(silica gel, benzene–ethanol, 5:1), and 0.18 g of the aminonitropyrazole X and 0.07 g of the nitropyrazole XI, mp 86-88°C (ethanol–water, 1:2) were obtained; according to the data of [6], mp 80-84°C. PMR spectrum ($CDCl_3$): 3.80 (3H, s, 1-CH_3); 6.82 (1H, d, 4-H); 7.42 ppm (1H, d, 5-H).

LITERATURE CITED

1. M. E. C. Biffin, D. J. Brown, and O. N. Porter, J. Chem. Soc., No. 17, 2159 (1968).
2. M. A. Khan and B. M. Lynch, Can. J. Chem., 49, 3566 (1971).
3. Yu. A. Manaev, M. A. Andreeva, V. P. Perevalov, B. I. Stepanov, V. A. Dubrovskaya, and V. I. Seraya, Zh. Obshch. Khim., 52, 2592 (1982).
4. M. A. Andreeva, M. I. Bolotov, Sh. G. Isaev, R. Ya. Mushii, V. P. Perevalov, V. I. Seraya, and B. I. Stepanov, Zh. Obshch. Khim., 50, 2116 (1980).
5. K.-Ch. Chang, M. R. Grimmett, D. D. Ward, and R. T. Weavers, J. Aust. J. Chem., 32, 1727 (1979).
6. M. R. Grimmett and K. H. R. Lim, Aust. J. Chem., 31, 689 (1978).
7. I. L. Finar and G. H. Lord, J. Chem. Soc., No. 7, 3314 (1957).

SYNTHESIS OF 3-AMINO-4-NITROPYRAZOLES

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UDC 547.772.1'773.07:543.422'51

3-Bromo-1,5-dimethyl-4-nitropyrazole does not react upon heating with aqueous ammonia, while 1,5-dimethyl-3,4-dinitropyrazole under the same conditions yields 3-amino-1,5-dimethyl-4-nitropyrazole, which is formed from 3-bromo-1,5-dimethyl-4-nitropyrazole in the presence of a copper catalyst. The amination of 1-methyl-3,4-dinitropyrazole-5-carboxylic acid is accompanied by decarboxylation, which is characteristic for 4-substituted 1-methylpyrazole-5-carboxylic acids upon heating in aqueous ammonia or water.

3- and 5-Amino-1-methyl-4-nitropyrazoles (I and II) were first obtained by the reaction of 4-methoxy-5-nitropyrimidine with methylhydrazine. However, Porter et al. [1] made a mistake in the structure assignment using the PMR spectra. Subsequently, 5-amino-1-methyl-4-nitropyrazole (II) was obtained as the result of a planned but rather complicated synthesis [2]. The simplest method for the synthesis of 5-amino-4-nitropyrazoles is the ammonolysis of 4-nitro-5-halopyrazoles, which has yielded 5-amino-1,3-dimethyl-4-nitropyrazole [3] and aminonitropyrazole II [4]. The possibility of obtaining 3-amino-4-nitropyrazoles by this method had not been examined, apparently, since 3-halopyrazoles, even with an electron-withdrawing group at C-4, do not undergo nucleophilic substitution in contrast to the corresponding 4,5-isomers [5]. To check this hypothesis in the case of ammonolysis, we synthesized 3-bromo-1,5-dimethyl-4-nitropyrazole (III).

The bromination of 1,5-dimethylpyrazole in acetic acid in the presence of sodium acetate yields, 3,4-dibromo-1,5-dimethylpyrazole (IV) which was synthesized previously by the bromination of 4-bromo-1,5-dimethylpyrazole in nitric acid [6]. Nitrodebromination of IV by a mixture of concentrated nitric acid and 95% sulfuric acid yielded bromonitropyrazole III. The position of the nitro group in this molecule is indicated unequivocally by the coincidence of the methyl group proton signals in its PMR spectrum with the same signals in the spectrum of 4-nitro-1,5-dimethylpyrazole (Table 1). 3-Bromo-1,5-dimethyl-4-nitropyrazole was isolated unchanged after heating for 5 h at 200°C with excess 25% aqueous ammonia. 3-Amino-1,5-dimethyl-4-nitropyrazole (VI) was obtained under the same conditions from 3-bromo-1,5-dimethyl-4-nitropyrazole in the presence of copper powder in high yield.

