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2-Spiroanellated 1,3-Benzodioxoles from the Reaction of 2,3-Dihydro-1*H*-pyrrol-3-ones with Tetrachloro-1,2-benzoquinone

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Summary. Novel spiro[1,3-benzodioxole-2,2′-(2′,3′-dihydro-1′*H*-pyrrol-3′-ones)] were obtained from 2-aminomethylene-2,3-dihydropyrrol-3(1*H*)-ones and tetrachloro-1,2-benzoquinone in ethanol at room temperature. However, in addition, 3,4-dichloro-7-methoxy-5-(4-methoxyphenyl)-5,10-dihydrophenazine-1,2-dione was formed in the reaction of 1-(4-methoxyphenyl)-2-(4-methoxyphenylaminomethylene)-4,5-diphenyl-1,2-dihydropyrrol-3-one with tetrachloro-1,2-benzoquinone.

Keywords. Spiro compounds; Dioxole; Haloquinone; Dihydrophenazine.

Introduction

1,3-Benzodioxoles, constituting acetals of carbonyl compounds with catechols, may be formed unexpectedly in a variety of ways from *o*-quinones. *o*-Chloranil reacts with *o*-phenylenebis(methylenetriphenyl phosphoranes) to 1,2-di(4,5,6,7-tetrachlorobenzo-1,3-dioxol-2-yl)benzene in low yield among other products [1], and with diarylmethylenetriphenyl phosphoranes 2-spiroanellated tetrachloro-1,3-benzodioxoles are formed [2].

The same type of benzodioxoles is found to be formed from *o*-chloranil and thiones [3–5] as well as from tetralones and 1-naphthols [6, 7] and various other active methylene compounds [8]. *Hassan* reported the formation of such spiro-1,3-benzodioxoles from *o*-chloranil and 2-arylisoindolines [9].

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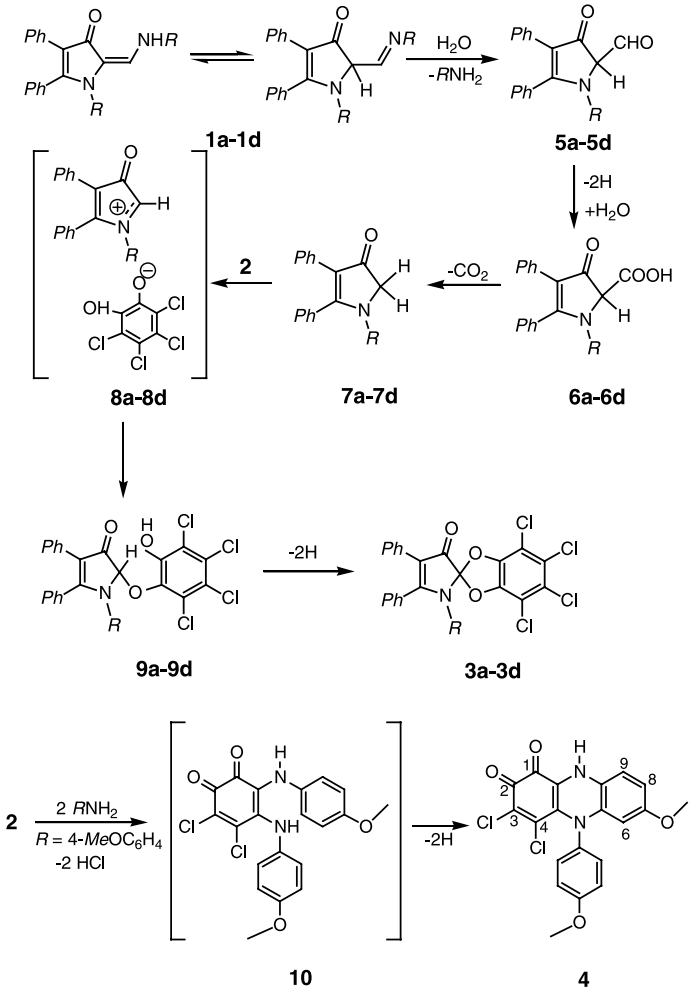
Results and Discussions

