Free-Radical Reagents. 2. Oxidation and Addition Products from the Reaction of Di-*tert*-butyliminoxyl with Phenols

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The blue, persistent free-radical di-*tert*-butyliminoxyl, t-$Bu_2C{=}NO^{\bullet}$ (1), oxidizes *p*-hydroquinones and catechol in organic solvents to the corresponding quinones in good yield. With simple phenols, the reaction takes three pathways. 2-Naphthol and 9-phenanthrol are oxidized to the corresponding *o*-quinones, while 1-naphthol, phenol, and 2,6-di-*tert*-butylphenol give 4,4-disubstituted oxime ethers. Para-substituted phenols afford cyclohexadienones with one di-*tert*-butyliminoxyl at the original para position. Some of these adducts can be prepared by cooxidation of 1–H and the phenol with ceric ion. Rate constants for some of the reactions of 1 with phenols have been measured by kinetic EPR spectroscopy.

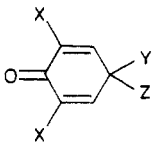
Phenolic oxidations are very widespread in natural systems,[1] and they are commercially important because of the extensive use of phenols as antioxidants[2] and as precursors for the synthesis of polymers.[3] We have studied the oxidation reactions of the blue free-radical di-*tert*-butyliminoxyl[4,5] (1) because of a possible analogy to the well-known, inorganic Fremy's radical (2), which characteristically oxidizes phenols to quinones in high yield.[6]

t-$Bu_2C{=}NO^{\bullet}$ (1) $\qquad$ $(^{-}O_3S)_2NO^{\bullet}$ (2)

Results

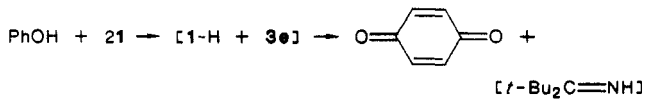
Stock solutions of 1 in pentane, prepared as described,[5] readily oxidized stoichiometric hydroquinones and catechol to the corresponding quinones in good yield (Table I). The byproduct 1–H, unlike the case with oxidations with 2, is soluble in organic solvents. The Experimental Section gives exemplary procedures for its separation from the phenol-derived products by fractional crystallization, sublimation of 1–H, preferential extraction of one product into a solvent, extraction of 1–H into methanolic base, or chromatography.

p-Cresol and its 2,6-di-*tert*-butyl derivative (BHT) gave colorless 1:1 adducts **3a** and **3b**, respectively, in the yields indicated in Table I. These compounds could also be prepared more conveniently by cooxidation of equimolar phenol and 1–H with 2 equiv of ceric ion.



3a, X = H, Y = Me, Z = t-Bu_2CNO
b, X = t-Bu, Y = Me, Z = t-Bu_2CNO
c, X = H, Y = Z = t-Bu_2CNO
d, X = t-Bu, Y = Z = t-Bu_2CNO
e, X = Y = H, Z = t-Bu_2CNO

Initial trials with phenol and 2 equiv of 1 in pentane gave black reaction mixtures from which only 1–H could be isolated. We then made a number of attempts to divert



the presumed intermediate para adduct of 1 and phenol (**3e**) with base. When the reaction was conducted in chloroform in the presence of aqueous NaOH, a 23% yield of benzoquinone could be detected by chromatography, but numerous other products were present.

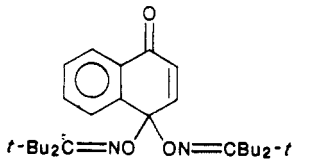
Table I. Products from 1 and Phenols

phenol	product, %	1–H, %
hydroquinone	quinhydrone, 99	76
2,5-di-*tert*-butylhydroquinone	t-$Bu_2C_6H_2O_2$, 69	68
o-catechol	*o*-benzoquinone, 80	63
2-methyl-1,4-naphthohydroquinone	vitamin K_3, 92	63
phenol	**3c**, 58	61
p-cresol	**3a**, 43	66
BHT	**3b**, 78	89
2,6-di-*tert*-butylphenol	**3d**, 81	36
1-naphthol	**4**, 87	68
2-naphthol	1,2-naphthoquinone, [82][a]	
9-phenanthrol	9,10-phenanthrenequinone, 51	66

[a] From visible absorption spectrum.

