saturated NaCl solution. The organic layer was dried over $MgSO_4$, filtered, and concentrated in vacuo. The residue was purified by preparative TLC (acetonitrile:ethyl acetate = 1:2) to afford **31** (8.5 mg, 17%) as colorless prisms.

Alternative Synthesis of 31. To a solution of **33** (9.6 mg, 0.027 mmol) in THF–*tert*-butyl alcohol (10:1, 0.5 mL) was added butyllithium (1.55 M in hexane, 25 mL, 0.039 mmol) at −78 °C. The mixture was stirred at −78 °C for 30 min and was added to a solution of sodium (12 mg, 0.52 mmol) in liquid ammonium (1.5 mL) precooled to −78 °C, and the resulting mixture was stirred for 1 h. Powdered NH_4Cl was added to the mixture until the blue color disappeared. The solvents were removed under reduced pressure, and the residue was treated with water and 1 M HCl to adjust the pH to 3. The mixture was stirred for 30 min at room temperature and made alkaline (pH 8) with saturated $NaHCO_3$ solution. To the resulting mixture were added dichloromethane (2 mL) and benzyloxycarbonyl chloride (0.1 mL, 0.69 mmol). After the mixture was stirred at room temperature for 10 h, the dichloromethane layer was separated, and the aqueous layer was extracted with a 1:3 mixture of ethanol and chloroform. The combined organic phase was dried over Na_2SO_4, filtered, and concentrated in vacuo. The residue was purified by preparative TLC (acetonitrile:ethyl acetate = 1:2) to afford **31** (3.9 mg, 58%) as colorless prisms: mp 129–130 °C (ethyl acetate–hexane); R_f 0.39 (acetonitrile:ethyl acetate = 1:2); $[\alpha]^{20}_D$ +8.7° (*c* 0.55, $CHCl_3$) [lit.[26e] mp 128.5–129.5 °C and $[\alpha]_D$ +8.6° (*c* 0.9, $CHCl_3$); lit.[28] mp 127–128 °C and $[\alpha]_D$ +9° (*c* 0.93, $CHCl_3$)]; ^1H NMR (DMSO-d_6) δ 3.3–3.8 (m, 3 H), 4.77 (t, J = 4.5 Hz, 1 H), 4.88 (dd, J = 9.8, 4.5 Hz, 1 H), 5.06 (s, 2 H), 7.34 (s, 5 H), 7.73 (d, J = 9.8 Hz, 1 H), 8.19 (br s, 1 H); ^1H NMR (acetone-d_6) δ 2.78 (br s, 1 H), 3.6–4.1 (m, 3 H), 4.15 (br s, 1 H), 5.08 (dd, J = 10.5, 6.0 Hz, 1 H), 5.10 (s, 2 H), 6.68 (br d, J = 10.5 Hz, 1 H), 7.36 (s, 5 H); IR (KBr) 3450, 3300, 1755, (sh), 1705, 1555, 1270, 1070 cm^{-1}; IR ($CHCl_3$) 3430, 1765, 1720, 1515, 1320, 1225, 1055 cm^{-1}; MS *m/z* (rel intensity) 250 (M^+, 0), 207 (19), 146 (8), 116 (42), 99 (13), 91 (100). The spectral data of **31** were identical with those reported [^1H NMR in DMSO-d_6[24a] or acetone-d_6[28a] and IR (KBr)[26f] or ($CHCl_3$)[28a]]. Physical data of **31** listed in ref 28a: mp 127.0–128.0 °C, $[\alpha]^{20}_D$ +9° (*c* 0.9305, $CHCl_3$); IR ($CHCl_3$) 3420, 1764, 1715, 1510, 1318, 1220, 1060 cm^{-1}; ^1H NMR (acetone-d_6) δ 3.7, 4.2, 5.1, 6.8, 7.35; MS *m/z* (CI-isob) 251 (MH^+).

Supplementary Material Available: ^1H NMR spectra of all compounds for which elemental analyses were not obtained (30 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

