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## Derivatives of Hydrazine

### III. Dithio- and Diselenocarbazic Acid

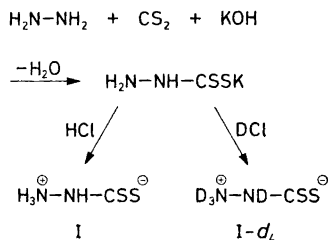
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In 1895 Curtius and Heidenreich<sup>1</sup> reported that dithiocarbazic acid (I) could not be prepared either by adding acids or benzaldehyde to hydrazinium dithiocarbazate, or by treating silver(I) dithiocarbazate with hydrogen sulfide. Instead,

decomposition products were obtained, which were later characterised by Losanitch.<sup>2,3</sup> These results contrast to those recently obtained<sup>4</sup> by an investigation of *N,N*-dimethyldithiocarbazic acid, which proved to be moderately stable in the crystalline state at room temperature. The stability was believed to arise from the compound existing principally in the dipolar hydraziniodithiocarbazate form, a form which might also be readily attained by unsubstituted dithiocarbazic acid. Even the possibility of (I) having a nonpolar structure does not necessarily prevent it from possessing the stability necessary for preparation. Thus, dithiocarbamic acid<sup>5</sup> has recently been described and found to be more stable than expected.

The preparation of (I) has been accomplished by the sequence of reactions shown in the following reaction scheme:



The preparation of potassium dithiocarbazate from hydrazine, potassium hydroxide, and carbon disulfide in aqueous ethanol has been described by Busch and Starke.<sup>6</sup> However, the yield of pure product was very small owing to the formation of an oily contaminant, probably arising from the formation of potassium xanthate as by-product. It was proposed by Professor K. A. Jensen, and confirmed by experiment, that the shortcoming of this method could be avoided by using dioxane as solvent.

When hydrochloric acid was added to the potassium salt at 0°C (I) could be prepared without difficulty. The experiment reported by Curtius and Heidenreich<sup>1</sup> was therefore repeated, and it was found that (I) could equally well be prepared from hydrazinium dithiocarbazate by addition of hydrochloric acid provided that the reaction mixture was kept in an ice-bath. Elemental analysis showed (I) to lose sulfur rapidly at room temperature and a correct sulfur analysis was not obtained.

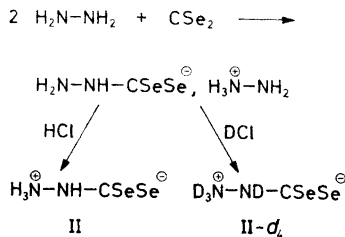
Dithiocarbazic acid also decomposes slowly at  $-40^{\circ}\text{C}$ .

In support of the assumption that (I) exists in a dipolar form, it is soluble in water and dimethylsulfoxide, but insoluble in common organic solvents such as tetrachloromethane, chloroform, and benzene. The structure of (I) was therefore only studied in the solid state by infrared spectroscopy using the KBr-pellet technique. The corresponding perdeuteriated acid, I- $d_4$ , was easily obtained for purposes of comparison with the IR spectrum of (I) by dissolving potassium dithiocarbazate in deuterium oxide and adding a solution of deuterium chloride in deuterium oxide.

The infrared spectrum of (I) showed the presence of a very strong, broad absorption region extending from ca.  $2500\text{ cm}^{-1}$  to  $3250\text{ cm}^{-1}$  with submaxima at ca. 2600, 2900, and  $3240\text{ cm}^{-1}$ . This absorption was displaced to the range ca.  $1950\text{ cm}^{-1}$  to  $2400\text{ cm}^{-1}$  in I- $d_4$  with the submaxima at 1980, 2210, and  $2410\text{ cm}^{-1}$ . Clearly, this absorption arises from NH/ND stretching vibrations, and the general appearance and location establish<sup>7</sup> its origin to be the  $\text{NH}_3^+/\text{ND}_3^+$  group of a dipolar form, except perhaps the submaxima at  $3240/2400\text{ cm}^{-1}$ , which might originate from the NH/ND group neighbouring the positively charged nitrogen atom. Of course, these observations do not exclude the presence of small amounts of the nonpolar form, since the SH stretching vibration from this would be situated around  $2500\text{ cm}^{-1}$ , hidden below the strong absorption. However, the relative proportion of this form can be estimated to be small from the observation that the infrared spectrum is almost devoid of absorption in the region between  $1580$  and  $1700\text{ cm}^{-1}$  where the  $\text{NH}_2$  deformation vibration should occur.

In the light of these results it appeared interesting to investigate the selenium analogue, diselenocarbazic acid (II). The preparation of II was accomplished without much trouble using a similar method in which hydrazinium diselenocarbazate is formed as an intermediate.

Diselenocarbazic acid (II) proved to be more stable to air in the dry, crystalline state than (I), a fact which can be attributed to a more complete conversion to a dipolar form. The solubility paralleled that of (I), but as hydrazinium diselenocarbazate was much less soluble in water than potassium dithiocarbazate it was difficult to obtain a high yield of II from an aqueous reaction mixture.



The characteristics of the NH/ND stretching regions of the infrared spectra of II and II- $d_4$  recorded in KBr-pellets were almost identical with those described above for I and I- $d_4$ , respectively. This result establishes the dipolar structure depicted for II. It was noted that the infrared spectra of I and II differed only in insignificant respects in the entire region from  $1100\text{ cm}^{-1}$  and upwards, but that two strong bands at  $1065\text{ cm}^{-1}$  and  $986\text{ cm}^{-1}$  in (I) had their counterparts at  $1020\text{ cm}^{-1}$  and  $896\text{ cm}^{-1}$  in II. This result agrees well with the proposal<sup>4</sup> that the band in the infrared spectrum of *N,N*-dimethyldithiocarbazic acid at  $1035\text{ cm}^{-1}$ , and in the selenium analogue at  $927\text{ cm}^{-1}$ , are mainly due to the asymmetric stretching vibrations of, respectively, the CSS- and CSeSe- groups.

