

after it had become completely colorless. The manganese dioxide was washed with 40 ml of hot water and extracted with boiling acetone. The acetone was removed by distillation, and the residue (1.1 g) was crystallized from alcohol to give 0.4 g (15.8%) of yellow crystals with mp 172-174° (from alcohol). IR spectrum,  $\nu$ ,  $\text{cm}^{-1}$ : 1690 (CO), 1540 (NO<sub>2</sub>, as), and 1345 (NO<sub>2</sub>, s). UV spectrum,  $\lambda_{\text{max}}$ , nm (log  $\epsilon$ ): 232 (4.12) and 300 (3.56). Found: C 55.9; H 3.9; N 14.2%. C<sub>14</sub>H<sub>11</sub>N<sub>3</sub>O<sub>5</sub>. Calculated: C 55.8; H 3.7; N 14%.

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#### 2,4,6-TRIS(METHYLSULFONYL)-3,5-DICHLOROPYRIDINE

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UDC 547.822.5.6:543.422.25

The reactions of 2,6-bis(methylthio)-3,4,5-trichloropyridine and its N-oxide with sodium hydrosulfide were studied. A method for the synthesis of 2,4,6-tris(methylsulfonyl)-3,5-dichloropyridine was developed.

We originally described 2,6-bis(methylsulfonyl)-3,4,5-trichloropyridine [1]. Continuing our research on the synthesis of polysulfone derivatives of pyridine we obtained 2,4,6-tris(methylsulfonyl)-3,5-dichloropyridine (I). Attempts to obtain sulfone I from 2,6-bis(methylsulfonyl)-3,4,5-trichloropyridine were unsuccessful. Its reaction with potassium hydrosulfide leads to replacement of one methylsulfonyl group by a mercapto group [1]. In addition, the reaction of 2,6-bis(methylthio)-3,4,5-trichloropyridine N-oxide (II) with potassium hydrosulfide does not give the desired results — a methylthio group rather than the chlorine atom in the 4 position is replaced to give 2-mercaptop-6-methylthio-3,4,5-trichloropyridine N-oxide, which was identified in the form of the methyl derivative.

In contrast to N-oxide II, the reaction of 2,6-bis(methylthio)-3,4,5-trichloropyridine (II) with sodium hydrosulfide proceeds readily in dimethylformamide (DMF) with replacement of the chlorine atom in the 4 position by a mercapto group to give 2,6-bis(methylthio)-4-mercaptop-3,5-dichloropyridine (IV) in quantitative yield. The difference in the chemical behavior of II as compared with unoxidized compound III is explained by the electronic effect of the N-oxide group, which activates the  $\alpha$  position considerably more markedly than the  $\gamma$  position in nucleophilic substitution reactions [2]. The manifestation of the electron-acceptor effect of the N-oxide group in II is also confirmed by the PMR spectrum, in which one observes a 0.04-ppm shift of the signals of the protons of the methyl group to the weak-field side as compared with the signals of the protons of III (Table 1). Methylation of IV with dimethyl sulfate in an alkaline medium gives 2,4,6-tris(methylthio)-3,5-dichloropyridine (V).

Institute of Organic Chemistry, Academy of Sciences of the Ukrainian SSR, Kiev. Translated from *Khimiya Geterotsiklicheskikh Soedinenii*, No. 3, pp. 369-371, March, 1976. Original article submitted March 11, 1975.

