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1,3-Dipolar Cycloaddition Reactions of Nitrile-N-oxides with *o*-Benzoquinones[#]

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Abstract

Di- and tri-substituted *o*-benzoquinones on reaction with nitrile N- oxides afforded novel mono spirodioxazole derivatives. The reaction of monosubstituted *o*-benzoquinones with stable nitrile oxides resulted in the formation of bis adducts.

Key words: o-Benzoquinones, nitrile oxide, dipolar cycloaddition, spirodioxazoles

o-Benzoquinones are unique conjugated 1,2-diones [1] that can exhibit diverse cycloaddition modes, participating either as carbodienes, heterodienes, dienophiles or heterodienophiles [2-10]. The presence of two potential dipolarophilic functionalities *viz.*, C=C and C=O, renders *o*-quinones very interesting from the vantage point of dipolar cycloaddition. Although dipolar cycloaddition reactions of *o*-benzoquinones can conceivably lead to novel heterocyclic compounds, there has been very little work on their reaction with various dipoles. There are isolated reports on the reaction of diazomethane [11] and certain mesoionic compounds [12] with *o*-benzoquinones. In addition there are sketchy investigations of the dipolar cycloadditions of nitrile-N-oxides with *o*-bromanil as well as unsubstituted *o*-benzoquinone [13a], phenanthrene-9,10-quinone and 1,2-naphthoquinone [13b]. It may be pointed out that in these cases, the products have not been characterized rigorously. Against this background, and in the context of our sustained interest in the cycloaddition reactions of *o*-quinones, we have undertaken an investigation of their 1,3-dipolar cycloaddition with nitrile N-oxides. A preliminary report of the work has been published [14] and the details of our expanded investigations are presented here.

[#] Dedicated with best regards to Dr. Lantz S. Crawley.

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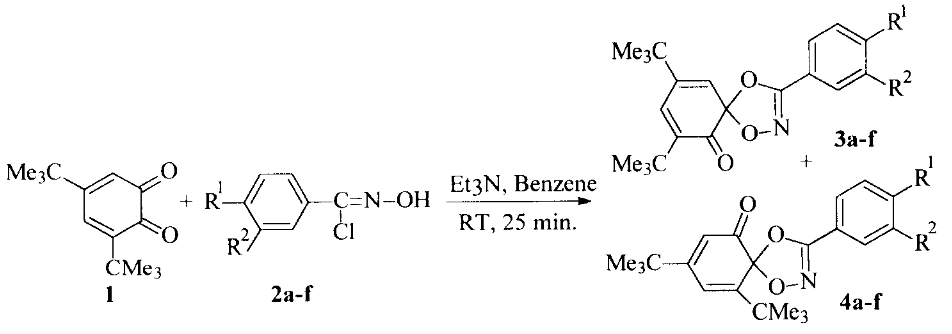
Results and discussion

3,5-Di-*tert*-butyl-1,2-benzoquinone **1** on treatment with 4-methyl benzohydroximoyl chloride **2a** and triethylamine afforded a mixture of yellow crystalline products in 80% yield (Scheme 1).



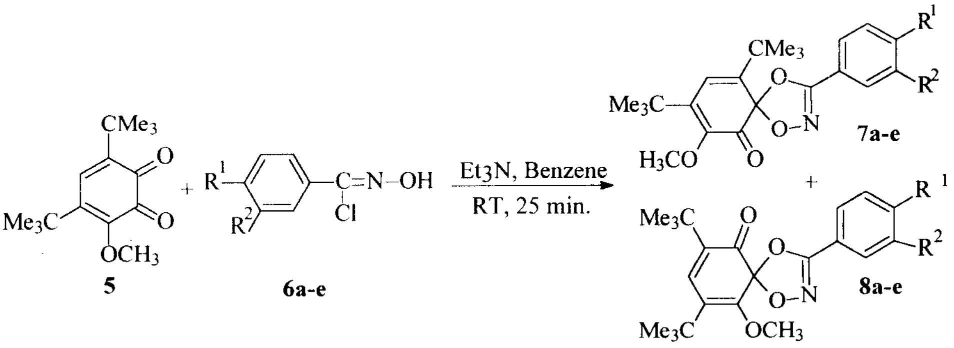
a. $R^1 = CH_3$; $R^2 = H$; **3a**:**4a** (3:1); 80%; b. $R^1 = OCH_3$; $R^2 = H$; **3b**:**4b** (1:1); 100%; c. $R^1 = R^2 = OCH_3$. **3c**:**4c** (1:1); 99%; d. $R^1 = Cl$; $R^2 = H$; **3d**:**4d** (1.6:1); 83%; e. $R^1 = H$; $R^2 = Cl$; **3e**:**4e** (2:1); 100%; f. $R^1 = R^2 = H$; **3f**:**4f** (1:1); 99%

Scheme 1

The products **3a** and **4a** were isolated as yellow solids after chromatography. Their structures were established by spectral analysis, including two doublet ^1H NMR spectroscopic signals at low field typical of 3,5-di-*tert*-butyl-1,2-benzoquinone moiety and one resonance for carbonyl carbon in the ^{13}C NMR spectra. The formulae were confirmed by elemental analysis and finally by single crystal X-ray analysis of **4a**[14].

The experiment was repeated with various nitrile oxides and in all cases the reaction proceeded smoothly to afford the spirodioxazoles (Scheme 1).

