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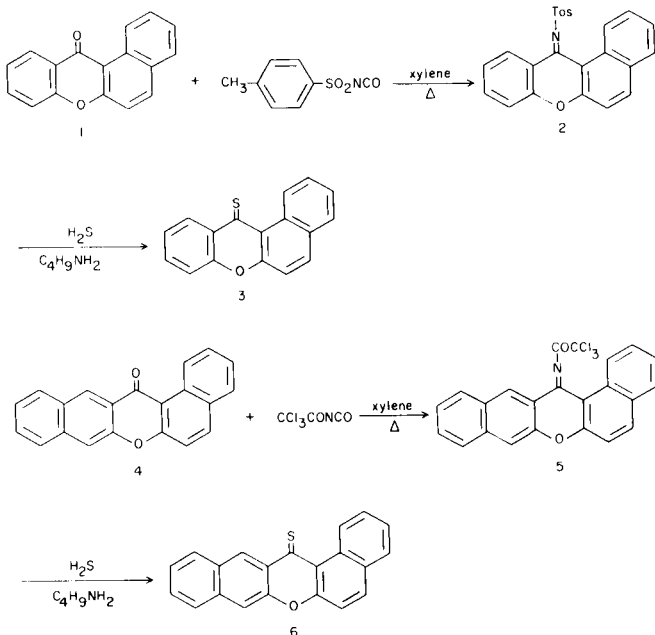
A general method for the preparations of pyranthiones is particularly useful for preparing substituted xanthiones which are unavailable by established procedures. Reaction of a xanthone with *p*-tosyl isocyanate or with trichloroacetyl isocyanate produces the corresponding imino derivatives, which upon treatment with *n*-butylamine followed by hydrogen sulfide gives the desired xanthione in good yield.

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The 4*H*-pyran-4-thiones are starting materials for pyran oximes and hydrazones (1) and 4,4'-bispyranylidene dimers (2). The thiones are usually prepared from the 4*H*-pyran-4-ones and phosphorus pentasulfide in high-boiling solvents such as xylene, toluene, pyridine, or dioxane (3). Another procedure involves allowing the pyranone to react with thionyl chloride or oxalyl chloride to give a geminal dichloride which is treated with thiolacetic acid (4) or potassium ethylxanthate (5) to give the thione. In the course of preparing a variety of pyranthiones, we were unable to prepare 3 and 6 from 1 and 4 by any of the published procedures including recently described methods employing the dimer of *p*-methoxyphenylthionophosphine sulfide (6) and phosphorus pentasulfide in acetonitrile and triethylamine (7). We now report a new method which seems to be general for the preparation of pyranthiones.

The method that we used to prepare 3 and 6 is shown in Scheme I.

Scheme I



Tolyl isocyanate did not react with 4, but the more active trichloroacetyl isocyanate gave the imine 5. The imines 2 and 5 reacted with hydrogen sulfide to give thiones, but the reaction was slow owing to the insolubility of the imines. Heating 2 and 5 with butylamine gave a soluble material (presumably the butylimino derivative) which rapidly gave 3 and 6 with hydrogen sulfide. We have previously described imines similar to 2 and 5 which were prepared from 2,6-diphenyl-4*H*-pyran-4-one (8), flavone (8), and 2,6-diphenyl-4*H*-thiopyran-4-one (9). These imines gave the corresponding 4-thiones with butylamine and hydrogen sulfide, but since all of the published procedures work in these cases, our method offers no advantages.

EXPERIMENTAL

12*H*-Benzo[*a*]xanthen-12-thione (3).

A mixture of 7.4 g. (0.03 mole) of 1 and 5.9 g. (0.03 mole) of *p*-toluenesulfonyl isocyanate in 120 ml. of xylene was refluxed for 20 hours. After cooling, the solid was collected, washed with methyl alcohol, and recrystallized from pyridine yielding 7.9 g. of 2: m.p. 241-242°.

Anal. Calcd. for C₂₄H₁₇NO₃S: C, 72.2; H, 4.3; N, 3.5. Found: C, 72.0; H, 4.6; N, 3.2.

A mixture of 7.9 g. of 2 in 20 ml. of *n*-butylamine was heated until solution was complete (about 10 minutes), and the excess amine was removed on a rotary evaporator. The residue was dissolved in 50 ml. of alcohol, and hydrogen sulfide was passed through the solution for 10 minutes. The solid was collected and recrystallized from toluene, yield 6.2 g. (79% from 2): m.p. 132-133°.

Anal. Calcd. for C₁₇H₁₀OS: C, 77.8; H, 3.8; S, 12.2. Found: C, 77.5; H, 3.6; S, 12.5.

14*H*-Dibenzo[*a,i*]xanthen-14-thione (6).

The procedure described for 3 was used but trichloroacetyl isocyanate replaced *p*-tosyl isocyanate. The m.p. of 5 was 242-243°, yield 90%.

Anal. Calcd. for C₂₃H₁₂Cl₃NO₂: C, 62.6; H, 2.7; Cl, 24.0. Found: C, 62.5; H, 2.8; Cl, 24.0.

The yield of 6 from 5 was 71%, m.p. 160-161°.

Anal. Calcd. for C₂₁H₁₂OS: C, 80.7; H, 3.9; S, 10.3. Found: C, 80.4; H, 3.7; S, 10.0.

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