

Heterocycles from 3,4,5,6-Tetrachloro-1,2-benzoquinone†

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Reactions of 3,4,5,6-tetrachloro-1,2-benzoquinone with active methylene derivatives, diethyl oxalate and diphenylacetylene, provided various novel heterocyclic derivatives.

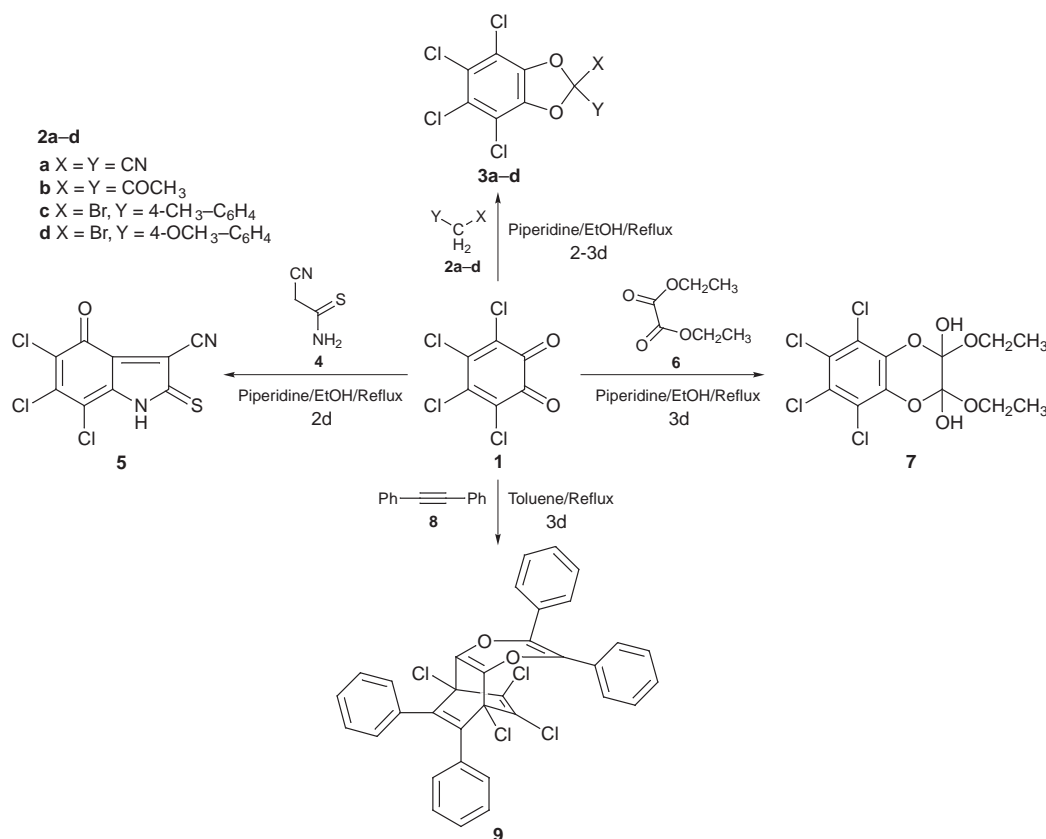
3,4,5,6-Tetrachloro-1,2-benzoquinone (*o*-CHL) has been extensively investigated in the context of Diels-Alder reactions,^{1–4} and considerable attention has recently been directed toward its other reactions. As a part of our programme to develop efficient procedures for the synthesis of heterocyclic compounds utilizing readily available reagents,^{5–9} reactions of (*o*-CHL) towards ethenyl[2.2]paracyclophanes¹⁰ and diimines¹¹ have been studied and its behavior has been found to vary from one substrate to another. The present study was of the reactions of *o*-CHL towards active methylene and α -dicarbonyl derivatives (*e.g.* diethyl oxalate) on the one hand and diphenylacetylene as a dienophile on the other.

The reaction of *o*-CHL (**1**) towards active methylene derivatives **2a–2d** proceeds in the presence of piperidine in refluxing ethanol. Chromatographic purification of the crude products yielded various benzo-1,3-dioxolane derivatives **3a–3d** in good yields (Scheme 1). The structures of these adducts were deduced largely from ¹³CNMR

and mass spectra as well as elemental analysis. For example, the ¹H NMR spectrum of compound **3a** did not reveal any proton signals, whereas the ¹³CNMR spectrum showed the O-C-O at δ 85.00.

The reaction of cyanothioacetamide (**4**) with compound **1** under the same reaction conditions as before gave product **5**. The mass spectrum and elemental analysis confirmed the molecular formula as C₉HCl₃N₂OS. The IR spectrum revealed the functional groups NH at ν_{\max} = 3420, CN at 2220, C=O, 1680 and C=S 1580 cm⁻¹. The ¹³C NMR spectrum confirmed the proposed structure (see Experimental section).