Reaction of Pyrazole Addition to Quinones

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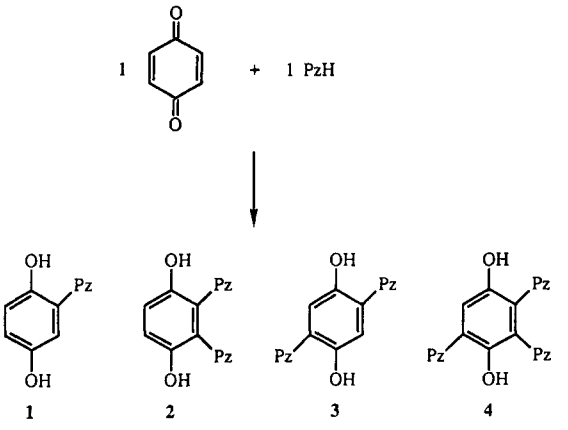
The reactions of pyrazole, 4-nitropyrazole, 3,5-dimethylpyrazole, and 4-chloro-3,5-dimethylpyrazole with 1,4-benzoquinone in dioxane have been analyzed. Mono- and 2,3-bis-adducts were obtained and only in the case of pyrazole was a 2,5-bis(pyrazol-1-yl)-1,4-dihydroxybenzene formed. Further oxidation of the mono- and bis-adducts with 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) afforded the quinones, which in turn added 1 mol of azole (pyrazole and imidazole) to yield tetrapyrazolylquinols. Nitration of the 2,3-bis(pyrazol-1-yl)- and 2,3-bis(3,5-dimethylpyrazol-1-yl)-1,4-dihydroxybenzenes has been performed to prepare the corresponding 4-nitropyrazolyl derivatives.

We have recently reported that some mono- and bis(pyrazol-1-yl)-1,4-dihydroxybenzenes, structurally related to 2-(2-hydroxy-5-methylphenyl)benzotriazole (Tinuvin P), exhibit excellent stability to light.[1] These compounds were easily prepared by addition reaction of pyrazoles to 1,4-benzoquinone in dioxane. Depending on the nature of the pyrazole, mono- and bis-adducts are obtained. This reaction was performed for the first time with 3,5-dimethylpyrazole and the single product obtained was erroneously identified as 2,5-bis(3,5-dimethylpyrazol-1-yl)-1,4-dihydroxybenzene.[2] We proved by X-ray diffraction analysis that the structure of this product is 2,3-bis(3,5-dimethylpyrazol-1-yl)-1,4-dihydroxybenzene.[1] Furthermore, a minor product, identified as 2-(3,5-dimethylpyrazol-1-yl)-1,4-dihydroxybenzene, was also formed. Other authors[3] extended the reaction, in ethanol medium, to unsubstituted pyrazole and 4-chloropyrazole, obtaining different mixtures of addition compounds. Together with our previous work, these results suggest that this reaction is stongly dependent on the nature of the pyrazole involved and also on the solvent.

Scheme I[a]



[a] **a**, Pz = pyrazole; **b**, Pz = 3,5-dimethylpyrazole; **c**, Pz = 4-chloro-3,5-dimethylpyrazole; **d**, Pz = 4-nitropyrazole; **e**, Pz = 4-nitro-3,5-dimethylpyrazole.

In this study we have investigated the influence of the substituent on the pyrazole ring on the course of the re-

(1) Catalán, J.; Fabero, F.; Guijarro, M. S.; Claramunt, R. M.; Santa María, M. D.; Foces-Foces, M. C.; Hernández Cano, F.; Elguero, J.; Sastre, R. *J. Am. Chem. Soc.* **1990**, *112*, 747.
(2) Grandberg, I. I.; Kost, A. N. *Zh. Obshch. Khim.* **1959**, *29*, 1099.
(3) Gauss, W.; Heitzer, H.; Petersen, S. *Ann. Chem.* **1972**, *764*, 131.

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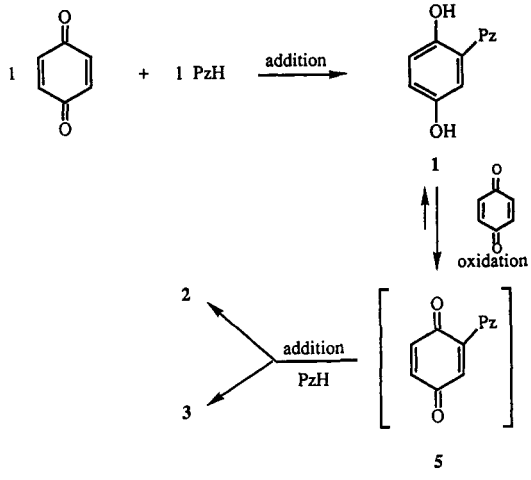
Table I. Relative Amounts of Compounds 1, 2, 3, and 4 from ^{1}H NMR Spectra of the Crude Reaction Mixtures

	1 (%)	2 (%)	3 (%)	4 (%)	reactn time (h)
a	57.0	29.0	14.0	traces	1
b	21.1	78.9			1
c	22.4	77.6			3.5
d	91.4	8.6			29
e	100				61

Scheme II



action, with the aim of obtaining a better understanding of this useful nucleophilic addition.

