthesis of dimethylamino derivatives by the direct methylation of the NH_2 group. Two methods for this sort of methylation have been described: reductive methylation with formaldehyde according to Leuckart [3,4], and methylation of the sodium salts of amines in aprotic solvents (ether, toluene, etc.) [5,6]. However, they both generally give low yields of the dimethylamino derivatives and lead to the formation of a mixture of various compounds that is extremely difficult to separate.

In this paper we have studied the methylation of N-anions of amines of the pyridine, isoquinoline, imidazole, and perimidine series in order to develop a convenient method for the synthesis of dimethylamino derivatives of nitrogen heterocycles. The development of two fundamental problems could be foreseen in the exhaustive alkylation of the amino group in nitrogen heterocycles through the sodium salts: 1) how to avoid the alkylation of the pyridine nitrogen atom; and 2) how to reduce the formation of the monomethylamino derivative to a minimum. We have found that both of these problems are successfully resolved by the methylation of the N-anions of heterocyclic amines with methyl iodide or dimethyl sulfate in liquid ammonia.† On the whole, this paper is divided into two parts – the preparation of the sodium (potassium) salts of the amines, and their alkylation.

We used three methods to generate the N-anions.

A) Ionization of the Amino Group by Means of Sodium Metal. This reaction was carried out by adding small lumps of sodium to a solution or suspension of the amine in liquid ammonia. The ionization proceeds very rapidly, as evidenced by the rapid disappearance of the initially displayed blue coloration char-

*See [1,2] for communications I and II.

† The alkylation of N-anions of heterocyclic compounds in liquid ammonia has been carried out previously primarily for secondary amines (pyrrole, indole, imidazole, etc.) [7]. One case of the alkylation of the NH_2 group in the 5-(7 or 8)-amino-6-methoxyquinoline with alkyl halides of complex structure (ω-haloalkylamines), in which the reaction gave the monoalkylamino derivative, has been described [8].

Rostov State University, Rostov-on-Don. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 9, pp. 1230-1237, September, 1971. Original article submitted June 17, 1970.

TABLE 1. Effect of the Conditions on the Results of the Methylation of the N-Anions of Some Amines

Source for the generation of N-anions	Conditions for the generation of N-anions	Methylation conditions		Yield, %		
		CH_3I, mole	solvent	$RN(CH_3)_2$	$RNHCH_3$	RNH_2
1-Methyl-2-azido-benzimidazole	2 g-atom of Na, NH_3	2	NH_3	80	traces	—
The same	The same	1	NH_3	42	traces	40
1-Methyl-2-amino-benzimidazole	The same	2	NH_3	80	traces	—
The same	The same	1	NH_3	41	traces	40
The same	The same	1	dioxane	—	70	—
The same	1.5 g-atom of $NaNH_2$, dioxane	1	dioxane	—	70	—
1-Methyl-5-azido-benzimidazole	2 g-atom of Na, NH_3	1	NH_3	43	6	33
The same	The same	2	NH_3	73	4	15
1-Methyl-2-amino-perimidine	The same	2	NH_3	75	15	—
The same	The same	1	NH_3	11	71	11
The same	1 g-atom of Na, NH_3	1	NH_3	10	38	50

acteristic for solutions of alkali metals in liquid ammonia. In most cases, a nonvanishing blue coloration appeared after the addition of 1 g-atom of sodium, which indicated the formation of a mono N-anion [9]:

$$R{-}NH_2 + Na \longrightarrow RNH^{\ominus}Na^{\oplus} + \tfrac{1}{2}H_2$$

Only 2-amino-1-methylperimidine and 2-amino-1-methylaceperimidine form dianions during the action of sodium in liquid ammonia because of the high acidity of an amino group in a markedly electron-deficient position [10].

