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THE REACTION OF ETHYLENE THIOUREA WITH CARBON DISULFIDE

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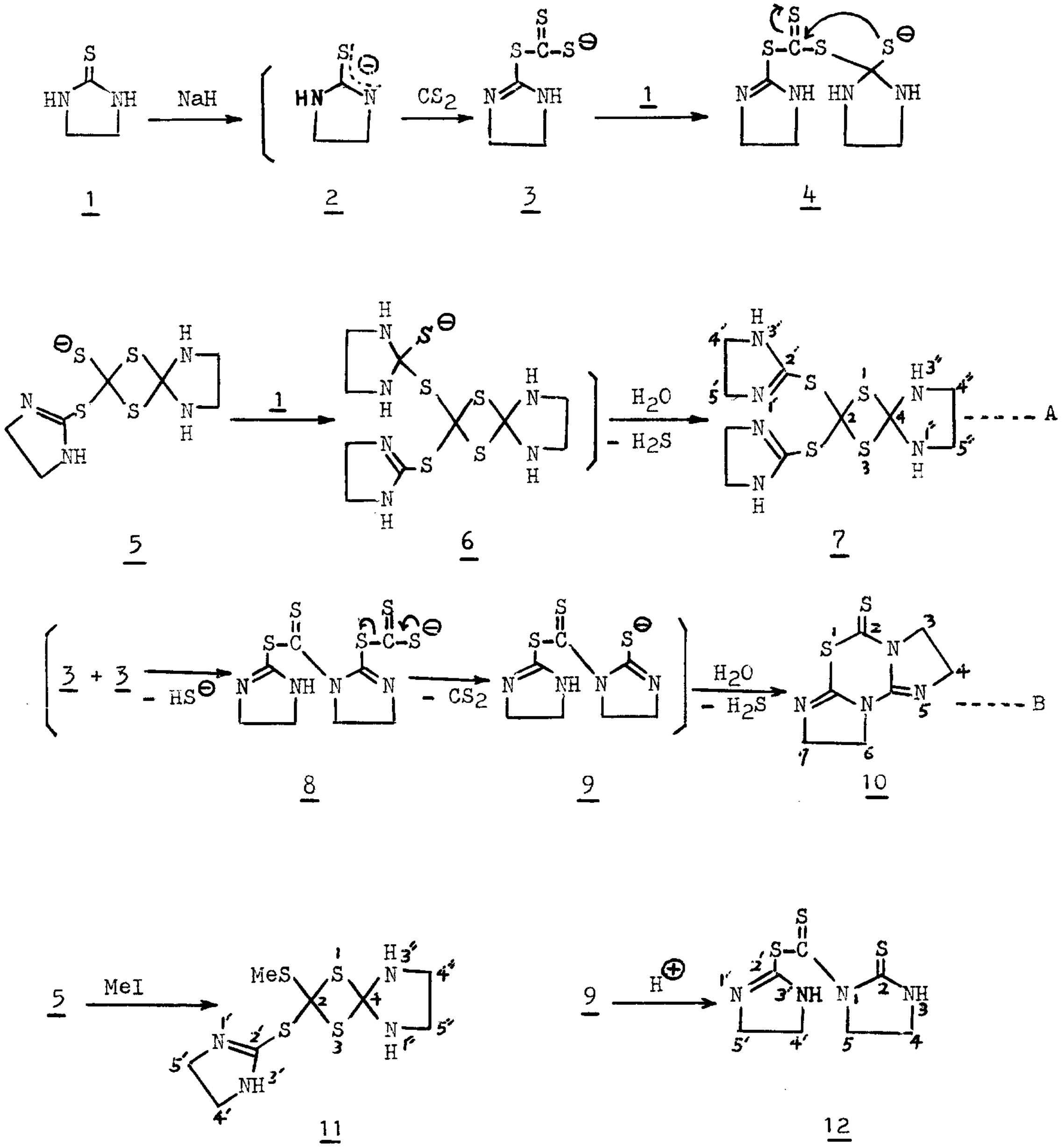
In the course of the synthesis of some heterocyclic compounds, the reaction of the cyclic urea with carbon disulfide has been studied. The reaction of the cyclic urea with carbon disulfide gave two expected compounds, such as dithiocarbamic acid and bisdithiocarbamic acid[2]. However, from the reaction of the cyclic thiourea with carbon disulfide a variety of unexpected compounds have been isolated as crystals.

