Tetrahedron Letters No. 18, pp 1687 - 1690, 1974. Pergamon Press. Printed in Great Britain.

REACTIONS OF N-CHLORO FORMIMIDOYL CHLORIDES WITH SULFUR [1]

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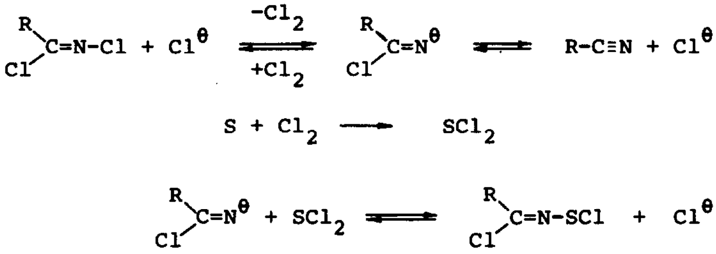
(Received in UK 21 March 1974; accepted for publication 27 March 1974)

The addition of chlorine to the cyanogen bond of some activated cyanides was reported earlier from this laboratory[2,3]. This addition results in the formation of N-chloro formimidoyl chlorides. We now wish to report on the reactions of these compounds with sulfur. Addition of catalytical amounts of chloride anion donating agents to the reactants causes exothermic reactions; no reaction is observed in the absence of catalyst. The first step can be envisaged as an insertion of sulfur into the nitrogen-chlorine bond to yield N-chlorothio formimidoyl chlorides:

Ia-d IIa-d

for which the following mechanism is proposed:



That the reactions follow the above course is confirmed by the observations that

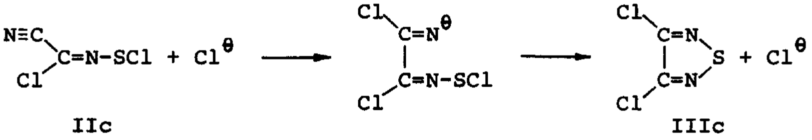
a. N-chloro formimidoyl chlorides (Ia-d) partly decompose in the presence of catalyst to give equilibrium mixtures with the free nitriles and chlorine, and
b. N-chlorothio formimidoyl chlorides (IIa-b) partly decompose in the presence of catalyst to give equilibrium mixtures with the free nitriles and sulfur dichloride.

The nature of the substituent R determines whether the N-chlorothio formimidoyl chlorides can be isolated as such, or are converted in consecutive reactions.

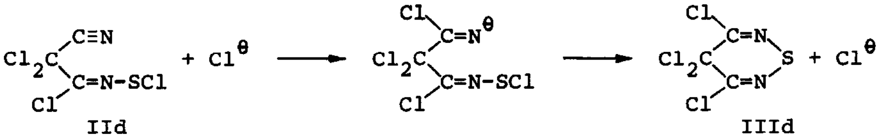
R= Cl. The reaction of N-chloro chloroformimidoyl chloride (Ia) with sulfur gives a mixture of N-chlorothio chloroformimidoyl chloride (IIa) and thiobis (isocyanide dichloride) (IIIa).

R= CCl_3. Treatment of N-chloro trichloroacetimidoyl chloride (Ib) with sulfur leads to the corresponding N-chlorothio trichloroacetimidoyl chloride (IIb); no consecutive reaction is observed.

R= CN. N-chloro cyanoformimidoyl chloride (Ic) reacts with sulfur to give 3,4-dichloro-1,2,5-thiadiazole (IIIc); intermediate formation of N-chlorothio cyanoformimidoyl chloride (IIc) is supposed.



R= CCl_2-CN. The reaction of N,2,2-trichlorocyanoacetimidoyl chloride (Id) with sulfur gives 3,4,4,5-tetrachloro-4H-1,2,6-thiadiazine (IIId); the N-chlorothio compound IId is assumed to be an intermediate.



Compounds IIa and IIIa have been prepared by Bacon et al.[4)] by reacting cyanogen chloride with sulfur dichloride; IIIc has been prepared by Vest[5)] in a similar way from cyanogen, and IIId by Kristinsson[6)] from dichloromalonitrile. IIId was prepared in our laboratory independently by reacting N,2,2-trichlorocyanoacetimidoyl chloride with sulfur and by reacting dichloromalonitrile with sulfur dichloride.

Catalyst: Three different sources of chloride anions have been used to catalyze the reaction of N-chloro formimidoyl chlorides with sulfur:

a. Tetrabutylammonium chloride, the most powerful catalyst in these reactions, can be applied for the synthesis of IIIc and IIId. The reactions must be performed in a suitable solvent e.g. dichloromethane. The chloride is soluble in many organic compounds and difficult to remove. By using this catalyst for the synthesis of IIa or IIb, reverse reactions yielding the nitriles and sulfur dichloride become apparent on purifying by distillation.

b. Tetramethylammonium chloride. This catalyst is less soluble than the former; reactions proceed much slower and may be performed without the use of a solvent. In most cases, the catalyst can be removed by filtration, when the reaction is complete.

c. N,N-dimethylformamide. It is supposed that in the presence of chlorinating agents, chloride anions are formed upon adding catalytical amounts of DMF. Reactions proceed faster than with tetramethylammonium chloride; usually the DMF-complex formed can be removed by filtration.

Experimental procedure:

Reaction of N-chloro formimidoyl chlorides with sulfur:

a. The reagents (Ia or Ib) are mixed at 0° without solvent and the catalyst is added. When the sulfur has dissolved, the mixture is kept overnight at room temperature, and distilled after removal of the catalyst.

