[4,4‴-Bis(4-cumylphenoxy)-4′,4‴-dinitrophthalocyaninato(2-)]copper(II) (9a) (Representative Procedure). The reaction was the same as the representative procedure up to the removal of the triethylamine hydrochloride. At this point 0.038 g (0.28 mmol) of anhydrous cuprous chloride was added to the reaction mixture, and it was stirred under nitrogen for 13 h at room temperature. After this time 0.046 g of sodium methoxide and 0.062 g of hydroquinone were added to the reaction mixture, and it was refluxed and stirred for an additional 6 h. The solvent was then stirred and the solid was purified as before: yield 72%; IR 3086 (w), 3058 (w), 3030 (w), 2966 (s), 2930 (w), 1613 (w), 1600 (s), 1533 (s), 1476 (s), 1339 (s), 1234 (s); ^{1}H NMR 7.26–6.95 (m br, 24 H), 1.53 (s br, 32 H); UV (5.0×10^{-6} M in THF) (log ϵ) 710 (4.61), 665 (4.59), 643 (4.46), 603 (4.14). Anal. Calcd. for $C_{52}H_{38}N_{10}O_6Cu$: C, 68.53; H, 3.89; N, 12.89. Found: C, 68.30; H, 4.15; N, 12.61.

[4,4‴-Bis(4-cumylphenoxy)-4′,4‴-dinitrophthalocyaninato(2-)]cobalt(II) (9b): yeild 58%; IR 3086 (w), 3058 (w), 3030 (w), 2965 (s), 2971 (w), 1613 (w), 1601 (s), 1527 (s), 1474 (s), 1333 (s), 1234 (s); ^{1}H NMR 7.30–6.80 (m br, 24 H), 1.56 (s br, 32 H); UV (9.2×10^{-6} M in THF) (log ϵ) 705 (4.45), 661 (4.34), 641 (4.32), 597 (4.00). Anal. Calcd. for $C_{52}H_{38}N_{10}O_6Co$: C, 68.82; H, 4.10; N, 12.95. Found: C, 68.59; H, 4.27; N, 12.63.

Acknowledgment. We are grateful to Dr. Randy Winans of Argonne National Laboratory for the FAB MS data. Part of this work was done at Clemson University Department of Chemistry in conjunction with disertation of J.G.Y.

Registry No. **2**, 89-40-7; **3**, 13138-53-9; **4**, 31643-49-9; **5a**, 125023-51-0; **5b**, 83482-57-9; **5c**, 96917-81-6; **6a**, 125023-52-1; **6b**, 125023-53-2; **6c**, 96917-83-8; **7** (6-NO_2), 41645-42-5; **7** (7-NO_2), 41645-43-6; **8a**, 125023-55-4; **8b**, 125023-56-5; **8c**, 125023-57-6; **9a**, 125023-54-3; **9b**, 125048-81-9; *p-tert*-butylphenol, 98-54-4; ammonia, 7664-41-7; phthalimide, 85-41-6.

Superoxide Oxidation: A Novel Route to Aromatic 1,2-Dicarboxylic Acids

Chariklia Sotiriou,† Wenni Lee, and Roger W. Giese*

Department of Medicinal Chemistry in the College of Pharmacy and Allied Health Professions, and Barnett Institute of Chemical Analysis and Materials Science, Northeastern University, Boston, Massachusetts 02115

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Potassium superoxide in aprotic media, in the presence of 18-crown-6 ether, effects a novel and mild oxidative cleavage of quinones, cyclic alcohols, and ketones fused to various aromatic hydrocarbons. Aromatic 1,2-dicarboxylic acids are obtained as major products, with highest yields in dimethylformamide, under oxygen or air. For example, the yield of pyrene-1,2-dicarboxylic acid is 82% from 9,10-dihydrobenzo[*a*]pyren-7(8*H*)-one and 88% from benzo[*a*]pyrene-7,8-dione. Minor side products include aromatic tetrones and 3-(2-carboxyaryl)propionic or 3-(2-carboxyaryl)propenoic acid, which provide mechanistic insights.

The chemical reactivity including mechanistic details for the reaction of potassium superoxide (KO_2) with organic substrates has been reviewed.[1,2] Two general reactivity patterns of KO_2 predominate in aprotic media depending on the substrate: oxidations and nucleophilic displacements. For the oxidations, H_2O_2 and O_2 generated in situ, along with O_2 bubbled through the reaction mixture, are the true oxidants.[1] Typically, the reactions are carried out in the presence of a crown ether to increase the solubility of KO_2 in aprotic solvents such as DMF, THF, toluene, or benzene.

One type of product that arises from the oxidative cleavage of susceptible substrates with KO_2 is an organic acid or diacid. San Fillipo, Jr., et al.[3] successfully used KO_2 to oxidatively cleave a series of α-keto, α-hydroxy, and α-halo carboxylic acids, esters, and ketones to the corresponding carboxylic acids. Moreover, it has been reported that diphenic acid is obtained from the KO_2 oxidation of 9,10-dihydroxyphenanthrene or the corresponding quinone.[4]

Among such KO_2 reactions, however, are lacking any reports of aromatic 1,2-dicarboxylic acid products. In fact, the literature indicates that such products are not obtained even when potential precursors are reacted with KO_2. For example, reaction of α-tetralone with KO_2 in toluene yields α-naphthol (38%) and 2-hydroxy-1,4-naphthoquinone (10%). Similar reaction of β-tetralone gives the latter product (27%), β-naphthol (5%), and 3-(2-carboxyphenyl)propionic acid (14%).[5] Using a higher concentration of KO_2 in THF, others have obtained a 75% yield of 2-hydroxy-1,4-naphthoquinone from both α- and β-tetralone.[6] The latter product is also isolated in 60% yield from the KO_2 reaction of either 1,2- or 1,3-dihydroxynaphthalene.[7] In another case, the reaction of KO_2 with 1,2-naphthoquinone is reported[2,8] to yield *cis*-2-carboxycinnamic acid and 2,3-benzo-4-(carboxymethyl)butyrolactone, although we question the stereochemistry assigned to the former product (see below).

