

11. Allerhand, A., Gutowsky, H. S., Jonas, J. and Meinzer, R. A. *J. Am. Chem. Soc.* **88** (1966) 3185 and references therein.
12. Ōki, M., Iwamura, H. and Hayakawa, N. *Bull. Chem. Soc. Japan* **36** (1963) 1542; Kurland, R. J., Rubin, M. B. and Wise, W. B. *J. Chem. Phys.* **40** (1964) 2426.
13. Alexander, S. *J. Chem. Phys.* **37** (1962) 967.
14. Glasstone, S., Laidler, K. J. and Eyring, H. *Theory of Rate Processes*, McGraw, New York 1941, p. 195 f.
15. McConnell, H. M. *J. Chem. Phys.* **28** (1958) 430.
16. Munday, R. and Sutherland, I. O. *J. Chem. Soc. B* **1968** 80.
17. Newman, M. S. and Hussey, A. S. *J. Am. Chem. Soc.* **69** (1947) 3023.
18. Mislow, K. and Raban, M. In Allinger, N. L. and Eliel, E. L., (Eds.), *Topics in Stereochemistry*, Wiley, New York 1967, Vol. I, Chap. 1.
19. Ronayne, J. and Williams, D. H. *J. Chem. Soc. B* **1967** 540, and references therein.

Received March 4, 1968.

N-Alkoxythiocarbamoylimidazoles

U. ANTHONI, Ch. LARSEN and
P. H. NIELSEN

Chemical Laboratory II (General and Organic Chemistry), University of Copenhagen, The H. C. Ørsted Institute, Copenhagen, Denmark

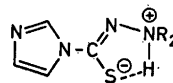
As part of a study of the thiocarbonyl group¹ we became interested in the title compounds, which might function as precursors for the very unstable alkoxy isothiocyanates (*N*-thiocarbonylalkoxyamines)² in analogy with the conversion of *N*-thiocarbonylimidazoles to *N*-isothiocyanatoamines.³ Staab and Walther⁴ have prepared *N*-benzyloxythiocarbamoylimidazole and shown that only its cyclohexylammonium salt is formed on attempted aminolysis with cyclohexylamine.

The reaction between *N,N*-thiocarbonyldiimidazole (I) and methoxyamine (IIa),

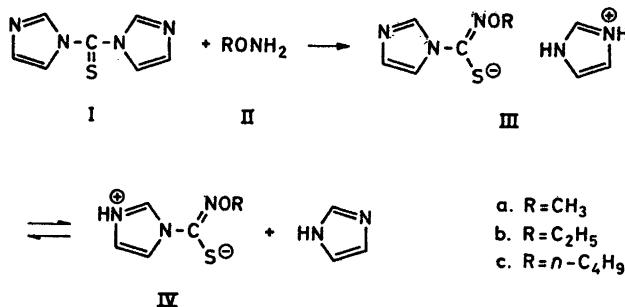
ethoxyamine (IIb), or butoxyamine (IIc) proceeds readily at room temperature to give imidazolium salts of *N*-alkoxythiocarbamoylimidazoles (IIIa–IIIc). Removal of imidazole from IIIa was effected by dissolving it in boiling acetone: *N*-methoxythiocarbamoylimidazole (IVa) precipitated in quantitative yield. Decomposition of IIIb or IIIc in an analogous way failed, probably because the products are soluble in acetone and the equilibrium accordingly is not displaced to the right.

The infrared and NMR spectra (in KBr and CDCl₃, respectively, except where otherwise stated) support the structures assigned to III and IV. In the NMR spectra of IIIa and IVa the CH₃–O singlets are observed at $\tau = 6.18$ ppm which indicates that the methoxythiocarbamoyl group is in the same state in both compounds. The imidazolium ion in IIIa gives rise to three signals at $\tau = 2.95$, 2.12, and ca. -4.2 ppm (ratio 2:1:2). The two former signals are displaced to $\tau = 2.76$ and 1.52 ppm in D₂O close to the positions ($\tau = 2.70$ and 1.55 ppm) observed for imidazolium chloride in D₂O. In addition, IIIa displays three partly resolved triplets with equal areas at $\tau = 3.04$, 2.27, and 1.30 ppm arising from the unprotonated imidazolyl group. As expected for the dipolar structure depicted for IVa the three corresponding peaks are observed at $\tau = 2.91$, 2.18, and 1.04 ppm, which indicates a deshielding of the C–H protons of the imidazole ring relative to the anion of IIIa. The signal from the NH⁺ proton in IVa is observed at $\tau = -1.05$ ppm; comparison with the above τ -value for the imidazolium ion points to the occurrence of inter- or intramolecular hydrogen bonding in IVa. The NMR spectra of IIIb and IIIc introduce no new features except the further signals arising from the alkyl groups.