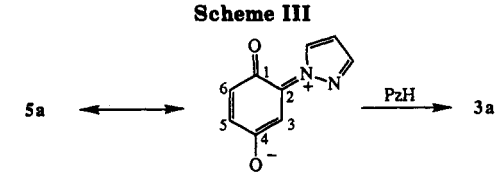
Results and Discussion

We have selected five pyrazoles with different nucleophilic character: unsubstituted pyrazole, 3,5-dimethylpyrazole, 4-chloro-3,5-dimethylpyrazole, 4-nitropyrazole, and 4-nitro-3,5-dimethylpyrazole. The reactions were performed in dioxane at 100° C and the crude mixtures were carefully analyzed by ^{1}H NMR (Scheme I). 2,3-Bis- and 2,5-bis-adducts were unequivocally distinguished in the ^{1}H NMR spectra by analysis of the isotopomer satellite bands around aromatic protons H_5–H_6 in 2,3-bis-adducts and H_3–H_6 in 2,5-bis-adducts.[1]

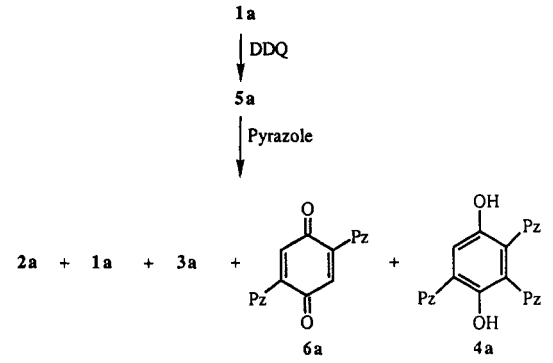
The relative amounts of the products obtained in each case are depicted in Table I. The results can be explained through a mechanism in which addition and oxidation processes are involved (Scheme II). However, formation of a charge-transfer complex prior to the nucleophilic addition can be also considered, as it has been postulated for piperidine addition.[4]

Due to the presence of the pyrazole ring, the intermediate mono-adducts 1 should have, in general, an oxidation potential slightly higher than that of 1,4-benzoquinone,[5] and, therefore, the oxidation step will be slow. However, if the pyrazole has a good nucleophilic character, as soon as the quinone **5** is formed, it will be trapped by the pyrazole to give the bis-adducts. Assuming a linear relationship between basicity and nucleophilicity (the Brönsted equation holds generally in the absence of steric effects), the pyrazoles thus far considered will react in the order of their increasing basicity: 4-nitropyrazole (pK_a = –2.0)[6] < 4-nitro-3,5-dimethylpyrazole (pK_a = –0.45)[6] < pyrazole

Scheme III



Scheme IV



(pK_a = 2.48)[6] < 4-chloro-3,5-dimethylpyrazole (pK_a about 3.0) < 3,5-dimethylpyrazole (pK_a = 4.06).[6] Thus, 3,5-dimethylpyrazole, which is a good nucleophile, yielded the corresponding 2,3-bis-pyrazolyl derivative **2b** as the major product. Pyrazole itself, with an intermediate nucleophilic character, afforded the mono-adduct **1a** as major product, together with the 2,3-bis- and 2,5-bis-adducts **2a** and **3a** and traces of the 2,3,5-tris-adduct **4a**. With 4-nitropyrazole, the influence of the two factors was clearly observed. Formation of mono-adduct **1d**, as almost the exclusive product after a long reaction time (29 h), reveals that the oxidation of **1d** by 1,4-benzoquinone is extremely difficult. The presence of the electron-withdrawing nitro group on the pyrazole should produce a remarkable increment of the oxidation potential of **1d**. Furthermore, the low nucleophilic character of 4-nitropyrazole makes it difficult to trap effectively the corresponding quinone **5d** in a manner such that the 2,3-bis-adduct **2d** is formed only in a very small amount.

Formation of 2,3-bis derivatives[7] as major products vs 2,5-bis derivatives suggests that the pyrazole ring orients similar to the cyano group[8] in contrast with methoxy[9] or chloro[10] groups. The fact that only pyrazole itself yielded a mixture of 2,3- and 2,5-bis-adducts **2a** and **3a** (relative ratio 68/32) is probably related to the absence of a substituent at position 5. Only for pyrazole could the quinone **5a** adopt a planar conformation (Scheme III) which allows the delocalization of the lone pair of N-1 over the quinone ring (something similar happens in 1-phenylpyrazoles).[11] The neutral resonance form **5** reacts toward nucleophiles at the position 3 with concomitant formation of bis-adducts **2**. However, the dipolar resonance form of **5a** shown in Scheme III has the position 3 deactivated toward a nucleophilic attack. It results that pyrazole nitrogen N-2 reacts on the position 5 leading to bis-adduct **3a**.

