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Studies of Dithiobiurets. II. The Thermal Decomposition of 1,1-Dimethyl-5-acetyl-2,4-dithiobiuret

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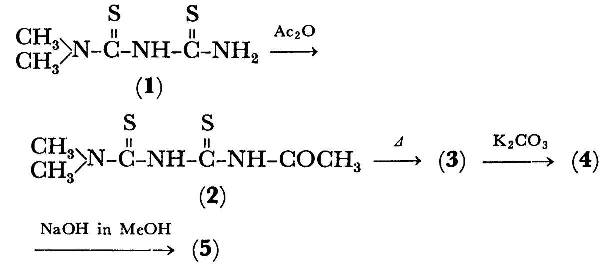
1,1-Dimethyl-5-acetyl-2,4-dithiobiuret (**2**), which is obtained by ordinary acetylation from 1,1-dimethyl-2,4-dithiobiuret (**1**), is thermally unstable and decomposes with a strong acidic odor, even at room temperature, upon standing more than 10 days.

We carried out the decomposition under various conditions and confirmed that a crystalline substance (**3**) was obtained in a 10% yield when **2** was heated at 100°C without a solvent or was refluxed in alcohol or acetone. Compound **3** shows a strong absorption band at 2030 cm^{-1} which corresponds to a SCN or NCS group and a carbonyl band at 1680 cm^{-1} in the infrared spectrum. It is soluble in water or diluted mineral acid and reacts with heavy metal ions, especially the Fe^{3+} ion, showing a pink color. An aqueous solution of it is acidic (pK_a'=4.5) and, upon neutralization with potassium carbonate, affords a crystalline substance (**4**) which gives analytical results corresponding to the molecular formula of $C_6H_9N_3OS_2$. Compound **4** is only two hydrogen atoms less than the starting acetyldithiobiuret **2** and still contains a singlet methyl proton at δ 2.35 ppm in addition to the *N*,*N*-dimethyl peaks in the NMR spectrum, but no absorption band appears in the carbonyl region of the infrared spectrum except for two sharp bands at 1580 and 1600 cm^{-1}. The high-resolution mass spectrum of **3** gave useful information for the structural elucidation of **3**. The molecular ion peak appeared at *m/e* 203; it consisted of $C_6H_9N_3OS_2$. The base peak was *m/e* 161, and the loss of the element of ketene (42 molecular units) was observed.

N,*N*-Dimethylthiocarbamoyl fragment was absent in **3** and **4**; the fragment peak at *m/e* 88, $Me_2N^+{=}C{=}S$, which was prominent in the mass spectrum of **2**, could not be observed in the spectra of **3** and **4**. Meanwhile, **4** was reconverted quantitatively to **3** by the addition of aqueous potassium thiocyanate to an acidic solution of **4**.

From the above results, it is clear that **3** is the hydrothiocyanate of **4**. When **4** was treated with methanolic sodium hydroxide, a yellow crystalline substance **5** was obtained; its molecular formula was identified with that of **4**. Compound **5** shows a carbonyl absorption band at 1710 cm^{-1} in the infrared spectrum, and a new singlet methylene signal appears at δ 4.50 ppm instead of the singlet methyl peak at δ 2.35 ppm in the NMR spectrum.



$$(CH_3)_2N\text{-}\overset{S}{\overset{\Vert}{C}}\text{-}NH\text{-}\overset{S}{\overset{\Vert}{C}}\text{-}NH_2 \xrightarrow{Ac_2O}$$ (1)

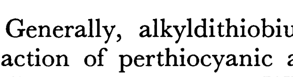
$$(CH_3)_2N\text{-}\overset{S}{\overset{\Vert}{C}}\text{-}NH\text{-}\overset{S}{\overset{\Vert}{C}}\text{-}NH\text{-}COCH_3 \xrightarrow{\Delta} (3) \xrightarrow{K_2CO_3} (4)$$ (2)

$$\xrightarrow{\text{NaOH in MeOH}} (5)$$

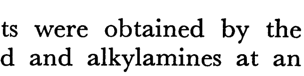
It showed the same molecular ion peak (*m/e* 203) as those of **3** and **4**, and the presence of the prominent ion peak at *m/e* 88 suggested that the acetyliminodithiazole system of **3** was rearranged to the *N,N*-dimethylthiocarbamoylthiazoline system. The structure of **5** was confirmed synthetically by the reaction of **1** and monochloroacetyl chloride described previously.[1] The acetyl methyl group in **2** was effected to be very active, and the dithiazole skeleton isomerized to the thiazoline one under alkaline conditions.