We wish now to report several unique compounds prepared from the reaction of ethylene thiourea with carbon disulfide and propose a reaction mechanism.

The following preparation of 2,2-bis(4',5'-dihydroimidazole-2'-thio)-1,3-dithietane-4-spiro-2''-imidazolidine (7) and 2-(4',5'-dihydroimidazole-2'-thio)-2-methylthio-1,3-dithietane-4-spiro-2''-imidazolidine (11) is representative.

The mixture of ethylene thiourea (1, 1 g, 9.8 mmol), sodium hydride (50 % oil dispersion, 1.5 g, 31 mmol), dry THF (10 ml, distilled over CaH_2), and diethyl carbonate (20 ml, dried over Zeolite) was stirred for 0.5 hr at 50-60°C under N_2 gas. To the reaction mixture was added dropwise a mixture of carbon disulfide (3 ml, 64 mmol) and HMPA (hexamethylphosphoric triamide, 5 ml, dried over Zeolite). The resulting mixture was stirred for 1 hr at room temperature and then poured into 100 ml of ice-water to afford a light yellow material. Recrystallization from pyridine gave 7 (0.75 g, 2.15 mmol, yield 66 %) as white prisms of mp 224-225°C[3,4]. The above filtrate was washed with benzene and then treated with a mixture of methyl iodide (2 ml) and ethanol (10 ml). The reaction mixture was kept to stand in refrigerator for 1 day to afford a light yellow material. Recrystallization from THF-H_2O gave 11 (0.38 g, 1.29 mmol, yield 26 %) as light yellow plates of mp 195-196°C[3,5].

Scheme I



The reaction mechanism shown in A of Scheme I may be considered to hold for the conversion of 1 into 7. As soon as the HMPA was added to the reaction mixture, the reaction of 1 with sodium hydride began along with the evolution of hydrogen to give a metalated compound (2), which immediately reacted with carbon disulfide to afford 3. And 3 reacted with 1 to give 5 and then 6 via an intermediate compound (4). When the reaction mixture was poured into ice-water, 6 was converted into the stable isolated compound (7) along with the evolution of hydrogen sulfide. The presence of 5 was confirmed by the isolation of 11 on treatment with methyl iodide. This mechanism also might be supported by the fact that both 7 and 11 could not be isolated when 1 was completely converted into 3 by the procedure of 1 hr's stirring with HMPA, followed by adding carbon disulfide. To the reaction solution prepared by the above procedure was added 1 g of ethylene thiourea to give 7 and 11 in yields of 24 % and 23 %, respectively. A pronounced decrease of total yield (47 %) seems to be ascribable to a side-reaction caused by the excess of 3.

In this reaction the use of N,N-dimethylacetamide instead of ethyl carbonate as an accelerator lowered the yield of 7 (44 %). On the other hand, the use of DMSO gave 7 in 50 % yield and 3,4,6,7-tetrahydro-bis-imidazo[2',3'-c : 2',3'-e]-2-thiono-1,3,5-perhydrothiadiazine (10)[3,6] in 16 % yield. Because 3 is very soluble in DMSO, it can undergo a dimerization reaction shown in B of Scheme I as a competitive reaction. When 1 was completely converted into 3 by the same method as that mentioned above, 10 was obtained in 48 % yield as a main product and 7 in 9 % yield as a by-product. When the above aqueous solution prepared by the use of DMSO was acidified, 2'-(4',5'-dihydroimidazolyl) 2-thionoimidazolidine-1-dithiocarboxylate (12) was obtained as light yellow material. Recrystallization from THF-petroleum ether gave light yellow prisms of mp 220-221°C^{dec} [3,7]. The above result shows the presence of 9 in this reaction.

Scheme II shows several characteristic mass patterns for 7 and 11.

References and Notes

(1) Department of Chemistry, Faculty of Science, Josai University.

(2) T.Takeshima, M.Ikeda, M.Yokoyama, N.Fukada, and M.Muraoka, JCS, Perkin Trans. 1, in press.

(3) Elemental analysis and mass spectrum gave satisfactory results.

