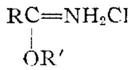
Imidoester Hydrochlorides

BY C. A. MACKENZIE, G. A. SCHMIDT AND L. R. WEBB[1]

A number of imidoester hydrochlorides were made by the Pinner reaction. These compounds are listed in Table I.

TABLE I

IMIDOESTER HYDROCHLORIDES



$$\underset{\displaystyle OR'}{RC}{=}NH_2Cl$$

R	R′	Dec. pts., °C.	Chlorine, % Calcd.	Chlorine, % Found
$ClCH_2CH_2-$	$C_6H_5CH_2-$	79–81	15.2	15.1
$ClCH_2CH_2-$	*m*-$NO_2C_6H_4CH_2-$	89–90	12.7	12.7
$ClCH_2CH_2-$	*p*-$NO_2C_6H_4CH_2-$	89–90	12.7	12.7
$ClCH_2CH_2-$	C_6H_5-	130–131	16.6	16.6
C_6H_5-	$C_6H_5CH_2-$	90–91	14.3	14.3
C_6H_5-	*m*-$NO_2C_6H_4CH_2-$	105–106	12.1	12.1
C_6H_5-	*p*-$NO_2C_6H_4CH_2-$	122–123	12.1	12.1
C_6H_5-	C_2H_5-	128–129	19.6	19.6
CH_3-	$C_6H_5CH_2-$	102–103	19.1	19.1
CH_3-	*m*-$NO_2C_6H_4CH_2-$	115–116	15.8	15.8
CH_3-	*p*-$NO_2C_6H_4CH_2-$	114–116	15.8	15.8
			Nitrogen, % Calcd.	Nitrogen, % Found
$ClCH_2CH_2-$	*n*-C_4H_9-	102–103	7.0	6.9
$ClCH_2CH_2-$	*n*-$C_7H_{15}-$	103–105	5.8	5.7

The reactions were carried out both in the presence of ether and in its absence. Better yields were obtained when ether was not used; however, in such cases, longer periods of time were required for complete crystallization to occur. With either method the yields of product exceeded 75%. The nitriles and alcohols (and ether) were used in equimolar quantities and were saturated with dry hydrogen chloride, then placed in stoppered flasks in a refrigerator until crystallization was complete. Crystallization was complete, usually within a 24-hour period although benzyl imidobenzoate hydrochloride, in the absence of ether, required seven days.

It was not found possible to recrystallize the salts without considerable decomposition occurring; for this reason these compounds should be prepared only from carefully purified reagents. They may be stored indefinitely in a refrigerator; if they are left in a desiccator at room temperature they may decompose. When benzyl β-chloroimidopropionate hydrochloride was stored at room temperature it completely decomposed in about four days to benzyl chloride and β-chloropropionamide.

n-Heptyl β-chloropropionate was obtained as the hydrolysis product of *n*-heptyl β-chloroimidopropionate hydrochloride. *Anal.* Calcd. for $C_{10}H_{19}O_2Cl$: Cl, 17.2. Found: Cl, 17.2; b.p. 86° (2 mm.); d^{25} 0.9715; n^{25}D 1.4360.

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On the Structure of Nitrogen Hydrogen Sulfide

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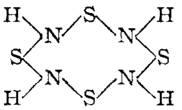
In the course of a spectroscopic study of nitrogen tetrasulfide, we had occasion to prepare a sample of nitrogen hydrogen sulfide, $N_4S_4H_4$, and examine its infrared spectrum in the region 280–3700 cm.$^{-1}$. The spectra were taken of a Nujol mull of the powder. The regions from 670–1700, and from 1700–3700 cm.$^{-1}$ were covered on a Beckmann IR-2 spectrometer at the Spectroscopy Laboratory of the University of Connecticut, using rock salt and lithium fluoride prisms. The region 280–670 cm.$^{-1}$ was covered on a Perkin–Elmer spectrometer, at the Spectroscopy Laboratory of the Massachusetts Institute of Technology, using potassium bromide and thallium bromide–iodide prisms. The absorption peaks in cm.$^{-1}$ observed in the above regions are 293(m), 407(s), 462(s), 516(m), 541(m), 693(w), 712(w), 828(s), 1262(m), 1296(m), 1302(m), 3220(s), 3285(s) and 3320(m), respectively.

The sample was prepared by the method of Meuwesen,[1] by reduction of nitrogen tetrasulfide, N_4S_4, in benzene with alcoholic $SnCl_2$.

It is believed that $N_4S_4H_4$ has a cyclic structure, based on the fact that it is prepared by reduction from cyclic[2] N_4S_4. However, while most observers believe,[1,3] on the basis of chemical evidence, that the hydrogens are bound to the sulfur atoms, in $N_4S_4H_4$, the presence of strong bands at 3220, 3285 and 3320 cm.$^{-1}$, and the absence of any bands in the region 2600 cm.$^{-1}$ in the infrared spectrum, indicates the presence of NH rather than of SH bonds in the molecule.

On the basis of the above data, and the lack of chemical evidence for the presence of nitrogen–nitrogen or sulfur–sulfur bonds,[1,3,4] we feel that the most likely structure for $N_4S_4H_4$ is



and that the compound should be called cyclotetrathiotetraimine.

[1] A. Meuwesen, *Ber.*, **62**, 1959 (1929).

[2] C. S. Lu and J. Donahue, THIS JOURNAL, **66**, 818 (1944).

[3] Sidgwick, "The Chemical Elements and Their Compounds," Oxford University Press, New York, N. Y., Vol. II, 1950, p. 893.

[4] A. Meuwesen and H. Holch, *Ber.*, **64B**, 2301 (1931).