In contrast, here we report that high yields of aromatic 1,2-dicarboxylic acids can be obtained by the reaction of KO_2 with any of the above precursors, and various related compounds. This is essentially achieved by balancing the molar ratio of KO_2:crown ether:substrate in an appropriate solvent, under oxygen or air.

Results and Discussion

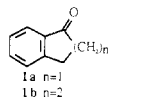
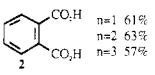
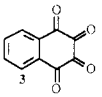
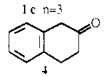
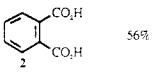
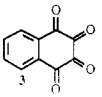
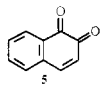
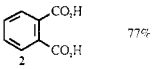
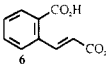
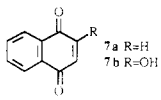
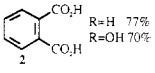
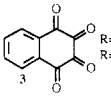
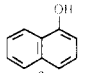
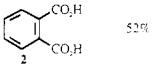
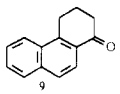
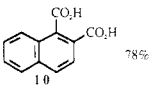
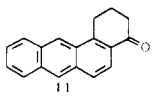
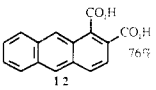
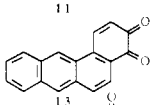
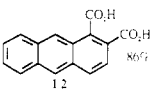
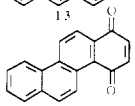
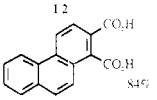
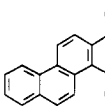
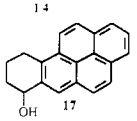
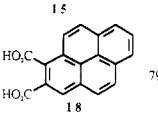
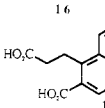
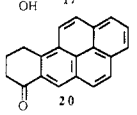
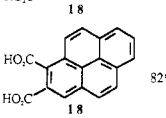
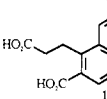
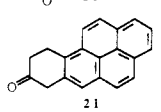
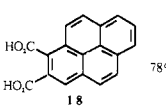
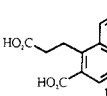
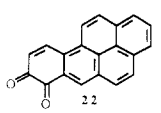
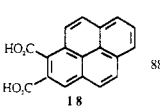
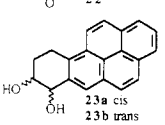
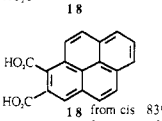
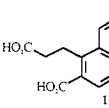
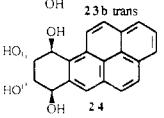
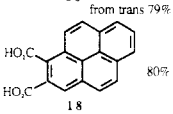
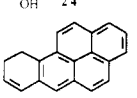
Table I summarizes the reactions that we have conducted with KO_2. As can be seen, a variety of aromatic

†Current address: Department of Chemistry, Harvard University, Cambridge, MA 02138.

(1) Sawyer, D. T.; Valentine, J. S. *Acc. Chem. Res.* **1981**, *14*, 393.
(2) Lee-Ruff, E. *Chem. Soc. Rev.* **1977**, *6*, 195.
(3) San Fillipo, J., Jr.; Chern, C.-I. *J. Org. Chem.* **1976**, *41*, 1077.
(4) Moro-oka, Y.; Foote, C. S. *J. Am. Chem. Soc.* **1976**, *98*, 1510.
(5) Lissel, M. *Tetrahedron Lett.* **1984**, *25*, 2213.
(6) Hocquaux, M.; Jacquet, B.; Vidril-Robert, D.; Maurette, M.-T.; Oliveros, E. *Tetrahedron Lett.* **1984**, *25*, 533.
(7) Vidril-Robert, D.; Maurette, M.-T.; Oliveros, E. *Tetrahedron Lett.* **1984**, *25*, 529.
(8) Lee-Ruff, E.; Lever, A. B. P.; Rigaudy, J. *Can. J. Chem.* **1976**, *54*, 1837.

0022-3263/90/1955-2159$02.50/0

Table I. KO_2 Oxidation of Various Derivatives of Aromatic Hydrocarbons[a]

compound	major product, yield	minor product, yield
 1a n=1 1b n=2 1c n=3	 n=1 61% n=2 63% n=3 57%	 n=2 2%, b
 4	 56%	 5%, b
 5	 77%	 2%
 7a R=H 7b R=OH	 R=H 77% R=OH 70%	 R=H 7% R=OH no other product
 8	 52%	no other product
 9	 78%	not isolated
 11	 76%	not isolated
 13	 86%	not isolated
 14	 84%	 8%
 17	 79%	 11%
 20	 82%	 9%
 21	 78%	 15%
 22	 88%	not isolated
 23a cis 23b trans	 18 from cis 83% from trans 79%	 19 from cis 6% from trans 6%
 24	 80%	no other product
 25	86%	no other product

[a] The oxidations were carried out with 1 mg of starting material, a 100-fold molar excess of KO_2, and a 40-fold excess of 18-crown-6-ether in 1 mL of DMF for 20 h at room temperature. Product yields were obtained by HPLC. [b] Traces of 3-(2-carboxyphenyl)-propionic acid were detectable in <1% yield.

precursors are transformed by this reagent into aromatic 1,2-dicarboxylic acids in good yields. These reactions are effective for cyclic substrates fused to benzene, naphthalene, and other polyaromatic hydrocarbons, as long as some degree of initial oxidation is present in the ring that is fused to the aromatic moiety. Even compounds **1b**, **4**, and **5** all give a good yield of phthalic acid, whereas previously[5-7] (see above), products other than this were obtained by KO_2 oxidation.