Analogous reaction was observed with 3-methoxy-4,6-di-*tert*-butyl-1,2-benzoquinone **5** and different benzonitrile oxides **6a-e**. In all these cases, however, an inseparable mixture of regioisomers was obtained in 1:1 ratio. The results are summarized in Scheme 2.

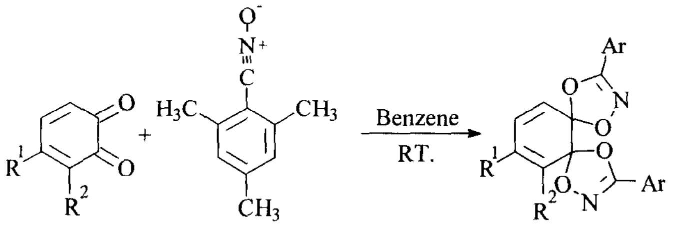


a. $R^1 = CH_3$, $R^2 = H$; **7a**:**8a** (1:1); 100%; b. $R^1 = H$; $R^2 = Cl$; **7b**:**8b** (1:1); 96%; c. $R^1 = H$; $R^2 = NO_2$. **7c**:**8c** (1:1); 97%; d. $R^1 = R^2 = OCH_3$; **7d**:**8d** (1: 1); 100%;e. $R^1 = Cl$; $R^2 = H$; **7e**:**8e** (1: 1); 98%.

Scheme 2

The products were isolated as mixtures after column chromatography. Their structures were established by spectral analysis, the ratio of isomers (1:1) was obtained from the integration of methoxy proton signals which appeared as singlets. There was one resonance each for carbonyl carbon and C=N. Most of the other carbon atoms presented twin signals representing the two isomers. The formulae assigned were supported by satisfactory elemental analysis.

3-Methoxy-1,2-benzoquinone **9a**, 4-*tert*-butyl-1,2-benzoquinone **9b** and 4-methyl-1,2-benzoquinone **9c** on reaction with the nitrile oxides **6a-e** gave complex mixtures. However **9a-c** afforded isolable products with mesityl nitrile oxide **10**. For example, 3-methoxy-1,2-benzoquinone **9a**, on treatment with **10** afforded a yellow semisolid in 59% yield (Scheme 3), whose structure was assigned as **11a** by spectroscopic analysis. Similarly the structures of **11b** and **c** were established by spectral and elemental analysis.

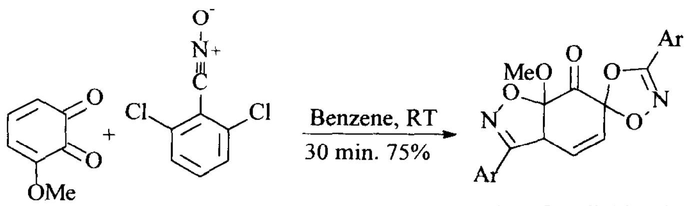


9a-c **10** **11a-c** Ar = Mesityl-

a. $R^1 = H$; $R^2 = OCH_3$; 30 min; 59%; b. $R^1 = CMe_3$; $R^2 = H$; 15 min; 69%; c. $R^1 = CH_3$; $R^2 = H$; 30 min; 49%.

Scheme 3

The reaction of 3-methoxy-1,2-benzoquinone **9a** with 2,6-dichlorobenzonitrile oxide **12** afforded a pale yellow crystalline solid in 75% yield (Scheme 4), whose structure was assigned as **13a** by spectral and elemental analysis.

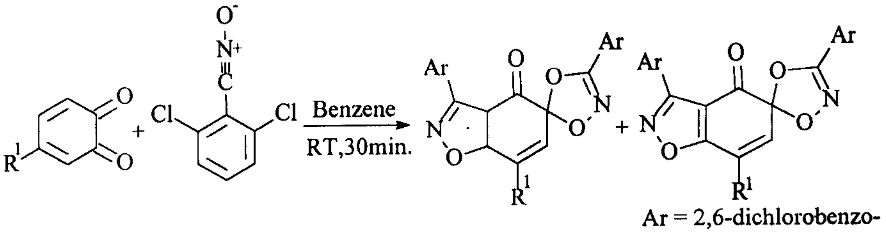


Ar = 2,6-dichlorobenzo-

9a **12** **13a**

Scheme 4

The reaction of 4-*tert*-butyl-1,2-benzoquinone **9b** and 3-methyl-1,2-benzoquinone **9c** with 2,6-dichlorobenzonitrile oxide **12** afforded products resulting from addition to both C=C and C=O. For instance, treatment of 4-*tert*-butyl-1,2-benzoquinone **9b** with **12** afforded two products in 59% yield and these were assigned structures **14b** and **15b** based on spectral analysis (Scheme 5).

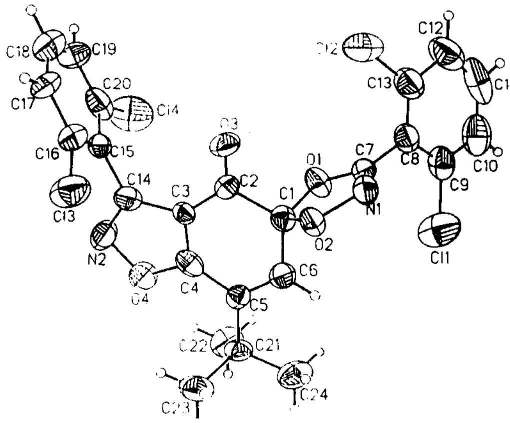


9b,c **12** **14b,c** **15b,c**

b. $R^1 = CMe_3$; 59% (2.5:1); c. $R^1 = CH_3$; 80% (4.3:1)

Scheme 5

The formulae assigned were confirmed by elemental analysis and finally by single crystal X-ray analysis of **14b**.