2-Naphthol with 1, on the other hand, led to a succession of vivid colors, culminating with the appearance of an orange precipitate identified as *o*-naphthoquinone. Spectroscopic experiments subsequently showed that 2-naphthol consumed about 4.1 equiv of 1 and generated 81% of the *o*-quinone product.

9-Phenanthrol and 1 similarly gave 9,10-phenanthrenequinone. When a 4.5-fold excess of 1 reacted with 1-naphthol under the same conditions, however, no 1,4-naphthoquinone could be detected, but a cream solid, mp 108.5 °C, to which we assigned the novel bis-oxime structure[7] **4**, was isolated in 87% yield.



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† MTU Dean's Fellow, summer 1985.

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(2) (a) Schnabel, W. *Polymer Degradation*; Hanser International: Vienna, 1981; pp 49–50. (b) Howard, J. A. In *Free Radicals*; Kochi, J., Ed.; Wiley-Interscience: New York, 1972; Vol. 2, Chapter 12.
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0022-3263/86/1951-5390$01.50/0

Table II. Rate Constants for Reactions of 1 with Phenols (Acetonitrile, 22 °C)

compound	$[compound]_0$, M	$10^4\,[1]_0$, M	$10^4 k_{obsd}$[a]
PhOH	0.0063	6.75	299
p-ClC_6H_4OH	0.00905	6.87	394
p-BrC_6H_4OH	0.0226	7.39	218
p-$O_2NC_6H_4OH$	0.0070	6.63	<4.9
p-$CH_3C_6H_4OH$	0.00578	6.87	1940
BHT	0.00394	6.87	>5000[b]
p-$MeOC_6H_4OH$	0.00357	6.87	>5000[b]

[a] The mean of three measurements (average SD = 9%) in $M^{-1}\,s^{-1}$ from fit of ESR decay to the equation $\ln (h_0/h_t) = k_{obsd}[AH]_0 t$, where h is the peak-to-peak height of one of the three multiplets of 1 in the partially resolved derivative spectrum, recorded with a Varian E9 spectrometer. [b] Reaction complete within preparation time.

The acid-sensitive acetal group in 4 immediately suggested an explanation for the unsatisfactory results with the reaction of phenol with only 2 equiv of 1. Indeed, when phenol was reacted with excess 1, a pale yellow, light-sensitive 2:1 adduct **3c** was isolated by chromatography. 2,6-Di-*tert*-butylphenol afforded an analogous, yellow product **3d** in good yield, and the latter compound could also be prepared by a cooxidation of 1–H and the phenol with ceric ion. All of these adducts were rather labile, and poor resolution of ^1H NMR spectra obtained for **3c** in $CDCl_3$ was traced to apparent dissociation to give 1, identified by its characteristic ESR spectrum. Satisfactory, well-resolved ^1H NMR spectra were obtained in acetone-d_6 and benzene-d_6. The spectra of the adducts showed two kinds of *tert*-butyl groups (syn and anti) derived from 1, and other resonances in the numbers and positions consistent with the assigned structures.

A low-temperature ^1H NMR spectrum of the freshly prepared reaction products from *p*-cresol and 1 in $CDCl_3$ showed only resonances ascribed to 1–H, **3a**, excess *p*-cresol, and solvent-derived protons.

Kinetic ESR studies of the reactions of phenol and substituted phenols under pseudo-first-order conditions showed a trend toward faster reaction rates with electron donation into the aromatic ring (Table II). In this respect, the radical 1 resembles *tert*-butylperoxyl[2b] and aroyl *tert*-butyl nitroxides.[8]

Discussion

The oxidation of hydroquinones with 1 deserves little comment because this transformation can be accomplished so many other ways, and even directly from the parent hydrocarbon and ceric ion.[9] There may be some advantage in our approach, however, where the quinone product precipitates directly from nonaqueous solution (e.g., *o*-benzoquinone), and in the fact that 1 shows no acidic or basic properties.

