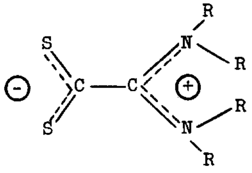
**Tetrahedron Letters No.37, pp. 3257-3260, 1965. Pergamon Press Ltd.
Printed in Great Britain.**

ZWITTERIONIC FORMAMIDINIUMDITHIOCARBOXYLATES

David H. Clemens, Anthony J. Bell and Joseph L. O'Brien
Research Laboratories, Rohm & Haas Company, 5000 Richmond Street
Philadelphia, Pennsylvania

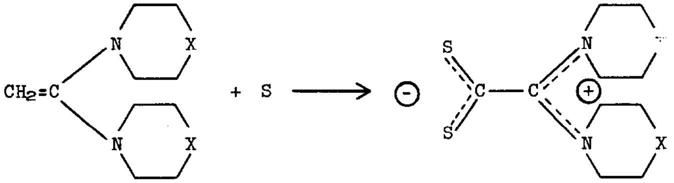
(Received 13 July 1965)

A recent communication by Winberg and Coffman[1] describing the preparation of compounds with the unique zwitterionic structure I, from tetraaminoethylenes and carbon disulfide prompts us to report some related studies.



I

In contrast to the recently reported[2] reaction of simple enamines with sulfur to produce thiocarboxamides, we have found that the enediamines[3 a-g] react readily with sulfur under similar conditions to produce high melting, colored solids to which structure I has been assigned (eq. 1).



(1)

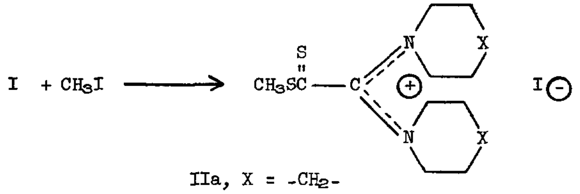
Ia, X = -CH$_2$-

Ib, X = -O-

Thus, when 6.0 g. (0.187 g. atom) of flowers of sulfur was added to a solution of 12.0 g. (0.062 mole) of 1,1-di-(1-piperidinyl)-ethylene in 350 ml. of chloroform the reaction mixture immediately took on a dark purple color. After standing overnight it was evaporated to dryness, and the residual solid was washed with methanol and carbon disulfide, leaving 8.0 g. (50% yield) of dark red N,N'-bis-pentamethyleneformamidiniumdithiocarboxylate (Ia) m.p. 234-235°. Anal. Calcd. for $C_{12}H_{20}N_2S_2$: C, 56.20; H, 7.86; N, 10.93; S, 25.10; molecular weight, 256.43. Found: C, 56.07; H, 7.90; N, 10.63; S, 25.10; molecular weight, 250. The n.m.r. spectrum consists of only two peaks at τ 6.42 and 8.27 previously shown to be highly characteristic of the bis-pentamethyleneamidinium moiety[3g] and the infrared spectrum has a strong band characteristic of amidinium salts at 6.4μ.

In a similar manner, N,N'-bis-3-oxapentamethyleneformamidiniumdithiocarboxylate (Ib), m.p. 233-236° with decomposition, was obtained from 1,1-di-(1-morpholinyl)-ethylene.

In agreement with the findings of Winberg and Coffman[1] both Ia and Ib are readily alkylated by treatment with methyl iodide in acetonitrile at room temperature to produce the corresponding dithiocarboxymethylformamidinium salts, IIa and IIb (eq. 2). The n.m.r. spectrum of IIa consists of three peaks at τ 6.25, 7.05 and 8.22 with approximate area ratios of 8/3/12, and the infrared spectrum has a strong band at 6.3μ. Complete elemental analyses in agreement with theory were obtained for IIa and IIb.

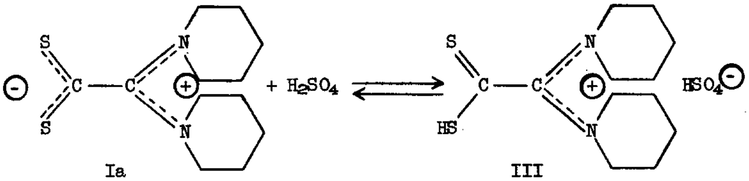


(2)

IIa, X = -CH$_2$-

IIb, X = -O-

A study of the ultraviolet spectrum of these compounds in varying strengths of sulfuric acid was instructive. In dilute sulfuric acid Ia has a maximum at 360 mμ and the spectrum is essentially identical to that obtained in methanol (λ max. 362 mμ). In concentrated sulfuric acid Ia has a maximum at 321 mμ, close to the value observed for the methyl thioester, IIa in methanol (328 mμ). Since dithioacids are known to have ultraviolet spectra very similar to their esters[4], it appears that protonation of Ia is occurring to give III (eq. 3). In support of this hypothesis, it has been shown that the spectral changes are reversible and that Ia can be isolated unchanged by dilution of its concentrated sulfuric acid solution with water.



Ia III (3)

Although the limited stability of Ia in sulfuric acid solution* precludes an accurate determination of the pKa of III by the method of Hammett[5,6] a reasonably good approximation can be obtained. Thus the ultraviolet spectrum of Ia in 39.5% sulfuric acid shows approximately equal amounts of the protonated and unprotonated species indicating a pKa of ca. -2 for III[6]. The confirmation of the expected high acidity** of the conjugate acid of I lends further support to the proposed structure.

---

* The half life of Ia in concentrated sulfuric acid is about 5 hours.

** An argument for the high acidity of III may be made as follows: the pKa of $(CH_3)_3\overset{\oplus}{N}CH_2COOH$ is 1.8. The approximate pKa difference between an oxyacid and a dithioacid may be estimated by the difference between acetic acid (pKa = 4.75) and dithioacetic acid (pKa = 2.55) to be ca. 2.2. Thus one might estimate the pKa of the hypothetical acid $(CH_3)_3\overset{\oplus}{N}CH_2CSSH$ to be ca. -0.4. III would be expected to be somewhat stronger due to the possibility of resonance forms in which the positive charge resides on the carbon adjacent to the - CSSH group.

REFERENCES

(1) H.E. Winberg and D.D. Coffman, *J. Am. Chem. Soc*. **87**, 2776 (1965)

(2) R. Mayer and J. Wehl, *Angew. Chem. Int'l. Ed*., **3**, 705 (1964).

(3) (a) S.M. McElvain and B.E. Tate, *J. Am. Chem. Soc*., **67**, 202 (1945); (b) J.F. Arens and Th. R. Rix, *Koninkl. Ned. Akad. Wetenschap. Proc*., **57B**, 270 (1954); (c) H. Baganz and L. Domaschke, *Chem. Ber*., **95**, 2095 (1962); (d) K.C. Brannock, R.D. Burpitt and J.G. Thweatt, *J. Org. Chem*., **28**, 1697 (1963); (e) R.H. Hasek, P.G. Gott, R.H. Meen and J.C. Martin, *ibid*. **28**, 2496 (1963); (f) R.H. Hasek, P.G. Gott and J.C. Martin, *ibid*. **29**, 2513 (1964); (g) D.H. Clemens, A.J. Bell and J.L. O'Brien, *ibid*. **29**, 2932 (1964).

(4) A. Hantzsch and W. Bucerius, *Chem. Ber*., **59**, 793 (1926)

(5) L.A. Flexser, L.P. Hammett and A. Dingwall, *J. Am. Chem. Soc*., **57**, 2103 (1935).

(6) L.P. Hammett and A.J. Deyrup, *ibid*., **54**, 2721 (1932).