*J. Org. Chem.* **1984**, *49*, 1969–1974

chromatography[25] were used throughout for product separation. Eastman chromagram precoated (silica gel on polyethylene) sheets impregnated with a fluorescent indicator were employed in thin-layer chromatographic operations. Isocyanates were purchased from the Aldrich, Eastman Organic, and Pfalts & Bauer Chemical Companies and distilled prior to use. *p*-Nitrophenyl isocyanate was recrystallized from anhydrous petroleum ether.

**Reactions of Phosphoranes 1 with Aryl Isocyanates 2. Preparations of 2,3-Dihydro-1*H*-imidazo[1,2-*b*]pyrazol-2-ones 13 and 4,9-Dihydropyrazolo[5,1-*b*]quinazolines 10. General Method.** A solution of the phosphorane 1 (2.0 mmol) and isocyanate 2 (2.5 mmol; $R^1$ = *p*-$O_2NC_6H_4$, 4.0 mmol) in 20 mL benzene was stirred under reflux for the amount of time indicated in Table I. After removal of solvent in vacuo, the reaction mixture was chromatographed on a silica gel column, eluting with ethyl acetate/hexane. This yielded the following in order of elution ($R^1$ = 2-$CF_3C_6H_4$, reverse order).

(a) **2,3-Dihydro-1*H*-imidazo[1,2-*b*]pyrazol-2-one (13)** as a colorless solid. Recrystallization from ethanol or ether/petroleum ether afforded an analytical sample. Isolated yields (Table I), melting points (Table I), IR (Table II), $^1H$ NMR (Table IV), $^{13}C$ NMR (Table VI), and mass spectral data (Table VII) are collected separately.

(b) **4,9-Dihydropyrazolo[5,1-*b*]quinazoline (10)** as a slightly yellow solid. Recrystallization from ether/petroleum ether afforded an analytical sample. Isolated yields (Table I), melting points (Table I), IR (Table II), $^1H$ NMR (Table III), $^{13}C$ NMR (Table V), and mass spectral data (Table VII) are collected separately.

**Reactions of Phosphoranes 1 with Alkyl or 2,6-Dimethylphenyl Isocyanates 2. Preparations of 2,3-Dihydro-1*H*-imidazo[1,2-*b*]pyrazol-2-ones 13. General Method.** A solution of the phosphorane 1 (2.0 mmol) and isocyanate 2 (2.5 mmol) in 20 mL of benzene was stirred under reflux for the amount of time indicated in Table I. After removal of solvent in vacuo, the reaction mixture was chromatographed on a silica gel column, eluting with ethyl acetate/hexane, to yield a 2,3-dihydro-*1H*-imidazo[1,2-*b*]pyrazol-2-one (13). Recrystallization from ether/petroleum ether afforded a colorless analytical sample. Isolated yields (Table I), melting points (Table I), IR (Table II), $^1H$ NMR (Table IV), $^{13}C$ NMR (Table VI), and mass spectral data (Table VII) are collected separately.

**Acknowledgment.** The generous support of the National Institute of General Medical Science (Grant No. GM 27620) is gratefully acknowledged. We thank Dr. Roger Crecely of the University of Delaware for obtaining and discussing the $^1H$ and $^{13}C$ NMR spectra, reported in this work, with us. We thank the mass spectroscopy lab of the University of Delaware for the mass spectral data. Purchase of the Bruker WM 250 was supported, in part, by a grant (GM 27616) from the National Institutes of Health.

**Registry No.** **1** (R = $CH_3$), 81724-92-7; **1** (R = $CH_3CH_2$), 89726-08-9; **1** (R = $CH_3CH_2CH_2$), 89726-09-0; **1** (R = $CH_2$ = $CHCH_2$), 81724-93-8; **1** (R = $C_6H_5CH_2$), 81724-94-9; **2** (R′ = $C_6H_5$), 103-71-9; **2** (R′ = 2-$CF_3C_6H_4$), 2285-12-3; **2** (R′ = 1-$C_{10}H_7$), 86-84-0; **2** (R′ = 2,6-$(CH_3)_2C_6H_3$), 28556-81-2; **2** (R′ = $CH_3$), 624-83-9; **2** (R′ = Bu-*t*), 1609-86-5; **2** (R′ = 4-$CH_3OC_6H_4$), 5416-93-3; **2** (R′ = 4-$CH_3C_6H_4$), 622-58-2; **2** (R′ = 4-$ClC_6H_4$), 104-12-1; **2** (R′ = 4-$CF_3C_6H_4$), 1548-13-6; **2** (R′ = 4-$O_2NC_6H_4$), 100-28-7; **10a**, 89726-10-3; **10b**, 89726-12-5; **10c**, 89726-14-7; **10d**, 89726-16-9; **10e**, 89746-10-1; **10f**, 89726-19-2; **10g**, 89726-21-6; **10h**, 89726-23-8; **10n**, 89726-30-7; **10o**, 89726-32-9; **10p**, 89726-34-1; **10q**, 89746-11-2; **10r**, 89746-12-3; **13a**, 89726-11-4; **13b**, 89726-13-6; **13c**, 89726-15-8; **13d**, 89726-17-0; **13e**, 89726-18-1; **13f**, 89726-20-5; **13g**, 89726-22-7; **13h**, 89726-24-9; **13i**, 89726-25-0; **13j**, 89726-26-1; **13k**, 89726-27-2; **13l**, 89726-28-3; **13m**, 89726-29-4; **13n**, 89726-31-8; **13o**, 89726-33-0; **13p**, 89726-35-2; **13q**, 89726-36-3; **13r**, 89726-37-4.