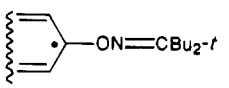
The isolation of para adducts from *p*-cresol and BHT finds analogies in the adducts of these phenols with $HO_2^{\bullet}$,[10] *t*-$BuO_2^{\bullet}$,[11] and 2,3-dichloro-5,6-dicyano-1,4-benzoquinone.[12] The oxidations of 2-naphthol and 9-phenanthrol by 1 are directly analogous to the classic Teuber reaction of **2**. In a number of reactions of **2** with phenols, unstable intermediates have been isolated and ascribed variously to C–N and C–O addition (**5a**, **5b**).[13]

$RON(SO_3^-)_2$ **5a** $RN^+(O^-)(SO_3^-)_2$ **5b** $RN^+(O^-)=CBu_2$-*t* **5c**

We assume that our addition compounds are oxime ethers and not nitrones (**5c**) because the latter would engender substantial steric strain from both *tert*-butyl groups, and because the adducts displayed solubility characteristics that were not at all consistent with the presence of two polar nitrone groups in the molecules.

Barton and co-workers[14] found that the Fremy's analogue $(PhS)_2N^{\bullet}$ gave a higher yield of product arising from addition to the ortho position of phenol, and they ascribed this result to the higher free spin density at the 2- and 6-positions of the intermediate phenoxyl radical. This explanation is clearly not a general one, since **3c** appears to be the only product from 1 and phenol. The reaction of phenoxyl with 1 and **2** appears to respond more to steric factors in giving the less hindered para adduct.[15]

Where the reagent 1 distinguishes itself from Fremy's radical and even from organic analogues such as acyl alkyl nitroxides[8] is in the formation of the unusual geminal dioximes **3c**, **3d**, and **4**. 2,5-Cyclohexadienones similar to these are valuable synthetic intermediates[16] and have been the subject of numerous photochemical studies.[17] The preference for these structures over other possible products may reflect a relatively slower rate of O–N scission in the presumed intermediate **6** vs. coupling with 1 compared



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with the analogous reactions of intermediates from phenols and other radicals. The enhanced thermodynamic stability of the O–C–O sequence[18] may explain why the geminal bis-oxime ethers are preferred over adducts to two sites in the aromatic ring.

We have noted that the selectivity of 1 toward H abstraction in related substrates does not follow the order of published C–H bond strengths. These studies are still in progress and will be reported separately.

Experimental Section

References to 1 in the following procedures refer to stock solutions 0.04–0.3 M in pentane[5] that were stored <–15 °C and warmed to room temperature before use.

Phenols and hydroquinones were commercial samples that were purified by conventional techniques if their appearance indicated that this was necessary. Low-melting phenols were added directly to 1, whereas higher melting ones (hydroquinones, 9-phenanthrol, etc.) were first dissolved in a minimal quantity of ether unless another solvent is indicated. Most ^1H NMR spectra were recorded with a Varian XL200 instrument, and resonances are given in δ from Me_4Si. The kinetic ESR data were obtained from degassed solutions in sealed 5-mm Pyrex tubes with a Varian E9 spec-

(7) Geminal oxime ethers have been prepared by unrelated routes: (a) Kirsch, S. J.; Schelling, H. *J. Org. Chem.* **1979**, *44*, 3970–3972. (b) Gieren, A.; Lamm, V. *Acta Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem.* **1978**, *34*, 3837–3840.

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(9) Ho, T.-L.; Hall, T.-W.; Wong, C. M. *Synthesis* **1973**, 206.

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(11) Coppinger, G. M.; Campbell, T. W. *J. Am. Chem. Soc.* **1952**, *74*, 1469–1471.

(12) Becker, H.-D. *J. Org. Chem.* **1965**, *30*, 982–989.

(13) (a) Teuber, H.-J.; Gotz, N. *Chem. Ber.* **1956**, *89*, 2654–2669. (b) Teuber, H.-J.; Thaler, G. *Chem. Ber.* **1959**, *92*, 667–693. (c) Magnusson, R. *Acta Chem. Scand.* **1964**, *18*, 759–768.

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(15) Cf. the principle of steric separation: Mendenhall, G. D. *Sci. Prog. (Oxford)* **1979**, *65*, 1–18.

(16) See: Koelsch, P. M.; Tanis, S. P. *Kodak Lab. Chem. Bull.* **1980**, *52*, 1–7.

