CONTROLLED OXIDATION OF BENZYL ETHERS ON IRRADIATED SEMICONDUCTOR POWDERS

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Abstract - Irradiation of a suspension of powdered TiO_2, a photoactive semi-conductor, in oxygen saturated acetonitrile leads to mild selective oxidation of substrates containing a benzylic methylene by conversion of that carbon to a carbonyl group. The method is shown to be synthetically useful for the preparation of esters from ethers and ketones from hydrocarbons. A critical analysis of the products and of the possible intermediates results in a plausible mechanistic pathway for these photooxidations.

INTRODUCTION

Recent investigations have shown that the ultimate chemical fate of radical pairs can be significantly influenced by the environment in which the pair is generated. Thus, the three-dimensional cavities in micelles[1], zeolitis[2], clays[3], or on surfaces exert a pronounced effect on spin correlation and competitive escape routes for paired radical species. Since these "supercages" cause such dramatic changes in product distributions obtained from neutral radical pairs, the perturbation of the reactivity of their charged ion radical pairs might be excepted to be even more profound.

Generation of radical anion-radical cation pairs can be readily accomplished by photoinduced electron exchange. In homogeneous solution, this electron transfer, eqn (1), is thought to occur

$$D + A \xrightleftharpoons{h\nu} D^{\overset{+}{\cdot}} + A^{\overset{-}{\cdot}} \tag{1}$$

efficiently if the singlet excitation energy exceeds by about 4 kcal/mole the difference between the donor's oxidation potential and the acceptor's reduction potential. Excitation of either the donor or the acceptor can often accomplish the necessary activation.

Mediating sensitizers can also be employed to initiate the necessary electron exchange. Whether demonstrable chemical reaction will be observed after this primary photochemical electron exchange will depend on the kinetics of the subsequent chemical reactions of the radical ions thus generated. The thermal back reaction (reverse of eqn 1) is favored both by electrostatic attraction within the charged ion radical pair and by simple thermodynamics, and this energy dissipative reverse electron exchange almost always reduces the quantum yield of products derived from the individual ion radicals. Efficient chemical transformation can be accomplished only if this troublesome back reaction can be inhibited. Here again, cage effects can affect net reactivity in a quite significant way, by either enhancing inter-actions between the constituent ion radicals or by inhibiting such interactions by adsorption or hydrophobic effects.

Semiconductor powders are unique materials for inducing analogous reactions[4]
By definition, semiconductors possess band structure in which a series of closely
spaced, filled levels (the valence band) are separated by an energy gap from a
second series of vacant, closely spaced levels (the conduction band). In the ground
state, the valence band electrons are highly localized and the material displays
insulating electrical properties. Upon reduction, however, the conduction band is
populated and metal-like conductive behavior can be obtained.

Alternatively, the conduction band can be populated by photoexcitation.
Promotion of an electron from the valence band renders the surface highly active
as an oxidant toward adsorbed electron donors; i.e. the irradiated surface can
act as an excited electron acceptor. The high energy electron, promoted to the
conduction band by photoexcitation, is likewise available for catalyzing reductions
of adsorbed acceptors.
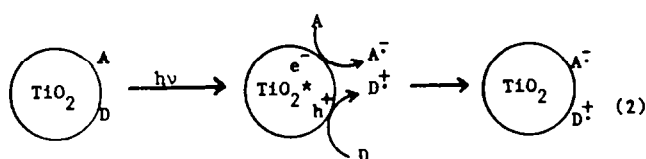
Thus, photoexcitation of a semiconductor powder suspended in a polar solvent
generates an electron-hole pair, which upon chemical interaction respectively with
acceptors and donors, is converted to a surface-bound radical cation-radical anion
pair, eqn 2. Because these radical fragment are strongly adsorbed to the surface,
the course of subsequent reactions will depend on the altered chemical reactivity
of the bound radical ion pair. Significantly different reactions may be observed,
indeed may be expected, on such surfaces, compared with that observed from the
same radical ion pair generated in an isotropic solvent cage in homogeneous
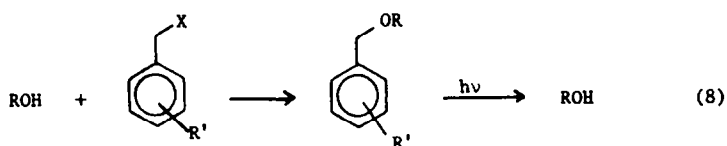solution.