**Supplementary Material Available:** Spectroscopic data in Tables II–VII (8 pages). Ordering information is given on any current masthead page.

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[25] Taber, D. F. *J. Org. Chem.* **1982**, *47*, 1351.

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# Oxidative Cleavage of Substituted Naphthalenes Induced by Irradiated Semiconductor Powders

Marye Anne Fox,* Chia-Chung Chen, and Janet N. N. Younathan

*Department of Chemistry, University of Texas at Austin, Austin, Texas 78712*

*Received November 22, 1983*

Electron-rich members of a series of substituted naphthalenes react with oxygen to give ring-cleaved products upon long wavelength ultraviolet irradiation of $TiO_2$ powders suspended in oxygen-saturated acetonitrile solutions of the arene. Reactivity within the series parallels trends in the oxidation potential, i.e., the species with the less positive oxidation potential appears to react more efficiently. A mechanism involving sensitized formation of the substituted naphthalene cation radical is suggested for the semiconductor-mediated photocatalysis.

Recent interest in photoreactions occurring at surfaces and in new methods for the activation of oxygen to effect the functionalization of hydrocarbons has stimulated the investigation of irradiated semiconductor powders as redox photocatalysts. The photoelectrochemical properties of excited metal oxides render them effective photooxidation catalysts,[1] but so far only limited use of these sensitizers for synthetically useful conversions has been described.

In particular, the photoinduced oxidation of aryl systems has been peripherally studied. The $TiO_2$-photocatalyzed oxidative cleavage of aryl olefins gives rise, in excellent chemical yields, to carbonyl compounds by initial oxygenation of the double bond,[2,3] but no oxygenation of the aryl rings could be detected. Similarly, the semiconductor-sensitized photooxidation of aryl amines, e.g., aniline or toluidine[4] and of alkylbenzenes, e.g., toluene,[5] leads to products involving side chain oxidation. In contrast, the photooxygenation of benzene,[6] benzoic acid,[7] or toluene[8]

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[1] Bard, A. J. *Science (Washington D.C.)* **1980**, *207*, 139.

[2] Fox, M. A.; Chen, C. C. *J. Am. Chem. Soc.* **1981**, *103*, 6757.

[3] Kanno, T.; Oguchi, T.; Sakuragi, H.; Tokumaru, K. *Tetrahedron Lett.* **1980**, 467.

[4] Kasturirangan, H.; Ramakrishnan, V.; Kuriacose, J. C. *J. Catal.* **1981**, *69*, 216.

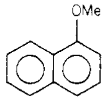
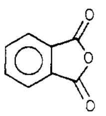
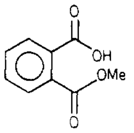
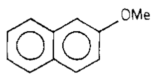
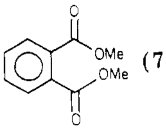
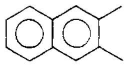
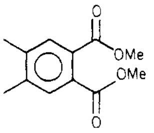
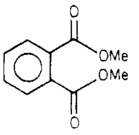
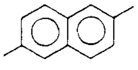
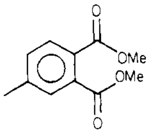
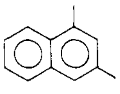
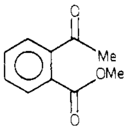
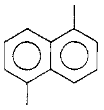
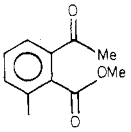
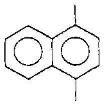
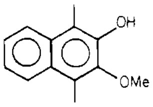
[5] (a) Mozzanega, M. N.; Herrmann, J. M.; Pichat, P. *Tetrahedron Lett.* **1977**, 2965. (b) Fujihara, M.; Satoh, Y.; Osa, T. *Nature* **1981**, *293*, 206.

[6] Izumi, I.; Dunn, W. W.; Wilbourn, K. O.; Fan, F. R. F.; Bard, A. J. *J. Phys. Chem.* **1980**, *84*, 3207.