Since the starting substance **2** was presumed to be oxidized to yield **4**, **2** was oxidized under various conditions. When **2** was oxidized with iodine in alcohol or acetic acid, deacetylation occurred at the same time and gave the product **6**, which was stable; however, its free base could not be isolated. As for other non-acidic conditions, the potassium-permanganate oxidation of **5** in acetone affords **4** in a 20% yield. When **6** was treated with acetic anhydride in the presence of an equimolar triethylamine, a crystalline substance which was identified with **4** was obtained.

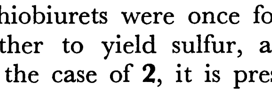
From the above results, the thermal decomposition product **3** from **2** was confirmed to be the hydrothiocyanate of 3-acetylimino-5-dimethylamino-3*H*-1,2,4-dithiazole (**4**).



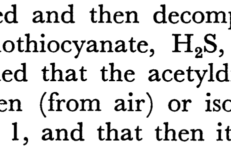
(3)



(4)

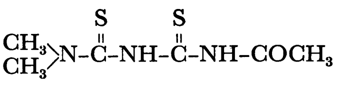


(5)

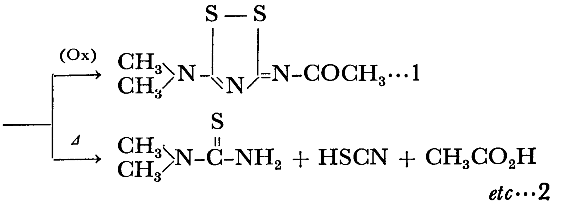


(6)

Generally, alkyldithiobiurets were obtained by the reaction of perthiocyanic acid and alkylamines at an ordinary temperature. When perthiocyanic acid was treated with amines at a higher temperature, alkyldithiobiurets were once formed and then decomposed further to yield sulfur, aminothiocyanate, H_2S, *etc.*[2] In the case of **2**, it is presumed that the acetyldithiobiuret **2** is oxidized by oxygen (from air) or isolated sulfur, as is shown in Scheme 1, and that then its salt is formed with the thiocyanic acid which is derived from the decomposition of **2**, as is shown in Scheme 2.



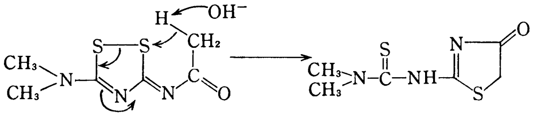
$$(CH_3)_2N\text{-}\overset{S}{\overset{\Vert}{C}}\text{-}NH\text{-}\overset{S}{\overset{\Vert}{C}}\text{-}NH\text{-}COCH_3$$



etc$\cdots$2

An analogous reaction was observed by Fairfull *et al*, in the preparation of 1-(2-pyridyl)dithiobiuret.[3] They reacted perthiocyanic acid with 2-aminopyridine and thus obtained 2-aminopyridine hydrothiocyanate.

The reaction mechanism from **4** to **5** was considered to be as in the following scheme:



(4) (5)

Experimental

Preparation of Starting Products. 1,1-Dimethyl-2,4-dithiobiuret **1** was prepared from aqueous dimethylamine and perthiocyanic acid by the method of Dixit.[2] 1,1-Dimethyl-5-acetyldithiobiuret **2** was obtained by the standard acetic anhydride-pyridine method.

*The Thermal Decomposition of **2**, the Preparation of 3-Acetylimino-5-dimethylamino-3*H*-1,2,4-dithiazole **3**.* *Procedure 1*: 1,1-Dimethyl-5-acetyldithiobiuret **2** (10 g) was heated for 1 hr at 100°C in a round-bottomed flask; then a 100 m*l* portion of acetone was added, and the insoluble crystalline substance was filtered off and washed with acetone. Recrystallization from methanol gave 1 g of white needles melting at 183—184°C with decomposition. IR: 2020 cm^{-1} (S-CN), 1690 (C=O), 1610 (C=N). NMR: δ 3.45 ppm (broad s, 6H, NMe_2), 2.18 (s, 3H, Ac). Mass: *m/e* 205, 204, 203, 188, 163, 162, 161, 146, 128, 116, 102, 97. UV: λ_{max} (in alc) 274, 302 mμ. Found: C, 31.65; H, 3.92; N, 21.46; S, 36.20%. Calcd for $C_7H_{10}N_4OS_3$: C, 32.06; H, 3.81; N, 21.37; S, 36.64%.

