The Synthesis of New Meso-ionic Compounds from Cyanomethyl Dithiobenzoate[1]

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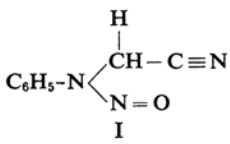
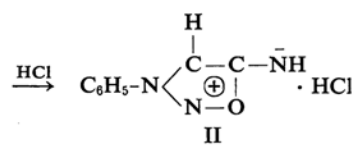
In our previous paper on meso-ionic compounds,[2] it was reported that 3-phenylsydnoneimine hydrochloride (II) was prepared by the action of hydrogen chloride upon *N*-nitrosoanilinoacetonitrile (I). Recently, the synthesis of sydnoneimine hydrochlorides and sydnoneimines substituted with an acyl-, carbamoyl- or thiocarbamoyl- group at the exocyclic nitrogen atom has been reported by Daeniker and Druey.[3]



I



II

The formation of a sydnoneimine ring involves both a bond formation by the intramolecular addition between polar groups, i. e., a nitroso and a cyano group, and a proton transfer to a nitrogen of the cyano group. As the thioketo group is a strong polar group like the nitroso group, it is reasonable to expect that ring formation would occur with cyanomethyl dithioesters by means of a similar mechanism. The present paper reports the synthesis of a new type of meso-ionic compound, "dithioloneimine,"* containing two sulfur atoms in a ring.

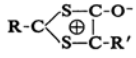
The reaction of potassium dithiobenzoate

1) This paper is the part XVII of studies on meso-ionic compounds.

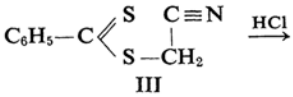
2) H. Kato, M. Hashimoto and M. Ohta, *J. Chem. Soc. Japan, Pure Chem. Sec.* (*Nippon Kagaku Zassi*), **78**, 707 (1957).

3) H. U. Daeniker and J. Druey, *Helv. Chim. Acta*, **45**, 2426 (1962).

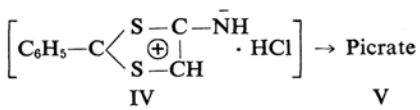
* The free base of IV is referred to as "dithioloneimine" and was derived from an unknown "dithiolone" with the structure written below. The synthesis of dithiolone is now under way in our laboratory.



with chloroacetonitrile in ethanol or in methanol gave a red, oily product, identified as cyanomethyl ester III, which could be purified neither by crystallization nor by distillation even in a nitrogen atmosphere because of decomposition; therefore, the oily intermediate was used for further experiments. When dry hydrogen chloride was passed into an ethereal solution of III, dithioloneimine hydrochloride was separated out; it was very hygroscopic in air and was identified as the picrate.

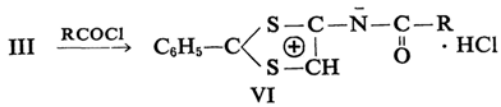


III

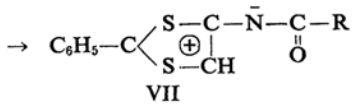


IV V

In contrast to sydnoneimine hydrochloride, which is easily acylated with acyl chlorides in the presence of alkali, IV seemed to be very unstable towards alkali and could not be acylated in the presence of weak alkali. By the action of benzoyl chloride on III in an ethereal solution, the hydrochloride of the *N*-benzoyl derivative VIa was obtained. When acetyl chloride was used in place of benzoyl chloride, the hydrochloride of the *N*-acetyl derivative VIb was obtained.



VI

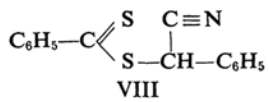


VII

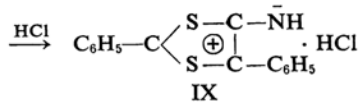
VIa R=C_6H_5 VIb R=CH_3

These hydrochlorides of *N*-acyldithioloneimines are yellow, but their free bases are brilliant red. It is known that some dithioesters show thermochromism in a solution. For example, a solution of methyl α-dithionaphthoate in ethyl benzoate is yellow-orange, but it becomes red-orange when heated.[4] Yellow crystals of VIa or of its solution in benzene or in xylene turn red when heated and then become yellow again when cooled.

When α-chlorophenylacetonitrile was treated with potassium dithiobenzoate, an oily intermediate VIII was obtained which gave 2, 5-diphenyldithioloneimine hydrochloride when treated with hydrogen chloride. Unexpectedly, when VIII was treated with benzoyl chloride, the same dithioloneimine hydrochloride was obtained. The reason for the formation of this hydrochloride instead of the *N*-benzoyl derivative is not clear.



VIII



IX

The structural evidence for dithioloneimines based on elementary analysis and its infrared spectrum. The disappearance of the C≡N stretching band at 2260 cm^{-1} and the appearance of a CH stretching band at 3020~3050 cm^{-1} suggest the formation of a meso-ionic ring. A CO stretching band of *N*-acylsydnoneimine hydrochlorides was observed at 1720 cm^{-1},[3] but in case of *N*-acyldithioloneimine hydrochlorides, this band shifts to 1650~1670 cm^{-1}.