(4) Muzalikrishna, U.; Krishnamurthy, M. *Indian J. Chem.* **1983**, *22A*, 858.

(5) Determinations of oxidation potentials of compounds **1a–d** are in progress. Up to now, we have measured the oxidation potential of **1a** in acetonitrile: E_0 = 0.735 V. E_0 of 1,4-benzoquinone and DDQ in the same conditions are 0.715 V and 1.150 V, respectively. Measurements were made by voltammetry (Pt electrode) using Ag/AgCl as reference electrode.

(6) Catalán, J.; Abboud, J. L. M.; Elguero, J. *Adv. Heterocycl. Chem.* **1987**, *41*, 187.

(7) We have obtained this 2,3-bis isomer in the reaction of 3,5-dimethylpyrazole and 1,4-benzoquinone in ethanol. This compound was previously misassigned as 2,5-bis isomer **3**.

(8) Thiele, J.; Meisenheimer, J. *Ber.* **1900**, *33*, 675.

(9) (a) Erdtman, H. G. H. *Proc. R. Soc. London, Ser. A.* **1933**, *143*, 177. (b) Mackenzie, H. A. E.; Winter, E. R. S. *Trans. Faraday Soc.* **1948**, *44*, 159, 171, 243.

(10) Burton, H.; Praill, P. F. G. *J. Chem. Soc.* **1952**, 2546.

(11) (a) Elguero, J. Pyrazoles and their Benzo Derivatives. In *Comprehensive Heterocyclic Chemistry*; Pergamon: Oxford, 1984; Vol. 5. (b) Katritzky, A. R.; Taylor, R. *Adv. Heterocycl. Chem.* **1990**, *47*, 161.

The bis-adduct corresponding to an attack at position 6 is never observed, in agreement with the results obtained with more conventional nucleophiles such as cyano, methoxy, or chloro. The presence of a nucleophilic substituent at position 2 deactivates position 6 by resonance interaction with the C=O at position 4.

The low oxidative character of 1,4-benzoquinone (E_0 = 0.715 V)[5] was evidenced when it was heated with **1a** in dioxane in the absence of additional pyrazole. Only traces of quinone **5a** were detected in the ^{1}H NMR spectrum of the reaction crude. However, this quinone was easily obtained by treatment with the strong oxidant DDQ (E_0 = 1.150 V).[5] The subsequent pyrazole addition reaction in refluxed dioxane was also studied. The ^{1}H NMR spectrum of the reaction mixture, after 1 h, revealed the products shown in Scheme IV and 22% of starting materials. The presence of quinone **6a** points out that its redox potential must be lower than those of compounds **2a** and **5a**. Compound **4a** should be formed by pyrazole addition to quinone **6a**. In fact, after 16 h the reaction was completed, and the ^{1}H NMR spectrum showed the absence of **6a**, with **2a** being the major product.

The DDQ oxidation procedure was extended to bis-adducts **2a**, **2b**, and **3a**, yielding the corresponding quinones **7a**, **7b**, and **6a**. Subsequent addition of 1 mol of pyrazole allowed the introduction of two new pyrazole rings to yield the tetrakis-substituted hydroquinones **8a** and **8b**, together with the hydroquinones **2a**, **2b**, and **3a**. Related tetrakis-substituted quinones have been previously obtained by a substitution reaction of chloranil with pyrazoles.[3] Compound **8a**, due to its low solubility in dioxane, was easily separated from hydroquinones **2a** and **3a**. However, compound **8b** was more difficult to isolate since it presented very similar solubility properties to those of compound **2b**.

In order to prepare mixed tetrakis derivatives, the reaction of quinone **7b** with azoles different from those linked to the quinoid ring was investigated. ^{1}H NMR analysis of the crude reaction mixtures revealed the formation of tris and tetrakis derivatives **9** and **10** in the case of pyrazole and the tetrakis derivative **11** in the case of imidazole. Addition of imidazole to 1,4-benzoquinone in acetonitile to give bis-adducts has been reported previously.[12]

Finally, the direct nitration of **2a** was attempted to improve the preparation of **2d**, a compound normally difficult to obtain by the general reaction. Treatment of **2a** with a mixture of concentrated nitric and sulfuric acids afforded quinone **7d** in high yield. Former oxidation of **2a** to quinone **7a** prevented the nitration of the benzene ring. Subsequent reduction of **7d** with hydroquinone gave compound **2d** in satisfactory yield. This procedure also allows the preparation of 2,3-bis(4-nitro-3,5-dimethylpyrazol-1-yl)-1,4-dihydroxybenzene (**2e**) from **2b**.

