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REACTIONS OF γ-THIAPYRAN (WITH Cl_2, Br_2 and I_2) AND THE PREPARATION OF ITS 1,1-DIOXIDE

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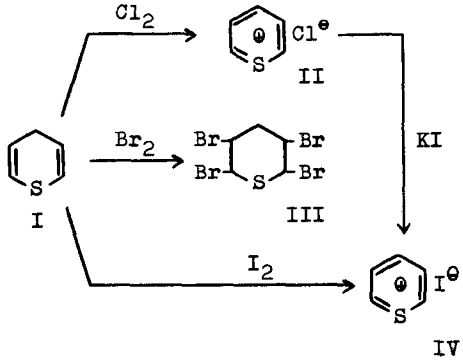
γ-Thiapyran[1] (I) exhibits an interesting difference in chemical behaviour with respect to the halogens Cl_2, Br_2 and I_2, as is shown in the following scheme:



Reaction with chlorine.

I, dissolved in $CHCl_3$ and treated at -40° with a solution of Cl_2 in $CHCl_3$, yielded almost quantitatively thiapyrylium chloride II, a very hygroscopic white substance, melting from 90-92°.* The U.V. spectrum (in water, containing 1%

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[1] J. Strating, J.H. Keijer, E. Molenaar and L. Brandsma, Angew. Chemie, 74, 465 (1962).

* All melting points, given in this paper, were determined with a melting point microscope.

HCl) showed two maxima at 245 and 284 mμ, in agreement with data reported in the literature for the thiapyrylium cation.[2,3] For identification II was converted into the iodide IV by treating an aqueous solution of II with KI. Analysis and melting point of the latter[3,4] were correct. The U.V. spectrum showed a maximum at 284 mμ and a broad one at 226 mμ (from the iodide ion) which concealed the second characteristic maximum at 245 mμ of the thiapyrylium cation.

Reaction with bromine.

I, dissolved in $CHCl_3$ and treated at -35° with a solution of Br_2 in $CHCl_3$, was converted into 2,3,5,6-tetrabromotetrahydrothiapyran III, yield 75%, m.p. 149-150° (white crystals from CCl_4).[5]

Anal. Found: C, 14.38; H, 1.46; Br, 75.77; S, 7.76
Calcd. for $C_5H_6Br_4S$: C, 14.38; H, 1.46; Br, 76.52; S, 7.67

The N.M.R. spectrum[6] showed a triplet at 3.1 (the two protons at C_4), a multiplet centered at 4.7 (the two protons

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[2] A. Lüttringhaus and N. Engelhard, Angew. Chemie, 73, 218 (1961).

[3] I.Degani, R. Fochi and C. Vincenzi, Tetrahedron Letters, No.18, 1167 (1963).

[4] R. Pettit, ibid., No.23, 11 (1960).

[5] Additionally a small amount (1 - 2%) of a orange-red substance is formed, insoluble in CCl_4, which was a 1 : 1 mixture of thiapyrylium bromide (identified by conversion into the iodide IV) and compound III.

[6] N.M.R. spectra were measured in $CDCl_3$ solution, using a Varian A-60 spectrometer. All signals are reported in p.p.m. as δ values (c.p.s./60), the internal standard tetramethyl silane being taken as δ = 0.0.

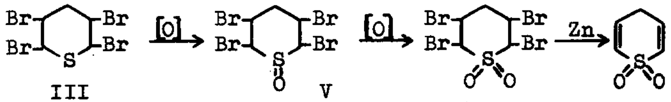
of C_3 and C_5) and a doublet at 5.2 (protons at C_2 and C_6) with relative intensities 1 : 1 : 1.

Reaction with iodine.

Under the conditions as described above, I did not react with iodine. However, when I and iodine were dissolved in a mixture of acetone and water, the iodine colour disappeared in about 1 hr. and thiapyrylium iodide IV could be isolated (yield 50%). Under these conditions, I and bromine did not give thiapyrylium bromide; only a small amount of compound III and tarry products were obtained.

Preparation of γ-thiapyran-1,1-dioxide.

We were unable to convert γ-thiapyran (I) into the 1,1-dioxide by direct oxidation, probably because of the extremely reactive allylic hydrogen atoms at position 4. Only black tarry products were obtained. However, it proved to be possible to prepare the sulfone of γ-thiapyran (VII) in a fairly good yield according to the following scheme:



III V VI VII

To III, dissolved in a mixture of AcOH and Ac_2O (4 : 1), kept at 75° was carefully added an excess of 30% H_2O_2, at such a rate that the temperature did not rise above 80°. The conversion to the sulfoxide V was complete when the temperature remained at 75°: white needles (recrystallized from ethanol), melting from 157-160° (dec.) were obtained in a yield of 80%.

Anal. Found: C, 13.95; H, 1.32; Br, 73.77; S, 7.39
Calcd. for $C_5H_6Br_4OS$: C, 13.85; H, 1.40; Br, 73.69; S, 7.39

Oxidation of V to the sulfone VI appeared to be extremely difficult; a prolonged reaction time and higher temperature were rewuired;[7] yield 75%, m.p. 185-186° (white crystals from $CHCl_3$).

Anal. Found: S, 7.28; Br, 71.79
Calcd. for $C_5H_6Br_4O_2S$: S, 7.13; Br, 71.09

I.R. spectroscopy and thin layer chromatography (using silica gel plates and benzene) are excellent methods to distinguish between the compounds III, V and VI.

When a refluxing solution of the sulfone VI in 90% alcohol was treated with zinc dust, VII was obtained in a yield of 50%, b.p. 100-102°/0.6 mm, melting from 56-58° (white needles from benzene-petroleum ether 3 : 1).

Anal. Found: C, 46.36; H, 4.65; S, 24.42; mol.weight 142.6
Calcd. for $C_5H_6O_2S$: C, 46.19; H, 4.65; S, 24.67; mol.w. 130.2

In contrast to γ-thiapyran, the 1,1-dioxide VII is a stable compound. The U.V. spectrum (in water) showed a maximum at 265 mμ, ε = 3800. The I.R. spectrum contained except the sulfone absorptions at 1305 cm^{-1} and 1120 cm^{-1} two $>C=C<$ absorptions at 1640 cm^{-1} and 1580 cm^{-1}. The N.M.R. spectrum showed absorptions at 3.9 (methylene protons at C_4), 6.3 (protons at C_3 and C_5) and 6.6 (protons at C_2 and C_6) with the relative intensities of 1 : 1 : 1.

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[7] In a typical experiment 0.047 mole of III, after being converted into V (without isolation) had to be heated for another 8.5 hrs. at 100° to obtain 0.036 mole of VI (77%).

[8] Compare the formation of Δ^2-dihydrothiapyran-1,1-dioxide by debromination of the corresponding dibromo compound with zinc dust, as described by E.A. Fehnel, J. Am. Chem. Soc., 74, 1569 (1952).