B) Ionization of the NH_2 Group by Means of Alkali Metal Amides. Monosodium salts are usually obtained when this method is used in aprotic solvents. In liquid ammonia, however, it is difficult to determine whether mono- or di-N-anions are formed in solution. Since the amide ion is a stronger ionizing agent than sodium or potassium in liquid ammonia [2], there is no doubt that in this case 2-aminoperimidines will form dianions. 2-Aminoarylimidazoles apparently react with $NaNH_2$ in liquid ammonia to form anions of both types with predominance of the monoanion [2]:

$$R{-}NH_2 + NaNH_2 \longrightarrow R{-}NH^{\ominus}Na^{\oplus} + R{-}N^{\circledcirc}Na_2^{\oplus} + NH_3$$

C) The success of methods A and B is determined by the activating effect of the pyridine nitrogen atom, as, for example, in aminopyridines and 2-aminoimidazoles. If, however, the amino group is far removed from the pyridine nitrogen atom, as, for example, in 5-aminobenzimidaloles, its ionization does not proceed via methods A and B because of the low acidity.* In such cases it is best to use the recently discovered [1, 11] reductive cleavage of aryl azides with sodium in liquid ammonia, which, as assumed, leads to the formation of dianions. The problem of the stability of the dianions of weakly acidic amines in liquid ammonia and their possible ammonolysis at present remains open to discussion.

$$R{-}N_3 + 2\,Na \longrightarrow R{-}N^{\circledcirc}Na_2^{\oplus} + N_2$$

Methylation of N-Anions. Amines of the benzimidazole series (Table 1) have been studied in greatest detail with respect to the effect of solvents, reagent ratios, and methods used to generate the anions. The results, together with the indexes in Table 2, make it possible to draw the following conclusions.

1) The results of the methylation of N-anions in liquid ammonia are almost independent of the method used to generate them. Partial hydrogenation of the π systems by the hydrogen formed during the ionization of the amino group was observed only during the generation of the N-anions of 2-aminopyridine and 1-aminoisoquinoline via method A. In such cases, the sodium salts are best obtained via method B.

*The ionization of the amino group of aniline, the pK_a of which in liquid ammonia is about 27 [9], proceeds similarly under very severe conditions.

TABLE 2. Dimethylamino Derivatives of Heterocyclic Compounds [RN$(CH_3)_2$] Obtained by Direct Methylation of N-Anions

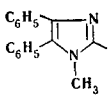
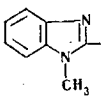
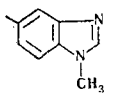
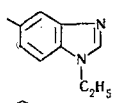
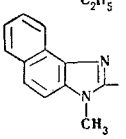
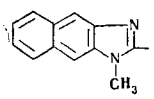
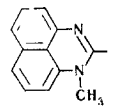
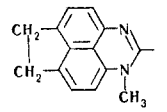
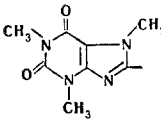
R	Method used to gener. N-anions	mp, °C (from hexane)	bp, °C (mm)	Empirical formula	Found, %			Calc., %			Yield, %
					C	H	N	C	H	N	
1	2	3	4	5	6	7	8	9	10	11	12
	B	—[1]	196	—	—	—	—	—	—	—	55[2]
	B	—[3]	100(8)	—	—	—	—	—	—	—	56
	C	—	100(8)	—	—	—	—	—	—	—	55
	A	112—113	—	—	—	—	—	—	—	—	67
	B	112—113	—	—	—	—	—	—	—	—	80
	B	—	123(5)	—	—	—	—	—	—	—	78
	B	146	—	$C_{18}H_{19}N_3$	78,2	6,8	15,3	77,9	6,9	15,1	59
	A	—	145(5)	—	—	—	—	—	—	—	80
	C	—	145(5)	—	—	—	—	—	—	—	80
	C	99—100	—	$C_{10}H_{13}N_3$	68,3	7,5	23,8	68,5	7,5	24,0	75
	C	81—82	—	$C_{11}H_{15}N_3$	69,8	8,2	22,3	69,8	7,9	22,2	60
	B	—[4]	140(9)	$C_{14}H_{15}N_3$	74,7	7,1	18,65	74,6	6,7	18,6	86
	A	106—107	—	$C_{14}H_{15}N_3$	74,5	7,0	18,5	74,6	6,7	18,6	61

