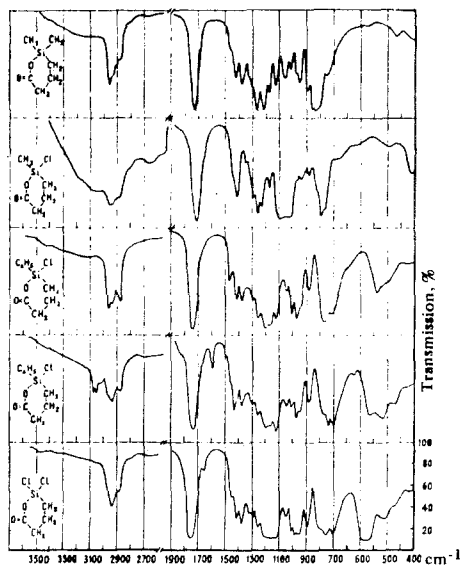


to give 17.5 g IV, as a viscous colorless oil. Found: M 138; 135. Calculated M 144.2. Compounds V-VIII were synthesized similarly.



IR spectra of compounds prepared

The table gives physical constants and analytical data for all the compounds prepared. The figure gives their IR spectra.

REFERENCES

1. V. F. Mironov and N. S. Fedorov, KhGS [Chemistry of Heterocyclic Compounds], 453, 1966.
2. L. H. Sommer, U.S. Patent no. 2589446, 1952; C. A., 47, 1953.
3. R. H. Leitheiser, Diss. Abs., 17, 2818, 1957.
4. N. V. Komarov and N. V. Semenova, Izv. AN SSSR, OKhN, 1879, 1965.

8 January 1966

State Scientific Research Institute
for the Chemistry and Technology
of Heteroorganic Compounds of
the Elements, Moscow

LETTERS TO THE EDITOR

REACTION OF PYRAZINE DI-N-OXIDE WITH ACETIC ANHYDRIDE AND BENZENESULFONYL CHLORIDE

A. S. Elina and I. S. Musatova

Khimiya Geterotsiklicheskikh Soedinenii, Vol. 3, No. 1, p. 183, 1967

UDC 547.861+593.544

Previously American workers, who had studied the reaction of N-oxides of the pyrazine series with acetic anhydride, reported that di-N-oxides of pyrazine unsubstituted in the ring, unlike N-oxides of pyridine and quinoline, do not react with acetic anhydride [1]. Those authors did not find any change in UV spectrum for samples of the reaction mixture, and finally recovered the starting pyrazine di-N-oxide (I). Continuing a study of rearrangements of N-oxides of 6-membered ring aromatic diazines, we investigated the reaction of I with acetic anhydride and benzenesulfonyl chloride. The reaction of I with acetic anhydride was followed by paper chromatography, using the system 5% acetic acid-BuOH. When I was boiled with acetic anhydride and a sample of the reaction solution chromatographed, the spot of the starting di-N-oxide I (R_f 0.13, in UV light dark-violet spot) was observed to gradually decrease, and after 6 hr boiling, it was hardly visible. Also, after 2 hr boiling the chromatogram showed new spots, one with R_f (0.36-0.37, dark-violet in UV light) corresponding to pyrazine mono-N-oxide, and three other spots due to unknown substances (R_f 0.49-0.51, azure; R_f 0.67-0.69, azure; brown spot at start). Only a very inconsiderable amount of I (up to 1%) was recovered from the solution of reaction products. Removal of the acetic anhydride left an oily mixture of products, whose composition is being studied. Previously one of us showed that quinoxaline di-N-oxide reacts with benzenesulfonyl chloride at room temperature to give

the benzenesulfonate of 2-chloroquinoxaline 1-N-oxide [2]. Under the same conditions the di-N-oxide of pyrazine does not react, unlike that of quinoxaline; it reacted with benzenesulfonyl chloride only when heated (75-100° for 8 hr). The reaction led to the isolation of the benzenesulfonate of compound I (30.8%) (bp 139-141°. Found: N 10.77; S 11.84%. Calculated for $C_4H_4N_2O_2 \cdot C_6H_5O_2S$. N 10.36; S 11.84%) and a substance mp 131-132° (8.7%), containing covalently linked chlorine. A solution of this compound in 2.5 N NaOH was heated for a short time; after cooling and acidifying the solution gave a color reaction with $FeCl_3$, characteristic of a cyclic hydroxamic acid. In view of these results the compound, mp 131-132°, was tentatively assigned a structure 2-chloropyrazine 1-N-oxide. Found: Cl 27.51; N 21.6%. Calculated for $C_4H_3ClN_2O$: Cl 27.19; N 21.46%. The study of this reaction is being continued.

REFERENCES

1. B. Klein, J. Berkowitz, and N. E. Hetman, J. Org. Chem., 26, 126, 1961.
2. A. S. Elina, ZhOKh, 34, 2809, 1964.

3 January 1966

Ordzhonikidze All-Union Scientific Research
Chemical and Pharmaceutical Institute, Moscow