(17) E.g.: Zimmerman, H. E.; Lynch, D. C. *J. Am. Chem. Soc.* **1985**, *107*, 7745–7756 and preceding papers in this long series.

(18) Schleyer, P. R.; Jemmis, E. D.; Spitznagel, G. W. *J. Am. Chem. Soc.* **1985**, *107*, 6393–6394 and references therein.

trometer. Data were collected with a PDP 11/03 computer and analyzed with a program written by Stephen Traxler. Most visible and UV spectra were obtained with a HP Model 8451A diode array spectrometer. IR spectra were recorded with a PE Model 735B or 283B spectrometer. Liquid chromatography was carried out with a HP Model 1084B instrument with UV detection. Melting points are uncorrected. Mass spectra were recorded on a HP Model 5985B instrument, and exact masses were recorded with a VG Analytical Model 70-250S. Combustion analyses were performed by Spang Microanalytical Laboratories.

The individual workup of reaction mixtures with **1** follows. The methods used to identify the byproduct **1**–H are indicated parenthetically. Unless otherwise stated, the reactions were complete within a few minutes after mixing.

Hydroquinone (81.3 mg, 0.738 mmol) and 2 equiv of **1** gave a yellow solution containing 107 ± 5% benzoquinone from the absorption maxima at 433 and 456 nm. Concentration to dryness and extraction with water left **1**–H, 100 mg (65%) after crystallization from ethanol (IR, mp).

A solution of hydroquinone (113 mg, 1.03 mmol) and 1 equiv of **1** was concentrated to remove some ether and then cooled to −30 °C to give green quinhydrone, 110 mg after filtration and washing with hexane, mp 167 °C dec (lit.[19] mp 171 °C). The filtrate was concentrated to dryness and sublimed to give 1 mg of yellow crystals (discarded) and then 122 mg of **1**–H (mp, IR[4]).

2,5-Di-*tert*-butylhydroquinone (160 mg, 0.72 mmol) in 100% EtOH (5 mL) and **1** was concentrated to dryness (<20 torr), dissolved in hexane (15 mL), and extracted with 15 5-mL portions of 1.7 M methanolic NaOH. The combined methanolic extracts were back-washed with pentane. Neutralization of the extracts with acetic acid and dilution with water gave **1**–H, which was recrystallized from ethanol: 150 mg (IR, mp). The combined pentane solutions were concentrated to dryness and sublimed (0.8 torr, <75 °C) to give yellow 2,5-di-*tert*-butylbenzoquinone, 110 mg, mp 148–151 °C subl (lit.[19] mp 152.5 °C). The IR spectrum was identical with a published spectrum of the compound.[20]

Catechol and 2 equiv of **1** by the procedure for conversion of hydroquinone to quinhydrone gave a red precipitate of *o*-benzoquinone, identified by its IR spectrum.[21]

2-Methyl-1,4-naphthohydroquinone (210 mg, 1.21 mmol) and **1** gave a yellow solution, which was concentrated to dryness (<20 torr). The residue was extracted with boiling water, leaving 258 mg of **1**–H (IR, mp). The aqueous extracts were cooled in ice to give 112 mg of vitamin K_3, mp 99 °C (lit.[19] mp 107 °C). An additional 80 mg, mp 99–100 °C, was isolated from the filtrate by ether extraction followed by recrystallization from pentane. The IR spectra of both crops were identical with a published one.[20]

Phenol (13.7 mg, 0.146 mmol) and 4.5 equiv of **1** were allowed to stand for 30 min at 25 °C followed by 17 h at −16 °C. The pale blue liquid was decanted from **1**–H (27.9 mg) onto a 10 cm × 6 mm dry column of basic alumina (Brockmann I, Aldrich) and eluted with 1:1 ether–pentane. The early fractions were concentrated to give 34.1 mg of **3c**, which was immediately recrystallized from about 1 mL of pentane at −60 °C. The resulting pale yellow cubes were dried at <1 torr with protection from light: 27.7 mg, mp 81–82 °C slight dec.