The results shown in Table I were achieved by using a 100-fold molar excess of KO_2 and a 40-fold molar excess of 18-crown-6 ether over the aromatic substrate in DMF. Typically, 1 mg of each compound was allowed to react for 20 h, at room temperature, in the dark, under dry O_2 or air. The reaction was then quenched with water, and reverse-phase HPLC was used to determine the product yields. As demonstrated below, the reactions of Table I can be scaled up with similar product yields. Authentic samples of several products, not available commercially, were prepared by essentially the same reaction (product **3** from **7a**, **6** from **5**, **10** from **9**, **12** from **11**, **15** and **16** from **14**, **18** and **19** from **20**) using either 50 or 100 mg of the aromatic precursor, a 30-fold molar excess of KO_2, and a 12-fold molar excess of 18-crown-6 ether. These products were then isolated by semipreparative HPLC, fully characterized, and used as external standards for yield determination.

The results shown in Table I demonstrate that the scope of this KO_2 reaction is broad. It is successful for α-tetralones and homologues ranging in the size of the fused ring (**1a–c**) and independent of the size of the aromatic moiety (**1a–c**, **9**, **11**, **20**). Both β-tetralone (**4**) and the functionally similar 9,10-dihydrobenzo[*a*]pyren-8(7*H*)-one (**21**) undergo the reaction to the corresponding aromatic 1,2-dicarboxylic acids, as do the aromatic *o*-quinones **5**, **13**, **22** and the aromatic *p*-quinones **7a,b**, **14**. 7,8,9,10-Tetrahydrobenzo[*a*]pyrene-7,8-diol, whether cis (**23a**) or trans (**23b**), reacts to give pyrene-1,2-dicarboxylic acid (**18**) as does the corresponding 7-hydroxy compound **17**, and the tetrol **24**. Interestingly, even 1-naphthol (**8**) reacts to give phthalic acid (**2**). One of the compounds tested, however, reacts differently with KO_2: 9,10-dihydrobenzo[*a*]pyrene (**25**) fully aromatizes forming benzo[*a*]pyrene (**26**).

Several other compounds such as naphthalene, anthracene, phenanthrene, pyrene, 3-phenylpropionic acid, *trans*-cinnamic acid, 3-(2-carboxyphenyl)propionic acid, 3-(2-carboxyphenyl)propenoic acid (**6**), and 3-(2-carboxypyrenyl)propionic acid (**19**) fail to react with KO_2. Apparently, the lack of reactivity with KO_2 can be attributed to the absence of any carbonyl or hydroxyl groups, or any sufficiently active CH sites, in these compounds.

We isolated and characterized three types of minor products from these KO_2 oxidations, as shown in Table I. The first are tetrones, formed as intermediates in a 2–8% yield, from incomplete KO_2 oxidation of **1b**, **7a**, and **14**. We have demonstrated that treating pure tetrone **3** with KO_2 gives phthalic acid. The second kind of side products are 3-(2-carboxyaryl)propionic acids, namely 3-(2-carboxyphenyl)propionic acid and **19**. These are terminal products for reasons explained above and arise from oxidative cleavage at a CHOH site (**19** from **17**), at a C=O site (3-(2-carboxyphenyl)propionic acid from **1b**, and **19** from **20** or **21**), or at a CHOHCHOH site (**19** from **23a,b**) that is situated in α, β, or α and β positions of a saturated six-membered ring relative to the fused aromatic moiety. The third minor product is *trans*-3-(2-carboxyphenyl)propenoic acid (**6**) derived from 1,2-naphthoquinone (**5**) and appears to be a terminal product as well. Presumably the corresponding cis compound is formed initially and then is isomerized to the more stable trans isomer. Others have reported that this reaction yields the

Table II. Effect of Reaction Conditions on the Oxidation of 20 by KO_2

reaction conditions[a]	molar ratio of CE[b] vs KO_2	products (% yield)[c] 18	19
DMF		57	11
DMF/crown ether	1:10	64	7
	1:5	68	8
	2:5	82	9
	1:1	82	9
DMSO		35	19
DMSO/crown ether	2:5	35	14
THF		17	58
THF/crown ether	2:5	73	12
benzene/crown ether	2:5	66	12

[a] 9,10-Dihydrobenzo[*a*]pyrene-7(8*H*)-one (**20**, 1 mg) was reacted with a 100-fold molar excess of KO_2 in DMF (1 mL), for 20 h, at room temperature. [b] CE = 18-crown-6-ether. [c] Product yields were determined by HPLC.

corresponding cis isomer but they did not present supporting evidence for their assignment.[2,8]

Even though we did not isolate all of the minor side products, likely structures can be suggested by analogy. For example, based on HPLC analysis, 3-(2-carboxyaryl)propionic acids apparently are formed as minor side products from the reaction of **9** and **11** with KO_2, analogously to the KO_2 reaction of **17** and **20**. Similarly, **13** and **22** appear to react with KO_2 in the same way as **5**.