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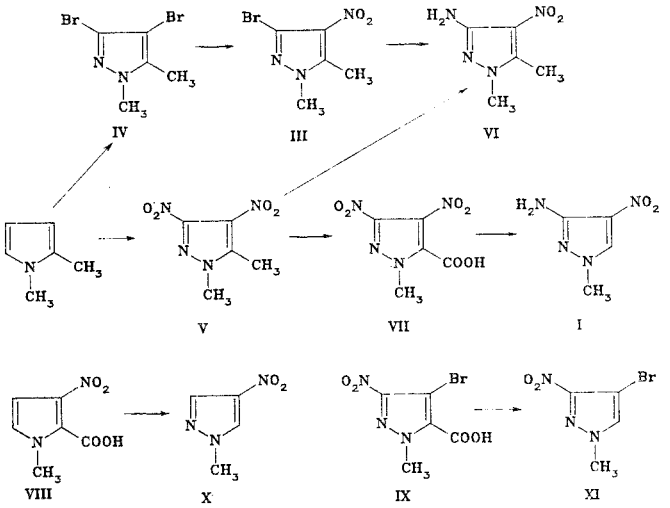
Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 12, pp. 1676-1679, December, 1983. Original article submitted March 29, 1983.

0009-3122/83/1912-1326$07.50

TABLE 1. Substituted 1-Methylpyrazoles

Compound	R	R¹	R²	Mp, °C	PMR spectrum, ppm			Found, %			Chemical formula	Calculated, %			Yield, %
					CH_3	R	R²	C	H	N		C	H	N	
IV	Br	Br	CH_3	51—52[a]	3,65	—	2,15	—	—	—		—	—	—	73
III	Br	NO_2	CH_3	96—98[b]	3,70	—	2,48	27,5	2,7	19,1	$C_5H_6BrN_3O_2$	27,3	2,7	19,4	26
	H	NO_2	CH_3	—	3,70	8,03	2,47	—	—	—	—	—	—	—	—
VI	NH_2	NO_2	CH_3	209—210[c]	3,45	5,98	2,37	38,1	5,4	36,1	$C_5H_8N_4O_2$	38,5	5,1	35,9	84
VII	NO_2	NO_2	COOH	178—180[d] (decomp.)	4,08	—	—	28,0	1,9	25,7	$C_5H_4N_4O_6$	27,8	1,9	25,9	37
I	NH_2	NO_2	H	194—196[e]	3,53	6,08	8,33	—	—	—	—	—	—	—	61
X	H	NO_2	H	90—91[d]	3,90	8,18	8,80	—	—	—	—	—	—	—	93
XI	NO_2	Br	H	156—158[c]	3,95	—	8,27	23,6	2,1	20,5	$C_4H_4Br_4N_3O_2$	23,3	1,9	20,4	58

[a]From petroleum ether; according to Elguero et al. [6], mp 60°C (after distillation). [b]1:1 ethanol—water. [c]Ethanol. [d]Water. [e]According to Khan and Lynch [2], mp 200°C.



o-Dinitrobenzene is readily converted by ammonolysis into o-nitroaniline [7]. The rate of the aramination of 1,2,4-trinitrobenzene is significantly greater than that of the same reaction for 2,4-dinitrobromobenzene [7]. Using these results, we carried out the amination of 1,5-dimethyl-3,4-dinitropyrazole (V) under the conditions indicated above and obtained 3-amino-1,5-dimethyl-4-nitropyrazole (VI) in good yield. The formation of one of the two possible aminonitropyrazoles in this case is apparently a consequence of the nature of the electron density distribution in the pyrazole ring [8]. The purity and structure assignment of VI were confirmed by PMR and mass spectroscopy (Table 1). Aminonitropyrazole VI was also synthesized by the reduction of dinitropyrazole V by sodium hydrosulfide in water and $SnCl_2$ in acetic acid.

1,5-Dimethyl-3,4-dinitropyrazole was oxidized by potassium dichromate in sulfuric acid to 1-methyl-3,4-dinitropyrazole-5-carboxylic acid (VII). The amination of this compound was found to be accompanied by decarboxylation to give 3-amino-1-methyl-4-nitropyrazole (I); the absence of a carboxylic acid group in this compound was shown by IR spectroscopy. The PMR spectrum of the compound obtained was identical to the spectrum of the compound for which the structure of 5-amino-1-methyl-4-nitropyrazole was erroneously assigned by Porter et al. [1].