Anal. Calcd for $C_{24}H_{40}N_2O_3$ (404.58): C, 71.24; H, 9.97; N, 6.93. Found: C, 71.42; H, 9.82; N, 6.88. ^{1}H NMR (C_6D_6): δ 1.183 (18 H), 1.342 (18 H), 6.19 (d, J = 10.4 Hz, 2 H), 7.28 (d, J = 10.4 Hz, 2 H). IR (Nujol): ν 1675, 1630, 1167, 1071, 1050, 972, 925 (br), 870 (br) cm^{-1}.

In another experiment, phenol (20 mg, 0.21 mmol) in chloroform (2 mL) containing 1 drop of 50% NaOH was treated with 0.45 equiv of **1** with shaking. After 30 min, the brown organic solution was analyzed by HPLC (C18 10μ column, 30% aqueous MeOH, 1 mL/min). A peak at 3.0 min showed a spectrum and retention time identical with those of an authentic sample of benzoquinone (yield 23%).

***p*-Cresol** and **1** gave successive crops of **3a** and **1**–H in the total yields indicated in Table I. The compound was conveniently prepared from *p*-cresol (357 mg, 3.30 mmol) and **1**–H (521 mg, 3.31 mmol) in MeOH (45 mL) by addition of 2 equiv of methanolic ceric ammonium nitrate, filtration (suspended CeO_2?), and dilution with water (45 mL). The cream solid was filtered after several hours, washed with 25% aqueous MeOH, and dried (<2 torr): 375 mg, mp 77.5–79.5 °C. A further crop of 224 mg, mp 72–75 °C, was isolated by dilution of the filtrate with water and standing at 5 °C (total yield, 69%). IR (Nujol): ν 1672 (s), 1630, 1608, 1575, 1390, 1362, 1300, 1240, 1220, 1180, 1080 (s), 1070 (s), 920–950 (s), 890, 855 (s) cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 1.12 (9 H), 1.35 (9 H), 1.476 (3 H), 6.16 (d, J = 10 Hz, 2 H), 6.90 (d, J = 10 Hz, 2 H). Exact mass calcd for $C_{16}H_{26}NO_2$ (M + H$^+$) 264.19635, found 264.1967.

BHT (300 mg, 1.36 mmol) and **1** were concentrated (<20 torr) to dryness, and the residue was sublimed (0.6 torr, <65 °C, 6 h). The yellow sublimate of **1**–H was crystallized from ethanol: 190 mg (mp, IR). The residue from the sublimation was crystallized from ethanol to give 400 mg of **3b**, mp 91.2–91.7 °C.

Anal. Calcd for $C_{24}H_{41}NO_2$: C, 76.75; H, 11.00; N, 3.73. Found: C, 76.02; H, 11.29; N, 3.77. Exact mass calcd for $C_{24}H_{42}NO_2$ (M + H$^+$) 376.32155, found 376.3214. Mass spectrum: major m/e at 376 (M + 1), 220, 219, 205, 189, 177, 163, 156, 135, 119, 100, 69, and 57 (P). ^{1}H NMR ($CDCl_3$): δ 1.080 (9 H), 1.191 (18 H), 1.348 (9 H), 1.384 (3 H), 6.525 (2 H). IR (Nujol): ν 2710, 1665, 1650 (s), 1620, 1390, 1360 (s), 1330, 1245, 1225, 1200, 1160, 1080, 1060, 880–940 (s), 845, 815, 738, 690 cm^{-1}.

The same compound was isolated in 88% yield by addition of 3.50 g (6.38 mmol) of ceric ammonium nitrate in MeOH (20 mL) to a mixture of **1**–H (0.50 g, 3.18 mmol) and BHT (0.72 g, 3.27 mmol) in MeOH (40 mL), followed by water (10 mL). After drying, the resulting crystals showed mp 87.5–88 °C.

2,6-Di-*tert*-butylphenol (57.0 mg, 0.276 mmol) and 5 equiv of **1** were allowed to stand overnight at 25 °C protected from light. After decanting from large crystals of **1**–H (31.5 mg, 36%), the solution was concentrated (<20 torr) to a green-white solid and triturated five times with MeCN. The solid was dried (<1 torr): 115.9 mg (81%), mp 88.5–89.5 °C.