The outcome of the KO_2 reaction on our substrates (Table I) is a function of the reaction time, solvent, relative concentration of KO_2 and crown ether, and the degree of exposure to O_2. All of the oxidations studied here are facilitated by the presence of air or oxygen. Nitrogen degassed solutions did not react to completion within the time period allowed for the reaction to proceed (typically 20 h). The effect of solvent and crown ether on the reaction was examined in detail for the oxidation of **20**. As shown in Table II, the highest yield of the aromatic 1,2-dicarboxylic acid **18** (82%) from ketone **20** is obtained in DMF and in the presence of crown ether. The latter operates as a phase-transfer catalyst, and its effect is also demonstrated in Table II: increasing the molar ratio of crown ether vs KO_2 from 1:10 to 1:1, while keeping the molar excess of KO_2 constant, increases the yield of product **18**, with a maximum yield reached at a ratio of 2:5. On the other hand, there is little effect of crown ether on the reaction in DMSO, an observation made previously.[9] Interestingly, 3-(2-carboxypyrenyl)propionic acid (**19**) becomes the major product (58%) in THF when crown ether is absent.

The importance of the reaction time and of the molar excess of KO_2 vs substrate is shown in Figure 1. Each data point represents the yield of pyrene-1,2-dicarboxylic acid (**18**) from 100 mg of **20** reacting with a different molar excess of KO_2 in DMF, while the molar ratio of crown ether vs KO_2 is kept constant at the optimum ratio of 2:5, established in Table II. Three significant conclusions are evident from the data in Figure 1. First, the KO_2 reaction of the types of compounds shown in Table I can be scaled up with high yields. Second, even a relatively low KO_2 molar excess over substrate gives a high yield of pyrene-1,2-dicarboxylic acid (**18**): an 8-fold molar excess of KO_2 over **20** yields 68% of **18** in 20 h and the corresponding yield from a 16-fold molar excess of KO_2 is 74%. The maximum yield of **18** (78%) can be obtained with a 32-fold molar excess of KO_2 over **20** after 20 h at room temperature. Third, pyrene-1,2-dicarboxylic acid (**18**) is a relatively stable product towards KO_2. Further experiments established that the yield of **18** does not change even after 40 h of reaction with a 100- or even a 200-fold molar excess of KO_2. On the other hand, the yield of phthalic acid (**2**) from **1b** falls from 63% after 20 h to 45% after 40 h under the same reaction conditions.

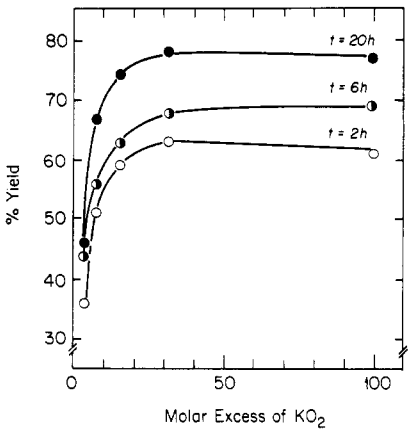


Figure 1. Yield of dicarboxylic acid **18** from ketone **20** as a function of time and molar excess of KO_2. **20** (100 mg) was oxidized with a 4-, 8-, 16-, 32-, and 100-fold molar excesses of KO_2 using a molar ratio of KO_2 to 18-crown-6 ether of 5:2 in DMF (20 mL), at room temperature, under oxygen.

In order to better understand the failure of others to obtain aromatic 1,2-dicarboxylic acids in KO_2 oxidations, we repeated the reaction of α-tetralone (**1b**) with KO_2 exactly as described in the literature,[6] using 1 g of α-tetralone, a 4-fold molar excess of KO_2 and a stoichiometric amount of crown ether relative to the substrate, in THF, for 5 h, at room temperature, under nitrogen. Based on HPLC analysis, the major product at this point was 2-hydroxy-1,4-naphthoquinone (**7b**) in 75% yield as reported.[6] We also observed a small amount of phthalic acid (<5%), which probably escaped detection previously due to the use of less sensitive analytical techniques. Eventually, the yield of phthalic acid rose to approximately 20% at the expense of 2-hydroxy-1,4-naphthoquinone when the reaction was allowed to continue for an additional 15 h. When the same reaction of α-tetralone was performed using the above literature conditions but in DMF under oxygen, phthalic acid was obtained in 40% yield after 5 h. Thus, it seems that the failure of prior workers to observe *any* aromatic 1,2-dicarboxylic acid from potential precursors can be mainly attributed to a solvent effect in combination with the absence of oxygen and a short reaction time.

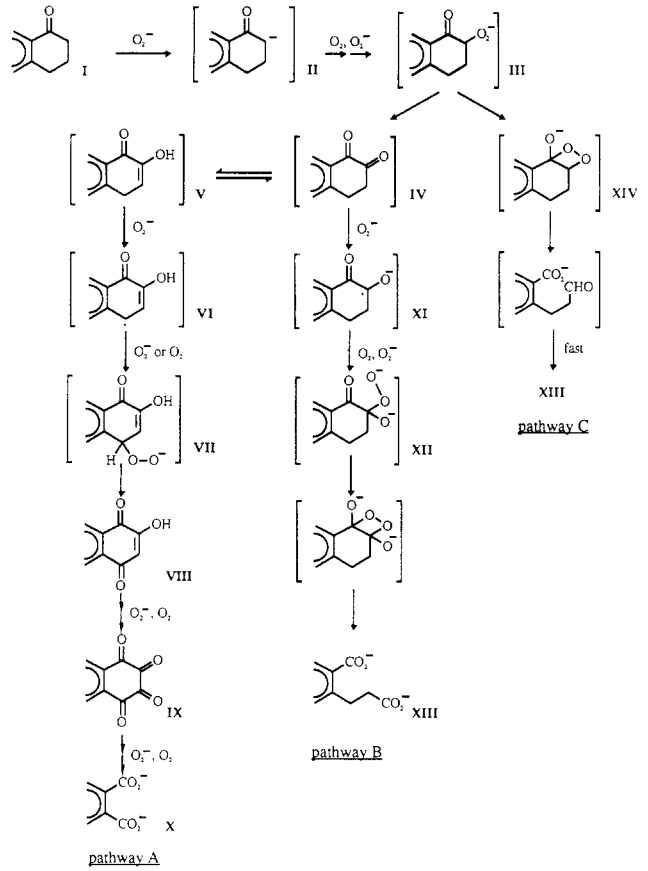
Mechanistic Insights. In Scheme I, we postulate, based on prior literature and our results, a likely sequence of steps to account for the major and minor products that we observe. This scheme is shown for substrates of the cyclohexanone type fused to aromatic moieties, but it is applicable to all of the substrates of Table I. Species in brackets have not actually been observed because either they are inherently unstable (anionic species and radicals) or they are very reactive under our conditions (e.g. IV, V).