Recently we have reported the formation of several 2-aminomethylene-2,3-dihydro-4,5-diphenylpyrrol-3(1*H*)-ones **1a**–**1d** from diphenylcyclopropen one and symmetric glyoxal bisimines [10]. These constitute in fact monoenamines of 1,3-dicarbonyl compounds and are analogous to active methylene compounds. We became interested in the reactions of 2-aminomethylene-2,3-dihydro-4,5-diphenylpyrrol-3(1*H*)-ones **1a**–**1d** with quinones and found to our surprise, that when treated with equimolar amounts of *o*-chloranil (**2**) in ethanol at room temperature, products **3a**–**3d** were obtained (Scheme 1). In the case of **1d**, a second product **4** was collected in addition



a: *R* = cyclohexyl
b: *R* = 2-*Me*C$_6$H$_4$
c: *R* = 4-*Me*C$_6$H$_4$
d: *R* = 4-*Me*OC$_6$H$_4$

Scheme 1

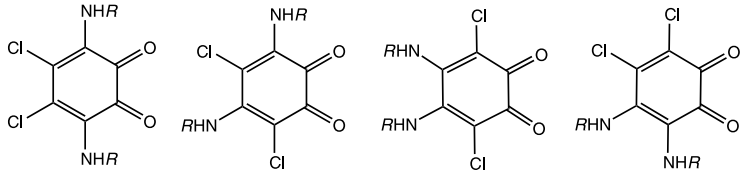
to **3d**. Yields of products **3** could be increased (up to 86% in the case of **3b**) when two equivalents of **2** were applied.

The products **3a**–**3d** were characterized as follows: The IR spectra of the solids showed C=O absorptions in the range of 1705–1710 cm^{-1}. In addition, at $\bar{\nu} = 1025$ (C–O–C=C) [11] and 909 cm^{-1} (O–C–O) [11] signals were observed. The elemental analyses supported the compositions, and the mass spectra showed the molecular ions as 4Cl-atom clusters in 4:3:2 ratios (for *e.g.* **3c** at $m/z = 569$, 571, and 573) demonstrating that substitution of chlorine atoms had not occurred. The mass, ^1H, and ^{13}C-NMR spectra clearly revealed that one *N*-organyl group and exocyclic methine carbon atom of **1a**–**1d** were lost during the process. Thus, all compounds **3a**–**3d** showed a signal for a quaternary carbon atom in the range $\delta = 109.3$–114.1 ppm, which was assigned to the spiro carbon atom C-2 (C-2′). All other ^1H and ^{13}C signals fell into expected shift ranges and showed the expected multiplicities (see Experimental).

The structure of phenazine **4** was assigned on the basis of elemental analysis and spectral data. Its ^1H NMR spectrum showed two singlets at $\delta = 3.70$ and 3.89 ppm for the two methoxy groups, two doublets at $\delta = 6.23$ and 8.03 ppm for 6-H, 9-H, and a doublet of doublet at $\delta = 7.23$ ppm for 8-H along with the AA′ BB′-system of the aromatic protons of the anisyl ring at $\delta = 7.17$ and 7.53 ppm. Moreover, the mass spectrum of phenazine **4** displayed a molecular ion at $m/z = 416$ as 2Cl-atom clusters (see Experimental).

When two chlorine atoms in **2** are substituted by *R*-NH, four isomers are possible: One *para*, one *meta*, and two *ortho* (Scheme 2). Only *ortho* isomers would be capable to form phenazine structures, and only that disubstitution product we envisaged, namely the open structure **10** (Scheme 1), can form a dehydrogenation product being capable to form a twofold hydrogen bonded dimer. If the phenazine structure was formed from the second *ortho*-isomer (**C**), such dimerization would not be possible. The IR in KBr between 3600 and 2000 cm^{-1} is reminiscent of an amino acid dimer. The proposed formula for **4** has an α-aminocarbonyl entity. Such units are prone to form dimers bridged by two C=O · · · H–N bridges.

The formation of **3a**–**3d** is rationalized as follows (Scheme 1): admission of moisture and an original water content of the solvent (ethanol) are crucial for the loss of the –CH=N–*R* unit observed. Hydrolysis of **1** liberates the amine and generates the aldehyde **5**, which is oxidized to carboxylic acid **6**, which under the reaction conditions may well undergo decarboxylation to generate **7**. Hydride abstraction by **2** (analogous to that reported for isoindolines in their reaction with **2** [9]) generates the ion pair **8** which in turn collapses to **9**. The latter is subject to a



Scheme 2

dehydrogenating cyclization forming **3**. The quinone **2** is very likely acting as dehydrogenating agent throughout, although air oxygen also may affect the transformation of **5** into **6**. In addition, the amine liberated is electron rich as *p*-anisidine, thus chances for displacement of chlorine in **2** are increased, and the product of disubstitution (**10**) may be dehydrocyclized to the by-product **4**.