The same compound resulted from 491.5 mg (2.38 mmol) of the phenol, 760.1 mg (4.83 mmol) of **1**–H, and 4.74 g (8.65 mmol) of ceric ammonium nitrate in methanol as described for *p*-cresol, with only 10 mL of water added to the filtrate. The yellow solid product, mp 95 °C, weighed 803.3 mg (65%). Anal. Calcd for $C_{32}H_{56}N_2O_3$ (516.788): C, 74.37; H, 10.92; N, 5.42. Found: C, 74.45; H, 10.88; N, 5.42. ^{1}H NMR (acetone-d_6): δ 1.221 (18 H), 1.227 (18 H), 1.362 (18 H), 7.06 (2 H). ^{1}H NMR ($CDCl_3$): δ 1.184, 1.226, 1.324, 6.984. IR (Nujol): ν 1669, 1643 (s), 1322 (s), 1240, 1200, 1160, 1080, 1040, 1007, 992, 961 (s), 928, 908, 885 (s), 810, 721 (br) cm^{-1}.

1-Naphthol (8.00 mg, 55.5 mmol, resublimed) and 5 equiv of **1** were concentrated to half-volume (steam bath) and, after 1 h, concentrated (<20 torr) to dryness. The solids were allowed to stand overnight with about 2 mL of MeCN, isolated by centrifugation, and triturated several more times with MeCN. After drying at <1 torr, the off-white **4** (14.4 mg, 87%) showed mp 110 °C.

Anal. Calcd for $C_{28}H_{42}N_2O_3$ (464.636): C, 73.97; H, 9.31; N, 6.16. Found: C, 74.01; H, 9.27; N, 6.27.

Mass spectrum: major m/e at 242 (M − 1 − C_4H_9), 176, 175, 160, 159, 158 (naphthoquinone), 130, 115, 111, 105, 104, 102, 100, 84, ($C_4H_{10}CN$), 46, 57 (P). ^{1}H NMR ($CDCl_3$): δ 1.126 (18 H), 1.346 (18 H), 6.45 (d, J = 10.6 Hz, 1 H), 7.644 (d, J = 10.6 Hz, 1 H). The latter two doublets were shown by the usual techniques to be coupled and are ascribed to H2 and H3, respectively, of the naphthalene ring. The other aromatic protons appeared as a series of finely split doublets (J = 2 Hz) at 7.42, 7.46, 7.50, 7.56, 7.59, ca. 7.63, 7.79, 7.83, 8.05, and 8.09. IR (Nujol): ν 1678 (s), 1640, 1599, 1325, 1301, 1009, 990, 960, 920, 901, 873 (s), 765 cm^{-1}. From another experiment, with 22.2 mg of 1-naphthol as starting material, the MeCN washings were concentrated (air stream) and sublimed (100 °C, <20 torr) to give 48.1 mg (68%) of impure **1**–H (HPLC retention time).

2-Naphthol (68.2 mg, 0.473 mmol) in a little ether was added dropwise to 2 equiv of **1**. The addition was halted when the blue color of **1** was discharged. The mixture became pale green, then yellow, followed by the formation of a red precipitate. The solid

(19) *Handbook of Chemistry and Physics*, 66th ed.; CRC: Boca Raton, FL, 1985. Melting points in Beilstein references cited in this handbook were usually lower.

(20) *Standard Grating Spectra*; Sadtler Research Laboratories, Inc.: Philadelphia, 1966.

(21) Otting, W.; Staiger, G. *Chem. Ber.* **1955**, *88*, 828–833.

was filtered off and washed with pentane, giving 14.4 mg (0.091 mmol) of orange 1,2-naphthoquinone, sintered 125 °C, mp ca. 133–139 °C dec. Melting points between 121 and 146 °C are cited in the literature.[19] The IR spectrum (Nujol mull) matched a published one except for a small systematic shift in the wavelengths.[22]

For quantitation, 90 μL of 0.425 M 2-naphthol in ether was injected into 1.05 mL of 0.15 M 1 in hexane. After 5 min, the mixture was diluted to 4.0 mL. This solution showed λ_{max} 536 nm (abs = 0.28), and the absorbance at 800 nm was 0.034. A 0.0162 M solution of the quinone in ether showed λ_{max} 536 nm (abs = 0.578). From these data and ϵ = 4.7 at 800 nm for 1 (in cyclohexane), we calculated that 4.1 mol of 1 was consumed per mole of the quinone produced, assuming that the ϵ values were unchanged by the slight differences in solvent.

