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NEW SYNTHESES OF THIAPYRYLIUM AND 1-THIANAPHTALENIUM CATIONS

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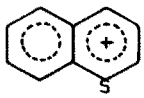
THIAPYRYLIUM cation (I) was first prepared by R. Pettit through expansion of the thiophen ring[1] and successively by A. Luttringhaus and N. Engelhard starting from 1-thia-3-cycloexen-5-ol.[2]

1-Thianaphtalenium cation (II) was prepared by several authors starting from 1-thiachroman-4-one,[3,4] and in one step synthesis from thiophenol and propargylaldehyde.[5]

I



II

We have obtained the cation (I) through two new synthetic routes.

1-Thia-γ-pyran (III) was converted to thiapyrylium chloride with PCl_5 in CCl_4 at room temperature.

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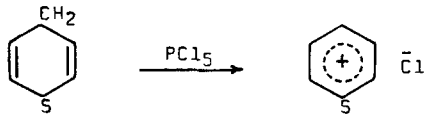
[1] R. Pettit, Tetrahedron Letters N° 23, 11 (1960).

[2] A. Luttringhaus and N. Engelhard, Angew. Chem. 73, 218 (1961).

[3] A. Luttringhaus and N. Engelhard, Ber. 93, 1525 (1960).

[4] W. Bonthrone and D. H. Reid, Chem. & Ind. 1192 (1960).

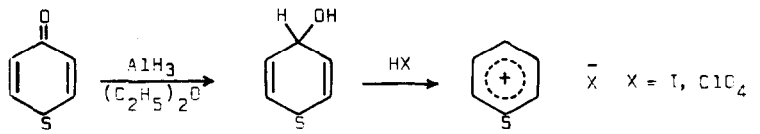
[5] N. Engelhard and A. Kolb Angew. Chem. 73, 218 (1961).



III

This method is similar to that employed for the preparation of tropylium chloride from tropilidene and PCl_5.[6] The 1-thia-γ-pyran has been recently synthetized[7] and its conversion to thiapyrylium chloride occurs with high yelds (>90%). The chlorine ion was easily substituted with ClO_4^- e I^- by treating an acueous solution of the thiapyrylium chloride with $HClO_4$ (70%) and HI (d=1,70) respectively. The ultraviolet spectrum of thiapyrylium perchlorate in water (containing 1% $HClO_4$) shows two maxima at 245 and 284 mμ, in agreement with the data reported in the literature.[2] Thiapyrylium iodide, orange-red needles, melts at 209°C (dec.), as described[1] by R. Pettit.

1-Thia-γ-pyran (IV)[8] was reduced with AlH_3 to the alcohol (V) and the latter, by treatment with $HClO_4$ or HI was converted to thiapyrylium perchlorate or iodide respectively.



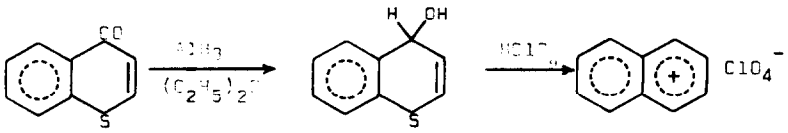
IV V

[6] D. N. Kursanov and M. E. Volpin, Dokl. Akad. Nauk S.S.S.R. 113, 339 (1957).

[7] J. Strating, J. H. Keijer, E. Molenar and L. Brandsma, Angew. Chem. 74, 465 (1962).

[8] G. Traverso, Ber. 91, 1224 (1957)

By analogy with the latter method 1-thianaphtalenium perchlorate has been prepared by AlH_3 reduction of 1-thiachromone (VI)[9] to the alcohol (VII) followed by treatment with $HClO_4$.



VI VII

1-Thianaphtalenium perchlorate is identical with the compound described[3] by A. Luttringhaus and N. Engelhard: yellow crystals, m.p. 228°C; the ultraviolet spectrum in CH_3COOH solution (containing 1% $HClO_4$) shows absorption maxima at 258, 335 and 385 mμ.

[9] F. Montanari and A. Negrini, Ricerca Sci. 27, 3055 (1957).