Refluxing compound **1** with diethyl oxalate (**6**) under the previous reaction conditions gave product **7**. The disappearance of the carbonyl groups on the one hand, and the appearance of the hydroxy groups on the other, indicated that nucleophilic addition of the hydroquinone form of *o*-CHL to the carbonyl groups led to the proposed structure **7**.



Scheme 1

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† This is a **Short Paper** as defined in the Instructions for Authors, Section 5.0 [see *J. Chem. Research (S)*, 1999, Issue 1]; there is therefore no corresponding material in *J. Chem. Research (M)*.

It was reported that *o*-CHL reacts with phenylacetylene to give a cycloadduct in which the diene *o*-CHL acts as a 4 π system.¹² Reaction of **1** with diphenylacetylene (**8**) in 1:1 ratio using toluene as a solvent gives the cycloadduct

9. The elemental analysis as well as the mass spectrum confirms its molecular formula as $C_{34}H_{20}Cl_4O_2$. The IR spectrum did not reveal any carbonyl group. The spectral data are in accord with the proposed structure in which two molecules of diphenylacetylene have reacted with *o*-CHL, at the diene the other at the α -dicarbonyl site, both via [2 + 4] cycloaddition. To our knowledge this type of bicycloaddition is hardly known for *o*-CHL. The former reaction was repeated using a 1 : 2 ratio of diphenylacetylene and *o*-CHL, giving the same cycloadduct **9** in about 97% yield.

Experimental

Melting points are uncorrected. The IR spectra were recorded on a Nicolet 320 FT-IR spectrometer, using KBr pellets, 1H and ^{13}C NMR spectra on a Bruker AM 400 (400.134 and 100.60 MHz) with chemical shifts relative to $SiMe_4$ as internal standard. TLC was carried out on silica gel PF₂₅₄ (Merck), 20 × 48 cm, using the solvents listed below. Zones were detected by quenching of indicator fluorescence upon exposure to 254 nm UV light. Elemental analyses were carried out by the Microanalysis center at Cairo University. Electron-impact mass spectra of the products were recorded using a Finnigan MAT 8430 spectrometer at 70 eV. Compound **1** and the starting materials were obtained commercially.

General Procedure for Synthesis of Compounds 3a–3d, 5 and 7.—To a stirred solution of *o*-CHL (**1**, 1 mmol) in 10 ml of absolute ethanol was added dropwise a solution of compounds **2a–2d**, **4** or **6** (1 mmol) in 20–30 ml of absolute ethanol. The mixture was then refluxed for 2–3 d (reaction progress followed by TLC). The precipitate formed was collected and dissolved in the minimum volume of acetone. The residue was subjected to PLC chromatography using toluene or toluene–ethyl acetate (5 : 1) as eluent. The pure products were recrystallized from appropriate solvents.

3a: 79% yield, mp 240–242 °C (ethanol); (Found: C, 34.70; Cl, 45.60; N, 8.90. $C_9Cl_4N_2O_2$ requires C, 34.87; Cl, 45.76; N, 9.04); δ_C (CDCl₃) 85.00 (O–C–O), 115.12 (CN), 126.10, 129.10, 130.45; ν_{max}/cm^{-1} 2220 (CN), 1110 (O–C–O); m/z 312 [M^{+4}] (28), 310 (62), 308 [M^{+4}] (100), 306 (38), 270 (34), 225 (20), 226 (48), 212 (38), 176 (22), 112 (12%).

3b: 60% yield, mp 210–212 °C (ethanol) (Found: C, 38.30; H, 1.90; Cl, 41.40. $C_{11}H_6Cl_4O_4$ requires C, 38.41; H, 1.76; Cl, 41.23%); δ_H (CDCl₃) 2.30 (s, 6H, COCH₃); δ_C (CDCl₃) 20.18 (CH₃), 80.19 (O–C–O), 125.12, 128.80, 129.00, 198.00 (CO); ν_{max}/cm^{-1} 2990–2890 (Aliph. CH), 1700 (C=O) m/z 346 [M^{+4}] (22), 344 (58), 342 [M^{+4}] (100), 340 (28), 305 (46), 266 (18), 248 (22), 216 (12), 170 (14), 76 (22%).

