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SYNTHESIS OF SOME STYRYL DYES FROM 3-ETHYL-2-THIO-4-SELENAZOLIDONE

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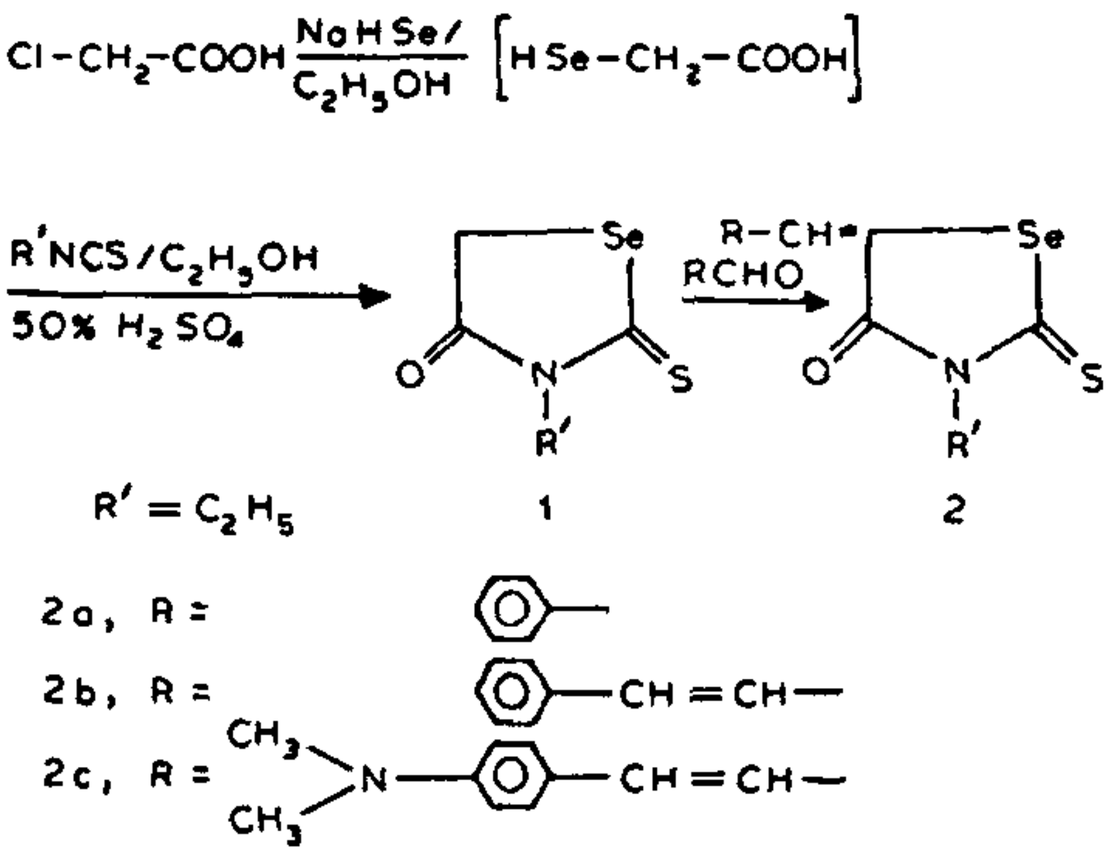
THE body of information found in chemical literature on the synthesis of 2-thio-4-selenazolidones[1,2] is meagre. A literature search was undertaken to synthesize some styryl dyes using thioselenazolidones. Surprisingly, no report has appeared hitherto on the syntheses of styryl dyes using the above mentioned selenium heterocycle. Incidentally the synthesis of thioselenazolidone itself appears to be accomplished by a circuitous method[1,2] which involves the reduction of diselenodiglycolic acid and a subsequent reaction of the resulting selenoglycolic acid with alkyl/aryl isothiocyanates. As the above method involves three steps viz. the preparation of diselenodiglycolic acid, its reduction to selenoglycolic acid and the final reaction of the same with appropriate isothiocyanates, we focussed our attention on the preparation of selenoglycolic acid through a simpler procedure. In this context, it is worth mentioning that the facile and easy preparation of sodium hydroselenide[3] *in situ* in ethanol solution and its reaction on organic compounds containing replaceable chlorine atoms have given impetus to numerous nucleophilic displacement reactions involving hydroselenide anion. Extending the above methodology to chloroacetic acid, selenoglycolic acid was prepared *in situ* which in turn was reacted with ethylisothiocyanate in the same pot to get 3-ethyl-2-thio-4-selenazolidone (1) in moderate yield.

Having achieved the one pot synthesis of the thioselenazolidone (1) our subsequent interest was to prepare some styryl dyes (2). They were synthesized by reacting thioselenazolidone with appropriate aldehydes in the presence of sodium hydroxide. The structures of the products were fully attested by elemental analysis and PMR spectral data.