Procedure 2: A suspended solution of 1,1-dimethyl-5-acetyldithiobiuret **2** (10 g) in 20 m*l* of ethanol was refluxed for 4 hr and then cooled. The solution turned dark red at that time. The precipitated white needles were collected and washed with cold ethanol. The yield was 1.2 g.

Procedure 3: A mixture of the dithiobiuret (10 g) in 50 m*l* of acetone and 5 m*l* of picoline was refluxed for 5 hr, when the precipitate was then collected, 1.2 g of white or pale pink needles were obtained.

*3-Acetylimino-5-dimethylamino-3*H*-1,2,4-dithiazole **4**.* *As Obtained from the Hydrothiocyanate **3***: The hydrothiocyanate (2 g) was dissolved in 20 m*l* of 3.5 N-hydrochloric acid and made alkaline with an excess of aqueous potassium carbonate. The white precipitate was filtered and recrystallized from isopropyl alcohol to give 1.4 g of white needles, melting at 160—161°C. IR: 1600, 1570 cm^{-1}. NMR: δ 2.38 ppm (s, 3H, Ac), 3.28, 3.47 (s,s, 6H, NMe_2). UV: λ_{max} (in alc) 298 mμ (log *e* 4.3). Mass: *m/e* 203 (M^+), 161, 141, 97, 82. Found: C, 35.27; H, 4.67; N, 20.68; S, 31.46%. Calcd for $C_6H_9N_3OS_2$: C, 35.47; H, 4.43; N, 20.69; S, 31.53%.

*As Obtained from the Potassium-permanganate Oxidation of **2**.* 1,1-Dimethyl-5-acetyldithiobiuret (1 g) was dissolved in

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[1] I. Iwataki, This Bulletin, **45**, 3218 (1972).

[2] S. N. Dixit, *J. Indian Chem. Soc.*, **38**, 44 (1961).

[3] A. E. S. Fairfull and D. A. Peak, *J. Chem. Soc.*, **1955**, 796.

40 m*l* of acetone, and then 3 g of potassium permanganate in 60 m*l* of acetone were stirred in, drop by drop, at room temperature. After the manganese dioxide had been filtered off, the solvent was distilled off and the residue was dissolved in water and made alkaline with potassium carbonate. The precipitate was filtered and dried to give 0.2 g of **4**.

*As Obtained from the Acetylation of 5-Dimethylamino-3-imino-*3H-*1,2,4-dithiazole hydroiodide* ***6***: The hydroiodide **6** which was prepared by Dixit's method[2] (5 g) was suspended in 20 m*l* of acetone, and then 5 m*l* of acetic anhydride and 2 g of triethylamine were stirred in. After 30 minutes, the solution was poured into ice water and neutralized with potassium carbonate to give 3 g of **4**.

The Preparation of the Dithiazole Hydrothiocyanate ***3*** *from* ***4*** *with Thiocyanic Acid.* 3-Acetylimino-5-dimethylamino-3*H*-1,2,4-dithiazole **4** (0.1 g) was dissolved in 3.5 N-hydrochloric acid (3 m*l*), and then 1 g of potassium thiocyanate in 1 m*l* of water was added. The white needles thus precipitated were collected. The mp, IR, and NMR coincided with those of **3**.

The Isomerization of ***4*** *to* ***5****, the Preparation of 2-(3,3-Dimethylthioureido)thiazolin-4-one.* A solution of the dithiazole **4** (0.3 g) in 8 m*l* of ethanol and 2 m*l* of 5N-KOH was kept at room temperature for 15 hr, and then poured into ice water and acidified with hydrochloric acid. The precipitate was extracted with chloroform, dried over magnesium sulfate, and evaporated *in vacuo*. Recrystallization from methanol gave 0.1 g of yellow scalies melting at 208—209°C Ref. 1: mp 208—209°C).