TABLE 2 (continued)

1	2	3	4	5	6	7	8	9	10	11	12
	A	69—70	—	$C_{14}H_{15}N_3$	74,8	7,0	18,4	74,6	6,7	18,6	75
	A	150	—	$C_{16}H_{17}N_3$	76,3	6,7	16,5	76,5	6,8	16,7	62
	B	112—113	—	$C_{16}H_{19}N_5O_2$	61,3	6,0	22,1	61,3	6,1	22,3	20[5]

[1]The picrate melted at 182° (from alcohol) [16].
[2]In addition, about 3% of 2-methylaminopyridine and 30% of the starting 2-aminopyridine were isolated.
[3]The picrate had mp 179° (from alcohol. Found %: C 44.4; H 3.9. $C_7H_{10}N_2 \cdot C_6H_3N_3O_7$. Calculated %: C 44.4; H 3.7.
[4]The picrate melted at 218° (from alcohol). Found %: N 18.2. $C_{14}H_{15}N_3 \cdot C_6H_3N_3O_7$. Calculated %: N 18.4.
[5]Also isolated were 8% 7-benzyl-8-methylaminotheophylline (mp 232-233°) and 50% of the starting amine.

2) The methylation of the N-anions of heteroaromatic amines in liquid ammonia proceeds exclusively at the extra-annular nitrogen atom. We could not detect compounds with an imino structure in the reaction products by thin-layer and gas-liquid chromatography. This indicates that the ambident character of the N-anions of the amines that we studied is expressed only weakly in liquid ammonia. Exceptions are possible during the methylation of sodium salts in aprotic solvents. (See the results from [12] presented below.)

3) The methylation of the monoanions of amino compounds is practically impossible to stop at the step involving the formation of a monomethyl-substituted compounds, regardless of the amount of methylating agent. In most cases the reaction leads to the formation of almost exclusively the dimethylamino-substituted compound with a small or insignificant admixture of the monomethylated product, which is readily separated. This observation served as our basis for the development of a method for the preparation of dimethylamino derivatives of nitrogen heterocycles of the most diverse structures; according to this method, the N-anions of heteroaromatic amines are methylated in liquid ammonia by two equivalents of methyl iodide or, with poorer results, dimethyl sulfate. The reaction is a general one, proceeds very rapidly, and, as a rule, ensures a good yield of the desired product (Table 2). Together with the availability of the starting amino compounds, all of this, in our opinion, makes this method the most convenient one for the synthesis of dimethylamino derivatives of nitrogen heterocycles. A relatively high yield was obtained only in the methylation of the N-anions of 2-aminopyridine and 7-benzyl-8-aminotheophylline. This is apparently explained by the somewhat reduced reactivities of these N-anions because of the electron-acceptor effect of the pyridine nitrogen atom and the two carbonyl groups. As a result, the specific weight of the competitive ammonolysis of methyl iodide increases. Since much unchanged amine is found in the reaction products, the yield with respect to the amine that has reacted should be considered to be quite high in these experiments. The yield can be raised somewhat by using excess methyl iodide. The formation of quaternary salts (the Menschutkin reaction) in liquid ammonia proceeds very slowly (according to our observations).

The yield of 4-dimethylaminopyridine in the methylation of the N-anion of 4-aminopyridine reaches 80%, while in ether the reaction forms 1-methyl-4-pyridoneimine, i.e., with transfer of the reaction center, according to the results in [12]. Our method has great advantages for the synthesis of hard-to-obtain 5-dimethylaminobenzimidazoles and 2-dimethylaminoimidazoles (uncondensed).