Consistent with this idea, a wide variety of organic functional group con-
versions can be effected in preparatively useful yields on irradiated semiconductor
suspensions. For example, conjugated carbon-carbon double bonds[5] (eqn 3) or electron
rich arenes (eqn 4) are oxydatively cleaved[6], and amines[7] (eqn 5), sulfides[8] (eqn 6)
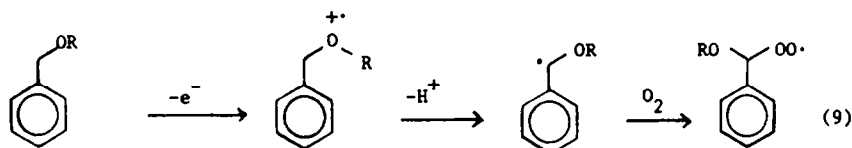and simple olefins[5] (eqn 7) are oxygenated.
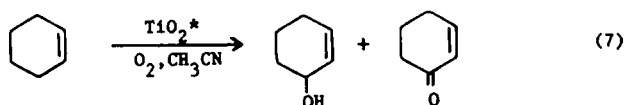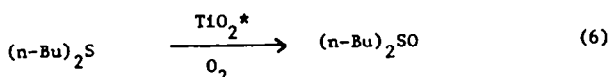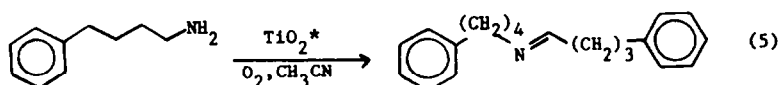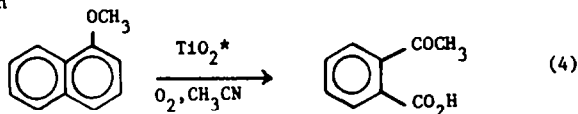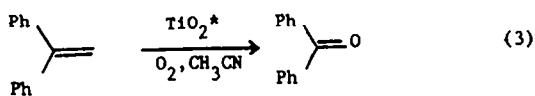
Reactivity is controlled by the relative band positions of the semiconductor and the oxidation potential of the organic substrate, by adsorption equilibria, and by restricting of redox reactants to one-electron exchange.

Mechanistic study has shown that the critical step in such conversions often involves radical cation formation from an organic donor, oxygenation of which leads to observed product[9,10]. Intermediate formation of superoxide (by directed reduction of adsorbed oxygen) is also feasible[5].

Our interest in such photoinduced redox reactions prompted us to consider whether this method could be used for selective activation of benzyl ethers of varying oxidation potential are easily accessible and have found extensive use in synthesis as protecting groups for alcohols[11], eqn 8.

$$ROH \; + \; \overset{X}{\underset{R'}{\bigcirc}} \; \longrightarrow \; \overset{OR}{\underset{R'}{\bigcirc}} \; \overset{h\nu}{\longrightarrow} \; ROH \qquad (8)$$

We hoped that the semiconductor surface might differentiate the reactivity of the benzyl radical formed by either ring or functional group oxidation, eqn 9, from that observed in solution and might provide an alternate route for selective oxygenation.

$$\underset{\bigcirc}{OR} \; \overset{-e^-}{\longrightarrow} \; \underset{\bigcirc}{\overset{+\cdot}{O}\text{-}R} \; \overset{-H^+}{\longrightarrow} \; \underset{\bigcirc}{\cdot OR} \; \overset{O_2}{\longrightarrow} \; \underset{\bigcirc}{RO \quad OO\cdot} \qquad (9)$$

Accordingly, we have observed high yield conversion of a series of benzyl ethers to the corresponding benzoate esters. We disclose here our results and describe the critical mechanistic control of the intermediate radicals and radical ions attained on these photoactive surfaces.