Conclusions

Pyrazoles efficiently add to 1,4-benzoquinone in dioxane solution to give mono- and bis-adducts. The nucleophilic character of the pyrazoles and the oxidation potentials of the mono-adducts are decisive factors in the process. In general, formation of 2,3-bis derivatives is preferred.

The reactions described herein offer a simple and straighforward route to polyazolylquinones and hydroquinones, compounds with fascinating chemistry and interesting properties such as host lattices, photoprotection, antioxidants, and DNA intercalation.

(12) Kouno, K.; Ogawa, C.; Shimomura, Y.; Yano, H.; Ueda, Y. *Chem. Pharm. Bull.* **1981**, *29*, 301.

Experimental Section[13]

The ^{1}H and ^{13}C NMR spectra were recorded with a Bruker AC-200 (200 MHz, 50.3 MHz) instrument under standard conditions. IR spectra were measured on a FT-IR BOMEM BM-100 spectrometer.

Melting points, which are uncorrected, were obtained on a Büchi 530 apparatus. Mass spectra were recorded on a VG-12-250 spectrometer at 70 eV. Chromatographic purifications were performed at atmospheric pressure through columns using Merck silica gel 60 (70–230 mesh).

Products were purchased from commercial sources and the following compounds were prepared by described procedures: 3,5-dimethylpyrazole,[14] 4-chloro-3,5-dimethylpyrazole,[15] 4-nitropyrazole,[16] and 4-nitro-3,5-dimethylpyrazole.[17]

Reaction of Pyrazole with 1,4-Benzoquinone. General Method. A mixture of pyrazole and 1,4-benzoquinone (1:1 molar ration) in dioxane was heated under reflux for the time shown in Table I. The reaction was cooled and then the solvent was evaporated and the crude products were purified by column chromatography. The eluent used is listed for each compound. Compounds **1a**, **1b**, **2a**, **2b**, and **3a** have been described previously.[1]

2-(4-Chloro-3,5-dimethylpyrazol-1-yl)-1,4-dihydroxybenzene (1c): chromatographic eluent 3:7 hexane/ether (R_f 0.20); mp 231–233 °C; ^{1}H NMR (DMSO-d_6) δ 2.04 (s, 3 H), 2.15 (s, 3 H), 6.58 (d, 1 H, J = 2.7 Hz), 6.71 (dd, 1 H, J = 2.7, 8.7 Hz), 6.83 (d, 1 H, J = 8.7 Hz), 9.07 (s, 1 H), 9.27 (s, 1 H); ^{13}C NMR (DMSO-d_6) δ 9.6 (q), 11.2 (q), 106.6 (s), 114.6 (d), 116.9 (d), 117.2 (d), 126.6 (s), 137.2 (s), 144.1 (s), 144.6 (s), 149.9 (s); MS, m/z 238 (100, M$^+$).

2,3-Bis(4-chloro-3,5-dimethylpyrazol-1-yl)-1,4-dihydroxybenzene (2c): chromatographic eluent hexane/ether 3:7 (R_f 0.07); mp 283–284 °C; IR (KBr) 2250–2700 (OH), 3400 (OH) cm^{-1}; ^{1}H NMR (DMSO-d_6) δ 1.95 (s, 6 H), 2.02 (s, 6 H), 7.02 (s, 2 H), 9.71 (s, 2 H); ^{13}C NMR (DMSO-d_6) δ 9.4 (q), 11.0 (q), 105.8 (s), 118.0 (d), 124.8 (s), 138.5 (s), 144.0 (s), 146.3 (s); MS, m/z 366 (100, M$^+$).

2-(4-Nitropyrazol-1-yl)-1,4-dihydroxybenzene (1d): chromatographic eluent 4:6 hexane/ether (R_f 0.14); mp 217–218 °C; IR (KBr) 2300–2950 (OH), 3450 (OH) cm^{-1}; ^{1}H NMR (DMSO-d_6) δ 6.78 (dd, 1 H, J = 8.8, 2.9 Hz), 6.98 (d, 1 H, J = 8.8 Hz), 7.16 (d, 1 H, J = 2.9 Hz), 8.53 (s, 1 H), 9.21 (s, 1 H), 9.25 (s, 1 H), 9.81 (s, 1 H); ^{13}C NMR (DMSO-d_6) δ 110.3 (d), 116.4 (d), 118.0 (d), 126.1 (s), 131.3 (d), 135.7 (s), 135.8 (d), 141.5 (s), 150.2 (s); MS, m/z 221 (100, M$^+$).