X-ray structure of **14b**

In summary, di- and tri-substituted *o*-benzoquinones form mixtures of mono spirodioxazoles by addition of aryl nitrile oxides to the carbonyl group. The preferential addition to the carbonyl group may be attributed to the steric hindrance imparted by the substituents on the quinone. In the case of mono substituted 1,2-benzoquinones, mesityl nitrile oxide forms bis spirodioxazoles, while 2,6-dichlorobenzonitrile oxide affords bis adducts by participation of C=C and C=O bonds. This difference in reactivity may be attributed to electronic effects of the substituents on the nitrile oxide. It is noteworthy that the mono spirodioxazole formation may be viewed as a means to obtain partially protected *o*-benzoquinones.

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Experimental Details

All reactions were carried out in oven dried glass ware (120 °C) under an atmosphere of argon. Analytical thin layer chromatography was performed on silica gel TLC plates. Purification by gravity column chromatography was carried out using silica gel (100-200 mesh). Mixtures of ethyl acetate and hexane were used as eluent. IR spectra were run on a Perkin-Elmer Model 882 and Nicolet (impact 400D FT-IR) spectrophotometers. NMR spectra were obtained using chloroform-d as solvent. Chemical shifts are given in δ scale with TMS as internal reference. Benzonitrile oxides were prepared according to the literature procedures [15-16].

Spirodioxazoles **3a** and **4a**

4-Methyl benzohydroximoyl chloride (0.250 g, 1.5 mmol) in benzene (10 mL) was added to a solution of 3,5-di-*tert*-butyl-1,2-benzoquinone **1** (0.220 g, 1 mmol) and triethylamine (0.152 g, 1.5 mmol) in benzene (5 mL) and stirred at room temperature for 25 min. The reaction mixture was filtered to remove triethylamine hydrochloride and the solvent was evaporated *in vacuo*. The residue was chromatographed on a silica gel column (1% and 2% ethyl acetate-hexane) afforded **3a** (0.212 g, 60%) and **4a** (0.071 g, 20%) as yellow crystalline solids (m. p. 116-118 °C and 120-122 °C respectively).

Data for **3a**

IR (KBr) 2969, 1699, 1631, 1521, 1483, 1465, 1371, 1329, 1277, 1249, 1085, 1015, 936, 891, 818 cm^{-1}. ^1H NMR δ 7.48 (Ar, 4H), 6.85 (d, J = 2.4 Hz, 1H), 6.05 (d, J = 2.3 Hz, 1H), 2.40 (s, 3H), 1.25 (s, 9H), 1.15 (s, 9H). ^{13}C NMR δ 192.90, 159.70, 150.45, 143.35, 142.04, 134.25, 129.27, 127.00, 121.51, 119.66, 102.53, 35.02, 34.51, 29.08, 27.98, 21.50. Anal. calcd for $C_{22}H_{27}NO_3$: C 74.76%, H 7.70%, N 3.96%. Found: C 74.85%, H 7.68%, N 3.85%.

Data for **4a**

IR (KBr) 2979, 1685, 1631, 1485, 1473, 1351, 1189, 1119, 1092, 830, 659 cm^{-1}. ^1H NMR δ 7.51 (Ar, 4H), 6.50 (d, J = 1.7 Hz, 1H), 5.90 (d, J = 1.7 Hz, 1H), 2.40 (s, 3H), 1.30 (s, 9H), 1.15 (s, 9H). ^{13}C NMR δ 193.41, 163.79, 159.76, 151.17, 142.21, 129.36, 127.03, 125.27, 119.63, 115.39, 104.29, 36.93, 35.91, 29.92, 27.89, 21.53. Anal. calcd for $C_{22}H_{27}NO_3$: C 74.76%, H 7.70%, N 3.96%. Found: C 74.68%, H 7.68%, N 3.92%.

Spirodioxazoles **3b** and **4b**

Reaction of **1** (0.220 g, 1.0 mmol) with **2b** generated from 4-methoxy benzohydroximoyl chloride (0.279 g, 1.5 mmol), as described earlier yielded after recrystallisation from hexane **3b** (0.185 g, 50%) and **4b** (0.184 g, 50%) as yellow crystalline solids (m. p. 128-130 °C and 156-158 °C respectively).

Data for **3b**

IR (KBr) 2971, 2880, 1700, 1632, 1614, 1518, 1466, 1428, 1372, 1354, 1260, 1177, 1140, 1085, 936, 839 cm^{-1}. ^{1}H NMR δ 7.75 (Ar, 2H), 6.91 (Ar, 2H), 6.83 (d, J = 1.7 Hz, 1H), 6.03 (d, J = 1.76 Hz, 1H), 3.83 (s, 3H), 1.25 (s, 9H), 1.18 (s, 9H). ^{13}C NMR δ 192.86, 162.19, 159.48, 150.33, 143.35, 134.08, 128.81, 121.60, 114. 82, 114.67, 102.40, 55.25, 35.06, 34.56, 29.13, 28.05. Anal. calcd for $C_{22}H_{27}NO_4$: C 71.52%, H 7.37%, N 3.79%. Found: C 71.61%, H 7.33%, N 3.82%.