[7] Izumi, I.; Fan, F. R. F.; Bard, A. J. *J. Phys. Chem.* **1981**, *85*, 218.

0022-3263/84/1949-1969$01.50/0

**Table I. Oxidative Cleavage Products Formed on Irradiated[a] $TiO_2$ Powders**

| substrate | irradiation time, h | conversion,[b] % | esterification method[c] | product and yield[d] (%) |
|---|---|---|---|---|
|  1 | 24 | 100 | |  (20) +  (46) |
|  2 | 24 | 64 | A |  (73) |
|  3 | 24 | 65 | A |  (13) +  (83) |
|  4 | 48 | 100 | A |  (95) |
|  5 | 30 | 71 | B |  (50) |
|  6 | 48 | 62 | B |  (72) |
|  7 | 24 | 73 | B |  (79) |

[a] Rayonet Photochemical Reactor, 350-nm lamps, room temperature, 0.01–0.03 M solutions of naphthalenes (100–300 mg) and 50 mg of $TiO_2$ suspended in oxygenated anhydrous acetonitrile. [b] Conversion of starting material was based on GLPC analysis. [c] Esterification method: (A) $CH_3OH$, $H_2SO_4$; (B) $CH_2N_2$. [d] Products were identified by NMR analysis and yields were calculated against an internal standard after completion of the reaction.

induced by irradiation of aqueous suspensions of $TiO_2$ powders gives some ring hydroxylation in competition with more extensive oxidative cleavage to carbon dioxide. The ring hydroxylation is thought to involve a photo-Fenton reaction, i.e., primary photoelectrochemical formation of the solvent-derived hydroxy radical,[6,8] for such products disappear when the photocatalysis is conducted in nonaqueous media.[8]

We report here our investigation of the photocatalyzed oxygenation of some substituted naphthalenes in which ring cleavage is observed. By avoiding an aqueous environment, we have achieved control of subsequent oxidation, i.e., interrupted the oxidative sequence before complete oxidation (to carbon dioxide) occurs. This work represents the first study in which preparatively useful quantities of organic materials of intermediate oxidation level can be isolated.

## Results

Irradiation ($\lambda = 350 \pm 20$ nm) of a suspension of $TiO_2$ powder in anhydrous, oxygenated acetonitrile made 0.01–0.03 M in a substituted naphthalene led to oxidative cleavage of the arene. After esterification of the reaction mixture by treatment either with acidic methanol or with diazomethane, the products listed in Table I were isolated. A much slower reaction was observed with 1-methylnaphthalene (**8**) and with naphthalene (**9**) itself, but product isolation was not attempted for these compounds. 1-Cyanonaphthalene (**10**) gave no oxidation products even after prolonged irradiation. Although some tail absorption of the naphthalenes occurs in the wavelength region of the irradiation, the oxidative consumption of starting material was at least an order of magnitude more rapid in the presence of $TiO_2$ powders than in its absence. Stirring of the reactants with $TiO_2$ powder in the dark led to no discernible reaction.

The irradiation times required for the disappearance of **1**–**10**, together with the oxidative peak potential of each member of this series, are listed in Table II.

## Discussion

The observed ring cleavage induced by catalytic excitation of $TiO_2$ powder represents a new route to hydrocarbon oxidation. The isolation of preparatively useful quantities of highly functionalized benzenes indicates the possibility of important uses for such photocatalyses. The direct products of the photocatalyzed irradiation were acids (based on the response of the reaction mixture to wet ninhydrin paper), but for easier isolation, the reaction mixtures were esterified before quantitative analysis was undertaken.

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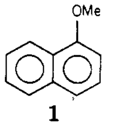
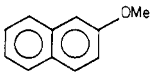
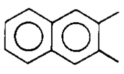
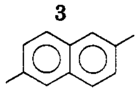
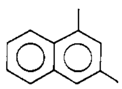
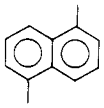
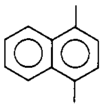
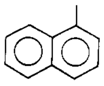
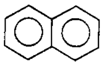
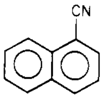
(8) Fujihara, M.; Satoh, Y.; Osa, T. *J. Electroanal. Chem. Interfacial Electrochem.* 1981, *126*, 277.

