1',3',3',8-Tetramethyl-4-chlorospiro(2H-1-benzopyran-2,2'-indoline) IIIb was obtained from enaminohydroxyketone Ib analogously to compound IIIa. It was eluted with 1:1 benzenehexane; colorless crystals, Rf 0.69, mp 115-117°C, 14% yield. Found: C 73.8; H 6.3; Cl 10.6; N 4.8%. C<sub>20</sub>H<sub>20</sub>ClNO. Calculated: C 73.7; H 6.2; Cl 10.9; N 4.3%.

<u>1',3',3'-Trimethyl-4-chloro-6-nitrospiro(2H-1-benzopyran-2,2'-indoline) (IIIc)</u> was obtained from enaminohydroxyketone Ic analogously to compound IIIa. It was eluted with 2:1 benzene-petroleum ether; Rf 0.62, bright yellow crystals, mp 170-173°C, 28% yield. Found, %: C 64.3; H 4.9; Cl 9.7; N 7.6; M 356.  $C_{19}H_{17}ClN_2O_3$ . Calculated, %: C 64.0; H 4.8; Cl 9.9; N 7.9; M 356.

<u>1',3',3'-Trimethyl-4-chloro(2H-1-naphtho[2,3-b]pyran-2,2'-indoline) (IIId)</u> was obtained from enaminohydroxyketone Id analogously to compound IIIa. A 1:1 benzene-hexane mixture eluted a colorless material with Rf 0.74, mp 135-137°C. Yield 39%. Found, %: C 76.3; H 5.8; Cl 10.1; N 4.4. C<sub>23</sub>H<sub>20</sub>ClNO. Calculated, %: C 76.3; H 5.6; Cl 9.8; N 3.9.

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NITRATION OF 4-HALO-1-METHYLPYRAZOLES IN SULFURIC ACID

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The rate of nitration of 4-bromo- and 4-chloro-1-methylpyrazoles with nitric acid in various concentrations of sulfuric acid is higher at position 5 than at position 3.

In the nitration of 4-bromo-1-methylpyrazole (I) with excess nitric acid in sulfuric acid, nitrodebromination takes place to give 1-methyl-4-nitropyrazole (II), and the nitro group enters positions 3 and 5 of the heterocycle to form 4-bromo-1-methyl-3,5-dinitropyrazole (III). It was assumed that compound III is obtained from 4-bromo-l-methyl-3-nitropyrazole (IV) which [like another possible mononitration product, 4-bromo-1-methyl-5-nitropyrazole (V)] was not separated and identified [1].

In order to study the features of nitration of compound I and 1-methyl-4-chloropyrazole (VI) we carried out the reaction at an equimolar ratio of halopyrazole to nitric acid in various concentrations (80, 90, 102.5%) of sulfuric acid. All the assumed nitration products, viz., compounds II-V, 1-methyl-3-nitro-4-chloropyrazole (VII), 1-methyl-5-nitro-4chloropyrazole (VIII), and 1-methyl-3,5-dinitro-4-chloropyrazole (IX), were obtained individually. They have characteristic differences in the  $R_f$  values of TLC and in their PMR spectra (Table 1), which were used in analyzing the nitration of 4-halo-1-methylpyrazoles (Table 2).

When 4-bromo-l-methylpyrazole is nitrated in 80% sulfuric acid, mainly nitrodebromination takes place. The only nitration product at the free heterocycle positions is 4-bromo-

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| TABLE 1. | PMR    | Spectra  | and R <sub>f</sub> |
|----------|--------|----------|--------------------|
| Values o | f Subs | stituted | 1-Meth-            |
| ylpyrazo | les    |          |                    |

| Com-                                         | R <sub>f</sub>                                       | PMR spectrum, ppm                                                    |                  |                                      |  |
|----------------------------------------------|------------------------------------------------------|----------------------------------------------------------------------|------------------|--------------------------------------|--|
| pound                                        |                                                      | CH3                                                                  | 3-н              | 5-H                                  |  |
| I<br>II<br>IV<br>V<br>VI<br>VII<br>VII<br>IX | 0,37<br>0,96<br>0,53<br>0,90<br>0,52<br>0,88<br>0,93 | 3,80<br>3,90<br>4,32<br>3,95<br>4,13<br>3,85<br>3,98<br>4,16<br>4,23 | 7,30<br>8,18<br> | 7,55<br>8,80<br>8,27<br>7,63<br>8,35 |  |

TABLE 2. Nitration of 4-Halo-1-Methylpyrazoles with Equimolar Amount of Nitric Acid in Sulfuric Acid at 100°C (after 1 h)

| Com-<br>pound H <sub>2</sub> SO <sub>4</sub><br>concen-<br>tration,<br>% | - Composition of reaction mixture, % |                                  |         |                                  |                           | Ratio of products<br>of nitrodehalogen- |                   |
|--------------------------------------------------------------------------|--------------------------------------|----------------------------------|---------|----------------------------------|---------------------------|-----------------------------------------|-------------------|
|                                                                          | 70                                   | I, VI                            | IV, VII | V. VIII                          | 111, 1X                   | 11                                      | tion              |
| VI<br>VI<br>VI<br>VI<br>VI                                               | 80<br>90<br>102,5                    | 40<br>55<br>10<br>15<br>18<br>19 |         | 10<br>45<br>40<br>69<br>54<br>63 | 5<br>10<br>13<br>18<br>15 | 50<br>40<br>10                          | 5:1<br>4:5<br>1:7 |