The decarboxylation of 4-substituted 1-methylpyrazole-5-carboxylic acids upon heating under pressure in aqueous ammonia or water is apparently characteristic for these compounds. Under these conditions, 1-methyl-4-nitropyrazole-5-carboxylic acid (VIII) and 4-bromo-1-methyl-3-nitropyrazole-5-carboxylic acid (IX) [9] yielded 1-methyl-4-nitropyrazole (X) and 4-bromo-1-methyl-3-nitropyrazole (XI), respectively. In contrast to VIII, isomeric 1-methyl-4-nitropyrazole-3-carboxylic acid (XII), obtained by the nitration of 1-methylpyrazole-3-carboxylic acid, remains unchanged upon heating with aqueous ammonia.

EXPERIMENTAL

The PMR spectra were taken on a Tesla BS-467 spectrometer at 60 MHz with HMDS and DMSO-d_6. The mass spectra were taken on an MKh-1309 mass spectrometer with 70 eV ionizing radiation and 150°C ionization chamber temperature. The IR spectra were taken on a UR-20 spectrometer.

3,4-Dibromo-1,5-dimethylpyrazole (IV). A sample of 21.0 ml (0.42 mole) bromine was added at 25°C to a solution of 20.0 g (0.20 mole) 1,5-dimethylpyrazole [14] and 37.0 g (0.27 mole) sodium acetate trihydrate in 100 ml acetic acid. The reaction mixture was heated to 85°C and maintained for 12 h. After cooling, the reaction mass was poured into 500 ml water. The aqueous layer was decanted. The oil was washed with two 100-ml portions of water. Then, 200 ml water was added. Sodium sulfite was introduced until the oily precipitate was decolorized. The aqueous layer was decanted. The residue was dissolved in carbon tetrachloride and the solution was dried over sodium sulfate. The solvent was distilled off and the residue was distilled in vacuum to yield 38.4 g IV.

3-Bromo-1,5-dimethyl-4-nitropyrazole (III). A sample of 7.62 g (0.03 mole) dibromopyrazole IV was added in portions to a mixture of 10 ml 97% nitric acid and 10 ml 95% sulfuric acid cooled to 20°C. The reaction mixture was stirred for 30 min at 25°C, then slowly heated to 60°C and maintained for 1 h. After cooling, the nitrated mass was poured onto ice. The residue was filtered off, washed with water until neutral, and dried to yield 1.7 g III. M^+ 219, 221, M 220.

Amination of 3-Bromo-1,5-dimethyl-4-nitropyrazole (III). A. A mixture of 0.9 g (3.0 mmole) bromonitropyrazole III and 10 ml 25% aqueous ammonia was heated in an autoclave at 190°C for 5 h. After cooling, the precipitate was filtered off and washed with water to yield 0.8 g starting bromonitropyrazole, as indicated by PMR spectroscopy and thin-layer chromatography.

B. Amination under analogous conditions of 0.5 g (2.3 mmole) III in the presence of 0.1 g metallic copper gave 0.3 g 3-amino-1,5-dimethyl-4-nitropyrazole VI. M^+ 156, M 156.

1,5-Dimethyl-3,4-dinitropyrazole (V) was obtained by the nitration of 1,5-dimethylpyrazole using 97% nitric acid in 20% oleum according to our previous procedure [10].

3-Amino-1,5-dimethyl-4-nitropyrazole (VI). A. A sample of 3.68 g (0.02 mole) 3,4-dinitropyrazole V and 30 ml 25% aqueous ammonia was heated in an autoclave for 5 h at 190°C. After cooling, the precipitate was filtered off to yield 2.54 g (82%) VI with mp 209-210°C (from ethanol).

B. A mixture of 9.2 g (0.05 mole) 3,4-dinitropyrazole V, 0.5 g magnesium sulfate, and 90 ml water was heated to 80°C and a solution of sodium hydrosulfide, prepared by passing hydrogen sulfide through a suspension of 12.0 g (0.05 mole) sodium sulfide hydrate in 40 ml water, was added dropwise and maintained at this temperature for 30 min. After cooling to 20°C, the mixture was maintained for 1 h. The precipitate was filtered off and washed with water to yield 5.2 g (66%) VI with mp 206-208°C (from ethanol).

C. Hydrogen chloride was passed through a suspension of 11.3 g (0.05 mole) stannous chloride hydrate in 30 ml acetic acid until the formation of a solution. Then 1.84 g (0.01 mole) 1,5-dimethyl-3,4-dinitropyrazole was added. The solution was heated to reflux and maintained until the disappearance of the starting compound as monitored by thin-layer chromatography on Silufol UV-254 plates with 5:1 chloroform–acetone eluent. The reaction solution was cooled. The residue was filtered off and washed with acetic acid. Then, the residue was dissolved in water and 10% aqueous sodium hydroxide to bring the pH to 10. The precipitate formed was filtered off to yield 0.88 g (56%) VI with mp 203-207°C.