Synthesis of 3-ethyl-2-thio-4-selenazolidone (1)

Chloroacetic acid (94.5 g, 1 mol) taken in ethanol (50 ml) was added dropwise to a freshly prepared sodium hydroselenide[3] solution, *in situ* in ethanol under nitrogen cover and was refluxed on a water bath for 2 h. After adjusting the pH of the solution to about 2 by adding 50% sulphuric acid, ethylisothiocyanate (85 g, 1 mol) was added in one lot and refluxed for 5 h. The reaction mixture was cooled, poured onto ice and extracted with chloroform. The chloroform layer was washed with water and dried (anhyd. Na_2SO_4). The solvent was removed under reduced pressure to get an oily liquid of thioselenazolidone which was further purified by vacuum distillation.

Yield: 83 g (40%); b.p. 120–125°C/12 mm;

PMR: (CCl_4) δ1.25(t, 3H, CH_2–CH_3, J = 6 Hz), 3.28(S, 2H, Ring CH_2) and 4.13(q, 2H, CH_2–CH_3, J = 6 Hz).

General procedure for the preparation of styryl dyes (2)

To a mixture containing equimolar quantities of 3-ethyl-2-thio-4-selenazolidone and appropriate aldehyde in ethanol (10 ml) was added 5 M aqueous sodium hydroxide (0.5 ml). The solution was left at room temperature for 2 h with occasional stirring. After the removal of ethanol the residue was extracted with ether. The ether layer was washed with saturated sodium bisulphite solution to remove the unreacted aldehyde and then with water and dried (anhyd. Na_2SO_4).. Removal of ether gave crude styryl dye which was further purified by passing through a silica gel column. The styryl dyes were recrystallized from appropriate solvents. The yield, m.p. and PMR data are given in table 1.

Table 1 *Yield, m.p. and PMR data*

Styryl dyes	Yield %	M p. °C (solvent)	PMR ($CDCl_3$) δ
2a	54	102–103 (Benzene)	1.23(t, 3H, CH_2–CH_3, J = 6 Hz) 4.00(q, 2H, CH_2–CH_3, J = 6 Hz) 7.06–7.86(m, 5H, aromatic protons) and 10.85(S, 1H, C_6H_5–CH=)
2b	59	115–116 (Chloroform)	1.25(t, 3H, CH_2–CH_3, J = 6 Hz), 4.17(q, 2H, CH_2–CH_3, J = 7.5 Hz), 6.70(d, 1H, C_6H_5–CH=CH–, J = 12 Hz) 6 84(d, 1H, C_6H_5–CH=, J = 15 Hz) 7.40–7.57(m, 5H, aromatic protons) and 7.92(d, 1H, –CH=CH–CH=, J = 12 Hz
2c	62	126–127 (Chloroform)	1.25(t, 3H, CH_2–CH_3, J = 7.5 Hz) 2.95(S, 6H, –$N(CH_3)_2$), 4.00(q, 2H, CH_2–CH_3, J = 6 Hz), 6.20–6.55(m, 3H, C_6H_4–CH=CH–), 7.00–7.30(m, 3H, C_6H_4–CH = CH–), and 9.20(d, 1H, –CH = CH–CH =, J = 9 Hz).

All the m.ps are uncorrected. Satisfactory elemental analysis were obtained for all compounds. NMR spectra were recorded on a spectrometer (Varian-90 MHz) with TMS as internal standard.

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EUGNONE, A NEW ANTHRAQUINONE FROM THE STEM BARK OF *SAPIUM EUGNIFOLIUM*

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Sapium eugnifolium Linn. (Euphorbiaceae) is used in the Indian system of medicine[1]. Anthraquinone has not been reported so far from this plant. We report here the isolation of a new anthraquinone eugnone (3-hydroxy-1, 6, 7-trimethoxy-2-methyl anthraquinone) and its characterization by colour reactions, spectral data and chemical methods.

The powdered stem bark of *S. eugnifolium* (3 kg) was extracted with ethanol under reflux from 180 h on a water bath. The ethanol from the percolates (20 l) was removed under reduced pressure on a water bath to get a syrupy mass which was then successively extracted with petroleum ether, benzene, chloroform and ethyl acetate. The excess of solvent was removed from the ethyl acetate extract under reduced pressure to get a yellowish solid mass which on TLC examination showed the presence of a single entity. It was loaded on a column of neutral alumina, eluted with $CHCl_3$–EtOAc (8:2) and crystallized as yellow coloured crystals from $CHCl_3$–MeOH (8:2):eugnone, (1), (yield 900 mg).

Eugnone (1), m.p. 278–280°C, $C_{18}H_{16}O_6$ (M^+328), showed UV-visible absorption maxima at 225, 250, 380, 405 nm and gave a positive Borntrager reaction[2] characteristic for an anthraquinone. The IR (KBr) spectrum of (1) showed characteristic absorptions for hydroxyl (3250–3350 cm^{-1}), methoxyl (2900), methyl (2830 and 1470) and carbonyl (1690) groups. The ^1H NMR spectrum (DMSO-d_6, δ, 90 MHz) of (1) showed a signal for an unchelated hydroxyl (11.20), three methoxyls (4.0) and one methyl group (2.40)[3]. Further, (1) showed two separate singlets (δ 8.16, 7.50 and 7.66) corresponding to one proton, at positions C-5 and C-8, and C-4, respectively.