2,3-Bis(4-nitropyrazol-1-yl)-1,4-dihydroxybenzene (2d): chromatographic eluent 4:6 hexane/ether (R_f 0.02); mp 234–236 °C; IR (KBr) 2250–3000 (OH), 3400 (OH) cm^{-1}; ^{1}H NMR (DMSO-d_6) δ 7.15 (s, 2 H), 8.25 (d, 2 H, J = 0.9 Hz), 9.06 (d, 2 H, J = 0.9 Hz), 10.25 (s, 2 H); ^{13}C NMR (DMSO-d_6) δ 119.0 (d), 123.2 (s), 134.2 (d), 135.5 (d), 136.2 (s), 145.2 (s); MS, m/z 332 (100, M$^+$).

2-(4-Nitro-3,5-dimethylpyrazol-1-yl)-1,4-dihydroxybenzene (1e). This compound was difficult to isolate since it presented similar R_f and solubility properties to those of hydroquinone. It was identified in the ^{1}H NMR (DMSO-d_6) spectrum of the reaction crude: 2.37 (s, 3 H), 2.45 (s, 3 H), 6.66 (d, 1 H, J = 2.8 Hz), 6.79 (dd, 1 H, J = 8.8, 2.8 Hz), 6.88 (dd, 1 H, J = 8.8, 0.4 Hz).

2,3,5-Tripyrazol-1-yl-1,4-dihydroxybenzene (4a): chromatographic eluent 95:5 chloroform/ethanol (R_f 0.47); mp 155–157 °C; IR (KBr) 2000–3300 (OH) cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 6.24 (dd, 1 H, J = 2.6, 2.0 Hz), 6.46 (dd, 1 H, J = 2.4, 1.9 Hz), 6.52 (dd, 1 H, J = 2.6, 2.0 Hz), 6.62 (dd, 1 H, J = 2.6, 0.5 Hz), 7.31 (s, 1 H), 7.46 (dd, 1 H, J = 2.4, 0.6 Hz), 7.69 (d, 2 H, J = 2.0 Hz), 7.82 (dd, 1 H, J = 1.9, 0.6 Hz); ^{13}C NMR ($CDCl_3$) δ 107.2 (d), 107.3 (d), 107.4 (d), 107.8 (d), 121.8 (s), 122.0 (s), 124.2 (s), 127.3 (d), 130.8 (d), 132.3 (d), 139.3 (d), 139.8 (d), 139.8 (s), 141.4 (d), 143.1 (s); MS, m/z 308 (100, M$^+$).

(13) Compounds **1d**, **2d**, **2e**, and **4a** gave satisfactory analytical data (±0.4% for C, H, N), and the purity of the other new compounds was established by ^{1}H NMR. The data are included as supplementary material.

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(15) Morgan, G. T.; Ackeiman, I. *J. Chem. Soc.* **1923**, 1308.

(16) Büchner, E.; Fritsch, M. *Ann. Chem.* **1893**, *273*, 165.

(17) Chang, K. C.; Grimmett, M. C.; Ward, D. D. *Aust. J. Chem.* **1979**, *32*, 1727.

Oxidation of 1a, 2a, 2b, and 3a with DDQ. To a stirred solution of hydroquinones **1a–3a** in dioxane was added a solution of the stoichiometric amount of DDQ in dioxane in small portions at rt. DDQ hydroquinone began to precipitate after 10 min. The mixture was left to stand for 1 h, and the precipitate was collected by filtration. The solvent of the filtrate was removed under reduced pressure to afford the crude quinones **4a**, **7a**, **7b**, and **5a**. The crude products were dissolved in the minimum amount of methylene chloride and filtered. Evaporation of the solution quantitatively yielded the quinone.

2-Pyrazol-1-yl-1,4-benzoquinone (5a): mp 79–81 °C; IR (KBr) 1679 (CO), 1666 (CO) cm^{-1}; ^1H NMR (DMSO-d_6) δ 6.61 (dd, 1 H, J = 2.7, 1.7 Hz), 6.89 (dd, 1 H, J = 10.0, 2.6 Hz), 7.00 (d, 1 H, J = 10 Hz), 7.02 (d, 1 H, J = 2.6 Hz), 7.89 (d, 1 H, J = 1.7 Hz), 8.42 (d, 1 H, J = 2.7 Hz); ^{13}C NMR ($CDCl_3$) δ 109.6 (d), 120.4 (d), 132.4 (d), 135.4 (d), 136.1 (d), 139.6 (s), 143.1 (d), 182.7 (s), 186.7 (s); MS, m/z 174 (100, M^+).