RESULTS

Preliminary experiments revealed that long wavelength uv irradiation of TiO_2 (anatase) powders suspended in a dry, oxygen-saturated acetonitrile solution of one of several benzylic ethers gave good conversion to the corresponding benzoate esters. All irradiation were conducted with a 450 W Hanovia medium-pressure Hg lamp which was cooled by a circulating $Bi(OAc)_3$ filter solution that cut off light below 355 nm. This experimental procedure ensured that the TiO_2 semiconductor would absorb the incident light. Control experiments established that irradiation in the absence of TiO_2 or of O_2 gave no ether oxygenation. The course of the photooxidation could be easily monitored by HPLC so that a comparison of the relative rates of disappearance of reactant and appearance of product could be made. Typical product yields at varying conversions are summarized in Table 1 for several benzyl ethers and arenes.

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<u>Table 1</u>: Photooxidation of Benzyl Substrates with $O_2/TiO_2/CH_3CN$

| Substrate	Irradiation Time (min)	% Reactant	Product	Chemical Yield (%) [a]	
1. $PhCH_2OCH_3$	0	100	$PhCO_2CH_3$	0	–
	60	76		20	83
	225	45		41	75
	339	35		46	71
	1320	11		71	80
2. $PhCH_2O(CH_2)_5CH_3$	120	65	$PhCO_2(CH_2)_5CH_3$	28	80
	1365	0		43	43
3. $PhCH_2OC(CH_3)_3$	85	90	$PhCO_2C(CH_3)_3$	11	~100
	1380	28		73	~100
4.	60	22		71	91
	215	2		95	97
5. $PhCH_2O(CH_2)_3Ph$	210	19	$PhCO_2(CH_2)_3Ph$	42	52
6. $4-CH_3OPhCH_2O(CH_2)_3Ph$	30	75	$4-CH_3OPhCO_2(CH_2)_3Ph$	16	64
	180	14		45	52
7. $PhCH_2Ph$	210	77	$\overset{O}{\overset{\|}{PhCPh}}$	16	70
	780	48		32	61
8.	60	84		16	100
	280	50		38	76
9.	40	71		15	52
	245	4		34	35
10.	1020	15		13[b]	15

(a) Based on moles of reactant consumed.

(b) Isolated yield.

The amount of TiO_2 photocatalyst necessary for efficient product formation was determined by observing rates and yield of product formation as a function of the amount of suspended catalyst. With less than 50 mg catalyst/300 mL of solution, the reaction began to slow measurably. This observation can imply either incomplete adsorption of the donor (i.e. the benzyl ether) as the available surface area of the catalyst is decreased or incomplete light absorption by the reduced quantity of suspended semiconductor. No significant differences were observed at higher (up to 500 mg/300 mL) TiO_2 levels.

The acetonitrile used was also found to be important although in a way which is still not entirely clear. All runs reported here were conducted in Fisher HPLC grade solvent. Trials using Fisher ACS grade solvent gave very slow conversions and poor yields. These reactions should be sensitive to water content of the acetonitrile since the TiO_2 will aggregate and remain poorly suspended if the solvent is wet. This, of course, reduces the effective absorption of light. However, even runs in dried ACS grade solvents (distilled from CaH_2 and then stored over 4A seives) seemed no better. Apparently solvent impurities can significantly influence the outcome of a reaction.

Chemical yields and product identification (benzoate esters and aryl ketones) obtained by oxidation of the benzylic ethers and hydrocarbons are shown in Table 1. In most cases, yields are given at both low and high conversion of substrate. Normally the yield of the product resulting from simple methylene to carbonyl oxidation was quite high at low conversion but then dropped off as the substrate was consumed because of secondary oxidation of the product. For instance, upon prolonged irradiation, carboxylic acid derivatives could be observed: benzoic acid from the simple benzylic arenes, phthalic acids from substrates like tetralin and 4-methoxytetralin, and salicylic acid from the benzofuran. In fact, the β-furanone is the most reactive product to further oxidation, perhaps because it has the highest percentage of enol content. These photocatalyzed reactions have appreciable synthetic utility since isolation of the esters and ketones in yields comparable to the analytical ones reported in Table 1, is quite simple. The reaction mixtures were filtered, the solvent evaporated and the residue subjected to flash chromatography on silica gel.