Data for **4b**

IR (KBr) 2978, 2880, 1688, 1630, 1611, 1520, 1463, 1350, 1311, 1258, 1182, 1123, 1093, 1029, 986, 860 cm^{-1}. ^{1}H NMR δ 7.78 (Ar, 2H), 6.93 (Ar, 2H), 6.47 (d, J = 1.4 Hz, 1H), 5.87 (d, J = 1.5 Hz, 1H), 3.83 (s, 3H), 1.27 (s, 9H), 1.20 (s, 9H). ^{13}C NMR δ 193.33, 163.50, 159.50, 151.19, 130.16, 129.67, 128.84, 125.12, 115.47, 114.76, 104.15, 55.27, 36.94, 35.92, 29.96, 27.94. Anal. calcd for $C_{22}H_{27}NO_4$: C 71.52%, H 7.37%, N 3.79%. Found: C 71.18%, H 7.21%, N 3.71%.

Spirodioxazoles **3c** and **4c**

Reaction of **1** (0.088 g, 0.40 mmol) with **2c** generated from 3,4-dimethoxy benzohydroximoyl chloride (0.120 g, 0.60 mmol), as described earlier yielded after recrystallisation from hexane **3c** (0.080 g, 50%) and **4c** (0.079 g, 49%) as yellow crystals (m. p. 110-112 °C and 166-168 °C respectively).

Data for **3c**

IR (KBr) 2971, 2914, 1690, 1613, 1582, 1523, 1468, 1432, 1372, 1277, 1139, 1098, 1031, 947 cm^{-1}. ^{1}H NMR δ 7.36 (Ar, 2H), 6.90 (Ar, 1H), 6.85 (d, J = 2.3 Hz, 1H), 6.05 (d, J = 2.3 Hz, 1H), 3.92 (s, 3H), 3.91 (s, 3H), 1.25 (s, 9H), 1.18 (s, 9H). ^{13}C NMR δ 193.00, 159.70, 151.95, 150.57, 148.99, 143.40, 134.30, 121.46, 120.77, 114.92, 110.77, 109.56, 102.59, 55.97, 35.10, 34.58, 29.11, 28.04. Anal. calcd for $C_{23}H_{29}NO_5$: C 69.15%, H 7.32%, N 3.51%. Found: C 69.21%, H 7.34%, N 3.54%.

Data for **4c**

IR (KBr) 2960, 2913, 1693, 1633, 1610, 1586, 1521, 1465, 1427, 1369, 1338, 1267, 1191, 1122, 1026, 925 cm^{-1}. ^{1}H NMR δ 7.36 (Ar, 2H), 6.91 (Ar, 1H), 6.50 (d, J = 1.7 Hz, 1H), 5.90 (d, J = 1.7 Hz, 1H), 3.93 (s, 3H), 3.91 (s, 3H), 1.28 (s, 9H), 1.20 (s, 9H). ^{13}C NMR δ 193.59, 163.85, 159.70, 152.13, 151.18, 149.07, 125.35, 120.77, 115.50, 114.86,110.80, 109.56, 104.07, 56.00, 37.00, 35.99, 30.00, 27.95. Anal. calcd for $C_{23}H_{29}NO_5$: C 69.15%, H 7.32%, N 3.51%. Found: C 69.18%, H 7.29%, N 3.52%.

Spirodioxazoles **3d** and **4d**

Reaction of **1** (0.220 g, 1.0 mmol) with **2d** generated from 4-chloro benzohydroximoyl chloride (0.224 g, 1.5 mmol), as described earlier yielded **3d** (0.230 g, 62%) and **4d** (0.080 g, 21%) as yellow crystalline solids (m. p. 150-152 °C and 146-140 °C respectively).

Data for **3d**

IR (KBr) 2971, 2880, 1699, 1634, 1603, 1496, 1409, 1370, 1327, 1277, 1249, 1142, 1092, 1013, 988, 937, 837 cm^{-1}. ^{1}H NMR δ 7.59 (Ar, 4H), 6.85 (d, J = 2.3 Hz, 1H), 6.04 (d, J = 2.3 Hz, 1H), 1.25 (s, 9H), 1.18 (s, 9H). ^{13}C NMR δ 193.00, 159.70, 150.95, 143.40, 137.82, 134.48, 129.03, 128.40, 121.20, 121.11, 102.00, 35.19, 34.61, 29.14, 28.04. Anal. calcd for $C_{21}H_{24}NO_3Cl$: C 67.46%, H 6.47%, N 3.75%. Found: C 67.51%, H 6.49%, N 3.78%.

Data for **4d**

IR (KBr) 2962, 2874, 1694, 1640, 1600, 1485, 1357, 1270, 1196, 1101, 1000, 838, 663 cm^{-1}. ^{1}H NMR δ 7.61 (Ar, 4H), 6.50 (d, J = 1.7 Hz, 1H), 5.90 (d, J = 1.7 Hz, 1H), 1.27 (s, 9H), 1.20 (s, 9H). ^{13}C NMR δ 193.00, 164.74, 159.79, 151.58, 138.71, 129.84, 129.12, 126.30, 121.72, 116.16, 104.44, 37.69, 36.74, 30.66, 28.65. Anal. calcd for $C_{21}H_{24}NO_3Cl$: C 67.46%, H 6.47, N 3.75. Found: C 67.22%, H 6.55%, N 3.52%.