In conclusion, the formation of a spirobenzodioxole from *o*-chloranil and a moderately active methylene compound generated *in situ* was observed. This case together with related examples from literature [6–8] demonstrate that the formation of benzodioxoles from active methylene compounds and electron deficient quinones may be a general reaction.

Experimental

The uncorrected melting points were determined on a *Reichert* Thermovar hot stage microscope. Elemental analyses were obtained on a Carlo Erba 1106 CHN analyzer; these values agreed favourably with the calculated ones. The IR (KBr) were recorded on a Perkin Elmer 983 spectrophotometer. The 300 MHz ^{1}H and 75 MHz ^{13}C NMR spectra were observed on a Bruker WM 300 instrument with *TMS* as internal standard and *DMSO*-d_6 or $CDCl_3$ as solvent. The ^{13}C signals were assigned on the basis of DEPT 135/90 spectra. The mass spectra (70 eV, electron impact mode) were recorded on an AMD 604 instrument. Preparative layer chromatography (plc) used air dried 1.0 mm thick layers of silica gel Merck PF_{254} and toluene:ethyl acetate (2:1) as developing solvent. Zones were eluted with acetone or ethyl acetate.

*General Procedure for Preparation of **3a–3d** and **4***

To a solution of 0.5 mmol of **1a**–**1d** in 10 cm^3 of ethanol at room temperature a solution of 1.0 mmol of **2** in 10 cm^3 of ethanol was added dropwise. The mixture was left standing overnight. It was subjected to plc using toluene:ethyl acetate = 2:1 as developing solvent. Zones were extracted with acetone, the fastest moving one contained **3a**–**3d**. In the latter case the slowest zone contained **4**.

4,5,6,7-Tetrachloro-1′-cyclohexyl-4′,5′-diphenylspiro[1,3-benzodioxole-2,2′-pyrrol]-3′(1′H)-one (**3a**, $C_{28}H_{21}Cl_4NO_3$)

Yield 0.16 g (58%), mp 224–225°C, yellow crystals (*EtOAc*); ^{1}H NMR ($CDCl_3$): $\delta = 0.93$–1.90 (m, 5cyclohexyl-CH_2), 3.52 (m, cyclohexyl-CH), 6.98–7.55 (m, 10Ar–H) ppm; ^{13}C NMR ($CDCl_3$): $\delta = 25.2$, 26.3, 32.1 (cyclohexyl-*C*H_2), 56.6 (cyclohexyl-*C*H), 109.3 (C-2 = C-2′), 126.4, 128.0, 128.1, 128.5, 129.2, 130.8 (aryl-*C*H), 113.0, 113.7, 125.9, 129.4, 129.9, 143.7, 176.7, 188.7 (qu *C*) ppm; IR (KBr): $\bar{\nu} = 1706$ (CO), 1230, 1165, 1136, 1073, 1025 (C–O–C=C), and 909 (O–C–O) cm^{-1}; MS: $m/z = 561$ (M+), 178.

4,5,6,7-Tetrachloro-1′-(2-methylphenyl)-4′,5′-diphenylspiro-[1,3-benzo-dioxole-2,2′-pyrrol]-3′(1′H)-one (**3b**, $C_{29}H_{17}Cl_4NO_3$)

Yield 0.24 g (86%), mp 195–196°C, yellow crystals (*EtOAc*); ^{1}H NMR ($CDCl_3$): $\delta = 2.19$ (s, CH_3), 6.79–7.61 (m, 14Ar–H) ppm; ^{13}C NMR ($CDCl_3$): $\delta = 19.0$ (CH_3), 114.0, 121.2, 125.9, 127.5, 128.3, 128.4, 128.9, 129.7, 130.5, 131.4 (all aryl *C*H), 114.1 (C-2 = C-2′), 119.7, 120.3, 124.0, 134.7, 138.1, 138.3, 139.4, 140.9, 176.7, 191.5 (qu *C*) ppm; IR (KBr): $\bar{\nu} = 1705$ (CO), 1260, 1167, 1136, 1075, 1025 (C–O–C=C), and 909 (O–C–O) cm^{-1}; MS: $m/z = 569$ (M+), 442, 336, 178, 91.

