OXIDATIVE OPENING OF THE 2,5-DIHYDROXY-3,4,6,7-TETRACHLOROCOUMARAN RING

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A method has been developed for the synthesis of (3,5,6-trichloro-1,4-benzoquinone-2-yl)chloroacetaldehyde by the oxidative ring opening of 2,5-dihydroxy-3,4,6,7-tetrachlorocoumaran with nitrogen oxides. The ion-radical salt of (3,5,6-trichloro-1,4-benzoquinone-2-yl)chloroacetaldehyde with N,N,N',N'-tetramethyl-p-phenylenediamine (1:1) has been synthesized. The reaction of 2,5-dihydroxy-3,4,6,7-tetrachlorocoumaran-3-yl) with pyridine gave N-(2,5-dihydroxy-4,6,7-trichlorocoumaran-3-yl) pyridine chloride, which is also formed from the opening of the coumaran ring.

It has been shown that the readily available [1] 2-(2-dialkylaminoethenyl)-3,5,6-trichloro-1,4-benzoquinone when heated in dioxane with concentrated hydrochloric acid gives 2,5-dihydroxy-3,4,6,7-tetrachlorocoumaran (I) [2].

The present work investigates the possibility of obtaining a halogen-substituted 1,4-benzoquinone containing a reactive chloroacetaldehyde group, by the oxidation of coumaran I. Such a compound could be used for the synthesis of a variety of substituted 1,4-benzoquinones which are otherwise hard to obtain, in particular those with an azole or other heterocyclic ring in the molecule. Moreover, it is known [3] that halogen-substituted 1,4-benzoquinones can be used as electron-attracting components for obtaining ion-radical salts with tetrathiafulvalenes – a new class of organic conductors.

We found that the oxidation of coumarin I with nitric oxide at room temperature was accompanied by a simultaneous opening of the coumaran ring to give (3,5,6-trichloro-1,4-benzoquinone-2-yl)chloroacetaldehyde (II). This oxidation was proposed as an original preparative method [4] for obtaining the aldehyde II.

The structure of the aldehyde II was confirmed by IR, UV, and PMR spectroscopy and by mass spectrometry. The IR spectrum contained a C=O absorption band from the α-halogen substituted aldehyde, two C=O bands from the 1,4-benzoquinone, and a band from the quinone C=C group; absorptions corresponding to an OH group or an aromatic system were absent. The UV spectrum was identical to the spectrum of chloranil [5]. The PMR spectrum (in $CDCl_3$) contained two doublets at 5.46 and 9.77 ppm with J = 0.75 Hz, corresponding to protons of the CHCl and CHO groups, respectively. In the mass spectrum,* a molecular ion corresponding to the molecular weight of the compound was observed. The isotopic peak ratio corresponded to that calculated for four chlorine atoms, confirming that these are present in the molecule.

Treatment of the aldehyde II with sodium hydrogen sulfite gave the coumaran I. Moreover, it appeared that the reduction of the quinone to the hydroquinone occurred first and was followed by the formation of (2,5-dihydroxy-3,4,6-trichlorophenyl)chloroacetaldehyde (IA), which was then converted to the cyclic isomer IC by intramolecular nucleophilic addition of the OH group to the C=O group. It is possible that the oxidation I → II also takes place through the intermediate formation of the open chain isomer IA in the reaction process. However, it could not be shown by IR or PMR spectroscopy that the ring-chain tautomeric equilibrium I ⇌ IA was present in the solution [2] (see scheme on top of following page).

Mixing hot equimolar solutions of compound II and N,N,N',N'-tetramethyl-p-phenylenediamine in acetonitrile gave the crystalline ion-radical salt III with donor-to-acceptor ratio of 1:1. In the UV spectrum of compound III, the cation-radical tetramethylphenylenediamine absorbed at 620 and 570 nm [6], and the quinone at 315 nm.