**Table II. Oxidation Peak Potentials[a] of Substituted Naphthalenes and Relative Rates[b] of Their Photooxygenation on $TiO_2$ in $CH_3CN$**

| substrate | $E_{ox}$, V vs. SCE | $T_{1/2}$, h[c] |
|---|---|---|
| <br>1 | 1.23 | 1.3 |
| <br>2 | 1.26 | 2.6 |
| <br>3 | 1.41 | 3.5 |
| <br>4 | 1.43 | 4.0 |
| <br>5 | 1.45 | 3.7 |
| <br>6 | 1.49 | 5.7 |
| <br>7 | 1.51 | 2.5 |
| <br>8 | 1.51 | 6.3 |
| <br>9 | 1.60 | 9.5 |
| <br>10 | 2.11 | *d* |

[a] All cyclic voltammograms are irreversible. [b] Irradiated in Rayonet reactor with 350-nm lamps. [c] Time required to consume 50% of the substrate. [d] No reaction was found after 9 h.

A plausible mechanism for the primary photochemical event is shown in Scheme 1. Band gap irradiation of semiconductor powders is known to generate an electron-hole pair.[1] Migration of the hole to the surface of the photocatalyst should induce rapid electron transfer from an adsorbed substrate whose oxidation potential is less positive than the valence band of the semiconductor (ca. +2.3 V for $TiO_2$ in $CH_3CN$[8]). The potentials listed in Table II indicate that the entire series of substituted naphthalenes could, in principle, react in this fashion.

With an adsorbed naphthalene in a nonoxidizable solvent, this process should lead to the formation of adsorbed cation radical. That such cation radicals are reasonable intermediates has been established by spectroscopic detection of olefin radical cations upon flash photolysis of colloidal $TiO_2$ suspended in olefinic acetonitrile solutions[9] and by substituent effects on the rate of catalyzed oxidation of 1,1-diphenylethylenes.[10]

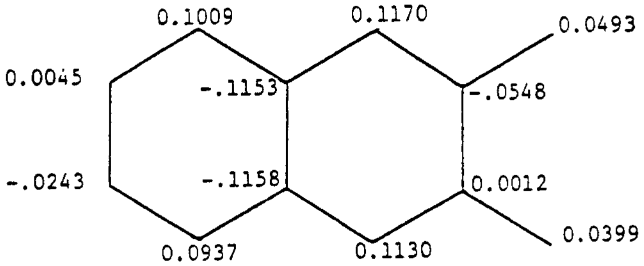


**Figure 1.** Charge distributions on radical cation of 2,3-dimethylnaphthalene (**3**) calculated by UMNDO.

The regiochemistry of the observed cleavage is also consistent with a positively charged intermediate. Except for **7**, all the substituted naphthalenes react by predominant or exclusive cleavage of the ring bearing electron-releasing substituents. With **10**, a species bearing a strong electron-withdrawing substituent, no oxidative cleavage could be observed within a reasonable irradiation period. With **3**, products resulting from the cleavage of either ring could be observed, the dominant (6:1) product being derived from preferential attack on the substituted (1,4) rather than the unsubstituted (5,8) ring. A UMNDO[11] calculation of the charge distribution in the radical cation derived from **3** provides a rationale for this preference, significantly higher positive charge being observed at the 1,4- than the 5,8-positions (Figure 1).

Furthermore, independent generation of the radical cation of **1** in homogeneous solution using dicyanobenzene as an electron acceptor sensitizer affords the same products as those obtained at the heterogeneous $TiO_2^*$/solution interface. Phthalic anhydride and monomethyl phthalic acid ester were obtained in 3% and 60% yields, respectively. Although this distribution differs from that found in the $TiO_2$-sensitized photolyses, the sum of the chemical yields of these closely related products essentially duplicated that found on the irradiated powder.

The required irradiation period for oxidative cleavage within the series tends to increase as the oxidative peak potential of the compound increases (Table II). Such an observation is consistent with the generation of a cation radical along the reaction coordinate, but the modest influence of arene oxidizability on the photooxygenation rate suggests that radical ion formation may not be involved in the rate-determining step. Rather, the efficiency of the reaction may be determined not by capture of the photogenerated hole, but rather by the competing rates of radical cation oxygenation and back electron transfer. Furthermore, the observation that rate differences can be seen in arenes of identical oxidizability, e.g., **7** vs. **8**, implies that some other factor, possibly steric in origin, contributes to the kinetics of these heterogeneous processes. A likely explanation of this effect involves differing adsorption equilibria of the variously substituted naphthalenes.

The adsorbed radical cation has several possible fates: recapture of the photoproduced electron to regenerate neutral adsorbed arene in an energy dissipative step, reaction with adsorbed ground-state oxygen or oxide sites on the semiconductor, or reaction with photogenerated superoxide either to form chemical bonds or through back electron transfer to generate adsorbed arene and singlet oxygen. The quantum efficiency of the reaction of 1 (0.07) is modest (as it is, apparently, for other members of the

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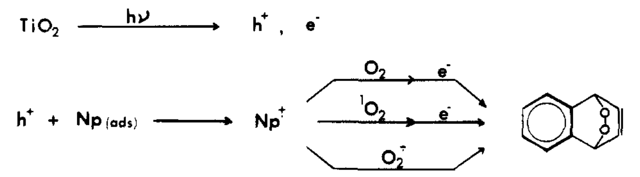
(9) Fox, M. A.; Lindig, B. A.; Chen, C. C. *J. Am. Chem. Soc.* **1982**, *104*, 5828.

