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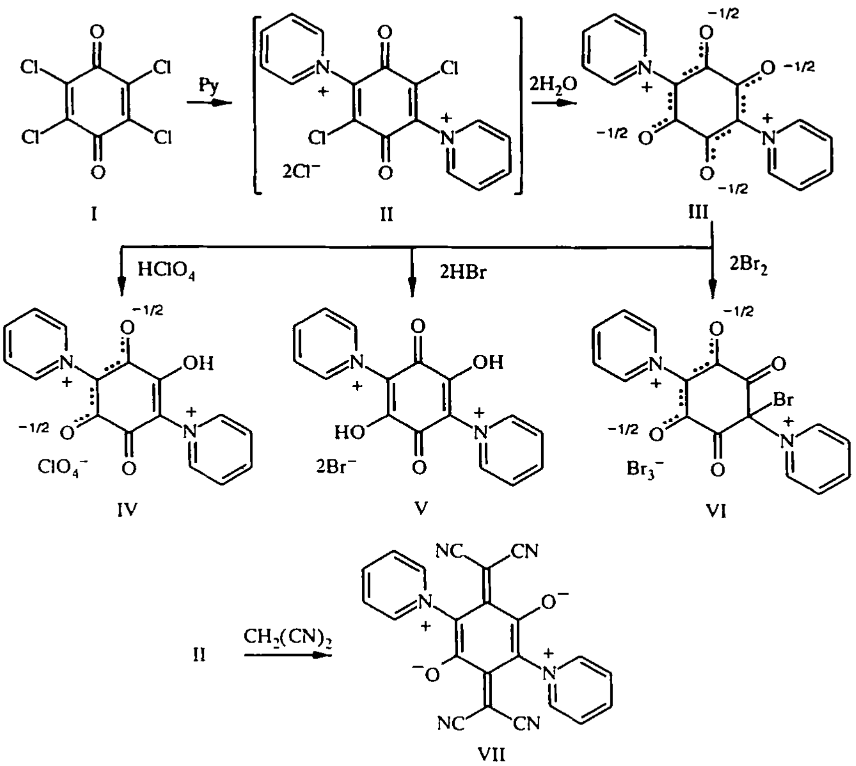
SYNTHESIS AND PROPERTIES OF DIPYRIDINIUM BETAINES OF DERIVATIVES OF 1,4-BENZOQUINONE AND TETRACYANOQUINODIMETHANE

V. A. Yanchishin, G. A. Karlivan, and R. É. Valter

Reaction of chloranil with excess pyridine gives the poorly stable 2,5-di(N-pyridinium)-3,6-dichloro-1,4-benzoquinone dichloride which is readily hydrolyzed to give the bisbetaine of 2,5-di(N-pyridinium)-1,4-benzoquinone-3,6-dioxide. Treatment with acid gives its mono- and bisprotonated derivatives as the perchlorate and dibromide and bromination gives the betaine 2-bromo-2,5-di(N-pyridinium)-5-cyclohexene-1,3,4-trione-6-oxide perbromide. The reaction of malonodinitrile with 2,5-di(N-pyridinium)-3,6-dichloro-1,4-benzoquinone dichloride in situ *gives the poorly stable bisbetaine of 2,5-di(N-pyridinium)-7,7,8,8-tetracyanoquinodimethane-3,6-dioxide.*

There are many examples known [1, 2] of the nucleophilic substitution of a chlorine atom in quinone molecules by nitrogen containing nucleophiles but the reaction with pyridine has been little studied. Treatment of chloranil with pyridine gave [3] "red and orange betaines," the structures of which were not strictly proved. In all probability, one of these is the bisbetaine of 2,5-di(N-pyridinium)-1,4-benzoquinone-3,6-dioxide (III). The compound has also been obtained [4] by oxidation of a mixture of hydroquinone and pyridine using iodine but its chemical properties were not examined. The action of pyridine on 2,3-dichlo-



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ro-1,4-naphthoquinone in butanol gave the betaine of 3-(N-pyridinium)-1,4-naphthoquinone-2-oxide [5], the reactions of which were studied in more detail [6-8].