Spirodioxazoles **3e** and **4e**

Reaction of **1** (0.220 g, 1.0 mmol) with **2e** generated from 3-chloro benzohydroximoyl chloride (0.284 g, 1.5 mmol), as described earlier yielded **3e** (0.235 g, 63%) and **4e** (0.139 g, 37%) as yellow crystalline solids (m. p.125-127°C and 129-131°C respectively).

Data for **3e**

IR (KBr) 2967, 2877, 1696, 1657, 1575, 1487, 1369, 1327, 1279, 1251, 1140, 1114, 1072, 941, 892 cm^{-1}. ^{1}H NMR δ 7.58 (Ar, 4H), 6.86 (d, J = 2.3 Hz, 1H), 6.04 (d, J = 2.3 Hz, 1H), 1.25 (s, 9H), 1.18 (s, 9H). ^{13}C NMR δ 193.00, 159.60, 151.03, 143.40, 134.79, 134.50, 131.68, 130.01, 127.10, 125.20, 124.28, 121.11, 102.05, 35.19, 34.61, 29.14, 28.04. Anal. calcd for $C_{21}H_{24}NO_3Cl$: C 67.46%, H 6.47%, N 3.75%. Found: C 67.55%, H 6.50%, N 3.72%.

Data for **4e**

IR (KBr) 2970, 2878, 1695, 1644, 1577, 1485, 1354, 1267, 1192, 1120, 1075, 997, 922, 811 cm^{-1}. ^{1}H NMR δ 7.60 (Ar, 4H), 6.51 (d, J = 1.7 Hz, 1H), 5.90 (d, J = 1.7 Hz, 1H), 1.27 (s, 9H), 1.20 (s, 9H). ^{13}C NMR δ 193.16, 164.08, 158.81, 150.83, 134.88, 131.82, 130.10, 127.10, 125.69, 125.23, 124.22, 115.44, 104.44, 37.03, 36.08, 30.00, 27.95. Anal. calcd for $C_{21}H_{24}NO_3Cl$: C 67.46%, H 6.47%, N 3.75%. Found: C 67.55%, H 6.44%, N 3.72%.

Spirodioxazoles **3f** and **4f**

Reaction of **1** (0.100 g, 0.45 mmol) with **2f** generated from benzohydroximoyl chloride (0.079 g, 0.50 mmol), as described earlier yielded **3f** (0.083 g, 49%) and **4f** (0.085 g, 50%) as yellow crystalline solids (m. p. 144-146 °C and 120-122 °C respectively).

Data for **3f**

IR (KBr) 2971, 2877, 1700, 1634, 1511, 1451, 1362, 1325, 1277, 1249, 1140, 1090, 1014, 938, 890 cm^{-1}. ^{1}H NMR δ 7.83 (Ar, 2H), 7.46 (Ar, 3H), 6.85 (d, J = 2.3 Hz, 1H), 6.05 (d, J = 2.3 Hz, 1H), 1.25 (s, 9H), 1.18 (s, 9H). ^{13}C NMR δ 193.00, 159.80, 151.60, 144.01, 134.45, 131.65, 128.66, 127.16, 122.30, 121.46, 102.50, 35.89, 35.60, 29.14, 28.07. Mass (EIMS): 339 (M$^+$), 309 (M-NO), 283, 222, 207, 149, 119, 105, 91, 57. Anal. calcd for $C_{21}H_{25}NO_3$: C 74.31%, H 7.42%, N 4.13%. Found: C 74.38%, H 7.40%, N 4.15%.

Data for **4f**

IR (KBr) 2976, 2880, 1688, 1630, 1583, 1475, 1454, 1349, 1249, 1184, 1120, 1092, 988, 922, 816 cm^{-1}. ^{1}H NMR δ 7.86 (Ar, 2H), 7.48 (Ar, 3H), 6.50 (d, J = 1.7 Hz, 1H), 5.90 (d, J = 1.7 Hz, 1H), 1.28 (s, 9H), 1.20 (s, 9H). ^{13}C NMR δ 193.00, 164.50, 159.90, 151.50, 131.77, 128.71, 127.13, 125.40, 122.10, 115.47, 104.60, 37.10, 36.20, 29.97, 27.95. Mass (EIMS): 339 (M$^+$), 309 (M-NO), 283, 222, 207, 164, 149, 119, 105, 91, 57. Anal. calcd for $C_{21}H_{25}NO_3$: C 74.31%, H 7.42%, N 4.13%. Found: C 74.35%, H 7.39%, N 4.18%.