DISCUSSION

The observed photooxidation reported in Table 1 demonstrate that semi-conductor catalyzed oxidation of carbon-hydrogen bonds can be highly regioselective and can be used as a useful synthetic method for controlled benzylic oxidation. Several examples of the selectivity involved include the preferential oxidation of a benzylic ether carbon as opposed to a simple benzylic center (eqn 10), oxidation of a benzylic center in preference to a carbon alpha to an ether (eqn 11) and oxidation at a benzylic site para to the electron donating methoxy group in preference to meta benzyl oxidation (eqn 12).
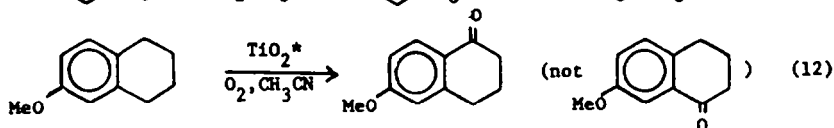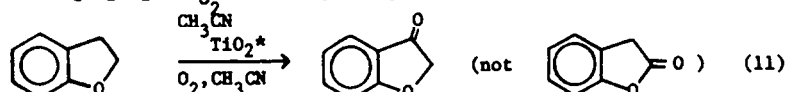
A plausible scheme for these conversions would seem to involve initial oxidation to the benzylic hydroperoxide after photocatalyzed formation of the organic cation radical in the primary photochemical step. Further oxidation to the carbonyl group could then produce the observed oxygenated product (eqn 13).

$$PhCH_2-X \xrightarrow{?} \underset{\underset{}{\overset{OOH}{|}}}{PhCH-X} \longrightarrow \underset{\overset{O}{||}}{PhC-X} + H_2O \qquad (13)$$
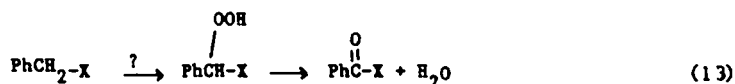
In fact, we had initially assumed that the hydroperoxide derived from ethers (i.e. X=O-R) would be unstable and this would lead to a mild method of benzylic cleavage. This would be analogous to a known electrochemical oxidative cleavage of benzylic ethers where hemiacetals are assumed to be the critical intermediate (eqn 14)[12].
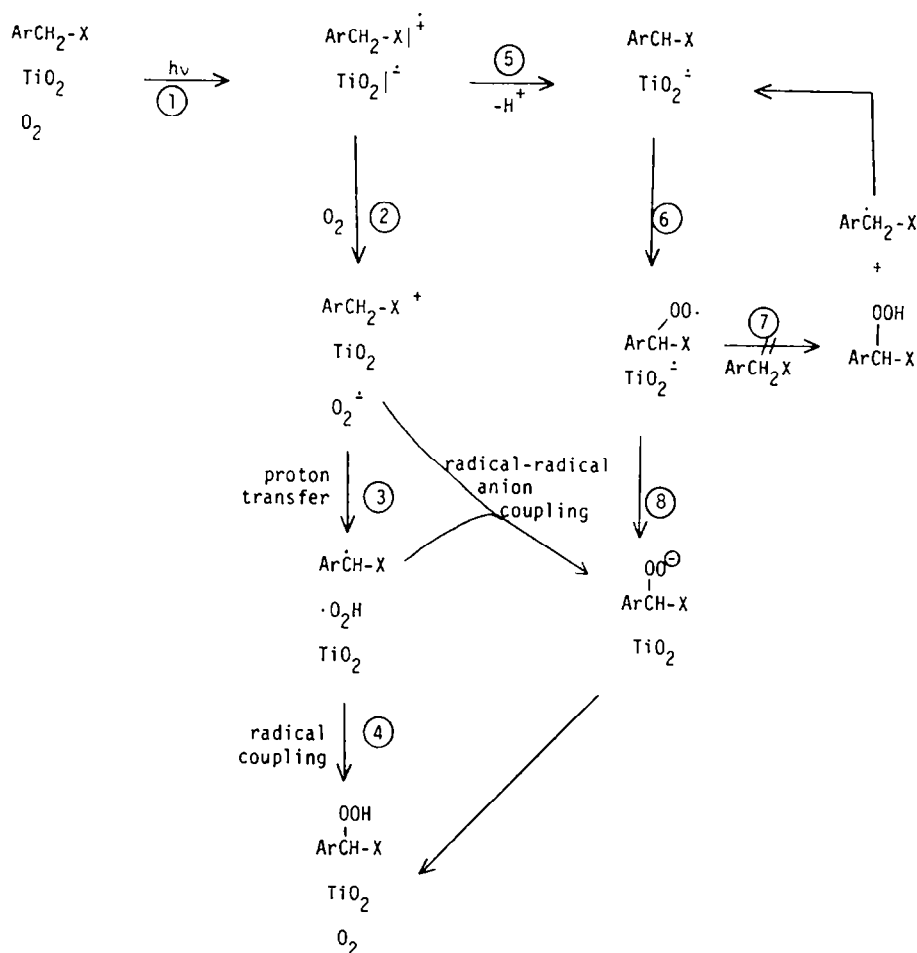

