PREPARATION OF 3-DIALKYLAMINO-4-(3,5,6-TRICHLORO-1,4-BENZOQUINON-2-YL)PYRAZOLES

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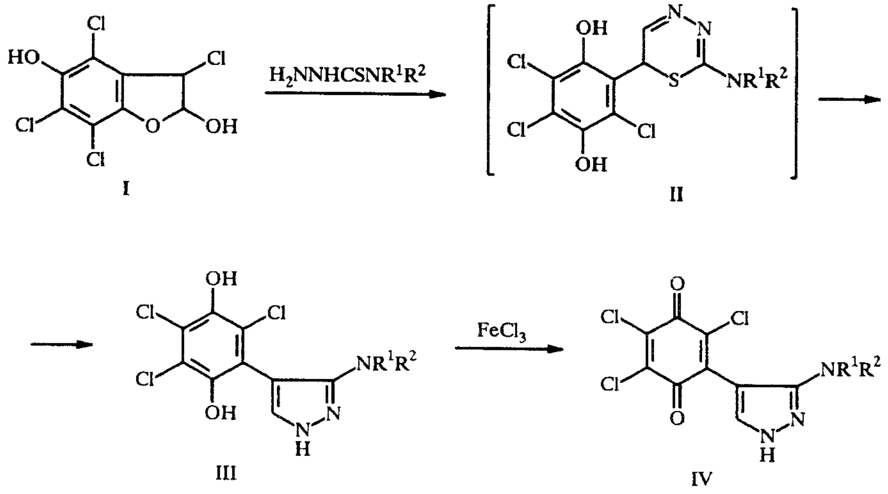
We report an original method of preparation which opens the way to new derivatives of pyrazole in which the pyrazole ring is connected via a C—C bond to a strong electron acceptor — trichloro-1,4-benzoquinone. We have previously prepared similar compounds having 2-aminothiazole [1] or 2-aminoselenazole [2] as electron donor parts in the molecule simultaneously with an electron-acceptor trichloro-1,4-benzoquinone fragment. These compounds are of interest in the study of intra- and intermolecular charge transfer.

We have established that in the reaction of 2,5-dihydroxy-3,4,6,7-tetrachlorocoumaran (I) [3] with 4,4-dialkylthiosemicarbazides, 3-alkylamino-4-(2,5-dihydroxy-3,4,6-trichlorophenyl)pyrazoles III are formed and these are readily oxidized by iron(III) chloride to the corresponding benzoquinones IV. It is suggested [4-6] that the pyrazole system is formed via the intermediate 1,3,4-thiadiazine II which readily undergoes extrusion of a sulfur atom with the formation of a pyrazole ring. Wide variation in the set of substituents R_1 and R_2 in the pyrazole ring is possible in this reaction, including those dictated by a search for biologically active compounds.



III, IV a $R^1 = R^2 = Et$; b $R^1, R^2 = (CH_2)_5$; c $R^1, R^2 = (CH_2)_2O(CH_2)_2$

3-Dialkylamino-4-(2,5-dihydroxy-3,4,6-trichlorophenyl)pyrazoles (IIIa-c). A mixture of 3 mmole compound I and 3 mmole of the appropriate thiosemicarbazide in 20 ml ethanol was stirred 3 h at 20°C and then at bp for 4 h, 0.2 g active carbon was added and the solution filtered hot. To the filtrate was added 5 ml hexane and after 24 h colorless crystals separated. The products were obtained in the form of the monohydrate and to remove the water they were heated at 80°C in vacuum over phosphorus pentoxide. The compounds did not have sharp melting points and decomposed above 240°C. PMR spectra (in DMSO-D_6, δ, ppm): IIIa 10.40 (1H, s, OH), 9.08 (1H, s, OH), 7.98 (1H, s, 5-H), 3.17 (4H, q, CH_2), 1.00 (6H, t, CH_3); IIIb 7.92 (1H, s, 5-H), 3.05 (4H, t, NCH_2), 1.48 (6H, m, CH_2); IIIc 9.67 (1H, s, OH), 9.58 (1H, s, OH), 7.66 (1H, s, 5-H), 3.56 (4H, t, OCH_2), 2.88 (4H, t, NCH_2). Yield 48-58%.

3-Dialkylamino-4-(3,5,6-trichloro-1,4-benzoquinon-2-yl)pyrazoles (IVa-c). To a solution of 0.5 g compound III in 30 ml ethanol at 20°C was added 50 ml 20% aqueous iron(III) chloride solution, the mixture stirred 20 min and then extracted twice with 20 ml chloroform. The extracts were dried over magnesium sulfate, the solution evaporated, and the residue recrystallized from 1:1 ethanol-ether (IVa, b) or from ethanol (IVc). Mp 201-203°C (IVa), 208-210°C (IVb), 238-240°C (IVc). IR spectra (in Nujol) (cm^{-1}): IVa 3168 (NH), 2968, 2930 (CH), 1680 (C=O), 1566 (C=C); IVb 3148 (NH), 2932, 2852 (CH), 1698,

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1684 (C=O), 1568 (C=C); IVc 3164 (NH), 2984 (CH), 1684 (C=O), 1570 (C=C). UV spectrum ($5 \cdot 10^{-5}$ mole/liter in ethanol) [λ_{max} nm (log ε)]: IVa 268 (3.94), 314 (3.77), 413 (2.94), 593 (2.80); IVb 270 (3.96), 334 (3.46), 420 (3.11), 589 (3.06); IVc 276 (4.05), 334 (3.55), 440 (3.12), 512 (3.10). PMR spectrum (in DMSO-D_6, δ, ppm): IVa 7.92 (1H, s, 5-H), 3.12 (4H, q, CH_2), 0.99 (6H, t, CH_3); IVb 7.90 (1H, s, 5-H), 2.92 (4H, t, NCH_2), 1.50 (6H, m, CH_2); IVc 7.53 (1H, s, 5-H), 3.56 (4H, t, OCH_2), 2.89 (4H, t, NCH_2). Yield 80-90%.

Elemental analyses of the compounds prepared were in agreement with calculated values.

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