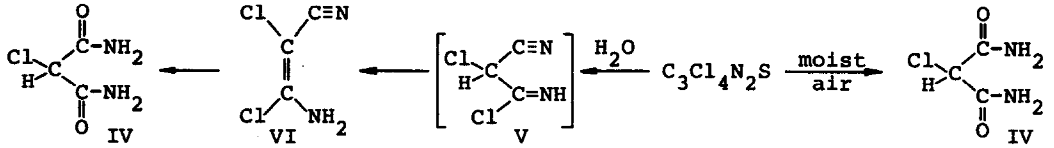
b. A solution of the N-chloro formimidoyl chloride (Ic or Id) in dichloromethane is added dropwise at 0° to a suspension of sulfur and the catalyst in the same solvent. When the sulfur has dissolved, the mixture is kept overnight at room temperature and distilled.

Reactions of trichloroacetonitrile and dichloromalonitrile with sulfur dichloride: Trichloroacetonitrile was converted into IIb and dichloromalonitrile into IIId. The first reaction is slow and can be performed by mixing the reagents with the catalyst (DMF) at room temperature and distilling after 24h. The second reaction is performed by adding the sulfur dichloride dropwise to a mixture of dichloromalonitrile and catalyst (tetrabutylammonium chloride) at 30-40°. After being kept overnight IIId can be distilled (under nitrogen) from the reaction mixture.

Compounds prepared: starting compound, catalyst, yield and side products given.
IIa + IIIa: Ia, DMF (0.5%), 70 and 25% resp., $ClC{\equiv}N$ and SCl_2.
IIa + IIIa: Ia, $(CH_3)_4NCl$ (1%), 50 and 30% resp., $ClC{\equiv}N$ and SCl_2.
IIb: Ib, DMF (0.5%), 55%, $CCl_3C{\equiv}N$ and SCl_2. IIb: $CCl_3C{\equiv}N$, DMF (0.5%), 68%.
IIIc: Ic, DMF (0.5%), 41%, $(C{\equiv}N)_2$ and SCl_2.
IIId: Id, DMF (0.5%), 70%. IIId: Id, $(C_4H_9)_4NCl$ (1%), 87%.
IIId: $CCl_2(C{\equiv}N)_2$, $(C_4H_9)_4NCl$ (1%), 90%.

Structure of new compounds prepared, and remarks on the structure of IIId:
IIb (C_2Cl_5NS): b.p.$_{11}$ 106-107°, n_D^{20} = 1.6005. The proposed structure of IIb was confirmed by elemental analyses, spectroscopic properties (IR: 1612 and 1594 cm^{-1} (doublet): C=N; Mass: $C_2{}^{35}Cl_5NS$, M^+ 244.821 (calc. 244.819)), and the identity of its cyclohexene addition product, ($C_8H_{10}Cl_5NS$): m.p. 52.5-54°.
IIId ($C_3Cl_4N_2S$): b.p.$_3$ 89-90°. In view of the structure of some of its reaction products, we had to consider both structures IId and IIId as possible for $C_3Cl_4N_2S$. On standing in moist air, $C_3Cl_4N_2S$ is converted rapidly into a solid, which proved to be 2-chloromalonamide (IV). This compound is identical with an authentic sample, prepared according to Conrad[7] (IR and NMR spectrum), although

a different melting point was observed; found for IV: 157-158°, lit.[7] 170°. When a solution of $C_3Cl_4N_2S$ in dichloromethane is treated for a short time (10 min) with ice water, 3-amino-2,3-dichloroacrylonitrile (VI) is obtained. This reaction is supposed to involve formation of chlorocyanoacetimidoyl chloride (V), which tautomerizes to VI. Examples of analogous tautomerism are found in literature[8]. On prolonged reaction with water IV is obtained.



VI: m.p. 119-121° dec.; IR: (KBr) 3430, 3305 (N-H stretch), 2200 (C≡N), 1625 (N-H def.) and 1580 cm^{-1} (C=C stretch); Mass: $C_3H_2{}^{35}Cl_2N_2$, M^+ 135.959 (calc. 135.959) NMR: A NMR spectrum of VI, recorded immediately after dissolving the solid in $CD_3C{\equiv}N$ showed one broad absorption at δ=6.2 only; a second spectrum of the same sample, recorded five minutes later, showed an additional small peak at δ=5.86. This peak (sharp) became more important in the course of time and is attributed to a hydrogen atom attached to a negatively substituted carbon atom, as found in its tautomer V. Therefore it is supposed that in solution an equilibrium is established between V and VI.

The IR spectrum of $C_3Cl_4N_2S$ shows no C=N absorption; this does however not exclude structure IId, since C≡N absorptions show varying intensities[9] and may be weak or even absent when an electronegative group is attached to a carbon atom in α-position to a cyano group. The mass spectrum is complicated: M^+ 236 ($C_3{}^{35}Cl_4N_2S$) is present, but the spectrum shows peaks up to 370 ($C_6{}^{35}Cl_6N_4S$) attributed to an ion-molecule reaction. The molecular formula was proved by elemental analyses and molecular weight determination (cryoscopic, in benzene: 216, 217 and 232). Final proof of structure was given by ^{13}C-NMR spectroscopy: IIId, contrary to IId, has two equivalent carbon atoms. In fact, apart from the solvent, two absorptions were found: CCl_4 (solvent) δ_C, ppm from TMS: 137.7 (>C=N) and 71.7 ($>CCl_2$); cf. spectrum of Id: 154.2 (>C=N), 110.0 (-C≡N) and 66.9 ($>CCl_2$).

Acknowledgement: We wish to thank Mr. G.A.M.Snelder for his assistance in the experimental work and Dr. J. de Wit (Groningen) for recording the ^{13}C-NMR spectra.

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