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LETTERS TO THE EDITOR

RECYCLIZATION OF 4H-PYRANS TO 4H-SELENOPYRANS

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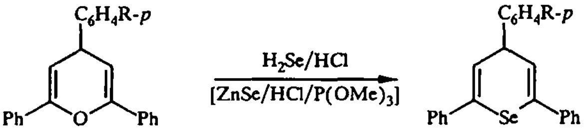
4H-Pyrans react with hydrogen sulfide under acid catalysis to give the corresponding 4H-thiopyrans [1].

We have found that 2,4,6-triphenyl-4H-pyran (Ia) reacts with hydrogen selenide under acid catalysis to give 2,4,6-triphenyl-4H-selenopyran (IIa). However, this reaction is complicated by pyran disproportionation when hydrogen selenide generated directly in the reaction mixture is used. We carried out a similar reaction in the presence of a mixture of ethers containing trimethyl phosphite [3], which was obtained by the reaction of PCl_3 with methanol. The presence of P(III) compounds in the reaction mixture suppressed disproportionation and permitted us to isolate 4H-selenopyrans IIa-c as pure compounds in good yield.



Ia- c

IIa- c

a R = H; b R = OMe; c R = Cl

A solution of 50 ml 5 N HCl in absolute methanol was saturated with hydrogen selenide in an argon atmosphere for 1 h and then a solution of 0.01 mole pyran I in 5 ml chloroform was added dropwise. The reaction mixture was stirred for 5 h. The hydrogen selenide stream was stopped and 50 ml ether was added. The mixture was thoroughly washed with water and dried. Ether was evaporated. The oily product was subjected to chromatography on a 30 × 500-mm alumina column using 4:1 hexane–ether as the eluent to give selenopyran IIa in 42% yield, mp 108-109°C (107.5-109°C [4]).

Synthesis of Selenopyrans in the Presence of Phosphorous Acid Derivatives (general method). A sample of 15 ml PCl_3 was added dropwise to 50 ml methanol with vigorous stirring and cooling. Then, 0.01 mole 4H-pyran and 0.012 mole ZnSe were added. The reaction mixture was stirred for 4 h. The crystalline precipitate was filtered off and recrystallized from methanol. Then, 50 ml ether was added to the reaction mixture. The solution was washed with water, dried over sodium sulfate, and evaporated. The product was recrystallized from methanol to give selenopyran IIa, mp 107.5-109°C in 63% yield.

2,6,-Diphenyl-4-(*p*-methoxyphenyl)-4H-selenopyran (IIb) was obtained in 32% yield, mp 104-106°C (104-105°C [4]). PMR Spectrum in $CDCl_3$: 7.24-7.54 (12H, m, H_{arom}), 6.89 (2H, d, J = 8.7 Hz, H_{arom}), 6.18 (2H, d, J = 4.4 Hz, β-H), 4.26 (1H, t, J = 4.4 Hz, γ-H), 3.80 ppm (3H, s, OMe).

2,6-Diphenyl-4-(*p*-chlorophenyl)-4H-selenopyran (IIc), mp 98-99°C. PMR spectrum in $CDCl_3$: 7.24-7.54 (14H, m, H_{arom}), 6.18 (2H, d, J = 4.4 Hz, β-H), 4.31 ppm (1H, t, J = 4.4 Hz, γ-H). Found: C, 68.04; H, 4.51; Cl, 8.51%. Calculated for $C_{23}H_{17}ClSe$: C, 67.74; H, 4.20; Cl, 8.69%.

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