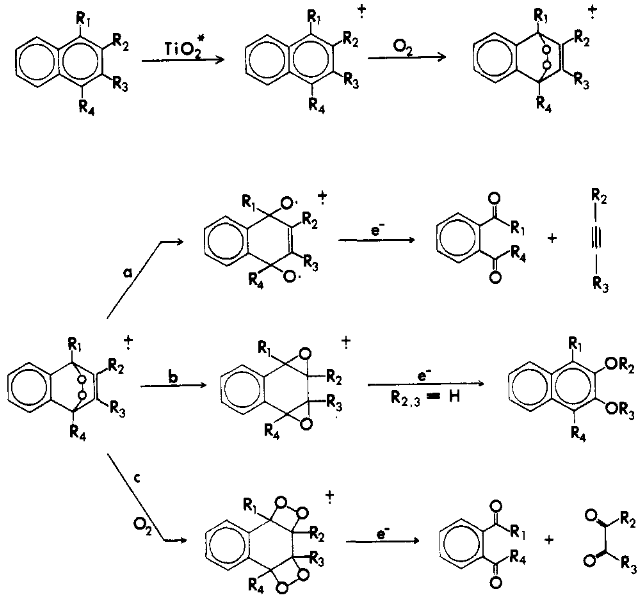
(10) Fox, M. A.; Chen, C. C. *Tetrahedron Lett.* **1983**, *24*, 547.

(11) Dewar, M. J. S.; Thiel, W. *J. Am. Chem. Soc* **1977**, *99*, 4899.

Scheme I



Scheme II



series; see relative rates, Table 2), although the chemical yield of the isolated products are reasonably high. This, together with the reported high quantum yield for electron–hole pair generation in irradiated $TiO_2$, requires that a significant deactivation route exist, probably involving inverse electron transfer.

The observed cleavage requires the presence of oxygen: deoxygenated solutions irradiated in parallel fashion do not give evidence of oxidation. Thus, either oxygen gas or a species derived from it must function as the effective source of oxygen atoms. As a working hypothesis, we assume that the observed oxidative cleavage is initiated by endoperoxide formation, three routes to which are shown in Scheme I. Such a species can undergo further oxidation and/or cleavage to give the observed products. This supposition is based on the observed stoichiometry of the reaction (3 mol of oxygen taken up per mol of 7 reacted) and by analogy to the demonstration by Rigaudy et al.[12] that rearrangement of such endoperoxides can give rise to products similar to those observed here. A possible route to the cleavage products is shown in Scheme II, path a. While the alkynes formed as side products in this route were not isolated (probably because of high volatility under the continuous stream of reactant (oxygen) gas or because of further oxidation and radical ion-induced polymerization), the formation of the substituted benzoic acids would imply the initial formation of substituted benzaldehyde (or acetophenone). Benzaldehyde can be shown independently to be oxidized under the reaction conditions.[13] This autooxidation must be rapid, in fact, for no trace of substituted benzaldehyde could be detected from any of the naphthalenes studied here. The phthalic anhydride obtained from the oxidative cleavage of 1 is almost certainly derived by loss of methanol from the initially formed monomethyl ester of phthalic acid, for the ratio of the anhydride to the ester continues to increase as the irradiation continues while the product mass balance remains high.

Scheme II can also accommodate the formation of 2,3-oxygenated product observed from 3 if the initially formed endoperoxide radical cation rearranges more rapidly than it can ring open: path b.

An alterante route to oxidative cleavage products in this series involves formation of a bis(dioxetane): path c. Such a species might be formed either directly from the substituted naphthalene or from further oxidation of the endoperoxide discussed above. Cleavage to aromatic carbonyl compounds would be accompanied by formation of a 1,2-dicarbonyl compound. Although aliphatic keto aldehydes formed in this pathway might not be isolable, biacetyl (the product expected from this route in the cleavage of 3) should persist unless its photocatalyzed destruction is more rapid than the disappearance of the substituted naphthalene. No evidence for its formation could be obtained, however, either by attempted isolation or GLPC detection of the compound itself or of its oxime derivative. Although the route shown in Scheme II remains possible for other members of the series, we can offer no solid supporting evidence for its occurrence.