Although O_2^- is a *very* weak oxidant[1,2,10] ($E°_{O_2^-/O_2^{2-}}$ = −2.02 V vs SCE in DMSO), it is known that it facilitates oxidations of acidic substrates in aprotic media by a sequence of steps initiated by abstracting an acidic proton from the substrate, like the proton α to carbonyl in I, to give the substrate anion II and the disproportionation

(9) Corey, E. J.; Nicolaou, K. C., Shibasaki, M.; Machida, Y.; Shiner, C. S. *Tetrahedron Lett.* **1975**, *37*, 3183.

(10) Cotton, F. A.; Wilkinson, G. *Advanced Inorganic Chemistry*, 4th ed.; John Wiley & Sons, Inc.: New York, 1980; p 490.

Scheme I



Scheme II

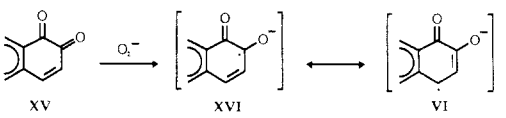


Table III. Effect of Temperature on KO_2 Oxidations[a]

substrate	temp, °C	reaction time, h	product yields (%)[b,c] X	XIII
1b	−20	30	35	45
	0	60	58	15
	25	20	65	8[d]
	80	2	68	7
20	−20	30	58	24
	0	60	67	11
	25	20	78	7
	80	2	76	5

[a] The oxidations were conducted with 100 mg of substrate, using a 32-fold molar excess of KO_2, and a molar ratio of crown ether/KO_2 = 2/5, in DMF (20 mL), under O_2. [b] Product yields were determined by HPLC. [c] Type X products are **2** from **1b** and **18** from **20** and type XIII products are 3-(2-carboxyphenyl)propionic acid from **1b** and **19** from **20**. [d] No yield of 3-(2-carboxyphenyl)-propionic acid from **1b** is reported in Table I since those data were obtained using 1 mg of substrate, and the small amount of 3-(2-carboxyphenyl)propionic acid detected by HPLC was difficult to quantify.

products of $HO_2^{\bullet}$ (H_2O_2 and O_2).[1] In turn, the substrate anion II is oxidized by oxygen to yield intermediate III,[11] which subsequently is able to form the α-diketone IV[12] (Scheme I). The keto form IV quickly establishes an equilibrium with its enol form V,[6,13] which can lose a benzylic hydrogen atom to O_2^-, to give the radical VI. This step is justifiable on the grounds that O_2^- reacting as a radical is able to abstract a hydrogen atom from substrates susceptible to a hydrogen atom transfer mechanism, to yield a substrate radical and HO_2^-.[1] The radical VI can then react with O_2^- (or O_2) to give the isolated intermediate VIII, which is en route to the major product X presumably through IX as data in Table I indicate.

The only other type of terminal product observed is the XIII type of diacid. Two pieces of data provide evidence that product X does not come from XIII, but that X and XIII originate from parallel mechanistic pathways (pathway A for X and pathway B and/or C for XIII) as indicated in Scheme I. First, we independently prepared 3-(2-carboxyphenyl)propionic acid, the type XIII product from α-tetralone (I, **1b**), by hydrogenation[14] of the commercially available 3-(2-carboxyphenyl)propenoic acid. This type XIII compound did not react with KO_2 under our conditions, proving that product X does not come from XIII. Similarly, we did not observe any conversion of the 3-(2-carboxypyrenyl)propionic acid (XIII, **19**) to the pyrene-1,2-dicarboxylic acid (X, **18**). Second, we independently proved that 3-(2-carboxyphenyl)propenoic acid (**6**), a minor product obtained from the KO_2 oxidation of 1,2-naphthoquinone (**5**), does not give phthalic acid under our oxidation conditions.

As shown in Scheme I, pathways B and C can both account for the formation of product type XIII. Pathway C has been proposed by Maurette for the formation of 4-(2-carboxyphenyl)butan-2-one from the superoxide oxidation of 2-methyl-1-tetralone.[6] The analogy of this reaction to the base-catalyzed autoxidation of cyclic ketones[12] and particularly of 2-methyl-1-tetralone[15] was claimed as a supporting evidence for this mechanistic route. We favor pathway B, however, in which the keto form IV is reduced by O_2^- (which in fact is a moderate reducing agent; $E°_{O_2/O_2^-}$ ranges from ca. −0.2 to −0.6 V vs NHE depending on the medium)[10] to give XI,[4] which can couple with another radical like O_2 (or O_2^-) to give XII that rearranges to XIII. Supporting evidence for pathway B comes from the behavior of 1,2-naphthoquinone (**5**) (Table I) which is unable to enolize and therefore is a good model of the keto form IV.[16] Although **5** cannot convert to XIV and finally to a type of product similar to XIII (i.e. **6**) via pathway C, it still yields some 3-(2-carboxyphenyl)propenoic acid (**6**). This is probably achieved by an initial reduction of 1,2-naphthoquinone (NQ) by superoxide to yield the radical anion XVI (Scheme II) similar to XI. This reduction, having $\Delta E° = \sim+0.36$ V ($E°_{NQ/NQ^{\bullet-}} = \sim-0.51$ V vs SCE in DMF/TEAP,[17] and $E°_{O_2/O_2^-} = -0.87$ V vs SCE in DMF/TBAP[18]) is favored thermodynamically. It is

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(14) Vogel, A. *Textbook of Practical Organic Chemistry*, 4th ed.; Longman Scientific & Technical: Essex, England, 1978; p 800.