1-Methyl-3,4-dinitropyrazole-5-carboxylic acid (VII). A solution of 5.5 g (35 mmoles) 1,5-dimethyl-3,4-dinitropyrazole V in 30 ml conc. H_2SO_4 was cooled to 20°C and a sample of 15.0 g (50 mmoles) potassium dichromate was added over 4 h in small portions (spontaneous heating was noted upon the addition of one half of the amount of the oxidizing agent and the solution was cooled during this period and maintained for 30 min without the addition of potassium dichromate). The reaction mass was stirred for 2 h at a temperature not higher than 45°C and was then heated to 75°C and maintained for an additional 2 h. After cooling, the reaction mass was poured onto 50 g ground ice. The solution obtained was extracted with four 50-ml portions of ether. The extract was dried over sodium sulfate. The solvent was distilled off. A sample of 100 ml 10% aqueous sodium carbonate was added to the residue.

This mixture was heated with stirring to 60°C and the starting dinitropyrazole V was filtered off. After extraction with four 50-ml portions of ether, the filtrate was acidified with hydrochloric acid to pH 1. The final product was extracted from the acidified solution with five 50-ml portions of ether. The extract was dried over sodium sulfate and the ether was distilled off to yield 2.64 g. IR spectrum (KBr): 1343, 1365, 1555 (NO_2), 1725 cm^{-1} (CO_2H).

3-Amino-1-methyl-4-nitropyrazole (I). A sample of 2.16 g (0.01 mole) dinitropyrazolecarboxylic acid VII and 15 ml 25% aqueous ammonia was heated in an autoclave at 190°C for 3 h. After cooling, the precipitate was filtered off and washed with isopropyl alcohol to yield 1.14 g I.

1-Methyl-4-nitropyrazole-5-carboxylic acid (VIII). A sample of 15.2 g 1-methylpyrazole-5-carboxylic acid was added in small portions to 5.5 ml nitric acid (d 1.52) and 30 ml 100% sulfuric acid at 20-25°C, stirred for 1 h at 30-40°C and 2 h at 75-80°C. After cooling, the reaction mass was poured onto ice and the precipitate was filtered off to yield 19.5 g (96%) VIII with mp 163-164°C (from water). Found, %: C 34.6; H 2.7; N 24.6. $C_5H_5N_3O_4$. Calculated, %: C 35.1 H 2.9; N 24.6.

4-Bromo-1-methyl-3-nitropyrazole-5-carboxylic acid (IX) was obtained by the nitration of 4-bromo-1-methylpyrazole-5-carboxylic acid according to our previous procedure [9] in 47% yield, mp 185-186°C (from 1:1 water–ethanol).

1-Methyl-4-nitropyrazole (X). A sample of 0.85 g (5 mmoles) 1-methyl-4-nitropyrazole-5-carboxylic acid VIII and 10 ml 25% aqueous ammonia was heated in an autoclave for 5 h at 190°C. After cooling, the precipitate was filtered off and the filtrate was evaporated. The precipitate obtained was filtered off, combined with the initial precipitate, and recrystallized from water to yield 0.59 g X.

By analogy, heating 1-methyl-4-nitropyrazole-5-carboxylic acid with 10 ml water yielded 1-methyl-4-nitropyrazole in 81% yield.

4-Bromo-1-methyl-3-nitropyrazole (XI). Heating 1.0 g (4 mmoles) 4-bromo-1-methyl-3-nitropyrazole-5-carboxylic acid IX and 10 ml 25% aqueous ammonia as described for nitropyrazole X yielded 0.45 g bromonitropyrazole XI.

1-Methyl-4-nitropyrazole-3-carboxylic Acid (XII). A sample of 15.2 (0.12 mole) 1-methylpyrazole-3-carboxylic acid was added in portions over 30 min to a nitrating mixture consisting of 5.5 ml 99% nitric acid and 30 ml 20% oleum at 25°C. Then the reaction mixture was heated at 80°C for 3 h. After cooling to 20°C, the reaction mixture was poured onto ice water. The precipitate formed was filtered off and washed with water to yield 16.7 g (81%) XII with mp 171-172°C (from water), 170-173°C [12]. The amide of 1-methyl-4-nitropyrazole-3-carboxylic acid has mp 163-165°C (from water).

A sample of 0.85 g (5 mmoles) acid XII and 10 ml 25% aqueous ammonia was heated under the conditions used for the preparation of nitropyrazole X. The solution obtained was acidified with hydrochloric acid to pH 1 and extracted with three 15-ml portions of ether. The extract was dried over sodium sulfate. The solvent was distilled off to yield 0.76 g starting XII, mp 169-170°C.