Experimental

2-Phenyldithioloneimine Picrate (V). — Thirty-eight grams of chloroacetonitrile were added drop by drop below 40°C to an ethanol solution (500 ml.) of potassium dithiobenzoate prepared from 98 g. of benzotrichloride by Crawholl's procedure;[5] the mixture was then stirred for an hour at room temperature under a slow stream of nitrogen. The filtration of the reaction mixture and the removal of the ethanol from the filtrate gave 47 g. of a red oil which was identified as III by its infrared spectrum but which could not be purified by distillation because it decomposed when heated above 80°C.

The red oil was dissolved in 100 ml. of ether and dried with sodium sulfate. Dry hydrogen chloride was passed through 10 ml. of an ethereal solution of III, the hygroscopic precipitate obtained was quickly dissolved in 10 ml. of ethanol, and 1 ml. of a saturated alcoholic solution of picric acid was added to the resulting solution. Then the alcoholic solution was heated to a boil; when it had cooled, there separated out red needles, which were recrystallized from ethanol (m. p. 157.5~158.5°C).

Found: C, 42.50; H, 2.30; N, 13.09. Calcd. for $C_{15}H_{10}N_4O_7S_2$: C, 42.66; H, 2.39; N, 13.26%.

2-Phenyl-1-*N*-benzoyldithioloneimine Hydrochloride (VIa).—To 20 ml. of the ethereal solution of III prepared above, 7.2 g. of benzoyl chloride were added while the mixture was shaken well, the mixture was then kept standing for a day at room temperature. The precipitate was filtered off and crystallized three times from ethanol to give 4.3 g. of yellow needles (m. p. 214~215°C (decomp.)), which showed λ_{max}^{EtOH} 398 mμ (ε 15100).

4) A. Schoenberg, S. Nickel and D. Cernik, *Ber.*, 65, 289 (1932).

5) J. C. Crawholl and D. F. Elliott, *J. Chem. Soc.*, **1951**, 2071.

Found: C, 57.42; H, 3.62; N, 4.28. Calcd. for $C_{16}H_{12}NOS_2Cl$: C, 57.57; H, 3.62; N, 4.19%.

2-Phenyl-*N*-acetyldithioloneimine Hydrochloride (VIb).—To 20 ml. of the ethereal solution of III, 4 g. of acetyl chloride were added while the solution was being cooled and shaken; the mixture was then kept standing for a day. The precipitate was filtered off, crystallized from ethanol, and recrystallized from isopropyl alcohol to give 4.5 g. of yellow crystals (m. p. 207°C (decomp.)), which showed λ_{max}^{EtOH} 398 mμ (ε 13800).

Found: C, 48.43; H, 3.45; N, 5.38. Calcd. for $C_{11}H_{10}NOS_2Cl$: C, 48.60; H, 3.71; N, 5.15%.

2-Phenyl-*N*-benzoyldithioloneimine (VIIa).—To 100 ml. of an aqueous solution of VIa (1 g.) 10 ml. of a saturated aqueous solution of sodium hydrogen carbonate was added, and the mixture was shaken with benzene. The benzene layer was then dried with sodium sulfate. The removal of the benzene gave 0.6 g. of red needles (m. p. 176~177°C (decomp.)), which showed λ_{max}^{EtOH} 472 mμ (ε 9090).

Found: C, 64.30; H, 3.48; N, 4.73. Calcd. for $C_{16}H_{11}NOS_2$: C, 64.63; H, 3.73; N, 4.71%.

2-Phenyl-*N*-acetyldithioloneimine (VIIb).—To 100 ml. of an aqueous solution of VIb (1 g.), 10 ml. of a saturated aqueous solution of sodium hydrogen carbonate was added, and the mixture was shaken with benzene. The benzene layer was then dried with sodium sulfate. The removal of the benzene gave 0.55 g. of red crystals, which was recrystallized twice from benzene-petrolium ether; m. p. 184~185°C (decomp).

Found: C, 55.63; H, 3.16; N, 5.56. Calcd. for $C_{11}H_9NOS_2$: C, 56.10; H, 3.86; N, 5.95%.

2, 5-Diphenyldithioloneimine Hydrochloride (IX).—7.6 g. of α-chlorophenylacetonitrile[6] which had been prepared from mandelonitrile[7] and thionyl chloride were added under a slow stream of a nitrogen current below 40°C to 100 ml. of potassium dithiobenzoate in ethanol prepared from 9.8 g. of benzotrichloride; the mixture was then stirred for an hour at room temparature. The filtration of the reaction mixture and the removal of ethanol of the filtrate gave a red oil, to which 20 ml. of water was added and extracted with two portions of ether of 50 ml. each. The ethereal layer was dried with sodium sulfate, and dry hydrogen chloride was passed through one-half of the ethereal layer. When the solution was kept standing for two days at room temparature, gave dark red crystals which were recrystallized from acetone (m. p. 166~167° (decomp.)), the crystals showed λ_{max}^{EtOH} 487 mμ (ε 21800).

Found: C, 58.42; H, 3.74; N, 4.52. Calcd. for $C_{15}H_{12}NS_2Cl$: C, 58.92; H, 3.92; N, 4.58%.

To the other half of the ethereal solution, benzoyl chloride was added; after the mixture had been kept standing over night, red crystals were filtered off. Recrystallization from acetone gave dark red needles which were identified as IX by their infrared spectrum and by elementary analysis.

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6) F. Barrow and F. J. Thorneycroft, ibid., **1934**, 722.
7) H. Gilman and A. H. Blatt, "Organic Syntheses," Coll. Vol. I, 336 (1961).