$$(14)$$
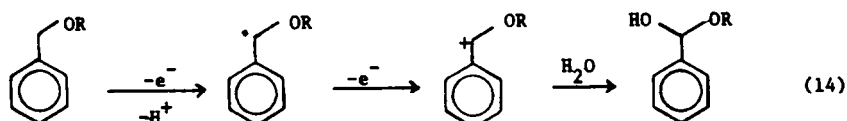
In fact, hydroperoxides of this type are surprisingly stable. They can be easily prepared by trapping with alcohol solvents of the intermediate zwitterion formed in the ozonolysis of alkenes (eqn 15)[13]. This hydroperoxide is distillable at reduced pressure at 50-70°C and only slowly decomposes to methyl benzoate above 100°.

$$PhCH=CH_2 \xrightarrow{O_3, CH_3OH} \underset{\underset{}{\overset{OOH}{|}}}{PhCH-OCH_3} \qquad (15)$$
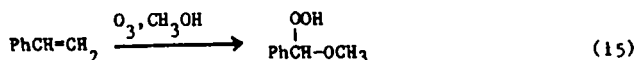
Moreover, in ether solution, it can be shaken with water for 15 min with no indication of hydrolysis! These observations suggest that the hydroperoxides formed would not cleave rapidly at room temperature in acetonitrile but would be long enough lived to undergo a second photochemically initiated oxidation.

The likely mechanistic steps leading to the oxidation of these benzylic substrates to the hydroperoxide are outlined in Scheme 1.

Scheme 1. Mechanistic Pathways for the TiO$_2$ Catalyzed Photooxidation of Benzylic
C-H Bonds to the Hydroperoxide

ArCH$_2$-X   ArCH$_2$-X|$\overset{+}{\cdot}$ ArCH-X

TiO$_2$ $\xrightarrow[\textcircled{1}]{h\nu}$ TiO$_2$|$\overset{\cdot}{\cdot}$ $\xrightarrow[-H^+]{\textcircled{5}}$ TiO$_2$$\overset{\cdot}{\cdot}$ $\longleftarrow$

O$_2$

O$_2$ $\Big\downarrow$ ⓶   ⓺ $\Big\downarrow$ ArCH$_2$-X

                                                                                +

ArCH$_2$-X $^+$,OO·   ⑦   OOH
                        ArCH-X $\xrightarrow[ArCH_2X]{\not\longrightarrow}$ |
TiO$_2$ TiO$_2$$\overset{\cdot}{\cdot}$ ArCH-X

O$_2$$\overset{\cdot}{\cdot}$

proton   radical-radical
transfer $\Big\downarrow$ ⓷   anion
                coupling $\Big\downarrow$ ⑧

ArCH-X   OO$^\ominus$
                                |
·O$_2$H   ArCH-X

TiO$_2$ TiO$_2$

radical $\Big\downarrow$ ④
coupling

OOH
|
ArCH-X

TiO$_2$

O$_2$

Considerable chemical precedent establishes that each of these individual steps
is reasonable. Little previous information, however, would allow us to exclude
one of the two reasonable pathways (i.e. 1   2   or   1   5).