2,3-Dipyrazol-1-yl-1,4-benzoquinone (7a): mp 172–174 °C; IR (KBr) 1672 (CO) cm^{-1}; ^1H NMR ($CDCl_3$) δ 6.42 (dd, 2 H, J = 1.8, 2.6 Hz), 7.00 (s, 2 H), 7.55 (d, 2 H, J = 1.8 Hz), 7.67 (d, 2 H, J = 2.6 Hz); ^{13}C NMR ($CDCl_3$) δ 108.1 (d), 133.3 (d), 133.3 (s), 135.4 (d), 142.6 (d), 181.8 (s); MS, m/z 240 (45.4, M^+).

2,5-Dipyrazol-1-yl-1,4-benzoquinone (6a): mp 214–215 °C; IR (KBr) 1660 (CO) cm^{-1}; ^1H NMR ($CDCl_3$) δ 6.53 (dd, 2 H, J = 2.8, 1.6 Hz), 7.39 (s, 2 H), 7.80 (d, 2 H, J = 1.6 Hz), 8.65 (d, 2 H, J = 2.8 Hz); ^{13}C NMR ($CDCl_3$) δ 110.1 (d), 119.3 (d), 133.1 (d), 139.6 (s), 143.7 (d) 182.1 (s); MS, m/z 240 (100, M^+).

2,3-Bis(3,5-dimethylpyrazol-1-yl)-1,4-benzoquinone (7b): mp 118–119 °C; IR (KBr) 1677 (CO) cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.00 (s, 6 H), 2.14 (s, 6 H), 5.89 (s, 2 H), 7.01 (s, 2 H); ^{13}C NMR ($CDCl_3$) δ 11.0 (q), 13.2 (q), 107.2 (d), 135.6 (d), 137.1 (s), 143.0 (s), 151.2 (s), 181.8 (s); MS, m/z 296 (100, M^+).

Addition of Pyrazole to Quinones 6a and 7a. To a solution of quinones **6a** or **7a** (100 mg, 0.42 mmol) in dioxane (10 mL) was added pyrazole (28 mg, 0.42 mmol). The reaction was stirred under reflux for 24 h. The precipitated tetrapyrazolylhydroquinone **8a** (74%) was collected and recrystallized from DMSO: mp 308–310 °C; IR (KBr) 2300–3080 (OH) cm^{-1}; ^1H NMR (DMSO-d_6) δ 6.32 (t, 4 H, J = 2.0 Hz), 7.49 (d, 4 H, J = 2.2 Hz), 7.59 (d, 4 H, J = 1.4 Hz), 9.71 (s, 2 H); ^{13}C NMR (DMSO-d_6) δ 106.5 (d), 126.8 (s), 132.7 (d), 140.5 (d), 141.8 (s); MS, m/z 374 (100, M^+).

Addition of 3,5-Dimethylpyrazole to Quinone 7b. To a solution of quinone **7b** (300 mg, 1.01 mmol) in dioxane (7 mL) was added 3,5-dimethylpyrazole (97 mg, 1.01 mmol). The reaction was stirred under reflux for 1 h and the resulting precipitate was collected and dried. The ^1H NMR spectrum of the precipitate revealed the presence of the hydroquinone **2b** together with the tetrakis(3,5-dimethylpyrazolyl)hydroquinone **8b**: ^1H NMR (DMSO-d_6) δ 5.76 (s, 4 H), 2.12 (s, 24 H).

Addition of Pyrazole to Quinone 7b. To a solution of quinone **7b** (200 mg, 0.68 mmol) in dioxane (6 mL) was added pyrazole (46 mg, 0.68 mmol). The reaction was stirred under reflux for 15 h. Then the reaction mixture was cooled and evaporated in vacuo. The ^1H NMR spectrum of the reaction crude revealed the presence of hydroquinone **2b** (44%), 2,3-bis(3,5-dimethylpyrazol-1-yl)-5-pyrazol-1-yl-1,4-dihydroxybenzene (**9**, 24%), and 2,3-bis(3,5-dimethylpyrazol-1-yl)-5,6-dipyrazol-1-yl-1,4-dihydroxybenzene (**10**, 31%).