3c: 70% yield, mp 180–182 °C (acetonitrile) (Found: C, 39.10; H, 1.50; Cl, 33.18. $C_{14}H_7BrCl_4O_2$ requires C, 39.20; H, 1.64; Cl, 33.07%); δ_H (CDCl₃) 2.50 (s, 3H, CH₃), 7.29 (dd, 2H, Ar H, $J = 10.00$), 7.40 (dd, 2H, Ar H, $J = 9.90$ Hz); δ_C (CDCl₃) 20.00 (CH₃), 110.00 (O–C–O), 120.40, 120.56, 122.70, 122.70, 124.90, 125.12, 126.78, 127.00, 128.80, 128.95, 129.00, 129.19; ν_{max}/cm^{-1} 3100–3000 (Ar H), 2980–2965 (Aliph. CH), 1115 (O–C–O); m/z 432 [M^{+4}] (20), 430 (48), 428 [M^{+4}] (100), 424 (28), 390 (18), 354 (54), 264 (20), 248 (60), 216 (12), 170 (14), 92 (22), 76 (10%).

3d: 75% yield, mp 162–163 °C (acetonitrile) (Found: C, 37.60; H, 1.40; Cl, 31.70. $C_{14}H_7BrCl_4O_3$ requires C, 37.79; H, 1.59; Cl, 31.88%); δ_H (CDCl₃) 3.80 (s, 3H, OCH₃), 7.20 (dd, 2H, Ar H,

$J = 9.80$), 7.30 (dd, 2H, Ar H, $J = 9.90$); δ_C (CDCl₃) 50.00 (CH₃), 108.00 (O–C–O), 120.50, 120.62, 122.68, 123.00, 125.00, 125.10, 126.70, 126.90, 129.00, 129.10, 130.10, 130.19; ν_{max}/cm^{-1} 3090–3000 (Ar H), 2982–2970 (Aliph. CH), 1110 (O–C–O); m/z 448 [M^{+4}] (18), 446 (48), 444 [M^{+4}] (100), 406 (30), 418 (22), 264 (28), 248 (20), 208 (42), 172 (14), 135 (88), 107 (10%).

5: 60% yield, mp 160–162 °C (ethanol) (Found: C, 37.25; H, 0.40; Cl, 36.28; N, 9.50. $C_9HCl_3N_2OS$ requires C, 37.07; H, 0.35; Cl, 36.48; N, 9.61%); δ_C (CDCl₃) 192.00 (C=S) 180.10 (C=O) 160.65, 140.00, 139.88, 138.18, 128.18, 120.44 (Ar C), 117.00 (CN); ν_{max}/cm^{-1} 3420 (NH), 2220 (CN), 1680 (C=O) 1580 (C=S) m/z 294 [M^{+3}] (30), 293 (58), 291 [M^{+4}] (100), 290 (78), 289 (50), 260 (28), 224 (16), 212 (82), 178 (18), 160 (44), 147 (22), 121 (10), 113 (26), 86 (44%).

7: 80% yield, mp 280–282 °C (ethanol) (Found: C, 36.64; H, 3.20; Cl, 36.10. $C_{12}H_{12}Cl_4O_6$ requires C, 36.57; H, 3.07; Cl, 35.99%); δ_H (CDCl₃) 1.50 (t, 6H, 2CH₃), 3.85 (s, 2H, 2 OH), 4.01 (q, 4H, 2CH₂); ν_{max}/cm^{-1} 3500 (OH), 2980–2890 (Aliph. CH), 1110 (O–C–O); m/z 398 [M^{+4}] (30), 396 (60), 394 [M^{+4}] (100), 392 (60), 356 (16), 303 (28), 246 (80), 211 (42), 174 (28), 89 (58%).

Synthesis of Compound 9.—To a refluxing stirred solution of diphenylacetylene (**8**) (2 mmol) in 50 ml of dry toluene, a solution of compound **1** (1 mmol) in 25 ml dry toluene was added with stirring during 1 h. A colorless precipitate began to be formed and increased with time of refluxing. After refluxing the mixture for 3 d the colorless precipitate was collected (*i.e.* the reaction was monitored by TLC till disappearance of the starting materials), washed several times with hot toluene, dried and recrystallized from DMF to give **9** in 97% yield, mp > 300 °C (Found: C, 67.64; H, 3.28; Cl, 23.34. $C_{17}H_{10}Cl_2O$ requires C, 67.79; H, 3.35; Cl, 23.55%); δ_H (DMSO-*d*₆) 6.95–8.30 (m, 20H, Ar H); ν_{max}/cm^{-1} 3020–2980 (Ar H), 1560 (C=C); m/z 606 [M^{+4}] (28), 604 (56), 602 [M^{+4}] (100), 600 (60), 558 (30), 532 (38), 498 (80), 462 (16), 440 (18), 285 (10), 255 (8), 220 (14), 205 (8), 105 (24%).

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