1-methyl-5-nitropyrazole. Isomer IV was not found. When sulfuric acid concentration is increased to 90% the conversion of starting compound I increases and its nitrodebromination and nitration go more quickly. At the same time when conversion of 4-bromo-1-methylpyrazole is incomplete the reaction product still contains dinitropyrazole III. When 1-methyl-4-chloro-pyrazole is nitrated in 80% sulfuric acid, along with chloropyrazole VIII dinitrochloropyrazole IX forms; there is no nitrodehalogenation. After nitration in 90% sulfuric acid 3-ni-tropyrazole VII is present in the reaction product. The reason for the formation of dinitropyrazoles III and IX when conversion of starting compounds I and VI is incomplete is that nitration at position 3 or 5 takes place in the form of bases unprotonated at  $N_{(2)}$ ; the equilibrium concentration of the latter in the nitration of 4-bromo-1-methylpyrazole the substituted pyrazole decreases. In the nitration of 4-bromo-1-methylpyrazole the sulfuric acid concentration she ratio of 1-methyl-4-nitropyrazole the sulfuric acid concentration takes place, in contrast to, e.g., bromobenzene [2].

In order to establish by which reaction path 4-halo-1-methyl-3,5-dinitropyrazoles form, we used the method of competing reactions, and carried out nitration of an equimolar mixture of 3-nitropyrazole IV and 5-nitropyrazole V, at 1:0.5 ratio of bromonitropyrazole to nitric acid. After the reaction, compounds III-V were separated in molar ratio 2:1:3. Increasing the amount of nitric acid (ingredient ratio 1:1:0.75) caused complete conversion of nitropyrazole IV, while the ratio of separated III and V was 4:3. These results are unequivocal evidence that the rate of nitration of 3-nitrosubstituted IV to dinitropyrazole III is significantly faster than that of the nitration of isomer V.



On the basis of these data we can consider that in the nitration of 4-halo-1-methylpyrazoles by an equimolar amount of nitric acid in sulfuric acid, 4-halo-1-methyl-3,5-dinitropyrazoles form mainly from 4-halo-1-methyl-3-nitropyrazoles. Therefore, the ratio of 4-halo-1-methyl-5-nitropyrazole to 4-halo-1-methyl-3,5-dinitropyrazole (Table 2) is evidence that the nitration rate of compounds I and VI at position 5 is faster than at position 3; this agrees with our results on the nitration of 4-bromo-1-methylpyrazole-3,5-dicarboxylic acid, 4-bromo-1,5-dimethylpyrazole-3-carboxylic acid, and 4-bromo-1,3-dimethylpyrazole-5-carboxylic acid [3].

## EXPERIMENTAL

PMR spectra were obtained on a Tesla BS-467 instrument (60 MHz, HMDS) in DMSO- $D_6$ . TLC was carried out on Silufol UV-254 plates, with chloroform eluent.

Nitro- and dinitrosubstituted 4-halo-1-methylpyrazoles III-V, VII-IX were obtained by the procedures of [4, 5].

<u>General Method for Nitration of 4-Halo-1-methylpyrazoles</u>. To the nitrating mixture, consisting of 0.65 g (0.01 mole) of 98% nitric acid and 10 ml of sulfuric acid of appropriate concentration cooled to 10°C, was added 0.01 mole of 4-halo-1-methylpyrazole gradually so that the temperature did not exceed 20°C. The reaction mixture was then heated to 100°C, held there for 1 h, cooled, and poured on ice. The precipitate was filtered off, and the filtrate was neutralized with 25% aqueous ammonia and extracted with chloroform. The dried extract was combined with the precipitate, the solvent was distilled off, and the residue was analyzed by TLC and spectroscopically. The proportions of the components of the reaction mixture, determined from the integral intensities of the characteristic signals in the PMR spectrum, are shown in Table 2.

Nitration of Mixture of 4-Bromo-1-methylnitropyrazoles IV and V. To the nitrating mixture, consisting of 0.35 g of 98% nitric acid and 10 ml of 90% sulfuric acid, was added 2.0 g of a 1:1 mixture of compounds IV and V gradually. The reaction mixture was heated to 100°C, held there for 1 h, then worked up and analyzed as in the preceding procedure. There was obtained 1.99 g of a mixture that contained, according to TLC and PMR, compounds III-V in 2:1:3 proportion.

Nitration of 2.0 g of 1:1 mixture of compounds IV and V was carried out similarly with a nitrating mixture consisting of 0.50 g of 98% nitric acid and 10 ml of 90% sulfuric acid. There was obtained 2.18 g of a mixture that contained, according to TLC and PMR, compounds III and V in 4:3 proportion.

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