Addition of Imidazole to Quinone 7b. To a solution of quinone **7b** (200 mg, 0.68 mmol) in dioxane (6 mL) was added imidazole (46 mg, 0.68 mmol). The reaction was stirred under reflux for 15 h. The reaction mixture was cooled and evaporated in vacuo. The ^1H NMR spectrum of the reaction crude revealed the presence of hydroquinone **2b** (36%) and 2,3-bis(3,5-dimethylpyrazol-1-yl)-5,6-diimidazol-1-yl-1,4-dihydroxybenzene (**11**, 64%).

Nitration of 2a or 2b. To a solution of **2a** or **2b** (0.41 mmol) in concentrated sulfuric acid (2.5 mL) was added a mixture of concentrated sulfuric acid (0.82 mL) and 95% nitric acid (1.1 mL). The mixture was left to stand at rt for 1 h and then poured into crushed ice. The resulting precipitate was collected and dried to yield 90 mg (66%) of **7d** or 81 mg (51%) of **7e** as a yellow solid.

2,3-Bis(4-nitropyrazol-1-yl)-1,4-benzoquinone (7d): mp 146–147 °C; IR (KBr) 1630 (CO) cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.16 (s, 2 H), 8.05 (s, 2 H), 8.59 (d, 2 H, J = 0.4 Hz); ^{13}C NMR (DMSO-d_6) δ 133.3 (s), 134.7 (d), 136.2 (d), 136.8 (s), 137.9 (d), 180.2 (s); MS, m/z 330 (100, M^+).

2,3-Bis(4-nitro-3,5-dimethylpyrazol-1-yl)-1,4-benzoquinone (7e): mp 217–218 °C; ^1H NMR ($CDCl_3$) δ 2.36 (s, 6 H), 2.53 (s, 6 H), 7.16 (s, 2 H); ^{13}C NMR ($CDCl_3$) δ 13.0 (q), 14.0 (q), 132.7 (s), 136.2 (d), 138.3 (s), 144.9 (s), 148.8 (s), 179.9 (s); MS, m/z 386 (100, M^+).

Reduction of 7d or 7e with Hydroquinone. To a solution of hydroquinone (0.3 mmol) in dioxane (6 mL) was added **7d** or **7e** (0.3 mmol). The reaction was stirred for 2 h at rt, and the solvent was evaporated in vacuo. Pure compounds were isolated by column chromatography using as eluent 3:7 or 4:6 hexane/ethyl acetate to yield **2d** (75%) or **2e** (70%).

2,3-Bis(4-nitro-3,5-dimethylpyrazol-1-yl)-1,4-dihydroxybenzene (2e): mp 317–319 °C; IR (KBr) 2600–3300 (OH) cm^{-1}; ^1H NMR (DMSO-d_6) δ 2.21 (s, 6 H), 2.41 (s, 6 H), 7.17 (s, 2 H), 10.20 (s, 2 H); ^{13}C NMR (DMSO-d_6) δ 12.0 (q), 13.5 (q), 119.4 (d), 122.1 (s), 130.2 (s), 144.5 (s), 145.7 (s), 145.9 (s); MS, m/z 388 (100, M^+).

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Registry No. **1a**, 123834-59-3; **1b**, 39736-42-0; **1c**, 133047-68-4; **1d**, 133047-65-1; **1e**, 133047-66-2; **2a**, 123834-58-2; **2b**, 123834-57-1; **2c**, 133047-74-2; **2d**, 133047-71-9; **2e**, 133047-72-0; **3a**, 39736-41-9; **4a**, 138152-18-8; **5a**, 138152-19-9; **6a**, 39736-44-2; **7a**, 138152-20-2; **7b**, 138152-21-3; **7d**, 138152-22-4; **7e**, 138152-23-5; **8a**, 138152-24-6; **8b**, 138152-25-7; **9**, 138152-26-8; **10**, 138152-27-9; **11**, 138152-28-0; 3,5-dimethylpyrazole, 67-51-6; pyrazole, 288-13-1; imidazole, 288-32-4; 1,4-benzoquinone, 106-51-4; 4-chloro-3,5-dimethylpyrazole, 15953-73-8; 4-nitropyrazole, 2075-46-9; 4-nitro-3,5-dimethylpyrazole, 14531-55-6.

Supplementary Material Available: Elemental analyses of compounds **1d**, **2d**, **2e**, and **4a** and ^1H and ^{13}C NMR spectra of compounds **1c**, **2c**, **1d**, **2d**, **1e**, **2e**, **4a**, **5c**, **6a**, **7a**, **7b**, **7d**, **7e**, **8a**, and **8b** (29 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.