The distinction between modes for oxidation on heterogeneous catalysts is difficult, but some evaluation of the possible involvement of singlet oxygen and/or superoxide can be made. That the observed reactivity is *not* derived from the attack of catalytically formed singlet oxygen on the substituted naphthalene is established by the contrasting product structure and kinetic behavior observed upon photocatalysis with irradiated $TiO_2$ and that reported for these compounds with singlet oxygen. Wasserman and co-workers have shown, for example, that a 1,4-endoperoxide is obtained in the reaction of singlet oxygen with 7, but that 1 completely resists reaction.[14] In contrast we find that 1 is oxygenated twice as rapidly as 7 at the surface of an irradiated semiconductor. Product distributions and relative rates obtained by de Boer and co-workers[15] for the reaction of singlet oxygen with mono- and dimethylnaphthalenes also differed significantly from those seen here.

The possibility that superoxide generated at the surface of the irradiated catalyst acts as the primary oxidant with homogeneous arene is unlikely. None of the naphthalenes **1**–**10** react with solubilized potassium superoxide upon stirring for periods comparable to the irradiation periods used here. Furthermore, the presence of a superoxide quencher, phenylglyoxylic acid, did not significantly affect the rate of the photooxygenation.

We conclude, therefore, that sensitized radical cation formation represents the initial chemical reaction in these oxidative cleavages. The adsorbed cation radical reacts with oxygen or a species derived from it which is strongly adsorbed to the surface of the metal oxide photocatalyst. As with our previous investigation of the oxidative cleavage of olefins, no evidence for the involvement of singlet oxygen or homogeneous superoxide was obtained. Mechanistic investigations of other organic redox reactions induced by irradiated semiconductor powders are continuing in our laboratory.

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## Experimental Section

**Solvents and Reagents.** Acetonitrile ($CH_3CN$, MCB) was distilled under $N_2$ from calcium hydride and stored over 4-Å molecular sieves (MCB). 2,2,2-Trifluoroethanol ($CF_3CH_2OH$, Aldrich, gold label) was distilled onto 4-Å molecular sieves.

Titanium dioxide ($TiO_2$, MCB technical grade, powder) was dried overnight at 110 °C and stored in a vacuum desiccator containing dry calcium chloride. Oxygen gas ($O_2$) was dried by passing through a drying tube (2 cm × 30 cm) containing dry calcium chloride.

Naphthalenes **1**–**10** were commercially available and were purified by sublimation or vacuum distillation before use.

**General Procedure for the Photooxygenation of Substituted Naphthalenes Catalyzed by $TiO_2$.** Two procedures were followed: procedure A for analytical purposes and procedure B for preparative purposes.

In a Pyrex test tube (procedure A, 1 cm × 7 cm; procedure B, 3 cm × 20 cm) equipped with a rubber stopper, a solution of substituted naphthalene (ca. 0.01–0.03 M, 100–300 mg per 100 mL) in $CH_3CN$ or in $CH_3CN/CF_3CH_2OH$ mixtures was treated with $TiO_2$ (ca. 5 mg per 100 mL solution) and was then shaken vigorously to give a cloudy heterogeneous solution which was then bubbled with $O_2$ for 0.5–1.0 h. The tube was sealed by a rubber stopper wrapped with aluminum foil, and the solution was irradiated at room temperature under a positive pressure of $O_2$. Irradiations were carried out in a Rayonet photochemical reactor (Southern New England Ultraviolet Co.) equipped with 350-nm lamps and a cooling fan or with a Hanovia 450-W medium-pressure mercury lamp equipped with a uranium sleeve filter (wavelengths greater than 360 nm) and an Ace Glass water-flow Cut-off safety device.

After a measured period of time, one of two procedures was followed. In procedure A, the suspension was filtered and the filtrate was tested for the presence of acid (wet ninhydrin paper) before being esterified (see below) and analyzed by gas–liquid phase chromatography (GLPC, Antek 400 flame ionization instrument, Column A, 5 ft × 1/8 in. 10% SE-30 on 50–80 mesh Chromosorb P column, 150 °C, peak areas by triangulation or with a 3390A Hewlett-Packard integrator). In procedure B, $TiO_2$ was removed from solution by vacuum filtration, the reaction mixture was esterified, and the solvent was removed by rotary evaporation. The resulting reaction mixture was characterized by NMR spectroscopy after the addition of a stoichiometric amount of internal standard (*cis*-stilbene). The resulting mixture was then separated and purified by GLPC or HPLC (Waters R-401 liquid chromatography system with a Prep-PAK silica column eluted with Skelly B: ethyl acetate mixtures).

Esterification was achieved either by stirring the mixture obtained by removing solvent from the filtered irradiation mixture with methanol containing sulfuric acid (the method of Boyer and Schoen[16]) or with diazomethane (method of de Boer and Backer[17]).

Isolated products were identified by comparison of their spectral properties (NMR, IR, MS) and melting points with those of authentic samples. Yields and structures of the isolated products obtained after partial conversion of starting material are listed in Table I.