4,5,6,7-Tetrachloro-1′-(4-methylphenyl)-4′,5′-diphenylspiro-[1,3-benzodioxole-2,2′-pyrrol]-3′(1′H)-one (**3c**, $C_{29}H_{17}Cl_4NO_3$)

Yield 0.19 g (65%), mp 250–252°C, yellow crystals (*Et*OA*c*); ^{1}H NMR ($CDCl_3$): $\delta = 2.22$ (s, CH_3), 6.95 (s, 4*p*-Tolyl-H), 7.12–7.35 (m, 10Ph–H) ppm; ^{13}C NMR ($CDCl_3$): $\delta = 21.1$ (CH_3), 110.5 (C-2 = C-2′), 127.0, 128.2, 128.4, 128.5, 129.3, 129.6, 129.9, 131.1 (all aryl *C*H), 112.3, 112.7, 125.7, 128.8, 129.4, 132.2, 138.2, 143.5, 173.2, 188.4 (qu *C*) ppm; IR (KBr): $\bar{\nu} = 1706$ (CO), 1250, 1215, 1162, 1149, 1131, 1070, 1025 (C–O–C=C), and 909 (O–C–O) cm^{-1}; MS: $m/z = 569$ (M+), 363, 178, 91.

4,5,6,7-Tetrachloro-1′-(4-methoxyphenyl)-4′,5′-diphenylspiro-[1,3-benzodioxole-2,2′-pyrrol]-3′(1′H)-one (**3d**, $C_{29}H_{17}Cl_4NO_4$)

Yield 0.19 g (65%), mp 248–250°C, yellow crystals (*Et*OA*c*); ^{1}H NMR ($CDCl_3$): $\delta = 3.71$ (s, OCH_3), 6.67 (d, $J = 9.0$ Hz, 2*p*-Anisyl-H), 7.00 (d, $J = 9.0$ Hz, 2*p*-Anisyl-H), 7.13–7.35 (m, 10Phenyl-H) ppm; ^{13}C NMR ($CDCl_3$): $\delta = 55.3$ (OCH_3), 114.5, 127.0, 128.2, 128.5, 129.24, 129.6, 130.1, 131.1 (all aryl *C*H), 110.3, 112.2, 112.7 (C-2 = C-2′), 125.8, 127.2, 128.8, 129.3, 143.4, 159.2, 173.3, 188.4 (qu *C*) ppm; IR (KBr): $\bar{\nu} = 1710$ (CO) 1251, 1163, 1118, 1055, 1025 (C–O–C=C), and 909 (O–C–O) cm^{-1}; MS: $m/z = 585$ (M+), 379, 178.

3,4-Dichloro-7-methoxy-5-(4-methoxyphenyl)-5,10-dihydrophenazine-1,2-dione (**4**, $C_{20}H_{14}Cl_2N_2O_4$)

Yield 0.076 g (36%), mp 264–265°C, reddish brown crystals (*Et*OA*c*); ^{1}H NMR (*DMSO*-d_6): $\delta = 3.70$ (s, OCH_3), 3.89 (s, OCH_3), 6.23 (d, $J = 2.5$, H-6), 7.17 (d, $J = 8.9$ Hz, 2*p*-Anisyl-H), 7.23 (dd, $J = 8.9$, 2.5 Hz, H-8), 7.53 (d, $J = 8.9$ Hz, 2*p*-Anisyl-H), 8.03 (d, $J = 8.9$ Hz, H-9) ppm; ^{13}C NMR (*DMSO*-d_6): $\delta = 55.6$, 55.7 (2OCH_3), 99.2, 114.2, 114.5, 130.4, 131.3 (all aryl *C*H), 103.9, 130.1, 131.4, 132.4, 133.8, 139.8, 150.8, 160.1, 161.7, 170.2 (qu *C*) ppm; IR (KBr): $\bar{\nu} = 3250$ (NH), 1662 and 1632 (CO) cm^{-1}; MS: $m/z = 416$ (M+), 383, 381 (M+ – Cl), 366, 338.

Acknowledgements

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