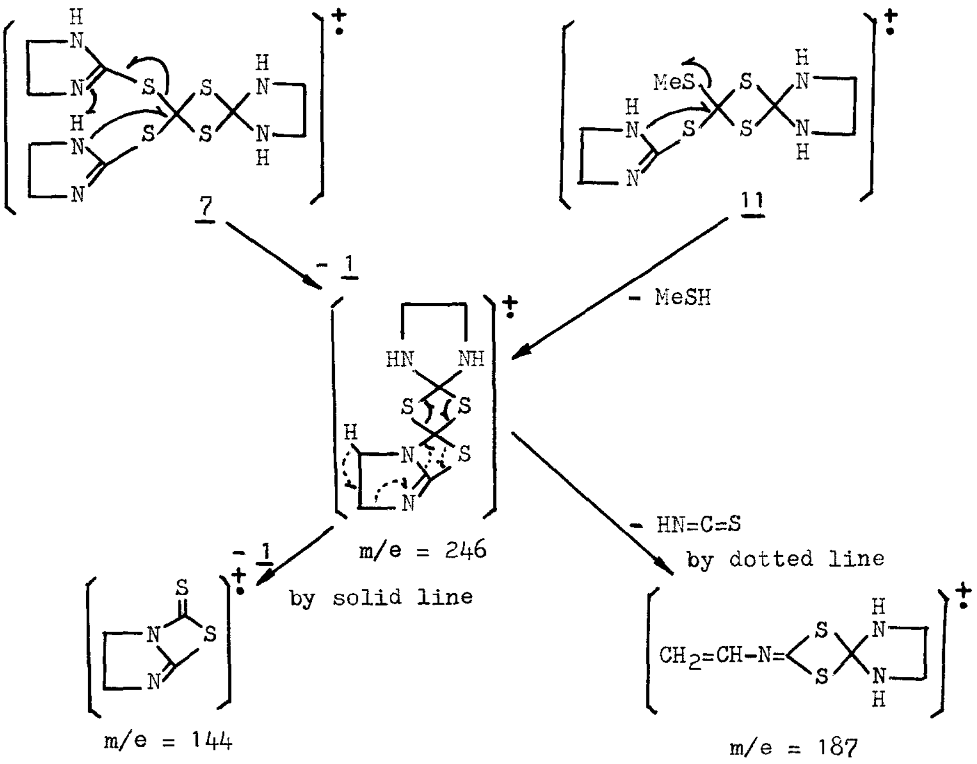
(4) ir (KBr) 3290, 3220, 3120 cm^{-1} (NH), 2925 (CH), 1560, 1548, 1528 (NH); uv$\lambda_{max}^{99\%\ EtOH}$ 262 nm (sh, ε= 27000), 280 (31500); nmr (DMSO-d_6) δ 12.24 (s, 2H, 3'-NH), 9.76 (s, 2H, 1'', 3''-NH), 4.38 (t, 2H, 5'-CH$_2$), 3.84 (s, 4H, 4'', 5''-CH$_2$), 3.46 (t, 4H, 4'-CH$_2$).

(5) ir (KBr) 3240 cm^{-1} (NH), 2900 (CH), 1562, 1545 (NH); uv$\lambda_{max}^{99\ \%\ EtOH}$ 264 nm (sh, ε= 30500), 272 (30800); nmr (DMSO-d$_6$) δ 12.16 (s, 1H, 3'-NH), 9.84 (s, 2H, 1'',3''-NH), 4.47 (t, 2H, 5'-CH$_2$), 3.84 (s, 4H, 4'',5''-CH$_2$), 3.50 (t, 2H, 4'-CH$_2$), 2.52 (s, 3H, CH$_3$).

(6) Recrystallization from EtOH gave white plates of mp 189-190°C. ir (KBr) 2970, 2950, 2920, 2865 cm^{-1} (CH), 1595 (C=N); uv$\lambda_{max}^{99\ \%\ EtOH}$ 245 nm (ε= 20000), 285 (28000); nmr (DMSO-d$_6$) δ 3.67-4.33 (m, 8H, 4CH$_2$).

(7) ir (KBr) 3220 cm^{-1} (NH), 2920 (CH), 1562, 1522 (NH); uv$\lambda_{max}^{99\ \%\ EtOH}$ 262 nm (ε= 6200), 280 (7200); nmr (DMSO-d$_6$) δ 12.20 (s, 1H, 3'-NH), 9.76 (s, 1H, 3-NH), 4.36 (t, 2H, 5'-CH$_2$), 3.80 (s, 2H, 4-NH), 3.46 (t, 4H, 4',5-CH$_2$).

Scheme II



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