Polypyridinium substituted benzoquinones [9] and tetracyanoquinodimethanes (TCNQ) [10] are of interest as very powerful electron acceptors for synthesis of charge-transfer complexes and ion-radical salts (see [11, 12] and citations in their literature). A specific method [9] has been proposed for preparation of 2,3,5,6-tetra(4-N,N-dimethylaminopyridino)-1,4-benzoquinone tetratriflate by reaction of chloranil with 1-trimethylsilyl-4-(N,N-dimethylamino)pyridinium triflate.

The aim of our work was to study the possible synthesis of 2,5-di- and 2,3,5,6-tetrapyridino substituted 1,4-benzoquinones and TCNQ in the nucleophilic substitution of chloranil with pyridine and malonodinitrile.

Reaction of chloranil (I) with pyridine in the molar ratio of 1:4 was carried out in refluxing aprotic solvents. In benzene, dioxane, and trichloroethylene tarring of the reaction mixture occurred but better results were obtained in acetonitrile or chloroform. The reaction product is 2,5-di(N-pyridinium)-3,6-dichloro-1,4-benzoquinone dichloride (II), obtained as red crystals which are poorly stable and very rapidly hydrolyzed by atmospheric moisture. We could not isolate this compound in the pure state and fully characterize it. Its IR spectrum showed 1,4-benzoquinone $C=O$ bands at 1697 and 1657 cm^{-1} [13]. The PMR spectrum showed only signals for pyridinium protons [14].

Hydrolysis of dichloride II gives the bisbetaine of 2,5-di(N-pyridinium)-1,4-benzoquinone-3,6-dioxide (III) which is poorly soluble in organic solvents. Its IR spectrum shows a strong band at 1558 cm^{-1} which can be assigned to an absorption vibration of the $O{=}C{=}C{=}C{=}O$ system [15]. The PMR spectrum shows only pyridine ring proton signals. Methylation of bisbetaine III with dimethylsulfate gives a product which is readily hydrolyzed by atmospheric moisture hence it could not be prepared in the pure state. Bisbetaine III is not acetylated by acetic anhydride in the presence of sulfuric acid and, in contrast to benzoquinone, is not reduced by sodium dithionite. We carried out a counter synthesis of bisbetaine III by reaction of hydroquinone with pyridinium perbromide (see [16]), but the yield in this reaction is significantly lower (16%).

Protonation of bisbetaine III by perchloric acid in methanol gives the stable monoperchlorate of 3-hydroxy-2,5-di(N-pyridinium)-1,4-benzoquinone-6-oxide (IV). The diprotonated form could not be separated. Monoperchlorate IV is stable in air but in water is hydrolyzed to give bisbetaine III. The IR spectrum of the crystalline monoperchlorate IV shows a broad band for the associated OH group at 2800 cm^{-1} (in acetonitrile at 3550 cm^{-1}) as well as a band for $C=O$ at 1648 cm^{-1}, the pyridine ring being at 1630 cm^{-1}, and an absorption band for $O{=}C{=}C{=}C{=}O$ at 1552 cm^{-1}.

Protonation of bisbetaine III in concentrated hydrobromic acid gives 3,6-dihydroxy-2,5-di(N-pyridinium)-1,4-benzoquinone dibromide (V). Compound V is stable in air but the action of water or alcohol causes hydrolysis to bisbetaine III once more. The IR spectrum of the crystalline dibromide V shows a broad band for associated OH at 2800 cm^{-1}, a benzoquinone $C=O$ band at 1674 cm^{-1}, and a pyridine ring at 1626 cm^{-1}. The vibration band for the $O{=}C{=}C{=}C{=}O$ system is absent.

The perbromide betaine of 2-bromo-2,5-di(N-pyridinium)-5-cyclohexene-1,3,4-trione-6-oxide (VI) can be separated from bromination of bisbetaine III. This compound brominates $C-H$ acids, e.g., malonic acid at room temperature. The IR spectrum of perbromide VI shows $C=O$ bands at 1770, 1756, and 1666 cm^{-1}, a band at 1628 cm^{-1} ($C=C$ and skeletal pyridinium ring vibrations), and an $O{=}C{=}C{=}C{=}O$ fragment vibration at 1562 cm^{-1}.

