gel (Mallinckrodt) and neutral alumina (Fisher) were used for column chromatography.

General Irradiation Procedure. Irradiations were carried out under an argon atmosphere in an immersion well apparatus (water cooled) with a Hanovia 450-W medium pressure mercury lamp (Pyrex filter). Methanol solutions (350 mL) of benzophenones (15–17.5 mmol) and acetone oxime (1.17 g) were irradiated for 4 h.[7] After the irradiation the solvent methanol was removed under reduced pressure and the residue was chromatographed over neutral alumina or silica gel[8] and eluted with hexane–ether (0–100%) mixtures and finally with methylene chloride. The pinacols[9] were eluted first in hexane–ether (<50%) followed by the diols **2** in more polar eluant mixtures. The melting points of the recrystalized products (capillary) are uncorrected. Yields represent the isolated amounts after chromatography.

1,1-Diphenyl-1,2-ethanediol (2, R = H): yield 44%, mp 120–121 °C; ^{1}H NMR ($CDCl_3$, 200 MHz) 1.80 (1 H, br, OH), 3.20 (1 H, br, OH), 4.17 (2 H, s, CH_2), and 7.20–7.46 ppm (10 H, m, Ar); ^{13}C NMR ($CDCl_3$, 75.4 MHz) 69.33 (t, CH_2OH), 78.54 (s, COH), 126.39 (d), 127.42 (d), 128.39 (d), and 143.81 ppm (s); mass spectrum (EI, 70 eV), *m/e* (relative intensity) 183 (100), 105 (87.5), and 77 (39); (30 eV) M^+ ion detected at *m/e* 214 (0.2).

1-Phenyl-1-*p*-tolyl-1,2-ethanediol (2, R = Me): yield 40%, mp 85 °C; ^{1}H NMR (CCl_4, 200 MHz) 2.28 (3 H, s, CH_3), 2.60 (1 H, br, OH), 3.46 (1 H, br, OH), 3.78 (2 H, br,[10] CH_2), 6.95–7.26 ppm (9 H, m, Ar); ^{13}C NMR (acedone-d_6, 75.4 MHz) 20.93 (q), 69.53 (t, CH_2OH), 78.63 (s, COH), 127.23 (d), 127.29 (d), 127.32 (d), 128.47 (d), 129.16 (d), 136.64 (s), 143.56 (s), and 146.66 ppm (s); mass spectrum (EI, 70 eV), *m/e* (relative intensity) 197 (100), 119 (26.5), 105 (49.5), 91 (9.5), and 77 (7.5); (30 eV) M^+ ion detected at *m/e* 228 (0.4).

1-Phenyl-1-(*p*-methoxyphenyl)-1,2-ethanediol (2, R = OMe): yield 32%, mp 105–106 °C; ^{1}H NMR (CCl_4, 200 MHz) 1.66 (1 H, br, OH), 2.92 (1 H, br, OH), 3.75 (3 H, s, OMe), 3.95 (2 H, slightly br,[10] CH_2), and 6.70–7.36 ppm (9 H, m, Ar); ^{13}C NMR (acedone-d_6, 75.4 MHz) 55.35 (q), 69.23 (t, CH_2OH), 78.49 (s, COH), 113.84 (d), 127.22 (d), 127.34 (d), 128.47 (d), 128.58 (d), 138.57 (s), 146.80 (s), and 159.27 ppm (s); mass spectrum (EI, 70 eV), *m/e* (relative intensity) 244 (3.2) M^+ ion, 227 (2.8), 213 (100), 135 (67.5), 105 (92), and 77 (28.5).

(7) VPC analysis (10% OV-101 on HP Chromosorb W at 40 °C) of aliquots withdrawn before and after irradiation indicated no loss of acetone oxime. A similar irradiation of benzophenone in the absence of acetone oxime gave pinacol and the diol **2** (R = H) in identical yields. The reaction was nearly complete after this period and only small amounts (<2%) of ketone were left unreacted.

(8) The photolysis products from 4-methyl- and 4-methoxybenzophenones showed some decomposition on an alumina column and hence were chromatographed on silica gel.

(9) Along with the pinacol(s), unchanged ketone and acetone oxime were also eluted: they were removed by washing the solid pinacol(s) with hexane. 4-Methyl- and 4-Methoxybenzophenones gave mixture of pinacols (*dl* and *meso*) in nearly a 1:1 ratio.

(10) This CH_2 signal appears as sharp singlet in $CDCl_3$ solvent and the observed broadening may be associated with enantiotopic properties of the methylene protons.