A systematic investigation of derivatives of dithio- and diselenocarbazic acids will shortly be submitted for publication in this journal.

*Experimental. Potassium dithiocarbazate.* A solution of carbon disulfide ( $2 \times 10^{-2}$  mol) in dioxane (25 ml) was added, over a period of 1–2 h, to a stirred suspension of pulverized potassium hydroxide ( $2 \times 10^{-2}$  mol) and anhydrous hydrazine ( $2 \times 10^{-2}$  mol) in dioxane (25 ml). The colourless precipitate was filtered off, washed with dioxane and then ether, and finally dried *in vacuo*. The yield was nearly quantitative. The salt may be recrystallized from a water/ethanol mixture, but is sufficiently pure for the next step in the synthesis.

*Dithiocarbazic acid (I).* A fresh, filtered solution of potassium dithiocarbazate (1.46 g) in water (8 ml) was cooled in an ice bath. 1 N hydrochloric acid (10 ml) was added dropwise to the stirred solution whereupon an almost colourless precipitate was formed. It was filtered off, washed with a small amount of cold water, and dried quickly in vacuum at room temperature. Attempts to store (I) overnight in a desiccator over calcium chloride resulted in complete decomposition. The m.p.

of freshly prepared material was 105–106.5°C with decomposition. (Found: C 11.30; H 3.99; N 26.03. Calc. for  $\text{CH}_4\text{N}_2\text{Se}_2$ : C 11.10; H 3.73; N 25.90).

*Diselenocarbazic acid (II)*. In the preparation of the selenium-containing compounds it proved important to use oxygen and peroxide-free solvents and to flush all apparatus with nitrogen before and during use. The moist compounds were extremely susceptible to oxidation as readily observed by the red colour of the selenium formed by the oxidation.

A solution of carbon diselenide (1.7 g) in dry ether (75 ml) was added, over a period of 2 h, to a stirred solution of anhydrous hydrazine (0.64 g) in dry ether (250 ml) cooled in an ice-bath. The sticky, red-black hydrazinium diselenocarbazate was precipitated at the walls of the reaction flask during the reaction and was finally separated from the supernatant by decantation. By addition of a small amount of absolute ethanol and scratching with a spatula the compound could be brought to crystallization. It was then filtered off, washed with ether, and rapidly dried in vacuum.

On attempting dissolution of the salt in water, varying amounts of an unidentified, insoluble material could be isolated. The filtered aqueous solution, saturated with hydrazinium diselenocarbazate, was cooled in an ice-bath. The precipitated salt disappeared when the calculated amount of 1 N hydrochloric acid was added over a period of 20 min to the stirred suspension. After some time the yellowish diselenocarbazic acid began to precipitate, and when the addition of hydrochloric acid was completed the acid was filtered off, washed with *small* amounts of cold water, and dried immediately *in vacuo*. The dry compound had a characteristic yellow-green colour. It decomposes on heating, but in a closed tube the m.p. could be determined to *ca.* 76°C with decomposition. When stored at  $-40^\circ\text{C}$  it is more stable than dithiocarbazic acid. (Found: C 5.77; H 1.97; N 13.57; Se 78.00. Calc. for  $\text{CH}_4\text{N}_2\text{Se}_2$ : C 5.95; H 2.00; N 13.87; Se 78.19).

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### *In vivo* Conversion of Vitamin $\text{A}_1$ to Vitamin $\text{A}_2$

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It is well known that vitamin  $\text{A}_2$  (3,4-dihydroretinol) predominates over vitamin  $\text{A}_1$  in fresh water fish intestines and liver.<sup>1</sup>  $\beta$ -Carotene is well established as provitamin  $\text{A}_1$  and Morton and Creed<sup>2</sup> found as early as 1939 that intake of  $\beta$ -carotene in perch and dace resulted in increased amounts of both vitamins  $\text{A}_1$  and  $\text{A}_2$  in the intestines and livers. This indicated a common provitamin for both forms of vitamin A. Besides  $\beta$ -carotene, the keto-carotenoids have been suggested as provitamins A, and particularly the widespread astaxanthine, 3,3'-dihydroxy-4-4'-diketo- $\beta$ -carotene.<sup>3-6</sup> A particular provitamin  $\text{A}_2$  has been implied, but has not been found in natural material.<sup>6</sup> Grangaud *et al.*<sup>7</sup> and more recently, Gross and Budowsky<sup>8</sup> found, however, evidence of a possible conversion of keto-carotenoids to  $\beta$ -carotene in fishes. Morcos and Salah<sup>8</sup> fed vitamin  $\text{A}_1$  to Nile fish (*Clarias lazera* and *Tilapia nilotica*), and they concluded that vitamin  $\text{A}_1$  cannot be converted by these species into vitamin  $\text{A}_2$  to any appreciable extent, if at all. Regarding the occurrence of vitamin  $\text{A}_2$ , the present authors showed in a survey of vitamin A in fishes<sup>9</sup> that vitamin  $\text{A}_2$  is present in comparable quantities in all fishes, regardless of marine or fresh-water environment, while higher concentrations of vitamin  $\text{A}_1$  mask the presence of vitamin  $\text{A}_2$  in most marine fishes.

We were able to confirm the conversion of vitamin  $\text{A}_1$  to vitamin  $\text{A}_2$  in a recent study on growth and uptake of nutrients in young rainbow trout. Investigating

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