LITERATURE CITED

1. M. E. C. Biffin, D. J. Brown, and O. N. Porter, J. Chem. Soc., C, No. 17, 2159 (1968).
2. M. A. Khan and B. M. Lynch, Can. J. Chem., 49, 3566 (1971).
3. M. A. Andreeva, M. I. Bolotov, Sh. G. Isaev, R. Ya. Mushii, V. P. Perevalov, V. I. Seraya, and B. I. Stepanov, Zh. Obshch. Khim., 50, 2116 (1980).
4. V. P. Perevalov, L. I. Baryshnenkova, M. A. Andreeva, Yu. A. Manaev, I. A. Denisova, B. I. Stepanov, and V. I. Seraya, Khim. Geterotsikl. Soedin., No. 12, 1672 (1983).
5. L. Paquette, Principles of Modern Heterocyclic Chemistry, Benjamin-Cummings (1968).
6. J. Elguero, R. Jacquier, G. Tarrago, and H. C. N. Tien Duc, Bull. Soc. Chim. Fr., No. 1, 293 (1966).
7. H. Fuer (editor), Chemistry of the Nitro and Nitroso Groups, Vol. 1, Wiley (1969).
8. I. L. Finar, J. Chem. Soc., B, No. 7, 725 (1968).
9. Yu. A. Manaev, M. A. Andreeva, V. P. Perevalov, B. I. Stepanov, V. A. Dubrovskaya, and V. I. Seraya, Zh. Obshch. Khim., 52, 2552 (1982).
10. M. A. Andreeva, Yu. A. Manaev, R. Ya. Mushii, V. P. Perevalov, V. I. Seraya, and B. I. Stepanov, Zh. Obshch. Khim., 50, 2106 (1980).

11. M. R. Grimmett and K. H. R. Lim, Aust. J. Chem., 31, 689 (1978).
12. V. Papesch and R. M. Dodson, J. Org. Chem., 30, 199 (1965).
13. S. P. Mal'tseva, Z. A. Borodulina, and B. I. Stepanov, Zh. Org. Khim., 9, 815 (1973).

A MASS SPECTROSCOPIC STUDY OF 2-X-ETHOXY-4,6-DICHLORO-symm-TRIAZINES

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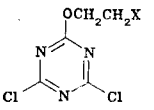
UDC 547.491.8'272'222'236'239:543.51

Defocusing and high resolution techniques were used to study the mass spectrometric decomposition of monoalkoxy-symm-triazines. Such decomposition was found to differ significantly from that of the corresponding dialkoxy and trialkoxy derivatives since, in addition to fragmentation of the side chain in various decomposition steps, decomposition of the heterocycle is also found with elimination of neutral ClCN, ClCNH$^{\bullet}$, and HOCN fragments.

Dichloro derivatives of symm-triazines are starting materials for the synthesis of trisubstituted triazines with important practical applications. The mass spectra of dialkoxytriazines [1] and trialkoxytriazines [2] have been studied rather thoroughly, while no information is available on the dissociative ionization of monoalkoxy-symm-triazines. A number of rearrangement processes upon thermolysis including quaternization of ring nitrogens [3] and transalkylation [4] have been reported specifically for monoalkoxy derivatives of symm-triazine containing the 2-chloroethoxy fragment. The thermolysis of 2-chloroethoxy-symm-triazines permits the synthesis of a number of new polycyclic heterocyclic compounds [4, 5].



I–V

I X=H; II X=CN; III X=N_3; IV X=Cl; V X=ONO_2

In the present work, we studied the dissociative ionization of 2-X-ethoxy-4,6-dichloro-symm-triazines (I-V) and compared the decomposition of these compounds with that for di- and trialkoxy derivatives. In addition, the mass spectral data may subsequently be used for identification of such compounds in complex mixtures of herbicides and their metabolites.

Despite the absence of molecular ions in individual cases in the mass spectra of the symm-triazines IV and V studied, a detailed analysis of the mass spectra using DADI and metastable defocusing methods and high resolution methods indicated general patterns for the decomposition of this class of compounds by the action of electron impact and a general scheme for the fragmentation:

*Deceased.

Lensovet Leningrad Technological Institute, Leningrad 198013. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 12, pp. 1680-1683, December, 1983. Original article submitted March 10, 1982; revision submitted March 30, 1983.

 0009-3122/83/1912-1330$07.50