The reaction of the coumaran I with pyridine gave N-(2,5-dihydroxy-4,6,7-trichlorocoumaran-3-yl)pyridine chloride (IV). The IR spectrum of this compound contained: a pyridine ring vibrational band, an aromatic absorption band, and a broad band

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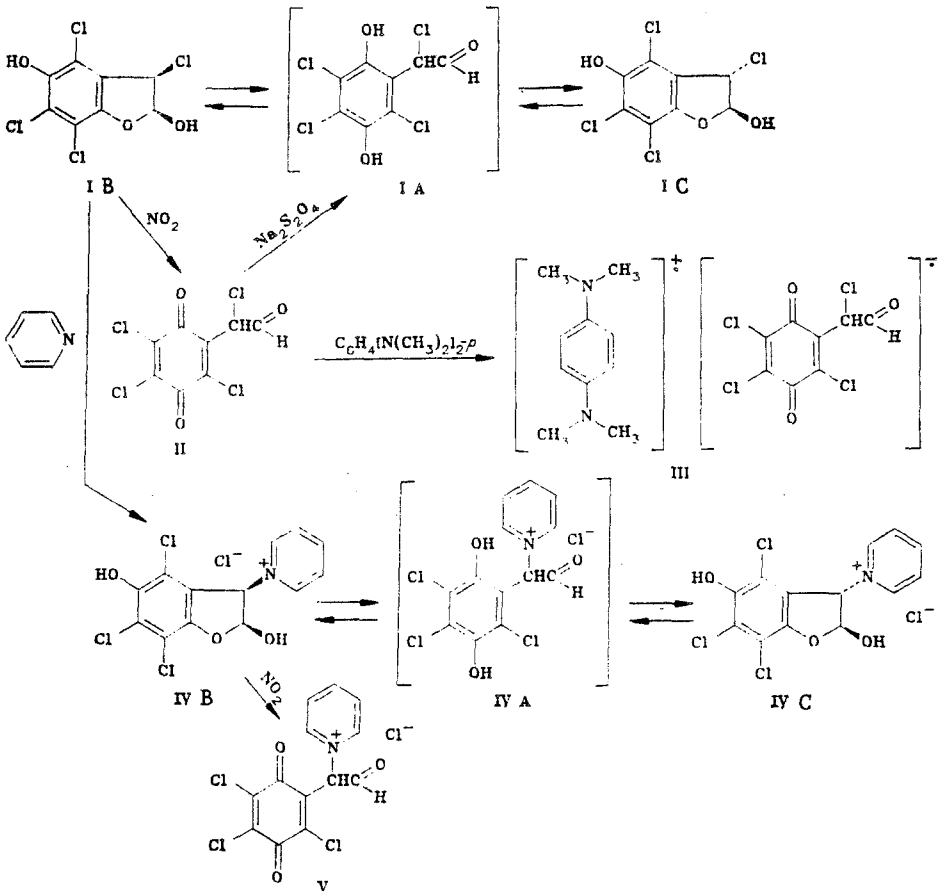

associated with the hydroxyl groups. The PMR spectrum of compound IV in DMSO-D_6 solution contained two doublets from the methine protons at 6.53 and 6.96 ppm, with $^3J_{23}$ = 6.45 Hz, which indicates a cis-orientation of these protons (structure IVB) [7]. In addition, the spectrum contained a pair of broad signals at 6.35 and 6.69 ppm (J < 1 Hz), corresponding to the trans-isomer IVC, of which 29% is present. The cis,trans-transition between the stereoisomers IVB and IVC, and the previously observed [2] IB ⇌ IC gives indirect evidence for the ring-chain equilibrium in solution. Such a transition could be realized only through the open-chain form of the aldehyde IVA. However, the presence of the aldehyde group in the solution of aldehyde IV could not be shown by IR or PMR methods: Apparently, the equilibrium concentration of the open form of IVA is too low to be detected by IR and PMR spectroscopy.

The oxidation of compound IV with oxides of nitrogen was accompanied by the opening of the coumaran ring to give the 1-[2-oxo-1-(3,5,6-trichloro-1,4-benzoquinone-2-yl)ethyl]pyridine chloride (V). The structure of the reaction product V was confirmed from an IR spectrum of its solution in dioxane, which contained absorption bands corresponding to the aldehyde and the quinone C=O groups.

EXPERIMENTAL

IR spectra were recorded on Specord IR-75 and IKS-14A instruments (mineral oil suspensions and solutions in dioxane). UV spectra were taken on a Specord UV-vis spectrophotometer. PMR spectra were obtained on a Bruker WH-90 DS, internal standard TMS. Mass spectra were taken on a Kratos MC-50, ionizing voltage 70 eV, temperature of the ionization chamber 150°C, direct introduction of the sample into the system.

