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THE REACTION OF THIOUREA WITH CARBON DISULFIDE

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Summary: A new type of compound (**7**) was obtained from the reaction of a metallated thiourea with carbon disulfide followed by methylation. A reaction mechanism involving a rearrangement of dimethylamino group was suggested.

In the course of the synthesis of some heterocyclic compounds from thiourea, it was found that a thiourea metallated by using n-BuLi reacted with carbon disulfide followed by methylation to form N,N-dimethylthiocarbamoyl thiocyanate (**7**), a new class of compound.

We wish now to report the preparation, the structural assignments, and the chemical properties of **7**, which can be produced by a rearrangement of dimethylamino group.

Compound **7** was prepared as follows. To a stirred mixture of thiourea (**1**, 1.5 g, 19.7 mmol) and dry THF (40 ml, distilled over CaH_2) was added dropwise 15 % solution of n-BuLi in hexane (37 ml, 59 mmol) under nitrogen with cooling in an ice-bath. After stirring for 20 min, the reaction mixture was dropped with 8 ml of methyl iodide and then stirred for 2 h at room temperature. The methylation reaction caused a violent boiling to give a transparent yellow solution, which was kept to stand in refrigerator for 1 day. Removal of the solvent and the unreacted methyl iodide from the reaction mixture left 23 g of yellow oil, which was thoroughly extracted with chloroform by shaking with water (150 ml) and chloroform (150 ml). After the extract had been dried over Zeolite A-3, the chloroform was removed on a rotary evaporator to afford 3.2 g of yellow oil.
When distilled on an oil-bath under reduced pressure, 1.5 g of yellow solution boiling at 51-2°C (2 Torr) and 1.1 g of the orange residue were obtained. The residue was collected, dissolved in a small amount of methanol, and kept to stand in refrigerator overnight to yield 0.3 g of **7** as white plates of mp 54-5°C (crude yield 39 %). The above distilled fraction was confirmed to be dimethyl trithiocarbonate (**8**, yield 56 %) by the infrared spectral comparison with an authentic sample prepared by Lecker's method[1].

The structure of **7** was determined on the basis of the following spectral data and experimental results together with elemental analysis.

The mass spectrum showed a parent ion of m/e 146. In ir spectrum a very strong absorption for thiocyanato group (2150 cm^{-1}) appeared.

A mixture of **7** (0.3 g), aniline (1.5 ml), and ethanol (1.5 ml) was refluxed for 1 h to afford 2-cyano-1-methyl-3-phenylisothiourea (**10a**) as white plates of mp 199-200°C[2] (recry. from ethanol). From cyclohexylamine 2-cyano-3-cyclohexyl-1-methylisothiourea (**10b**) was obtained as white plates of mp 120-1°C[2] in 50 % yield (recry. from 1 : 1 MeOH-H_2O).

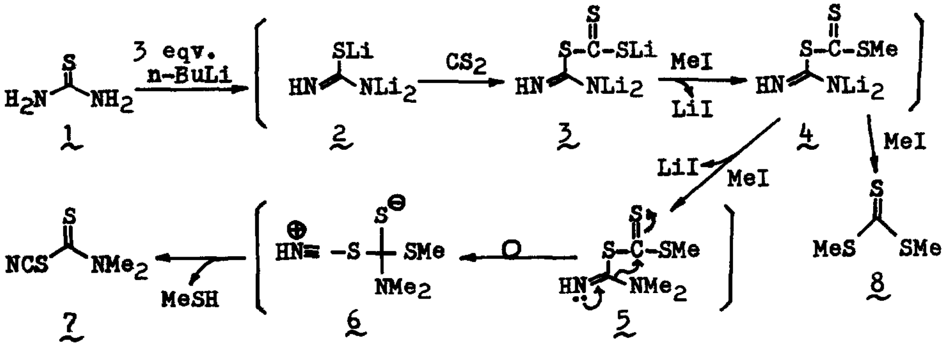
From these experiments the structure of N,N-dimethylthiocarbamoyl isothiocyanate for **7** was ruled out.

The reaction mechanism shown below may be considered to hold for the conversion of **1** into **7**. An intermediate **5** is converted into **6** by a rearrangement of dimethylamino group. Then **6** can be changed to **7** along with elimination of methanethiol. Compound **8** can be formed by a competitive reaction of **4** with methyl iodide.

The treatment with 1 eqivalent of n-BuLi gave both **8** (yield 40 %) and 4-amino-6-dimethylamino-2H-1,3,5-thiadiazine-2-thione [**9**, yield 1.5 %, light yellow prisms of mp 199-200°C[2] (recry. from DMSO-H_2O)]. Compound **9** can be prepared from the reaction of **1** with **3**, perhaps because n-BuLi is used in an amount insufficient for changing **1** into **3**.

In this reaction the use of NaH instead of n-BuLi gave the same result as that from 1 equivalent of n-BuLi. This suggests that more sluggish NaH can not yield a sufficient amount of **2**.

We are now examining the interesting properties of **7**.



References and Notes

(1) von H.Lecker, Ann., 445, 53 (1925).

(2) Elemental analysis and spectral data (ir, mass, and nmr) gave satisfactory results.

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