Spirodioxazoles **7a** and **8a**

Reaction of 3-methoxy-4,6-di-*tert*-butyl-1,2-benzoquinone **5** (0.100 g, 0.40 mmol) with **6a** generated from 4-methyl benzohydroximoyl chloride (0.135 g, 0.80 mmol), as described earlier afforded inseparable mixture of isomers **7a** and **8a** (0.171 g, 100%) as pale yellow solid. IR (film) 2962, 2874, 1694, 1634, 1573, 1472, 1351, 1276, 1188, 1087, 952, 878, 824 cm^{-1}. ^{1}H NMR δ 7.49 (Ar, 8H), 6.98 (s, 1H), 6.40 (s, 1H), 3.75 (s, 3H), 3.72 (s, 3H), 2.39 (s, 3H), 2.29 (s, 3H), 1.29 (s, 18H), 1.23 (s, 18H). ^{13}C NMR δ 191.29, 190.09, 159.94, 159.77, 149.11, 144.67, 142.17, 138.38, 129.38, 129.35, 127.09, 127.04, 119.57, 119.41, 105.91, 103.03, 60.00, 58.44, 36.62, 35.55, 34.86, 34.18, 29.81, 29.66, 29.22, 28.95, 21.55, 21.43. Anal. calcd for $C_{23}H_{29}NO_4$: C 72.04%, H 7.62%, N 3.65%. Found: C 72.18%, H 7.45%, N 3.49%.

Spirodioxazoles **7b** and **8b**

Reaction of 3-methoxy-4,6-di-*tert*-butyl-1,2-benzoquinone **5** (0.09 g, 0.36 mmol) with **6b** generated from 3-chloro benzohydroximoyl chloride (0.100 g, 0.72 mmol), as described earlier afforded inseparable mixture of isomers **7b** and **8b** (0.171 g, 100%) as pale yellow solid._IR (film) 2960,1697, 1637, 1571, 1483, 1439, 1357, 1269, 1077, 1033, 956, 884 cm^{-1}. ^{1}H NMR δ 7.60 (Ar, 8H), 7.02 (s, 1H), 6.45 (s, 1H), 3.79 (s, 3H), 3.72 (s, 3H), 1.31 (s, 18H), 1.24 (s, 18H). ^{13}C NMR δ 191.02, 189.89, 158.86, 158.68, 144.69, 144.18, 138.69, 134.73, 132.01, 131.71, 129.98, 127.98, 126.88, 126.40, 125.03, 123.93, 123.78, 107.50, 106.00, 60.29, 58.47, 36.51, 35.52, 34.93, 34.21, 29.68, 29.47, 29.05, 28.90. Anal. calcd for $C_{22}H_{26}NO_4Cl$: C 65.42%, H 6.49%, N 3.47%. Found: C 65.26%, H 6.67%, N 3.35%.

Spirodioxazoles **7c** and **8c**

Reaction of 3-methoxy-4,6-di-*tert*-butyl-1,2-benzoquinone **5** (0.100 g, 0.40 mmol) with **6c** generated from 3-nitro benzohydroximoyl chloride (0.160 g, 0.80 mmol), as described earlier afforded inseparable mixture of **7c** and **8c** (0.161 g, 97%) as yellow solid. IR (film) 2962, 1694, 1634, 1546, 1479, 1351, 1270, 1128, 1034, 953, 879, 744 cm^{-1}. ^{1}H NMR δ 8.70 (s, 2H), 8.39 (d, 2H), 8.21 (d, 2H), 7.71 (m, 2H), 7.04 (s, 1H), 6.48 (s, 1H), 3.78 (s, 3H), 3.73 (s, 3H), 1.31 (s, 18H), 1.25 (s, 18H). ^{13}C NMR δ 191.02, 189.87, 158.51, 158.29, 148.46, 145.50, 145.01, 144.05, 139.09, 132.59, 130.17, 130.12, 126.97, 126.29, 122.02, 106.85, 105.50, 60.76, 58.74, 36.72, 35.51, 34.89, 34.42, 29.89, 29.64, 29.40, 29.23. Anal. calcd for $C_{22}H_{26}N_2O_6$: C 63.76%, H 6.32%, N 6.76%. Found: C 63.38%, H 6.53%, N 6.58%.

Spirodioxazoles **7d** and **8d**

Reaction of 3-methoxy-4,6-di-*tert*-butyl-1,2-benzoquinone **5** (0.100 g, 0.40 mmol) with **6d** generated from 3,4-dimethoxy benzohydroximoyl chloride (0.170 g, 0.80 mmol), as described earlier afforded inseparable mixture of regioisomers **7d** and **8d** (0.171 g, 100%) as pale yellow solid. IR (KBr) 2969, 1694, 1640, 1607, 1510, 1472, 1378, 1344, 1270, 1148, 1034, 960, 879 cm^{-1}. ^{1}H NMR δ 7.26 (Ar, 6H), 7.03 (s, 1H), 6.42 (s, 1H), 3.95 (s, 6H), 3.80 (s, 3H), 3.74 (s, 3H), 1.31 (s, 18H), 1.25 (s, 18H). ^{13}C NMR δ 191.04, 189.86, 160.05, 159.80, 152.12, 149.02, 148.87, 144.78, 144.63, 144.54, 129.95, 126.07, 120.73, 114.62, 110.77, 109.43, 60.08, 58.50, 55.87, 36.57, 35.52, 34.90, 34.18, 29.74, 29.56, 29.11, 28.99. Anal. calcd for $C_{24}H_{31}NO_6$: C 67.11%, H 7.27%, N 3.26%. Found: C 66.98%, H 7.46%, N 3.10%.

