FORMATION OF SUBSTITUTED BENZOFURANONES-2 BY A NENITZESCU REACTION

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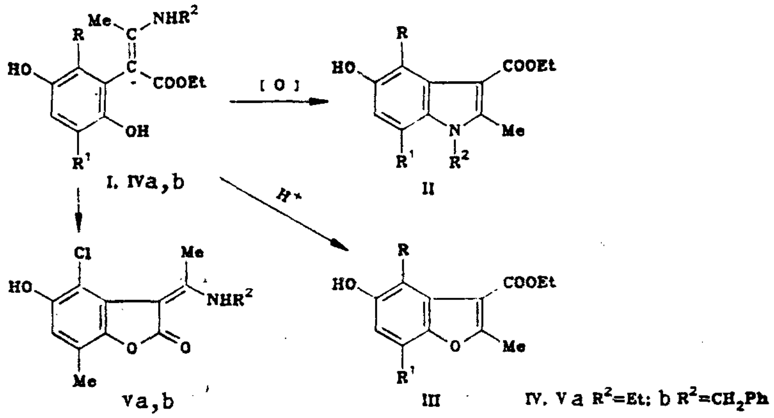
The Nenitzescu reaction is the synthesis of indoles from quinones and enamines [1]. It proceeds via formation of addition products by the Michael reaction (I), which are oxidized to substituted indoles (II), and then by heating in the presence of acid are converted to benzofuran derivatives (III) [1]. We have found that if enaminohydroquinones (IV) with bulky substituents in the benzene ring and at the enamine nitrogen are used as type (I) adducts, the treatment with acid is accompanied by closure not of the furan ring [type (III)], but of the butyrolactone ring to form benzofuranones (V). The reaction was carried out by boiling adducts (IVa, b) [2] in acetic acid in the presence of a catalytic amount of concentrated H_2SO_4. Previously such cyclization had been observed only in alkaline medium [3].

This process is probably due to the reduced rate of the acid hydrolysis of enamines in the presence of strong acid, which in turn is the result of the steric inhibition of enamine conjugation [4].



I, IVa,b

II

Va,b

III

IV, V a R^2=Et; b R^2=CH_2Ph

The relatively low yield of the resulting benzofuranones is apparently due to the complexity of separating these substances from the reaction mixture. TCL study of the mixtures showed that the main products are compounds (Va, b).

7-Methyl-5-hydroxy-2-oxo-4-chloro-3-(1-ethylaminoethylidene)-2,3-dihydrobenzofuran (Va). Mp 170-172°C (from methanol), 60% yield. IR spectrum (mineral oil): 1660 (C=O), 3280 cm^{-1} broad band (NH, OH). PMR spectrum ($CDCl_3$): 10.10 (br.s, NH), 6.63 (s, 6-H), 5.41 (br.s, OH), 3.50 (m, CH_2CH_3), 2.62 (s, =C–CH_3), 2.30 (s, 7-CH_3), 1.38 ppm (t, CH_2CH_3).

1-Benzylaminoethylidene-7-methyl-5-hydroxy-2-oxo-4-chloro-2,3-dihydrobenzofuran (Vb). Mp 110-112°C (from 1:1 hexane–acetone), 20% yield. IR spectrum (mineral oil): 1660 (C=O), 3320 cm^{-1} broad band (OH, NH). PMR spectrum ($CDCl_3$): 10.53 (br.s, NH), 7.32 (m, Ph), 6.64 (s, 6-H), 5.47 (br.s, OH), 4.66 (d, CH_2), 2.59 (s, =C–CH_3), 2.30 ppm (s, 7-CH_3).

Elemental composition and mass spectrometric molecular weight agree with the calculated values.

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FORMATION OF 2,3-DIHYDRO-3-CHLOROMETHYLNAPHTHO[1,2-b][1,4]-DITHIANE IN THE REACTION OF ALLYL 1-NAPHTHYL SULFIDE WITH SULFUR DICHLORIDE

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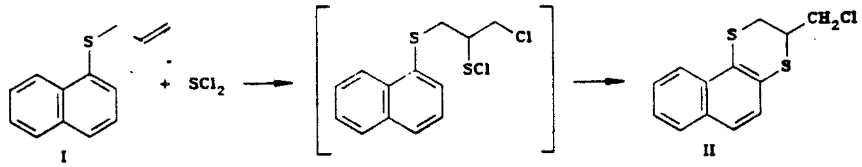
The reaction of 1,5-heterodienes with SCl_2 is one of the methods for synthesizing heterocyclic sulfur compounds that contain two heteroatoms in the ring [1-3]. In order to obtain a hitherto undescribed halosubstituted dithiane we extended this reaction to allyl-1-naphthyl sulfide (I), which represents allyl vinyl sulfide but with the vinyl segment as part of a naphthalene system. We obtained 2,3-dihydro-3-chloromethylnaphtho[1,2-b][1,4]dithiane (II) in 50% yield:



To a solution of 8 g (0.04 mole) of sulfide (I) in 40 ml of dry CH_2Cl_2 at –40°C in an argon atmosphere was added dropwise a solution of 4.15 g (0.04 mole) of freshly distilled SCl_2 in 10 ml of dry CH_2Cl_2. The reaction mixture was stirred for 1 h at –40°C and for 4 h at room temperature. Then it was washed with sodium bicarbonate solution and water. The organic layer was separated and dried with calcined $MgSO_4$. The solvent was distilled off and the residue was separated on a column of Silpearl grade silica gel, with 2:7:1 hexane–CCl_4–CH_2Cl_2 eluent.

Compound II. Yield 50%. PMR spectrum ($CDCl_3$): 2.90 (1H, m, 3-H), 3.32 (2H, m, CH_2Cl), 3.76 (2H, m, 2-H), 7.82 ppm (6H, m, arom.). Mass spectrum, m/z (I_{rel}, %): $[M + 2]^{+\cdot}$ 268 (30), $[M]^{+\cdot}$ 266 (100), $[M - CH_2Cl]^{+\cdot}$ 217 (27), $[C_{10}H_6S_2]^+$ 190 (52), $[C_{10}H_7SCH_2]^+$ 184 (57), $[C_{10}H_7]^+$ 127 (5).

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