If the irradiations were conducted with deaerated solutions under an atmosphere of nitrogen, no oxidation could be observed. If $TiO_2$ were omitted in the above procedures, the starting naphthalenes were consumed at a much slower rate that observed in the presence of the catalyst: with **1**, for example, the ratio of the rates of disappearance of **1** with and without the catalysts were consistently greater than 10. Solutions of the naphthalenes **1**–**10** stirred over $TiO_2$ in the dark for 2 days showed no consumption of starting material.

**Photooxygenation of 1-Methoxynaphthalene (1) Using Dicyanobenzene.** In a Pyrex test tube (3 cm × 20 cm) equipped with a rubber septum, 1-methoxynathalene (1.26 mmol) and dicyanobenzene (0.126 mmol) were dissolved in 50 mL of $CH_3CN$. After oxygen saturating the solution by passing a stream of $O_2$ through a glass frit immersed in the solution for 0.5 h, the mixture was irradiated at 350 nm under a positive pressure of $O_2$ for 24 h. For comparison, 50 mL of a $TiO_2$ suspension containing 1-methoxynapthalene (0.25 M) was irradiated simultaneously.

After removing the solvent by rotary evaporation, the reaction mixture was analyzed by NMR spectroscopy (3-pentanone, internal standard) and gave monomethyl phthalic acid ester as the major product (60%). Quantitative analysis by HPLC with a Waters P/N 27477 Porasil column eluted with Skelly B:EtOAc (2:1) showed phthalic anhydride to be present in 3% yield. Spectral properties of both compounds were identical with those of authentic samples.

**Photocatalyzed Oxygenation of 1,4-Dimethylnaphthalene (7).** The product obtained from the oxygenation of **7** showed different chemical behavior than other members of the series. After workup, but before treatment with diazomethane, a small portion of the residue was dissolved in methanol and the resulting solution was treated with 2 drops of a solution of $FeCl_3$ (10% in aqueous methanol). A persistent blue color characteristic of the presence of phenolic –OH was observed. A second portion of the methanolic solution, treated with 2 drops of KI (10% in aqueous methanol) gave a negative response for the presence of peroxide.

After treatment with diazomethane, a white solid was obtained, 1,4-dimethyl-3-methoxy-2-naphthol: mp 79–81 °C; NMR ($^1H$, Varian EM-390, $CDCl_3$) $\delta$ 8.00–7.83 (m, 2 H), 7.35–7.55 (m, 2 H), 3.85 (s, 3 H), 2.60 (s, 3 H), 2.57 (s, 3 H); ($^{13}C$, Varian EM-390, $CDCl_3$) $\delta$ 145.59, 145.12, 131.33, 128.44, 125.14, 124.24, 123.56, 123.34, 122.18, 114.18, 61.57, 11.50, 10.61; IR (Beckmann Acculab 7, $CHCl_3$) 3540, 1462, 1409, 1250, 1072, 1025 $cm^{-1}$; low-resolution mass spectrum (Dupont 21-491 mass spectrometer), *m/e* 202 (P, base), 187, 169, 159, 141, 128, 121, 115, 103; high-resolution mass spectrum (Dupont CEC-101) *m/e* calcd for $C_{13}H_{14}O_2$, 202.0994; found, 202.0996.

**Attempted Detection of Biacetyl from the Catalyzed Photooxygenation of 2,3-Dimethylnaphthalene (3).** After photooxygenation and filtration by the general procedure described above, the reaction mixture obtained after consumption of 65% of **3** was analyzed by distillation and by GLPC analysis (column A, 50 °C). No evidence for the presence of biacetyl in the reaction mixture could be obtained.

The reaction mixture was then treated with hydroxylamine according to the procedure of Shriner, Fuson, and Curtin[18] in order to form a solid derivative of any carbonyl compounds present. No solid precipitated during the reaction and no evidence for the presence of the oxime nor the dioxime of biacetyl could be found in the NMR spectrum of the mixture.

**Measurement of Relative Rates for Photooxygenation of 1–10.** The general procedure for the $TiO_2$-catalyzed photooxygenation was followed with 0.01 M acetonitrile solutions of **1**–**10**. Irradiation was conducted on a merry-go-round support mounted inside the Rayonet photochemical reactor equipped with long-wavelength UV ($\lambda$ = 350 nm) lamps. The concentrations of the starting materials were monitored by GLPC (Antek 400, column A, 120–160 °C) using an independently prepared calibration curve to correlate the substrate concentration with the chromatographic peak height. A plot of the disappearance of starting material with increasing irradiation time was constructed for each compound and the irradiation period ($\tau_{1/2}$) required to convert 50% of the starting material was obtained by extrapolation. Results are listed in Table II.

