SYNTHESIS OF 2-AMINO-5-(3,5,6-TRICHLORO-1,4-BENZOQUINON-2-YL)SELENAZOLES

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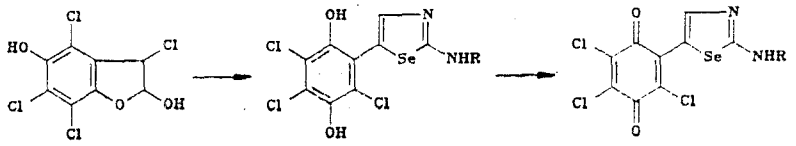
A convenient synthesis of compounds containing both electron donor (2-aminoselenazole) and electron acceptor (trichloro-1,4-benzoquinone) moieties is described. We have previously [1, 2] obtained similar compounds containing the 2-aminothiazole grouping as the electron donor portion of the molecule, these being of interest in studies of intra- and intermolecular charge transfer.

We have found that 2,5-dihydroxy-3,4,6,7-tetrachlorocoumarin (I) [3] reacts with selenourea or N-phenylselenourea in equimolar proportions in boiling ethanol to give 2-amino-5-(2,5-dihydroxy-3,4,6-trichlorophenyl)selenazoles (IIa, b) (compound (IIa) was isolated as its hydrochloride). This reaction makes it possible to obtain selenazoles (II) bearing a wide range of substituents on the nitrogen of the amino group.

Oxidation of the hydroquinone moiety in (IIa, b) to the quinone with ferric chloride in aqueous DMF at 20°C affords 2-amino-5-(3,5,6-trichloro-1,4-benzoquinon-2-yl)selenazoles (IIIa, b).



I II a,b III a,b

II, III a R=H; b R=Ph

(IIa) Hydrochloride. Colorless crystals, yield 83%. IR spectrum (in Nujol): 1575, 1627, 2817, 2923, 3052, 3210 cm^{-1}.

(IIb). Colorless crystals, yield 56%, R_f 0.62 (acetone—hexane, 1:1). IR spectrum (in Nujol): 1497, 1541, 1555, 1601, 3352 cm^{-1}.

(IIIa). Blue crystals, yield 84%, R_f 0.19 (acetone—hexane, 1:2). IR spectrum (in Nujol): 1490, 1522, 1588, 1620, 1649, 2665, 2880 sh, 2988, 3258 cm^{-1}. UV spectrum (in ethanol), λ_{max}, nm (ε): 250 (8400), 334 (10,400), 650 (4000).

(IIIb). Blue crystals, yield 81%, R_f 0.50 (acetone—hexane, 1:2). IR spectrum (in Nujol): 1496, 1507, 1569, 1595, 1612, 1667, 2840, 3192 cm^{-1}. UV spectrum (in ethanol), λ_{max}, nm (ε): 237 (12,500), 268 (10,800), 347 (19,400), 668 (8750).

Compounds (IIa, b) and (IIIa, b) did not have sharp melting points, and decomposed gradually above 200°C. Compounds (IIa, b) were recrystallized from ethanol—ether—hexane, 2:1:2. The homogeneity of (IIb) and (IIIa, b) was checked by TLC on Silufol UV-254 plates. The elemental analyses of the products corresponded to the calculated values.

LITERATURE CITED

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