The most important diagnostic feature of the infrared spectra of IIIa and IVa is the occurrence of intense absorption characteristic of the hydrogen-bonded imidazolium group in the range between 2500 and 3200 cm⁻¹.⁵ In contrast the spectra of 1-(*N,N*-dialkylthiocarbonyl)imidazoles,¹ which have the dipolar struc-



V



ture V, display the relatively weak and broad absorption in the 2500–2900 cm^{-1} region characteristic of ammonium and hydrazinium salts. This difference reinforces the above conclusions as regards the dipolar nature of IVa.

Experimental. Conditions and equipment used for the physical measurements have been summarized in an earlier paper.⁶

Reaction between methoxyamine (IIa) and N,N-thiocarbonyldiimidazole (I). Solvents such as chloroform, acetone, etc. brought about partial conversion of the initial product IIIa to IVa and imidazole. The best solvent for the reaction appeared to be anhydrous ether, but even in this case contamination of IIIa with small amounts of IVa was difficult to prevent. The details of the reaction are: To a saturated solution of (I) in anhydrous ether at room temperature was added, with stirring, one drop of methoxyamine. Within ten minutes the first crystals usually formed; if not, the reaction mixture was filtered and another drop of methoxyamine added. As soon as crystals had been obtained methoxyamine was added dropwise at a slow rate until the yellow colour of the reaction mixture almost had disappeared. After 15 min the precipitate was filtered off and dried. The colourless, crystalline salt IIIa, m.p. 75–77°C, was obtained in nearly quantitative yield. (Found: C 42.40; H 5.12; N 31.00. Calc. for $\text{C}_8\text{H}_{11}\text{N}_5\text{OS}$: C 42.65; H 4.92; N 31.09). The salt is easily soluble in water and acetone, but insoluble in ether. When a solution in acetone was heated to boiling a crystalline product (IVa) soon began to precipitate, and after 5 min the conversion was complete. The colourless substance IVa had a m.p. of 106–107°C. (Found: C 38.40; H 4.60; N 26.89. Calc. for $\text{C}_8\text{H}_7\text{N}_5\text{OS}$: C 38.20; H 4.49; N 26.74). Prolonged boiling of IIIa

with acetone causes another product, m.p. 120–121°C, to separate which has not been investigated further.

Reaction between ethoxyamine (IIb) and I. The reaction was performed as described above but proceeded at a slower rate. Accordingly, IIb should be added at a rate not exceeding 4 drops/min. A yellow-brown oil was often formed at the beginning of the reaction, and the analytically pure compound was obtained by discarding this. This shortcut lowered the yield of colourless, crystalline IIIb to 60–70%; m.p. 59–60°C. (Found: C 44.95; H 5.47; N 29.40. Calc. for $\text{C}_9\text{H}_{13}\text{N}_5\text{OS}$: C 45.17; H 5.47; N 29.27). Attempts to remove one mole of imidazole by treatment with different solvents resulted in a product with nitrogen and carbon contents lower than calculated for IVb.

Reaction between butoxyamine (IIc) and I. The reaction was performed as described for ethoxyamine. An 85% yield of colourless, crystalline IIIc was obtained; m.p. 65–66°C. (Found: C 49.59; H 6.50; N 26.31. Calc. for $\text{C}_{11}\text{H}_{17}\text{N}_5\text{OS}$: C 49.41; H 6.41; N 26.20).

1. Anthoni, U., Larsen, Ch. and Nielsen, P. H. *Acta Chem. Scand.* **22** (1968). *In press.*
2. Jensen, K. A., Burmester, S. and Bak, T. A. *Acta Chem. Scand.* **21** (1967) 2792.
3. Anthoni, U., Larsen, Ch. and Nielsen, P. H. *Acta Chem. Scand.* **20** (1966) 1714.
4. Staab, H. A. and Walther, G. *Ann.* **657** (1962) 104.
5. Bellocq, A.-M., Perchard, C., Novak, A. and Josien, M.-L. *J. Chim. Phys.* **62** (1965) 1334.
6. Anthoni, U., Larsen, Ch. and Nielsen, P. H. *Acta Chem. Scand.* **21** (1967) 1201.

Received March 13, 1968.