Attempts were undertaken in [10] to prepare polyonium derivatives of TCNQ but the authors were unable to obtain single compounds.

In situ reaction of malonodinitrile with dichloride II gave the bisbetaine of 2,5-di(N-pyridinium)-7,7,8,8-tetracyanoquinodimethane-3,6-dioxide (VII). This compound is poorly soluble in organic solvents, decomposes upon solution in mineral acids and in DMF and DMSO, and could not be separated as a single compound with satisfactory elemental analysis. Methylation of bisbetaine VII by dimethylsulfate gives an unstable product which rapidly decomposes in air. The IR spectrum of VII shows a $C=C$ band at 1614 cm^{-1}, $C\equiv N$ at 2196 cm^{-1}, and pyridine ring $C-H$ at 3062, 3082, and 3126 cm^{-1}. The UV spectrum of an acetonitrile solution showed strong maxima at 457 and 487 nm, typical of TCNQ derivatives [17]. The PMR spectrum showed only signals for pyridine protons.

While carrying out this investigation there appeared work [18] in which the reaction of chloranil with 4-tert-butylpyridine to give the bisbetaine corresponding to III was reported.

EXPERIMENTAL

IR Spectra were recorded on a Specord M-80 instrument for thin film suspensions in Nujol (region 1900-1500 cm^{-1}, NaCl prism) and in hexachlorobutadiene (3800-2000 cm^{-1}, LiF prism). Electronic spectra were taken on a Specord M-40 for solutions in water and acetonitrile (c = $5 \cdot 10^{-5}$ molar). PMR Spectra were obtained on a Bruker H-90 instrument for DMSO-D_6 solutions with chemical shifts measured relative to internal TMS standard.

2,5-Di(N-pyridinium)-1,4-benzoquinone-3,6-dioxide Bisbetaine (III). A. Pyridine (8.1 g, 100 mmole) was added with stirring to a refluxing solution of chloranil (6.1 g, 25 mmole) in acetonitrile (100 ml). The product was refluxed for 2 h and diluted with water (100 ml). After standing for 24 h at 5°C, the precipitate was separated, washed with water, and recrystallized from acetic acid to give III (6.7 g, 91%) as bright yellow crystals with mp >250°C. IR Spectrum (thin film): 3117, 3073, 3045, 1658, 1632, 1618, 1610, 1558 cm^{-1}. UV Spectrum (water), λ_{max} (log ε): 252 (4.00), 316 nm (4.41). PMR Spectrum (DMSO-D_6): 8.10 (3,5-H_2); 8.43 (4-H) and 8.75 ppm (2,6-H_2). Found, %: C 65.29; H 3.65; N 9.60. $C_{16}H_{10}N_2O_4$. Calculated, %: C 65.30; H 3.43; N 9.52.

B. Pyridine perbromide (6 g, 25 mmole) and pyridine (2 ml, 25 mmole) were dissolved in methanol (10 ml), a solution of hydroquinone (0.55 g, 5 mmole) was added, and the reaction mixture was heated using a reflux condenser for 3 h. The refluxing solution was diluted with hot water (25 ml) and then cooled. After 24 h the precipitate was washed with water and recrystallized from acetic acid to give III (0.23 g, 16%) as bright yellow crystals. The IR spectrum taken in the fingerprint region was identical to the spectrum of III prepared by method A.

3-Hydroxy-2,5-di(N-pyridinium)-1,4-benzoquinone-6-oxide Monoperchlorate (IV). Perchloric acid (0.45 ml, 5 mmole) was added to a suspension of bisbetaine III (0.3 g, 1 mmole) in methanol (10 ml). The mixture was heated to reflux, cooled after 1 h, and the precipitate formed was washed with a small amount of methanol to give IV (0.43 g, 80%) as orange crystals with mp >250°C (decomp.). IR Spectrum (thin layer): 3120, 2800 (broad), 3068, 1680, 1648, 1630, 1552 cm^{-1}; (acetonitrile) 3550 cm^{-1} (OH). Found, %: C 48.31; H 2.65; Cl 8.78; N 7.48. $C_{16}H_{10}N_2O_4 \cdot HClO_4$. Calculated, %: C 48.68; H 2.81; Cl 8.98; N 7.10.