Spirodioxazoles 7e and **8e**

Reaction of 3-methoxy-4,6-di-*tert*-butyl-1,2-benzoquinone **5** (0.135 g, 0.54 mmol) with **6e** generated from 4-Chloro benzohydroximoyl chloride (0.208 g, 1.08 mmol), as described earlier afforded inseparable mixture of isomers **7e** and **8e** (0.212 g, 98%) as yellow solid. IR (film) 2969, 2874, 1694, 1634, 1607, 1566, 1492, 1364, 1310, 1270, 1094, 1061, 1020, 946, 838 cm^{-1}. ^{1}H NMR δ 7.65 (Ar, 8H), 7.02 (s, 1H), 6.41 (s, 1H), 3.75 (s, 3H), 3.68 (s, 3H), 1.29 (s, 18H), 1.25 (s, 18H). ^{13}C NMR δ 191.20, 189.98, 159.24, 158.84, 150.41, 145.68, 138.81, 138.66, 137.92, 131.98, 128.97, 128.31, 126.30, 121.72, 120.58, 107.40, 106.82, 60.29, 58.50, 36.44, 35.60, 34.96, 34.24, 29.64, 29.50, 29.03, 28.93. Anal. calcd for $C_{22}H_{26}NO_4Cl$: C 65.42%, H 6.49%, N 3.47%. Found: C 65.29%, H 6.72%, N 3.42%.

Bis-spirodioxazole **11a**

To a solution of 3-methoxy catechol (0.140 g, 1.00 mmol) and mesityl nitrile oxide **10** (0.405 g, 2.5 mmol) in benzene (10 mL), silver carbonate (0.690 g, 2.5 mmol) was added and stirred at room temperature for 30 min. The inorganic material was removed by filtering through a short celite column. The filtrate was then concentrated *in vacuo* and the residue was charged on a silica gel column. Elution with 30% ethyl acetate in hexane afforded **11a** (0.270g, 59%) as a yellow semisolid. IR (film) 2968, 2917, 2866, 1667, 1616, 1452, 1327, 1248, 1073, 1022, 903, 852 cm^{-1}. ^{1}H NMR δ 6.92 (Ar, 4H), 5.62 (m. 1H), 5.35 (brs, 1H), 4.88 (m, 1H), 3.88 (s, 3H), 2.27 (m, 18H). ^{13}C NMR δ 158.95, 158.04, 143.29, 141.23, 140.96, 140.75, 138.99, 138.90, 138.81, 129.77, 128.31, 116.85, 105.80, 104.06, 55.45, 20.97, 19.53, 19.35. Anal. calcd for $C_{27}H_{28}N_2O_5$: C 70.42%, H 6.13%, N 6.08%. Found: C 70.64%, H 6.55%, N 5.98%.

Bis-spirodioxazole **11b**

A solution of 4-*tert*-butyl-1,2-benzoquinone (0.164 g, 1 mmol) and mesityl nitrile oxide **10** (0.405 g, 2.5 mmol) in benzene (15 mL) was stirred at room temperature for 15 min. The reaction mixture was concentrated *in vacuo* and the residue on silica gel column chromatography (5% ethyl acetate in hexane) afforded **11b** (0.335 g, 69%) as a pale yellow semisolid. IR (film) 2969, 2928, 2874, 1635, 1613, 1452, 1378, 1324, 1263, 1081, 1007, 919, 858 cm^{-1}. ^{1}H NMR δ 6.86 (Ar, 4H), 6.40 (m, 1H), 6.11 (m, 1H), 5.80 (brs, 1H), 2.24 (m, 18H), 1.16 (s, 9H). ^{13}C NMR δ 158.50, 157.90, 141.37, 140.67, 138.96, 138.71, 130.61, 128.62, 128.49, 126.80, 124.38, 124.01, 118.19, 110.81, 109.51, 34.51, 27.98, 21.21, 19.90, 19.71. Anal. calcd for $C_{30}H_{34}N_2O_4$: C 74.05%, H 7.04%, N 5.76%. Found: C 73.89%, H 7.31%, N 5.46%.

Bis-spirodioxazole **11c**

Reaction of 4-methyl catechol **9c** (0.155 g, 1.25 mmol) and mesityl nitrile oxide **10,** as described earlier for **11a** afforded **11c** (0.273 g, 49%) as colorless solid. IR (film) 2969, 2928, 2854, 1620, 1445, 1324, 1216, 1175, 1142, 1074, 1020, 912, 858 cm^{-1}. ^{1}H NMR δ 6.71 (Ar, 4H), 5.85 (brs, 1H), 5.21 (brs, 1H), 4.83 (m, 1H), 2.10 (m, 21H). ^{13}C NMR δ 158.91, 158.29, 141.55, 140.33, 139.59, 139.50, 130.18, 129.14, 125.21, 122.68, 118.31, 109.80, 109.39, 22.30, 21.95, 21.87, 20.46. Anal. calcd for $C_{27}H_{28}N_2O_4$: C 72.95%, H 6.35%, N 6.30%. Found: C 72.49%, H 6.91%, N 6.59%.