The primary formation of a dimethylamino-substituted compound during the methylation of the monoanions of heteroaromatic amines in liquid ammonia is probably explained, as in the case of the carbanion of phenylacetonitrile [13], by the stepwise character of the reaction. Anions of two types – $RNH^{\ominus}$ and $\overset{\ominus}{R}NCH_3$ – are present in solution during the methylation of the monoanions. The latter is formed as a result of ionization of the N–H bond in the monomethylated amine under the influence of excess sodium amide or sodium, or (when not enough of these bases are present) under the influence of the $RNH^{\ominus}$ anion.* Despite the high equilibrium concentration of the $\overset{\ominus}{R}NCH_3$ anion, its rate of methylation is apparently much higher than that of the initially formed $RNH^{\ominus}$ anion, and is thus methylated first. As a result, the dimethylamino derivative rather than the monomethylamino derivative accumulates in the reaction mixture. When equimolecular amounts of the base and the methylating agent are introduced into the reaction, about 50% of the amine is converted to the dimethylamino derivative, and the other half is regenerated.

4) In contrast to the monoanions, the methylation of the dianions of heteroaromatic amines is subject to definite regulation, and in liquid ammonia the process can be directed to favor the formation of monomethylamino or dimethylamino derivatives. Thus, for example, the action of 1 mole of methyl iodide on the dianion of 1-methyl-2-aminoperimidine leads to the formation of 71% of the monomethyl derivative and 11% of the dimethylamino derivative; about 10% of the starting amine is regenerated. If, however, this reaction is carried out with 2 moles of methyl iodide, the chief product (75%) is 1-methyl-2-dimethylaminoperimidine. The yield of 1-methyl-2-methylaminoperimidine in this case is 15%. The methylation of the dianion of 1-methyl-2-aminoaceperimidine gives similar results. This sort of behavior of the dianions becomes understandable when the scheme of their alkylation is examined:

$$\underset{\text{I}}{R{-}N^{\ominus\ominus}} \xrightarrow{CH_3I} \underset{\text{II}}{R{-}\overset{\ominus}{N}CH_3} \xrightarrow{CH_3I} R{-}N(CH_3)_2$$

In this case, the dianion (I) and anion (II) of the monomethylamino derivative are present in the reaction mixture. The reactivity of the dianion should, of course, be higher, and it should be alkylated first. This will lead to the accumulation of II in the reaction mixture, the methylation of which becomes appreciable only after dianion I vanishes or its concentration decreases sharply. It should be noted that less reactive anions generally correspond to more acidic amines. When the dianions of 2-aminoperimidines are methylated with 2 mole of methyl iodide, this leads to a more appreciable yield of the monomethylamino derivative because of the increase in the specific weight of the competitive ammonolysis of methyl iodide, which usually is not of substantial significance. The monoanions of acidic amines, which are capable of forming dianions, are still less reactive; monoanions of this sort behave anomalously as compared with the monoanions of other amines, and stepwise alkylation is not very characteristic for them. Thus the methylation of the monoanion of 1-methyl-2-aminoperimidine in liquid ammonia with 1 mole of methyl iodide gives 38% of 1-methyl-2-methylaminoperimidine and only 10% of the 2-dimethylamino derivative. About half of the starting amine remains unchanged.

Our conclusions regarding the peculiarities of the methylation of dianions are preliminary and may be formulated definitively after the detection of other amines that are capable of giving dianions and after a study of their reactivities.