(3,5,6-Trichloro-1,4-benzoquinone-2-yl)chloroacetaldehyde (II, $C_8H_2Cl_4O_3$). A thin layer of finely ground 2,5-dihydroxy-3,4,6,7-tetrachlorocoumaran (I) (2.9 g, 10 mmoles) was spread over the bottom of a Petri dish, placed in a covered desiccator in the presence of 40-50 ml of fuming nitric acid, and allowed to stand at room temperature for 2 h. The product obtained was dried in vacuum, first at room temperature, and then at about 60°C to give 2.9 g (100%), of yellow crystals mp 115-117°C. IR spectrum (in Nujol): 1744 (aldehyde C=O); 1698, 1662 (quinone C=O); 1580 cm^{-1} (C=C). UV spectrum (in ethanol), λ_{max} (log ε): 203 (4.30), 283 (4.01), 355 nm (2.74). PMR spectrum (in $CDCl_3$), δ: 5.46 (1H, d, J = 0.75 Hz, CHCl); 9.77 ppm (1H, d, J = 0.75 Hz, CHO). M^+ 286 (caused by ion with isotope ^{35}Cl).

Reduction of the Aldehyde II. A solution of compound II (1 g, 3.5 mmoles) in diethyl ether (20 ml) was shaken at room temperature with a solution of sodium hydrosulfite (2 g) in water (15 ml) until the organic layer was decolorized. The organic layer was washed with saturated sodium chloride, then dried with magnesium sulfate. The ether was evaporated in vacuum and the residue recrystallized from carbon tetrachloride to give 0.65 g (65%) of coumaran I mp 142-143°C (decomp.) (literature value mp 144-145°C (decomp.) [2]). There was no depression of melting point when mixed with an authentic sample of coumaran I, showing that the two compounds were identical.

Complex of (3,5,6-Trichloro-1,4-benzoquinone-2-yl)chloroacetaldehyde with N,N,N',N'-Tetramethyl-p-phenylenediamine (III, $C_8H_2Cl_4O_3 \cdot C_{10}H_{16}N_2$). To a boiling solution of compound II (0.29 g, 1 mmole) in acetonitrile (2 ml) was added a solution of tetramethyl-p-phenylenediamine (0.16 g, 1 mmole) in acetonitrile (2 ml), also heated to boiling. The reaction mixture was kept for 2-3 h in the dark at 0°C, the precipitated material filtered off, washed with acetonitrile, and dried in vacuum at room temperature. The ion-radical salt was obtained as dark-blue crystals with a metallic luster. Yield 0.4 g (45%), mp 85-87°C (decomp.). UV spectrum (in acetonitrile), λ_{max}: 315, 570, 620 nm.

N-(2,5-Dihydroxy-4,6,7-trichlorocoumaran-3-yl)pyridine Chloride (IV, $C_{13}H_9Cl_4NO_3$). To a solution of coumaran I (0.58 g, 2 mmoles) in anhydrous benzene (10 ml) in an atmosphere of argon at room temperature was added a solution of pyridine (0.16 ml, 2 mmoles) in anhydrous benzene (5 ml). The reaction mixture was kept at room temperature for 2 h, the precipitated material separated, and recrystallized from anhydrous ethanol. The product was obtained as colorless crystals, 0.46 g (62%), mp 202-203°C (decomp.). IR spectrum (in mineral oil): 1632 (pyridine ring); 1605, 1580 (aromatic ring); 3350, 3040 cm^{-1} (wide band, OH). PMR spectrum (in DMSO-D_6), δ: 6.35 (1H, s, J < 1 Hz, 2-H, IVC); 6.69 (1H, s, J < 1 Hz, 3-H, IVC); 6.53 (1H, d, J = 6.45, 3-H, IVB); 6.96 (1H, d, J = 6.45, 3-H, IVB); 8.19 (2H, m, β-pyridine ring protons); 8.71 (1H, m, γ-pyridine ring protons); 8.99 (2H, m, α-pyridine ring protons), 9.33 (1H, br.s, 2-OH); 10.36 ppm (1H, br.s, OH).

1-[2-Oxo-1-(3,5,6-trichloro-1,4-benzoquinone-2-yl)ethyl]pyridine Chloride (V). Compound IV (0.1 g, 0.35 mmole), spread as a thin layer in a Petri dish, was kept for 30 min at room temperature in a closed desiccator in the presence of fuming nitric acid (40 ml). The reaction product was dried in vacuum at room temperature to give 0.08 g (80%) of dark-red crystals, mp 60°C (decomp.). The compound was unstable, very hygroscopic, and quickly resinified. IR spectrum (in dioxane): 1731, 1665, 1642 cm^{-1}. UV spectrum (in ethanol), λ_{max} (log ε): 355 (3.38), 410 (3.08), 650 nm (3.26).

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