(22) Pouchert, C. J. *Aldrich Library of Infrared Spectra*, 3rd ed.; Aldrich Chemical Co.: Milwaukee, WI, 1981.

9-Phenanthrol. Aldrich technical grade product was partially purified by sublimation at <1 torr. From 52.8 mg (0.272 mmol) of phenanthrol and 5 equiv of 1, a yellow orange precipitate was obtained. After standing at 25 °C for 17 h, it was filtered off and washed with pentane: 28.6 mg, mp 205–207 °C (lit.[19] mp 208–210 °C). The IR spectrum matched a published spectrum of 9,10-phenanthrenequinone.[22]

The filtrates at −16 °C deposited 33.4 mg of pure 1-H (^{1}H NMR, mp), and a further crop was isolated on cooling to −60 °C (23.0 mg after crystallization from aqueous MeOH).

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Structural Effects Affecting Hydration of 1,2-Diones Studied by Linear-Sweep Voltammetry[1]

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Linear-sweep voltammetry was used for determination of values K_d^{CO} = [RCOCOR′]/[RCOC(OH)$_2$R′] and K_d^{COH} = [RCOCOH$^+$R′]/[RCOC(OH)(OH$_2^+$)R′] for some aliphatic and alicyclic 1,2-diketones. Values obtained were compared with data obtained from UV and NMR spectra. Dc polarographic data were used to choose the most reliable value. In all cases, the protonated form predominating in solutions of sulfuric acid is less strongly hydrated than the unprotonated form. The effect of ring size on the hydration in polycyclic species is discussed. Steric hindrance of the hydration due to the 7- and possibly the 1-methyl group in 2,3-camphorquinone has been confirmed.

Ketones undergo reversible hydration, resulting in formation of geminal diols, much less readily than aldehydes.[2] Presence of adjacent electronegative groups can, nevertheless, result in an increase in the hydration of the keto group. Effects of alkyl groups, halogenated alkyl groups, and carboxylic groups were successfully treated by a four-parameter linear-free-energy relationship.[3] This approach, nevertheless, fails to enable interpretation of the lack of hydration of most benzaldehydes, "neutral" heterocyclic aldehydes, alkyl aryl ketones, diaryl ketones, α,β-unsaturated aldehydes and ketones, or 1,3-diketones. Interpretation of the absence of hydration as due to resonance effects encounters problems of interpretation of strong hydration of all pyridine carboxaldehydes and other formyl derivatives of "basic" heterocycles. Effect of structure on hydration of 1,2-diketones, where the shift in favor of the hydrated form is due to the electron-withdrawing properties of adjacent carbonyl groups, has been discussed only qualitatively[4] based on the possibility of isolation of the particular hydrate. Sandris and Ourisson[4] did not have available values of equilibrium constants of the hydration–dehydration reaction but were able to propose that the stability of the hydrate depends on three factors: polar effects of substituents, ring strain, and steric effects of nonbound groups. Presence of halogens increases the stability of the hydrate. Ring strain (Bayer) causes five-membered cyclic 1,2-diketones to be more strongly hydrated than six-membered. Presence of methyl groups in 2,3-camphorquinone prevents formation of a crystallizable hydrate, which is possible for α-santenonequinone, bearing one less methyl group in position 7.

For the course of investigation of electroreduction of 1,2-diketones,[5] a knowledge of the equilibrium constant of the dehydration reaction (K_d = [nonhydrated form]/[hydrated form]) proved essential. In the search for a suitable method for determination of these constants, serious limitations were encountered: The use of UV spectra for the study of hydration of carbonyl compounds involves[6] an estimate of the molar absorptivity of the free carbonyl form. This always introduces a degree of uncertainty, but for 1,2-diketones, the situation is complicated by the unusual dependence of UV spectra on solvent composition.[5b] Thus, for 3,3,6,6-tetramethyl-1,2-cyclohexanedione, the

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