3,6-Dihydroxy-2,5-di(N-pyridinium)-1,4-benzoquinone Dibromide (V). Bisbetaine III (0.3 g, 1 mmole) was dissolved with heating in concentrated hydrobromic acid (10 ml). The solution was heated to reflux and left to crystallize. The precipitate was removed to give V (0.36 g, 80%) as orange needle crystals with $T_{decomp.}$ >250°C (without melting). IR Spectrum (thin film): 3118, 3074, 2800, 1674, 1640, 1626, 1506 cm^{-1}. UV Spectrum (concentrated HBr), λ_{max} (log ε): 268 nm (3.19). Found, %: C 41.71, H 2.68; Br 35.93; N 6.07. $C_{16}H_{10}N_2O_4 \cdot 2HBr$. Calculated, %: C 42.13; H 2.65; Br 35.04; N 6.14.

2-Bromo-2,5-di(N-pyridinium)-5-cyclohexene-1,3,4-trione-6-oxide Betaine Perbromide (VI). A solution of bromine (0.25 ml, 5 mmole) in CCl_4 (5 ml) was added dropwise with stirring to a suspension of bisbetaine III (0.3 g, 1 mmole) in CCl_4 (5 ml). The product was refluxed for 1 h, cooled, the precipitate separated and washed with hot CCl_4 (20 ml) to give VI (0.6 g, 98%) as light brown crystals with $T_{decomp.}$ >150°C (without melting). IR Spectrum (thin film): 3118, 3066, 1770, 1756, 1666, 1618, 1576, 1562 cm^{-1}. Found, %: C 31.01; H 1.57; Br 52.33; N 4.14. $C_{16}H_{10}Br_4N_2O_4$. Calculated, %: C 31.30; H 1.64; Br 52.07; N 4.56.

Reaction of Perbromide VI with Malonic Acid. A solution of malonic acid (0.1 g, 1 mmole) in diethyl ether (5 ml) was added with vigorous stirring to a suspension of perbromide VI (0.45 g, 0.7 mmole) in ether (5 ml). The mixture was held at room temperature for 2 h and then stirred, filtered, the filtrate evaporated, and the residue recrystallized from benzene to give product (0.14 g, 80%) as colorless needle crystals of bromomalonic acid with mp 105-106°C (decomp.). In the literature [19] the mp is reported as 113°C (decomp.). Its identity as bromomalonic acid was confirmed by mixed melting point.

2,5-Di(N-pyridinium)-7,7,8,8-tetracyanoquinodimethane-3,6-dioxide Bisbetaine (VII). Chloranil (1.2 g, 5 mmole) was dissolved with heating in acetonitrile (50 ml) and pyridine (1.6 ml, 20 mmole) was added with vigorous stirring. The mixture was heated using a reflux condenser for 1 h and a solution of malonodinitrile (0.8 g, 12 mmole) and pyridine (0.8 ml, 10 mmole) in acetonitrile (5 ml) was added with vigorous stirring to the hot reaction mixture. Stirring was continued for 1 h at 40-50°C and the product was cooled and held at 5°C for 24 h. The separated precipitate was washed with hot benzene and then chloroform to give VII (1.25 g, 64%) as grey-green crystals with $T_{decomp.}$ >250°C (without melting). IR Spectrum (thin film): 3126, 3082, 3062, 2196, 1702, 1684, 1614 cm^{-1}. UV Spectrum (acetonitrile), λ_{max}(log ϵ): 261 (4.31), 457 (4.42), 487 nm (4.46). PMR Spectrum (DMSO-D_6): 8.27 (3,5-H_2); 8.69 (4-H), and 8.93 ppm (2,6-H_2).

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