

identical with that of 1 (signals at τ 8.02 and 8.06 in ratio 2:1 and absence of end-of-chain methyl signal at τ 8.19). In particular two structures are being considered, a decapreno-carotenoid with linearly extended isoprenoid chain (2) and structure 3, the carbon skeleton of which is analogous with that of the structure recently assigned to *dehydrogenans*—P439 (4).^{10,11}

In the mass spectrum significant peaks due to the loss of up to two fragments of 58 mass units (acetone) from the molecular ion and from other major fragments are better accommodated by structure 3. The NMR-spectra so far obtained do not permit a differentiation between 2 and 3.

Further work on the structure of bacterioruberin including syntheses of model substances is in progress and further details will be published.

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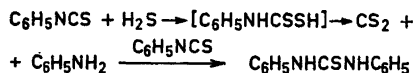
N-Isothiocyanatoamines

VI. The Reactivity of *N*-Isothiocyanatodiisopropylamine towards Hydrogen Sulfide, Thio- and Selenoamides

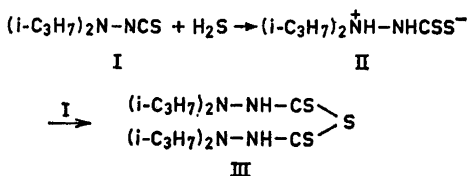
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Phenyl isothiocyanate is known to react with hydrogen sulfide at room temperature to form carbon disulfide and 1,3-diphenylthiourea.¹ The reaction probably takes place *via* phenyldithiocarbamic acid. This in turn undergoes spontaneous decomposition into carbon disulfide and aniline, which is converted to the thiourea by excess phenyl isothiocyanate.



In a related reaction,² phenyl isothiocyanate under forcing conditions eliminates hydrogen sulfide from thiourea to form, in addition to the above products, cyanamide. During our work on *N*-isothiocyanatoamines,³⁻⁷ we examined the reaction between *N*-isothiocyanatodiisopropylamine (I) and hydrogen sulfide, expected to give the stable *N,N*-diisopropyldithiocarbamic acid (II).^{7,8} However, the product obtained was identified as bis-(*N,N*-diisopropyldithiocarbazoyl)sulfide (III). The following mechanism is proposed.

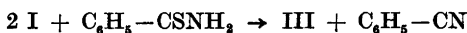


A sample of II was prepared⁷ from diisopropylhydrazine and carbon disulfide.

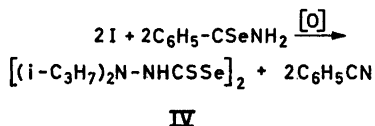
Acta Chem. Scand. **21** (1967) No. 9

Consistently with the above scheme, this compound reacted with I to give III. It should be noted that III is the first thiocarbazoyl sulfide to be described. The properties of this class of compound will be treated in detail elsewhere.⁹

Next, the reactivity of I towards various thioamides was investigated. No reaction was observed with thiourea or with secondary and tertiary thioamides. With thiobenzamide, 4-pyridinethiocarboxamide, and 2-hydroxythiobenzamide, I afforded crystalline III and the corresponding nitriles, *e.g.*



Since the yield of nitriles in this reaction was very poor, they were only identified in solution by infrared spectroscopy. It is interesting that the corresponding reaction between I and selenobenzamide proceeds with exclusive formation of bis-(*N,N*-diisopropylthiocarbazoyl) diselenide (IV).⁷ Very probably *N,N*-diisopropylselenothiocarbamic acid is first formed, but this compound has previously⁷ been shown to autoxidize very easily in ethanolic solution.



Experimental. Conditions and equipment used for the physical measurements were those described in part II of this series.⁴

Bis-(N,N-diisopropylthiocarbazoyl)sulfide (III). A solution of I in absolute ethanol⁵ was saturated with dry hydrogen sulfide several times and in between heated briefly to the boiling point. Cooling and scratching gave a colourless crystalline material in 70% yield; m.p. 150–151°C. (Found: C 48.10; H 8.85; N 15.75; S 27.40. Calc. for C₁₄H₃₀N₄S₂: C 47.96; H 8.63; N 15.98; S 27.43). This material was compared to an authentic sample prepared by treatment of bis-(*N,N*-diisopropylthiocarbazoyl)disulfide⁹ with potassium cyanide. The infrared spectra and melting points were identical and a mixed melting point was not depressed. A third sample of this compound was obtained in 70% yield by mixing ethanolic solutions of I and II. The solution was heated to the b.p. several times and allowed to stand. The compound was

filtered off next day and washed with a little ice-cold ethanol. The crude material was analytically pure but could be recrystallized, if necessary, from ethanol.

Reactions with thioamides. Ethanolic solutions of I (2 mmol) and thiobenzamide (1 mmol) were mixed and heated for some time to the b.p. Cooling and scratching gave a 50% yield of III. The infrared spectrum of the evaporated mother liquor showed that it consisted of benzonitrile contaminated with III and dimerized I. Owing to the volatility of the benzonitrile and the small amounts present, we did not succeed in isolating it pure. However, the infrared spectrum (in CHCl₃) left no doubt of the identity of the benzonitrile. In the hope that crystalline nitriles would prove easier to purify, the same experiment was repeated with 2-hydroxythiobenzamide and with 4-pyridinethiocarboxamide. In both cases, only small yields were obtained of the corresponding nitriles in purities estimated from the infrared spectra to be *ca.* 80%.

Reaction with selenobenzamide. Exploratory experiments showed that only IV was formed in this reaction. Accordingly equimolar proportions of solutions of I and selenobenzamide were mixed and allowed to react under different conditions. Irrespective of the solvent type (*e.g.* ethanol or methylene chloride) and the duration of heating, we obtained a 50–70% yield of IV and a solution containing benzonitrile. All attempts to purify the nitrile proved unsuccessful, probably owing to selenium-containing by-products. Again, the infrared spectrum was the best criteria for the presence of benzonitrile in the solutions.

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