4-THIAZOLIDINES, DERIVATIVES AND ANALOGS

IV. Synthesis of 4-Thione-1, 3-Thiazan-2-One and 2, 4-Dithione-1, 3-Thiazane*

A. P. Grishchuk, G. I. Roslaya, and S. N. Baranov

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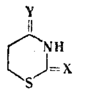
Heating thiazan-2, 4-dione (I) with P_2S_5 in xylene or toluene gives a hitherto unknown isomer of propiorhodanine (II), 4-thione-1, 3-thiazan-2-one (III), with an active thione group and more acidic properties than II. Reaction of I with P_2S_5 in dioxane gave 2, 4-dithionethiazane, (IV) in high yield, this being the most convenient method of preparing IV.

The method, offered by us, of synthesizing heterocyclic thio compounds by reacting oxo compounds with P_2S_5 in dioxane [1] made it possible in particular to obtain the hitherto unknown 2, 4-dithione-1, 2-dithiazane (IV), with active 4-thione and 5-methylene groups [2]. However use for that purpose as the starting material of the compound



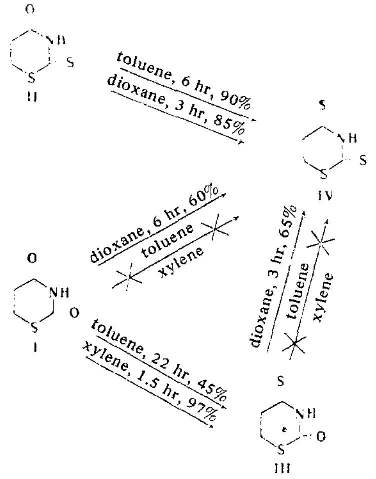
I X=O, Y=O
II X=S, Y=O
III X=O, Y=S
IV X=S, Y=S,

2-thione-1, 3-thiazan-4-one (II) makes the particular synthetic route to IV comparatively expensive and inconvenient, as synthesis of II necessitates preparation of ammonium dithiocarbamate, and a long time (some days) [3].

Conversion of II to IV in toluene [4] takes even longer than in dioxane, and complicates isolation of pure IV.

So instead of II we made use of readily accessible thiazan-2, 4-dione (I), prepared from β-chloropropionic acid and thiourea [5]. It was shown that in dioxane both oxygen atoms of I are easily replaced by sulfur atoms to give a high yield of IV, so that this method of synthesizing IV possesses considerable advantage. Reaction of I with P_2S_5 in toluene, run for comparison, showed that even 20 hr of heating converts only one CO group, that at position 4, to CS, and of the three possible thio compounds, only 4-thione-1, 3-thiazan-2-one (**III**), a hitherto unknown isomer of propiorhodanine **II**. However the same reaction takes place considerably faster (1 1/2 hr) in xylene, but does not take place at all in dichloroethane. With neither solvent is **IV** obtained.

These changes proceed according to the following equations:



It is evident that conversion of I to III in toluene and xylene has a selective character, also found with thiazolidin-2, 4-dione [6], which demonstrates the higher activity of the CO group at position 4 than at position 2.

Conversion of **I** to IV proceeds, undoubtedly via formation of **III**, and not **II**, and occurs only in dioxane,

Properties of Isomeric Thiazanes

Properties compared	II	III
Mp, °C	121.5–122	111.5–112
Refractive index $\begin{cases} n_g \\ n_p \end{cases}$	1.707 1.622	1.762 1.688
pH*	6.75	6.35
Solubility in nonpolar solvents	Low	Considerable
Condensation with aniline	Does not condense	4-Substitution product formed
Diazo coupling reaction	Negative	Positive

*For a 0.005 M solution in 70% MeOH at 20°.

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*For Part III see [6]

the medium which most facilitates formation of thio compounds. Furthermore, comparison of the times required for conversion of II to IV and I to III in toluene shows that the presence of the CS group at position 2 activates the CO group at position 4.

Our III is more acid and active, but is obviously a less polar compound than II. It also differs with respect to other properties listed in the table.

EXPERIMENTAL

2, 4-Dithione-1, 3-thiazane (IV). 2 g dry thiazan-2, 4-dione (I) was dissolved in 25 ml dioxane dried over Na and freshly distilled 2.4 g (0.011 mole) P_2S_5 introduced, and the whole refluxed for 6 hr. The solution was filtered, the dioxane vacuum distilled off, and excess MeOH, using active charcoal. A further portion of IV was obtained by diluting the MeOH filtrate with water. Total yield of purified IV, mp 108–109° C, 1.4–1.6 g (58–65%). Its properties were as previously described [2]. Found: N 8.54: S 58.85%, calculated for $C_4H_5NS_3$: N 8.54: S 58.92%.

4-Thione-1, 3-thiazan-2-one (III). 0.91 g (0.007 mole) I, 0.6 (0.0027 mole) P_2S_5 in 10 ml o-xylene were refluxed together, and a further 0.3 g (0.0014 mole) P_2S_5 added over a period of 1/2 hr. Even after 20 min refluxing, crystals of the new compound could be observed under the microscope, and after 1 1/2 hr, crystals of the starting I had completely disappeared. The solution was treated with charcoal, filtered, cooled to 0° C, and the precipitate of III filtered off. Yield 1 g (97%). Repetition of the synthesis with 5 times the amount of reagents, heating 2 1/2 hr, and further addition of P_2S_5 gives a quantitative yield of III. Recrystallized from CCl_4 it formed hexahedral pale yellow needles, mp 112° C. It was readily soluble in many solvents, crystallizing from water as long and almost colorless plates. Found: N 9.39; S 43.38%, calculated for $C_4N_5NOS_2$: N 9.25; S 43.56%. III unlike IV does not give a brown color with Cu^{2+} salts, but, like IV, and unlike II, in 5% NaOH it gives a red color with diazotized aniline, and also on boiling with p-dimethylbenzaldehyde in Ac_2O. The latter reaction for II proceeds considerably more slowly, than that for IV. Even when cold alkaline solutions of III give a positive nitroprusside reaction.

Conversion of III to IV is effected in 65% yield by boiling together for 3 hr 0.2 g (1 mM) III and 0.25 g (1.1 mole) P_2S_5 in 6 ml dry dioxane, then precipitating with water and recrystallizing from CCl_4. Found: N 8.39; S 58.77%, calculated for $C_4H_5NS_3$: N 8.58; S 58.92%.

4-Phenylamino-1, 3-thiazan-2-one. 0.117 g (0.001 mole) III, 0.095 g (0.001 mole) aniline, and 2 ml MeOH were heated together for 30 min on a steam bath, the products cooled, and the crystals filtered off. Yield 0. 4 g (68%), mp 150° C. Pale yellow prisms (ex MeOH), mp 156°–157° C (decomp). Readily soluble in acetone, not readily soluble in other solvents, insoluble in water. Found: N 13.58; S 15.24%, calculated for $C_{10}H_{10}N_2OS$: N 13.57: S 15.56%.

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L'vov State Medical
Institute