(15) Baillie, A. C.; Thomson, R. H. *J. Chem. Soc. C* **1966**, 2184.

(16) A reviewer has expressed concern regarding mechanistic pathway B and has suggested that the validity of this pathway can be tested by performing the KO_2 oxidation on authentic 3,4-dihydro-1,2-naphthoquinone (compound type IV) to see if XIII is formed. This suggestion is not helpful since it is known that 3,4-dihydro-1,2-naphthoquinone converts to 1,2-naphthoquinone (**5**) in the presence of O_2 and base.[28] As we have shown independently (see Table I), the latter quinone yields both X and XIII under our reaction conditions. Nevertheless, when the base is $O_2^{\bullet-}$, IV does not need to go through 1,2-naphthoquinone in order to give XIII because of the reducing power of $O_2^{\bullet-}$, as shown in pathway B.

(17) Meites, L.; Zuman, P. *CRC Handbook Series in Organic Electrochemistry*; CRC Press: Boca Raton, FL, 1976; Vol. I, p 407.

noteworthy that 1,2-quinones **5**, **13**, and **22** (Table I), although unable to enolize to an intermediate structurally similar to V, all yield 1,2-dicarboxylic acids (X) as major final products, apparently through the above mentioned reduction of the generalized substrate XV to XVI, which is a resonance form of VI (Scheme II).

Further support of pathway B for the formation of XIII comes from the effect of temperature on the product ratio of X vs XIII. It has been shown[12] that the base-catalyzed autoxidation of cyclic ketones similar to the generalized substrate I favors products of type IV to products of type XIII at low temperatures (e.g. −20 °C). At higher temperatures (>−8 °C) the major products are of type XIII. Thus, if it is assumed that products of type X originate from the α-diketone IV through pathway A and that products type XIII come from pathway C, one would anticipate more X at low temperature and XIII at higher temperature. However, the temperature data for the KO_2 reaction of compounds **1b** and **20**, presented in Table III, show exactly the opposite effect. Clearly, the mechanistic model for the base-catalyzed autoxidation of cyclic ketones is unable to explain the temperature effect. Our mechanistic scheme, however, easily rationalizes this effect. The α-diketone IV, even though it is less stable thermodynamically,[12,13] would equilibrate more slowly with its enol form V at a low temperature (−20 °C). This apparently allows more of IV to follow competitive pathway B, increasing the yield of product type XIII. The key difference then between the base-catalyzed autoxidation and the superoxide assisted oxidation of cyclic ketones is the reducing power of O_2^-, which gives rise to pathway B.

Conclusion

A facile transformation of various hydroxy and keto derivatives of aromatic hydrocarbons into 1,2-dicarboxylic acids has been achieved. The few procedures reported previously[19-22] to form aromatic 1,2-dicarboxylic acids other than phthalic acid are demanding in terms of availability of starting materials, number of steps, or use of harsh conditions. In contrast, our method is a single-step, mild oxidation which is applicable to a variety of precursors and furnishes a high yield of this type of product.

Experimental Section

Materials and Methods. KO_2, 18-crown-6 ether, DMF (HPLC grade), 1-indanone (**1a**), 1-benzosuberone (**1c**), α- and β-tetralones (**1b** and **4**), 1,2- and 1,4-naphthoquinones (**5** and **7a**, respectively), 2-hydroxy-1,4-naphthoquinone (**7b**), 1-naphthol (**8**), phthalic acid (**2**), 2-carboxycinnamic acid (**6**), 1,2,3,4-tetrahydrophenanthren-1-one (**9**), 3,4-dihydroxybenz[*a*]anthracen-1(2*H*)-one (**11**), 1,4-chrysenequinone (**14**), 9,10-dihydrobenzo[*a*]pyren-7(8*H*)-one (**20**), and benzo[*a*]pyrene (**26**) were obtained from Aldrich Chemical Co. and used as received except for DMF (dried over 40-nm molecular sieves) and 1,2-naphthoquinone (**5**), which was purified by flash column chromatography (silica gel, CH_2Cl_2) and subsequent recrystallization from CH_3OH. Benz[*a*]anthracene-3,4-dione (**13**) and tetrahydrobenzo[*a*]pyrene-*r*-7,*t*-8,9,*c*-10-tetrol (**24**) were purchased from the National Cancer Institute. 7,8,9,10-Tetrahydrobenzo[*a*]pyren-7-ol (**17**),[23] 9,10-dihydrobenzo[*a*]pyrene (**25**),[23] *cis*-[23] and *trans*-7,8-dihydroxy-7,8,9,10-tetrahydrobenzo[*a*]pyrene[24] (**23a,b**), 9,10-dihydrobenzo[*a*]pyren-8(*H*)-one (**21**),[23] and benzo[*a*]pyrene-7,8-dione (**22**)[25] were synthesized according to literature procedures.[26] 3-(2-Carboxyphenyl)propionic acid was prepared by hydrogenation[14] of 3-(2-carboxyphenyl)propenoic acid (**6**).