Bisadduct **13a**

Reaction of 3-methoxy catechol **9a** (0.210 g, 1.5 mmol) and 2,6-dichloro benzonitrile oxide **12** (0.705 g, 3.75mmol) as described earlier afforded **13a** (0.574 g, 75%) as a yellow solid. (m. p. 203-205 °C). IR (KBr) 3063, 2942, 2854, 1721, 1640, 1566, 1431, 1303, 1263, 1209, 912, 784 cm^{-1}. ^{1}H NMR δ 7.29 (m, 6H), 5.91 (dd, J = 3.5 Hz, 8.89 Hz, 1H), 5.82 (d, J = 3.4 Hz, 1H), 4.97 (d, J = 8.9 Hz, 1H), 3.78 (s, 3H). ^{13}C NMR δ 180.00, 154.95, 151.68, 151.20, 136.38, 135.34, 135.10, 132.97, 131.48, 128.46, 128.19, 126.75, 121.00, 110.55, 107.11, 55.89, 55.59. Anal. calcd for $C_{21}H_9N_2O_5Cl_4$: C 49.15%, H 2.16%, N 5.46%, Cl 27.64%. Found: C 48.46%, H 2.63%, N 5.25%, Cl 28.07%.

Bis adducts **14b** and **15b**

Reaction of 4-*tert*-butyl-1,2-benzoquinone **9b** (0.164 g, 1.00 mmol) and 2,6-dichloro benzonitrile oxide **12,** (0.470 g, 2.5 mmol) as described earlier for **11b** afforded **14b** (0.226 g, 42%) and **15b** (0.091 g, 17%) as colorless solids.

Specral data for **14b**

IR (film) 2969, 2915, 2874, 1708, 1661, 1620, 1566, 1438, 1317, 1270, 1202, 1121, 885, 791,730 cm^{-1}. ^{1}H NMR δ 7.24 (m, 6H), 6.49 (brs, 1H), 6.01 (d, 1H), 5.06 (d, 1H), 1.39 (s, 9H). ^{13}C NMR δ 184.53, 165.80, 154.90, 151.75, 136.35, 132.83, 131.31, 128.45, 128.20, 126.27, 121.24, 106.67, 79.17, 55.28, 37.20, 30.06. Anal. calcd for $C_{24}H_{18}N_2O_4Cl_4$: C 53.36%, H 3.36%, N 5.19%, Cl 26.25%. Found: C 53.01%, H 3.78%, N 5.01%, Cl 25.97%.

Spectral data for **15b**

IR (KBr) 2975, 1721, 1573, 1458, 1445, 1317, 1202, 1135, 993, 946, 919, 879, 791, 737 cm^1. ^{1}H NMR 7.41 (Ar, 6H), 6.43 (s, 1H), 1.47 (s, 9H). ^{13}C NMR 182.85, 174.70, 155.00, 154.27, 142.20, 136.66, 133.06, 129.01, 128.36, 128.20, 125.41, 121.27, 103.95, 35.15, 28.73. Anal. calcd for $C_{24}H_{16}N_2O_4$: C 53.56%, H 3.00%, N 5.20%, Cl 26.35%. Found: C 53.45%, H 3.18%, N 5.08%, Cl 26.05%.

Crystal data for **14b** $C_{24}H_{16}N_2O_4Cl_4$, colorless crystalline solid, 0.28x0.20x0.14 mm., monoclinic, space group $P2_1$, Unit cell dimensions: a = 12.5823(2) Å. alpha = 90 °, b = 17.5486 (2) Å, beat = 95.635 (1)°, c = 12.9804 (2) Å, gamma = 90 °. R indices (all data) R1 = 0.1364, WR2 = 0.1960, Volume Z = 2852.24 (7) Å ^{3}, 2. Density (Calculated) = 1.253 Mg/m^3. F(000) = 1096; Absorption coefficient = 0.444 mm^{-1}.

Bis adducts **14c** and **15c**

Reaction of 3-methyl catechol **9c** (0.223 g, 1.8 mmol) and 2,6-dichloro benzonitrile oxide **12,** (1.00 g, 5.31 mmol) as described earlier for **13a** afforded **14c** (0.576 g, 65%) and **15c** (0.133 g, 15%) as colorless solids.

Spectral data for **14c**

IR (KBr) 3076, 2950, 2820, 1735, 1654, 1560, 1431, 1303, 1202, 1128, 1088, 939, 892, 784 cm^{-1}. ^{1}H NMR δ 7.22 (m, 6H), 6.31 (s, 1H), 5.63 (d, J = 9.0 Hz, 1H), 5.00 (d, J = 9.3 Hz, 1H), 2.25 (s, 3H). ^{13}C NMR δ 183.17, 155.81, 154.85, 151.79, 136.37, 132.84, 131.39, 128.19, 127.70, 121.20, 106.48, 80.45, 55.59, 21.01. Anal. calcd for $C_{21}H_{12}N_2O_4Cl_4$: C 50.63%, H 2.43%, N 5.62%, Cl 28.47%. Found: C 50.98%, H 2.74%, N 5.53%, Cl 28.20%.

Spectral data for **15c**

IR (KBr) 3083, 2955, 2921, 2854, 1728, 1600, 1458, 1452, 1384, 1330, 1209, 1148, 1094, 993, 784 cm^{-1}. ^{1}H NMR 7.44 (Ar, 6H), 6.46 (s, 1H), 2.39 (s, 3H). ^{13}C NMR 182.70, 174.79, 155.93, 154.24, 136.62, 131.99, 128.33, 128.26, 128.21,125.26,121.22, 103.96, 15.55. Anal. calcd for $C_{21}H_{10}N_2O_4Cl_4$: C 50.84%, H 2.03%, N 5.65%, Cl 28.58%. Found: C 51.02%, H 2.38%, N 5.45%, Cl 28.32%.

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