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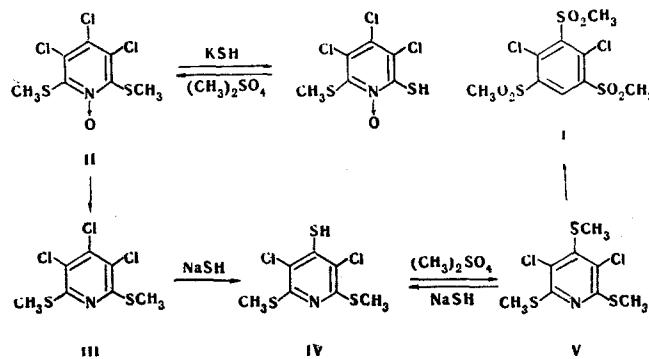
TABLE 1. Chemical Shifts and Ratio of the Intensities of the Protons of the  $\text{CH}_3$  Groups

Compound	R	$\text{R}'$	$\delta_{\alpha}$ , ppm	$\delta_{\gamma}$ , ppm	$J_{\alpha}/J_{\gamma}$
I*	$\text{SO}_2\text{CH}_3$	$\text{SO}_2\text{CH}_3$	3.45	3.40	2:1
II†	$\text{SCH}_3$	Cl	3.02	—	—
III	$\text{SCH}_3$	Cl	2.98	—	—
V	$\text{SCH}_3$	$\text{SCH}_3$	2.95	2.91	2:1
VI	Cl	$\text{SCH}_3$	—	3.01	—
VII	$\text{OCH}_3$	$\text{OCH}_3$	4.30	4.28	2:1

\* In trifluoroacetic acid.

†N-Oxide.

To prove the position of the mercapto group in III we recorded the PMR spectra of not only V but also of several model compounds (III, VI, and VII). As seen from Table 1, III and VI have simple spectra with one singlet; in VI the methylthio group is deshielded to a greater degree than in III ( $\delta_{\gamma}^{\text{VI}} > \delta_{\alpha}^{\text{III}}$ ). At the same time, the spectrum of V consists of two singlets for which inversion ( $\delta_{\alpha}^{\text{V}} > \delta_{\gamma}^{\text{V}}$ ) of the  $\delta_{\text{CH}_3}$  chemical shifts for the  $\alpha$  and  $\gamma$  positions (the assignment is confirmed by integration of the spectrum) as compared with III and VI is observed. A similar PMR spectrum is also observed for 2,4,6-trimethoxy-3,5-dichloropyridine (VII). The inversion of the chemical shifts in the PMR spectra of V and VII is apparently due to the different degree of double bond character of the C-Cl bonds in the  $\alpha$  and  $\gamma$  positions of the pyridine ring; this is sufficiently persuasively proved by the  $^{35}\text{Cl}$  nuclear quadrupole resonance method [3] and by the absence of such a difference for the doubly coordinated sulfur atom of the methylthio group [4].



An attempt to bring about more profound substitution of the chlorine atoms in V by the action of sodium hydrosulfide again leads to starting IV. 2,4,6-Tris(methylsulfonyl)-3,5-trichloropyridine was obtained by oxidation of V with hydrogen peroxide in trifluoroacetic acid.

#### EXPERIMENTAL

The PMR spectra of  $\text{CCl}_4$  solutions of the compounds were recorded with a Tesla BS-487 B spectrometer (80 MHz) at room temperature with hexamethyldisiloxane as the external standard.

Reaction of II with Potassium Hydrosulfide. A solution of 2.8 g (0.05 mole) of KOH in 250 ml of ethanol was saturated with  $\text{H}_2\text{S}$  at 0° for 30 min, after which 2.9 g (0.01 mole) of N-oxide II was added with stirring, and the mixture was refluxed for 30 min with simultaneous bubbling of  $\text{H}_2\text{S}$  through it. The solvent was then removed in vacuo, and the residue was dissolved in 150 ml of water. The solution was filtered, and 2.5 g (0.02 mole) of dimethyl sulfate was added dropwise to it with stirring at 20° in the course of an hour while maintaining an alkaline medium by the addition of potassium hydroxide. The resulting precipitate was separated, washed with water, and dried to give 1.8 g (62%) of 2,6-bis(methylthio)-3,5,6-trichloropyridine N-oxide with mp 210-212° (from aqueous ethanol) (mp 212-214° [5]); no melting-point depression was observed for a mixture of this product with an authentic sample.