Synthesis of 4,6-Dinitroresorcinol

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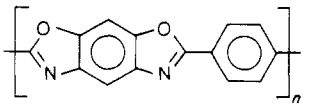
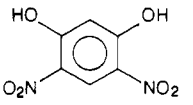
Polyhydroxy aromatics are typically difficult to nitrate directly in large quantities because of the exothermicity of the nitration reaction.[1] Also, the desired regiospecificity may be difficult to obtain in the nitration of phenols because of their reactivity. However, recent developments in the synthesis of the high strength, liquid crystalline polymer poly[*p*-phenylenebenzobis(oxazole)] (PBO)[2] require a high-yield, regioselective synthesis of 4,6-dinitroresorcinol (4,6-DNR)[2] as a polymer precursor.

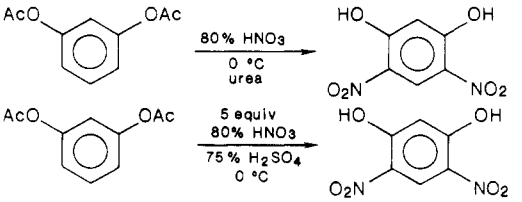


PBO



DNR

Most of the relevant organic literature pertains to the synthesis of 2,4-dinitroresorcinol.[3-6] Only a few references are available for the direct synthesis of 4,6-DNR, and only very low yields were obtained.[7] It is recognized that the 2,4-substitution evolves from prior nitrosation,[8] and thus we have focused on nitration with strict control of nitrosation reactions. Consequently, we have found that 4,6-DNR can be synthesized in high yield from resorcinol diacetate with nitric acid or mixed solutions of nitric acid/sulfuric acid containing large quantities of urea as a nitrous acid trap. Typical optimal yields for the two



systems are 44 and 60%, but the yields are quite sensitive to conditions. Our experiments demonstrated that if the nitric acid concentration or the sulfuric acid concentration is varied by 5% in either direction or if the temperature rises above +10 °C, an extremely low yield of 4,6-DNR is obtained.

In conclusion, we developed a convenient method for synthesizing 4-substituted resorcinols. This reaction requires the control of all prior nitrosation reactions to minimize the side reactions and to maximize both the regioselectivity of the reaction and the yield.

Experimental Section

Preparation of Purified Nitric Acid. Nitrous acid reacts with resorcinol or an acylated resorcinol to give 2-nitrosoresorcinol. Thus, control of nitrous acid is essential to obtain 4,6-DNR. The 90 wt % white fuming nitric acid and the 70 wt % nitric acid were prepared by bubbling dry oxygen or air through 90 wt % red nitric acid to remove the NO_2 or N_2O_4 until the nitric acid was colorless. Residual nitrous acid was then eliminated from either nitric acid concentration by addition of urea or hydrazine. Urea was added in excess to destroy any nitrous acid that might remain or that was formed during the nitration reaction.

Synthesis in Nitric Acid. *CAUTION*: This synthesis has inherent dangers. This reaction involves solutions of nitric acid and resorcinol diacetate, which have been known to react violently after an induction period (fume off)!! 2,4,6-Trinitroresorcinol (styphnic acid—*CAUTION*—explosive!!) is formed as a byproduct in this reaction.

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The 90 wt % nitric acid with the urea was added slowly with cooling to an equal amount of purified 70 wt % nitric acid to give 80 wt % nitric acid as required for the reaction. All reactions were performed under an inert atmosphere. The 1000 mL of 80 wt % white fuming nitric acid was then cooled to −10 °C. Urea (20 g) was slowly added to the reaction mixture as a nitrous acid trap. Next, 161 g (0.82 mol) of resorcinol diacetate was slowly added with stirring at a rate sufficient to maintain a temperature at or below 5 °C. Extreme caution must be used at this stage of the reaction, because adding the resorcinol diacetate too rapidly or allowing the temperature to rise above 0 °C can lead to a fume off. A yellowish-gold precipitate will slowly form in the nitric acid/urea solution. After approximately 2 h, the precipitate was collected by filtration with use of a glass filter paper. The remaining nitric acid solution was poured onto ice and filtered again to remove any additional precipitate. The precipitate was washed several times with water, dried, and recrystallized from ethyl acetate. The isolated yield of recrystallized material from the reaction was 56.4 g (44%). We can also isolate 4-nitroresorcinol and 2,4,6-trinitroresorcinol (styphnic acid) from the water/nitric acid mixture. Mass spectrum of 4,6-DNR: m/e 200 (M^+), 184 (M − O), and m/e 170 (M − NO).

Synthesis in Nitric Acid/Sulfuric Acid. *CAUTION*: This synthesis has inherent dangers. While in practice we have found this method to be considerably safer and more reliable than the corresponding nitric acid method above, this reaction involves solutions of sulfuric acid, nitric acid, and resorcinol diacetate, which have been known to react violently after an induction period (fume off)!! 2,4,6-Trinitroresorcinol (styphnic acid—*CAUTION*—explosive!!) is formed as a byproduct in this reaction.