^1H NMR spectra were recorded on a Varian XL-300 spectrometer with tetramethylsilane as internal standard. Mass spectra were obtained at 20 eV on a Nuclide 12-90 G mass spectrometer interfaced to Teknivent Vector/one data system. UV absorption spectra (in CH_3CN) were measured with a Perkin-Elmer Lambda 3B UV/vis spectrophotometer interfaced to Perkin-Elmer 3600 data station. Elemental analyses were performed by Atlantic Microlab Inc. Melting points were determined on a Thomas-Hoover apparatus and are uncorrected. High-performance liquid chromatography equipment consisted of a LDC (Laboratory Data Control) Gradient Master, two LDC Constametric III pumps, a Rheodyne 7125 injector, a UV Monitor at λ = 254 nm, and a SP (Spectra Physics) 4270 integrator. HPLC was carried out either on a Brownlee 4.6 × 220 mm RP-18, 5 μm analytical column at a flow of 1 mL/min or on a Dynamax 10 × 250 mm RP-18, 5 μm semipreparative column at a flow of 4 mL/min. Solvent A was 0.1 M acetic acid (pH 2.9) and solvent B was acetonitrile. Phthalic acid was analyzed with a 30-min gradient from 10 to 90% B. For naphthalene-, anthracene-, phenanthrene-, and pyrene-1,2-dicarboxylic acids the gradient was from 30 to 80% B in 20 min.

General Procedure for Oxidation. Finely powdered potassium superoxide (30 mol excess) and 18-crown-6 ether (12 mol excess) were suspended in dry DMF (15 mL). The substrate to be oxidized (50 or 100 mg) was dissolved in DMF (10 or 20 mL, respectively) and added dropwise within a few minutes to the KO_2 suspension. The mixture was stirred vigorously for 20 h at room temperature, in the dark, under oxygen atmosphere. The reaction mixture was then diluted with 10 mL of water to destroy the unreacted KO_2, and the solvents were evaporated under reduced pressure. To the residue was added 3 M HCl (~20 mL), and the mixture was subsequently extracted with three 30-mL portions of ethyl acetate. The combined organic extracts were dried (Na_2SO_4) and evaporated to dryness under reduced pressure. The residual solid was redissolved in THF and purified by reverse-phase HPLC (for conditions see above). This oxidation was also performed with 1 mg of starting material, using a 100-fold molar excess of KO_2 and a 40-fold molar excess of 18-crown-6 ether over substrate in DMF (1 mL). In the latter case, after 20 h, the reaction was quenched with water (1 mL) and an aliquot was injected directly into a reverse-phase HPLC column. Yields were determined using authentic products to construct calibration curves.

Naphthalene-1,2-dicarboxylic acid (10): mp 174–175 °C (lit.[19] mp 175 °C, lit.[20] mp 175–176 °C); ^1H NMR (acetone-d_6) δ 7.62–7.76 (m, 2 H, $H_{6,7}$), 8.01–8.15 (m, 4 H, Ar), 10.18 (br s, 2 H, CO_2H); UV λ_{max} (ϵ_M) 233 nm (47 800); MS *m/e* (relative intensity) 216 (M^+, 2), 198 (100), 154 (55), 126 (94).

Anthracene-1,2-dicarboxylic acid (12): mp 235–236 °C dec; ^1H NMR (acetone-d_6) δ 7.59–7.64 (m, 2 H, $H_{6,7}$), 8.01 (d, 1 H, H_4, $J_{3,4}$ = 9.1 Hz), 8.13–8.21 (m, 2 H, $H_{5,8}$), 8.24 (d, 1 H, H_3, $J_{3,4}$ = 9.1 Hz), 8.69 (s, 1 H, H_{10}), 8.74 (s, 1 H, H_9); UV λ_{max} (ϵ_M) 258 nm (81 300); MS *m/e* (relative intensity) 266 (M^+, 2), 248 (100), 176 (85). Anal. Calcd for $C_{16}H_{10}O_4$: C, 72.16; H, 3.79. Found: C, 72.42; H, 4.00.

Phenanthrene-1,2-dicarboxylic acid (15): mp >300 °C; ^1H NMR (acetone-d_6) δ 7.76–7.81 (m, 2 H, $H_{6,7}$), 7.99 (d, 1 H, H_9, $J_{9,10}$ = 7.9 Hz), 7.95–8.08 (m, 2 H, $H_{5,8}$), 8.29 (d, 1 H, H_4, $J_{3,4}$ = 8.9 Hz), 8.93 (d, 1 H, H_{10}, $J_{9,10}$ = 7.9 Hz), 9.04 (d, 1 H, H_3, $J_{3,4}$ = 8.9 Hz), 11.32 (br s, 2 H, CO_2H); UV λ_{max} (ϵ_M) 290 nm (14 700), 262 (57 700), 216 (26 100); MS *m/e* (relative intensity) 266 (M^+, 2), 248 (100), 204 (20), 176 (77). Anal. Calcd for $C_{16}H_{10}O_4$: C, 72.16; H, 3.79. Found: C, 72.01; H, 4.13.

Pyrene-1,2-dicarboxylic acid (18): mp >300 °C; ^1H NMR (acetone-d_6) δ 8.21–8.45 (m, 7 H Ar), 8.91 (s, 1 H, H_3), 11.94 (br s, 2 H, CO_2H); UV λ_{max} (ϵ_M) 342 nm (27 400), 326 (18 100), 281 (23 600), 269 (27 600), 254 (39 500); MS *m/e* (relative intensity) 29 (M^+, 2), 272 (47), 228 (14), 200 (100). Anal. Calcd for $C_{18}H_{10}O_4$:

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C, 74.47; H, 3.47. Found: C, 74.37; H, 3.41.