5) The different behavior of the mono- and dianions in the methylation in liquid ammonia can apparently be used for the solution of the difficult problem of the identification of the mono- and dianions of aromatic amines in liquid ammonia. There is an opinion that dianions are formed in the reductive cleavage of aryl and heteryl azides by sodium or potassium in liquid ammonia [1, 11]. However, for weakly acidic amines of the aniline, 5-aminobenzimidazole, and 2-aminobenzimidazole type, which form only monoanions by the action of sodium, it is logical to assume that their dianions will undergo ammonolysis to the corresponding monoanion in liquid ammonia:

$$R{-}N^{\ominus\ominus} + NH_3 \longrightarrow R{-}\overset{\ominus}{N}H + NH_2^{\ominus}$$

The methylation of the N-anions of 5-amino-1-methyl- and 2-amino-1-methylbenzimidazoles, generated from the corresponding azides, with 1 mole of methyl iodide to primarily the corresponding dimethyl-

*Liquid ammonia itself, as we established, does not cause ionization of the N–H bonds in the investigated amines and thus does not have a direct relationship to the formation of the N-anions.

amino derivative (Table 1) indicates, as it were, that we are actually dealing here with principally the monoanion rather than the dianion.

6) The methylation of the monoanions to the monomethyl derivative can be realized in aprotic solvents of the aromatic hydrocarbon or dioxane types, where the stepwise character of the reaction is not manifested to such a degree as in liquid ammonia. Thus the methylation of the sodium salt of 2-amino-1-methylbenzimidazole with methyl iodide in dioxane gave 70% of 1-methyl-2-methylaminobenzimidazole. This reaction proceeds extremely slowly in ether.

EXPERIMENTAL

Four typical examples of the methylation of the N-anions of heteroaromatic amines are presented below.

1. Sodium [0.46 g (0.02 g-atom)] was added in small portions to a solution of 1.47 g (0.01 mole) of 1-methyl-2-aminobenzimidazole in 50 ml of liquid ammonia. The mixture was stirred for 30 min at −70 to −33°, after which 2.84 g (0.02 mole) of methyl iodide was added, and the mixture was stirred at the same temperature for another 30 min. The cooling was then removed, and the ammonia was allowed to evaporate (this is possible without stirring). The residue was then extracted with ether to give 1.4 g (80%) of 1-methyl-2-dimethylaminobenzimidazole as a colorless oil with bp 145° (5 mm). The picrate had mp 186-187° (from alcohol). The compound was similar to that described in [14].

2. 1-Aminoisoquinoline [1.44 g (0.01 mole)] was added to a solution of sodium amide obtained from 0.46 g (0.02 g-atom) of sodium in 50 ml of liquid ammonia (with an iron nitrate catalyst). The sodium salt of this amine was soluble in liquid ammonia; this is, however, not a necessary condition for the successful methylation. The mixture was stirred at −70° for 15 min, 2.85 g (0.02 mole) of methyl iodide was added, and the mixture was stirred for another 30 min at −70 to −33°. The ammonia was evaporated, and the residue was treated with 25 ml of absolute ether. The solution was filtered through a small layer of aluminum oxide, and the ether was evaporated to give 1.38 g (81%) of practically pure 1-dimethylaminoisoquinoline as a colorless oil with bp 123° (5 mm). The picrate had mp 165-166° (from alcohol), which is in agreement with the melting point in [15].

3. Sodium [0.35 g (0.016 g-atom)] followed by 2.13 g (0.016 mole) of methyl iodide were added in small lumps to a suspension of 1.38 g (0.008 mole) of 1-methyl-5-azidobenzimidazole in 50 ml of liquid ammonia. The mixture was stirred for 1 h at −33°, after which the ammonia was evaporated. The residue was extracted with 25 ml of chloroform, and the extract was passed through a column filled with aluminum oxide with collection of the first fraction to give 1.05 g (75%) of colorless needles of 1-methyl-5-dimethylaminobenzimidazole with mp 99-100° (from hexane).

4. 1-Methyl-2-aminobenzimidazole [1.47 g (0.01 mole)] was refluxed in a stream of nitrogen with 0.6 g (0.015 mole) of finely ground sodium amide in 50 ml of absolute dioxane for 3 h. The mixture was cooled, 0.62 ml (0.01 mole) of methyl iodide in 10 ml of dioxane was added to it, and the mixture was refluxed for another hour. The precipitate was removed by filtration, and the dioxane was removed from the filtrate by distillation. The semicrystalline residue was triturated with a small amount of ether to give 1.2 g (70%) of 1-methyl-2-methylaminobenzimidazole as colorless crystals with mp 178-179° (from benzene). Found %: C 67.3; H 7.0; N 26.0. $C_9H_{11}N_3$. Calculated %: C 67.1; H 6.9; N 26.1.