As described above, 80 wt % nitric acid is purified to eliminate all NO_2, N_2O_4, or nitrous acid. Three molar equivalents (relative to the resorcinol diacetate) of purified nitric acid (46.5 g) was then added slowly to 1000 mL of 80 wt % H_2SO_4, which was cooled to −10 °C. Small amounts of urea were added to control any nitrous acid formed in the reaction. Resorcinol diacetate (47.53 g) was slowly added with stirring, while the reaction temperature was kept below 0 °C. A yellowish-gold precipitate slowly formed, and the reaction was worked up as described above after 1.5 h. The isolated yield of recrystallized 4,6-DNR was 60%.

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Evidence of Termolecular Complex Formation of Tetrabromo-*p*-benzoquinone with Certain Nonaromatic Donors

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In recent spectrophotometric studies of the interaction of *p*-chloranil and *p*-fluoranil as electron acceptors (Ac) with various electron donors (D), including ethers, amides, lactones, and related compounds, evidence has been obtained in some cases that 2:1 (D_2Ac) as well as 1:1 (DAc) complexes are formed.[1,2] Presumably in the termolecular complex the two donor molecules coordinate on opposite sides of the acceptor ring. Termolecular complex formation becomes more apparent as the donor strength increases and also is observed more frequently with *p*-fluoranil than with *p*-chloranil as the acceptor, no doubt in reflection of the relative acceptor strengths[3] of the two tetrahalobenzoquinones.

These earlier investigations of *p*-chloranil and *p*-fluoranil complexes have now been extended to determine the disposition of *p*-bromanil to undergo complex formation with a number of the same electron donors used previously. Since *p*-bromanil has been reported to be the weakest of the three *p*-tetrahaloanils,[3] it has seemed of interest to determine whether any detectable evidence that it engages in termolecular complex formation can be obtained.

Experimental Section

Materials. The sources of the donors and of the carbon tetrachloride used as solvent were the same as described previously.[1,2] The *p*-bromanil was obtained from Lancaster Synthesis.

Determination of Equilibrium Constants. For each donor investigated a series of carbon tetrachloride solutions of varying concentration of the donor and fixed concentration of *p*-bromanil (usually of the order of (7–8) × 10^{-4} M) were prepared at 25.0 °C. Generally eight to ten such solutions were used, the donor concentrations of which varied over more than a 10-fold range. To improve the chances of obtaining evidence of termolecular complex formation, the most concentrated solutions were of the order of 5–7 M, except in the cases of lactam donors (2–3 M). The spectrophotometric equipment that was used and the general method of determining the absorbances of these solutions at various wavelengths were the same as described previously.[1] In most instances the absorbance of each solution was measured at several wavelengths in the 390–310-nm range, at which the complexes absorb appreciably more than the free acceptor. Solutions containing lactones and triethyl orthoformate were also measured in the 330–260-nm range at a *p*-bromanil concentration level of 7 × 10^{-5} M.

In a few instances equilibrium constants for formation of *p*-fluoranil complexes of the donor used in the *p*-bromanil studies had not been previously determined. These were obtained for comparison purposes by essentially the same procedures as used in the earlier work on *p*-fluoranil complexes.[2]

The experimental data obtained at a particular wavelength for the series of solutions of varying donor concentration were treated graphically by the Ketelaar equation (1)[4] on the assumption that only a 1:1 complex with an equilibrium constant of K_c is formed (eq 2). In eq 1, $\epsilon_a = A/l[Ac]_t$ where A is the absorbance of the

$$\frac{1}{\epsilon_a - \epsilon_{Ac}} = \frac{1}{\epsilon_c - \epsilon_{Ac}}\left(\frac{1}{K_c[D]}\right) + \frac{1}{\epsilon_c - \epsilon_{Ac}} \quad (1)$$

$$K_c = [DAc]/[D][Ac] \quad (2)$$

solution of donor and acceptor, l is the light path length in centimeters, and $[Ac]_t$ is the total concentration of acceptor (free and complexed) in moles/liter; ϵ_{Ac} and ϵ_c are the molar absorptivities of free and complexed acceptor, respectively. The donor concentration, [D], was expressed in moles/liter. In those cases in which plots of $1/(\epsilon_a - \epsilon_{Ac})$ values at a particular wavelength vs corresponding 1/[D] values were linear over the entire donor concentration range, K_c values were calculated from the slopes and intercepts. In those cases in which the lines curved downward at higher donor concentrations, later reported K_c values were based on linear portions of the plots. In such cases, as has been discussed in detail recently,[1,2] a procedure based on the discussion of Deranleau[5] was applied in estimating K_1 and K_2 values (eq 3).

$$K_2 = [D_2Ac]/[D][DAc] \quad (3)$$

The K_1 values so obtained are K_c values that have been corrected in recognition of the formation of termolecular as well as bimolecular complexes. Less likely interpretations of the data are dealt with in the earlier publications.[1,2]

Results and Discussion

The K_c values for interaction of the various electron donors with *p*-bromanil are summarized in Table I. The corresponding values of K_c for the *p*-chloranil and *p*-

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