**Quantum Efficiency for the $TiO_2$-Catalyzed Photooxygenation of 1-Methoxynaphthalene (1).** A lower limit for the quantum yield for photooxygenation of **1** can be established by assuming negligible reflection by the responsive photocatalyst. Actinometry was conducted by using a Model 550-1 Radiometer-Photometer (EG&G Electro-optics) mounted on a light-shielded optical bench. A suspension of $TiO_2$ in acetonitrile containing **1** at the concentrations described in the general procedure was irradiated with a phosphor-coated low-pressure mercury arc (intensity = 641 joule/ $cm^2$ s) for 2 h. The consumption of **1** consumed/einsteins impinging on the catalyst powder) was calculated directly. The radiometer response under

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[16] Boyer, J. H.; Schoen, W. "Organic Syntheses"; Wiley: New York, 1963, Collect. Vol. 4, p 532.

[17] de Boer, Th. J.; Backer, H. J. "Organic Syntheses"; Wiley: New York, 1963; Collect. Vol. 4, p 250 and 102.

[18] Shriner, R. L.; Fuson, R. C.; Curtin, D. Y. "The Systematic Identification of Organic Compounds"; Wiley: New York, 1973; p 290.

our experimental conditions was calibrated by potassium ferrioxalate actinometry.[19]

**Stoichiometry in the Photocatalyzed Oxygenation of 1.** When the general procedure for the catalyzed photooxygenation was used, a 0.01 M solution of 1 containing 5 mg of suspended $TiO_2$ was saturated with oxygen and was maintained under 1 atm of oxygen during irradiation by using an oil-filled leveling bulb. The suspension was stirred during the irradiation to ensure equilibration of adsorbed oxygen on the surface of the photocatalyst. Uptake of oxygen was measured with the levelling bulb as the disappearance of 1 was monitored by GLPC (see above). Over the first 20% of reaction, approximately 3.0 ± 0.4 mol of oxygen were taken up for each mol of arene reacting.

**Attempted Reaction of 1-Methoxynaphthalene (1) and Naphthalene (10) with Superoxide.** Potassium superoxide (661 mg, 9.3 mmol) was solubilized by adding 18-crown-6 ether to 10 mL of dry acetonitrile. The resulting solution was treated with 1 or 10 (185 mg, 1.2 mmol) and the resulting solution was stirred at room temperature for 2 h. Neither GLPC nor NMR analysis (see above) showed formation of the photocatalyzed oxygenation products. Nor could any effect be noted on the rate of the photooxygenation if the solution was made 0.01 M in phenylglyoxylic acid, a known superoxide trap.[20]

**Measurement of Oxidation Potentials of 1–10.** Anodic peak potentials were measured by cyclic voltammetry, which was performed on a Princeton Applied Research (PAR) Model 173 potentiostat/galvanostat equipped with a PAR Model 175 universal programmer. The current–voltage curves were recorded on a Houston Instruments x–y recorder. The electrochemical cell was a standard three electrode cell equipped with a silver wire quasi-reference electrode, a platinum coil counterelectrode, and a platinum disk working electrode. Oxidation peak potentials are reported in volts vs. the standard calomel electrode (SCE) by using ferrocene as an internal standard.[21]

The electrolyte, tetra-*n*-butylammonium perchlorate (TBAP, Southwestern Analytical Chemicals Inc.) was recrystallized from a solution of EtOAc and Skelly B (1:1). The solvent, $CH_3CN$, was degassed by bubbling Ar for 3 h before use. For a typical run, a solution (0.1 M) of TBAP in $CH_3CN$ (10 mL) was injected into the standard cell. After the solution was bubbled with Ar again for 0.5 h, it was scanned to ensure the absence of electroactive impurities.

A solution of substrate ($2 \times 10^{-2}$ M) in $CH_3CN$ (1 mL) was then introduced into the cell by syringe. With a scan rate of 200 mV per second, a cyclic voltammogram (cv) was obtained by scanning the potential from 0.0 V to 2.2 V with the cell under an argon atmosphere at room temperature. Quasi-reversible waves were observed for each member of the series. Peak potentials for the anodic waves are listed in Table II. A solution of ferrocene[21] ($5 \times 10^{-2}$ M) in $CH_3CN$ (1 mL) was then injected into the cell and another cv was recorded.

**Calculation of Charge Distribution in the Radical Cation of 2,3-Dimethylnaphthalene (3).** Calculations were carried out using the spin unrestricted version of the MNDO[11] (Modified Neglect of Diatomic Overlap) semiempirical treatment. Equilibrium geometries were found by minimizing the energy of the radical ion with respect to all variables (bond lengths, bond angles, and dihedral angles between related atoms in a molecule), using the Davidon–Fletcher–Powell[22] optimization procedure.

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