2,6-Bis(methylthio)-4-mercaptop-3,5-dichloropyridine (III). A 1.7-g (0.03 mole) sample of freshly prepared sodium hydrosulfide in 50 ml of DMF was added to a solution of 2.7 g (0.01 mole) of III in 25 ml of DMF, after which the mixture was refluxed for 5 min and poured into ice water. The aqueous mixture was acidified with hydrochloric acid, and the resulting precipitate was removed by filtration to give 2.6 g (96%) of III with mp 141-142° (from aqueous methanol). Found: Cl 26.1; S 35.3%.  $\text{C}_7\text{H}_7\text{Cl}_2\text{NS}_3$ . Calculated: Cl 26.1; S 35.3%.

B) This compound (mp 141-142°) was similarly obtained from V in 100% yield.

2,4,6-Tris(methylthio)-3,5-dichloropyridine (IV). This compound, with mp 119-121° (from aqueous ethanol), was obtained in 95% yield from the potassium salt of IV and dimethyl sulfate as in the preparation of II. Found: Cl 24.7; S 33.4%.  $C_8H_9Cl_2NS_3$ . Calculated: Cl 24.8; S 33.6%.

2,4,6-Tris(methylsulfonyl)-3,5-dichloropyridine (I). A total of 10 ml (0.09 mole) of 30%  $H_2O_2$  was added to a cooled solution 2.8 g (0.01 mole) of V in 25 ml of trifluoroacetic acid, after which the mixture was allowed to stand at 20° for 12 h. It was then refluxed for 15 min and poured into ice water. The resulting precipitate was removed by filtration to give 3.2 g (85%) of a product with mp 285-287° (dec., from aqueous acetone). Found: Cl 18.6; S 25.1%.  $C_8H_9Cl_2NO_6S_3$ . Calculated: Cl 18.6; S 25.1%.

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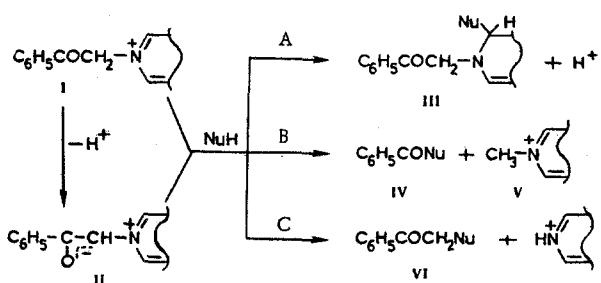
#### REACTIONS OF PYRIDINIUM AND ISOQUINOLINIUM PHENACYLIDES WITH NUCLEOPHILES

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UDC 547.829'852.3'838:542.938

The hydrolysis, alcoholysis, and hydrazinolysis of N-phenacylpyridinium bromide lead to the corresponding benzoic acid derivatives. In addition, 3,6-diphenylpyridazine is formed during hydrazinolysis. The hydrolysis and alcoholysis of N-phenacylisouquinolinium bromide lead to its dimerization, whereas hydrazinolysis gives a triazinoisouquinoline derivative.

The following three types of reactions, in addition to the formation of the corresponding ylids II (or through the intermediate formation of the latter), can be proposed for N-phenacylpyridinium and N-phenacylisouquinolinium cations (I) on reaction with nucleophiles:



We have investigated the hydrolysis, alcoholysis, and hydrazinolysis of N-phenacylpyridinium and N-phenacylisouquinolinium bromides under comparable conditions and have found that the behavior of these salts in these reactions differs markedly. A phenacylation reaction (type C) was not recorded in a single case. N-Phenacylpyridinium bromide reacts completely via a scheme of the B type on standing with aqueous alkali to

Donetsk Branch, L. V. Pisarzhevskii Institute of Physical Chemistry, Academy of Sciences of the Ukrainian SSR. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 3, pp. 372-374, March, 1976. Original article submitted January 3, 1975.

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