In all of the remaining cases the methylation products were purified by chromatography on aluminum oxide with chloroform as the solvent. The dimethylamino derivative was always eluted first. The monomethylamino derivative, which was eluted second, was usually formed in insignificant quantities, except for the experiments with 2-aminoperimidines.

1-Methyl-2-methylaminoperimidine. This was obtained as slightly greenish crystals with mp 165° (from aqueous alcohol). Found %: C 73.6; H 6.2; N 19.8. $C_{13}H_{13}N_3$. Calculated %: C 73.9; H 6.2; N 19.9.

1-Methyl-2-methylaminoaceperimidine. This compound was obtained in 20% yield as yellow-green crystals with mp 215° (from octane) by the methylation of the dianion of 1-methyl-2-aminoaceperimidine with 2 mole of methyl iodide in liquid ammonia. Found %: C 75.7; H 6.4; N 17.4. $C_{15}H_{15}N_3$. Calculated %: C 75.9; H 6.4; N 17.7.

1-Methyl-5-methylaminobenzimidazole. This compound was obtained as colorless crystals with mp 102-103° (from benzene). Found %: N 25.7. $C_9H_{11}N_3$. Calculated %: N 26.1.

The following previously unreported 5-azidobenzimidazoles were synthesized in yields of 85-90% for the generation of the N-anions of 5-aminobenzimidazoles.

5-Azidobenzimidazole. A solution of 1.33 g (10 mmole) of 5-aminobenzimidazole in 30 ml of hydrochloric acid (sp. gr. 1.18) was diazotized at 0° with a solution of 0.69 g (10 mmole) of sodium nitrite in 30 ml of water. The resulting diazonium salt solution was added to a solution of 0.78 g (12 mmole) of sodium azide in 2 ml of water. The mixture was stirred for 1 h at room temperature, neutralized with 40% sodium hydroxide, and extracted with ethyl acetate. The extract was dried with potassium carbonate, and the solvent was removed by distillation to give colorless flocculent crystals with mp 224-225° (from water). Found %: C 52.6; H 3.3. $C_7H_5N_5$. Calculated %: C 52.8; H 3.1.

The other 5-azidobenzimidazoles were similarly obtained.

1-Methyl-5-azidobenzimidazole. This compound was obtained as slightly yellowish, fibrous needles with mp 101-102° (from hexane). ν_{N_3} 2120 cm^{-1} (mineral oil). Found %: C 55.3; H 4.2; N 40.5. $C_8H_7N_5$. Calculated %: C 55.5; H 4.1; N 40.4.

1-Ethyl-5-azidobenzimidazole. This compound was obtained as colorless needles with mp 39-40° (from petroleum ether). ν_{N_3} 2120 cm^{-1}. Found %: C 57.6; H 5.1; N 37.2. $C_9H_9N_5$. Calculated %: C 57.7; H 4.8; N 37.4. The picrate had mp 194° (from alcohol).

1-Phenyl-5-azidobenzimidazole. This compound was obtained as colorless needles with mp 72-73° (from heptane). ν_{N_3} 2110 cm^{-1}. Found %: C 66.6; H 3.9; N 29.5. $C_{13}H_9N_5$. Calculated %: C 66.4; H 3.9; N 29.8.

1-Benzyl-5-azidobenzimidazole. This compound was obtained as colorless fibrous needles with mp 104-105° (from hexane), ν_{N_3} 2114 cm^{-1}. Found %: C 67.7; H 4.4; N 28.2. $C_{14}H_{14}N_5$. Calculated %: C 67.5; H 4.4; N 28.1.

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