3-(2-Carboxypyrenyl)propionic acid (19): mp 235 °C dec; ^{1}H NMR (DMSO-d_6) δ 2.81 (t, 2 H, $CH_2CH_2CO_2$, $J_{2,3}$ = 6.5 Hz), 3.77 (t, 2 H, $CH_2CH_2CO_2$, $J_{2,3}$ = 6.5 Hz), 8.15–8.38 (m, 7 H, Ar), 8.49 (s, 1 H, H_3); MS m/e (relative intensity) 318 (M^+, 100), 300 (15), 272 (34), 259 (79), 200 (38). Anal. Calcd for $C_{20}H_{14}O_4$: C, 74.54; H, 4.44. Found: C, 75.47; H, 4.38.

1,2,3,4-Naphthalenetetrone (3): mp 132 °C (lit.[27] mp 130–131 °C); ^{1}H NMR ($CDCl_3$) δ 7.63–7.82 (m, 2 H, $H_{6,7}$), 8.05–8.24 (m, 2 H, $H_{5,8}$); MS (positive chemical ionization, CH_4) m/e (relative intensity) 216 (M + 28, 19), 188 (M^+, 100).

1,2,3,4-Chrysenetetrone (16): mp 224–226 °C dec; ^{1}H NMR ($CDCl_3$) δ 7.70–7.78 (m, 2 H, $H_{8,9}$), 7.95–8.00 (m, 2 H, $H_{7,10}$), 8.05 (d, 1 H, H_6, $J_{5,6}$ = 8.5 Hz), 8.72 (d, 1 H, H_{11}, $J_{11,12}$ = 7.9 Hz), 8.91 (d, 1 H, H_5, $J_{5,6}$ = 8.5 Hz), 9.03 (d, 1 H, H_{12}, $J_{11,12}$ = 7.9 Hz); MS (positive chemical ionization, CH_4) m/e (relative intensity) 316 (M + 28, 22), 288 (M^+, 100). Anal. Calcd for $C_{18}H_8O_4$ (unstable compound): C, 74.99; H, 2.80. Found: C, 74.05; H, 2.75.

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Conformations of [*m*.3.3]Propellane Ketones and Alcohols†

Anand Natrajan, Joseph D. Ferrara, John D. Hays, Mahesh Khot, Jennifer Colonell, Wiley J. Youngs, and Chaim N. Sukenik*,[1]

Department of Chemistry, Case Western Reserve University, Cleveland, Ohio 44106

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We have prepared a series of [*m*.3.3]propellanediones (*m* = 3, 4, 10, 12, 22) and have studied various structural aspects of these diones and their ketol and diol reduction products. We have used X-ray crystallography to establish stereochemistry and to explore cyclopentyl ring conformations. The ^{1}H NMR spectra of the ketols and diols have also been used to probe their conformations. They provide evidence for intramolecular hydrogen bonding between the OH groups of some of the anti,anti (aa) diols. The folding needed for this interaction is also seen in the gas phase in the *i*-C_4H_{10} CIMS. For an aa diol, this leads to a bridged $[M + 1]^+$ ion. For an anti ketol, it promotes an intramolecular proton transfer leading to H_2O elimination from the $[M + 1]^+$ ion. This results in unusual stability for the protonated parent ion of an aa diol and enhanced fragmentation of the parent ion of an anti ketol, relative to their stereoisomers. The ease of the molecular puckering that is the key observation of both the NMR and CIMS work, is shown to be dependent on the size of the propellane polymethylene bridge.

As part of a research program on micelle-induced perturbations of organic reactions,[2] we have synthesized and determined the stereochemistry of the ketols and diols of some [*m*.3.3]propellanes (*m* = 3, 4, 10, 12, 22; Scheme I).[3] The structural work done to assign those propellane configurations prompted the following study of the conformations of the fused cyclopentyl rings of the [*m*.3.3]propellanes. We have determined the X-ray crystal structure of the [12.3.3]propellanedione to provide the first direct evidence for the conformation of such fused cyclopentanone rings. We have used ^{1}H NMR coupling constants to probe the solution conformations of the cyclopentanol rings. And, we have explored the ability of the two oxygen atoms in the anti,anti (aa) diols and the anti ketols to approach each other, by studying the solvent dependence of their ^{1}H NMR spectra and by obtaining their chemical ionization mass spectra (CIMS).

Results and Discussion

X-ray Crystallography. The single-crystal X-ray structures of the three [4.3.3]propellanediols have been reported by Kapon et al.[4] We have reported the structure of the [10.3.3] syn,syn (ss) diol.[3a] Comparison of these showed that, while *m* = 4 diols had relatively planar cyclopentanol rings, the *m* = 10 diol had puckered cyclopentanols whose OH-bearing carbons were bent down (away from the polymethylene ring) by 37°. Since no crystallographic data were available on any carbonyl-containing [*m*.3.3]propellanes, we solved the structure of a propellanedione.

The structure of [12.3.3]propellane-16,19-dione was determined by standard X-ray analysis. The molecular structure is shown in Figures 1 and 2. The five-membered rings are nearly planar with the root-mean-square deviation (rms dev) for the atoms defining the cyclopentanone plane for C(01), C(14), C(15), C(16), C(17), and O(01) at 0.134 (2) Å and C(01), C(14), C(18), C(19), C(20), and O(02) at 0.128 (2) Å. The rms deviation from the mean plane of

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