    Step   1   represents absorption of light by the metal oxide semiconductor to
generate an electron-hole pair. Electron transfer from the absorbed substrate will
produce an adsorbed radical cation. All of these substrates employed here have
oxidation potentials suitable for exothermic electron transfer to the valence
band of TiO$_2$ (+2.3V in CH$_3$CN): typical electrooxidative waves can be observed
by cyclic voltammetry at about +1.6V for oxygen substituted benzene rings and
at about +2.0V for the simple benzylic cases[12]. Since simple alkyl ethers are
oxidized at much more positive potentials, we assume that the charge density is
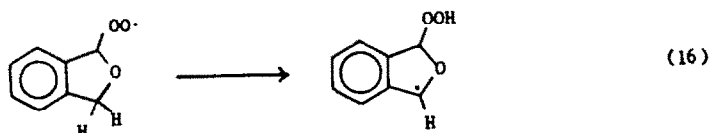located in the pi system rather than being localized on the potentially oxidizable
oxygen atom.

Step 2 involves the reduction of molecular oxygen to superoxide by the electron in the conduction band of photoexcited TiO_2. Again the potentials are permissive: the conduction band edge for TiO_2 lies at about -0.8V in CH_3CN and the reduction potential for O_2 is -0.78V in this same solvent[4]. Thus, trapping of the photogenerated electron by O_2 will be nearly thermoneutral. In fact there is no unambiguous evidence for the intervention of superoxide anion in any TiO_2 photooxygenations, but its formation would provide a method by which surface electron-hole recombination could be inhibited and would provide a rationale for the observed requirement for oxygen for any photocatalytic reactivity with these substrates. If superoxide is formed, the rest of the conversion is straightforward.

Step 3 involves benzylic deprotonation of the organic caution radical to produce a benzylic radical. Such a step would be rapid under our reaction conditions, for superoxide can function as a weak base (pK$_a$ of $HO_2^{\cdot}$ = 4.7)[14] and benzylic radical cations are certainly strong acids (pK of about -10)[15]. Coupling of the resulting radicals in step 4 gives the hydroperoxide. Alternatively, chemical combination of the benzylic radical from step 3 with superoxide (an oxygen radical anion) would lead directly to the conjugate base of this hydroperoxide. This Scheme would result in the observed regioselective oxygenation because of preferential deprotonation at the benzylic site adjacent to the ring position bearing the largest fraction of positive charge and spin density. Specific activation at precisely the sites observed in equations 10-12 would therefore be predicted.

If superoxide is not involved, then step 5 probably takes over where the the strongly acidic radical cation loses a proton to some acceptor, perhaps the solvent or the oxide surface. The radical then simply reacts with molecular oxygen in step 6 to give a peroxy radical. This is, of course, one of the steps in autoxidation, the second being abstractrion of a hydrogen from the neutral substrate to continue the chain; step 7 . In fact, these reactions could have been simply a method for the initiation of the autoxidation pathway as has been suggested previously for some other photo-oxidations[16].

However, this pathway cannot be operative here. The rate constant for step 7 has been measured for many benzylic substrates, including benzylic ethers, and typically has a value of 5 M^{-1} sec^{-1} [17]. At $10^{-3}M$ substrate, as in our experiments, this bimolecular process would occur with a pseudo first-order rate constant of only about 5×10^{-3} sec^{-1}. In fact, in common autoxidation studies, concentrations of substrate are usually held above 1.0 $\underline{M}$ so that this relatively slow chain propagating step can compete with termination reactions. Even then chain lengths of only 10 to 50 are observed.

If peroxy radicals are generated in these reactions they must be short lived enough to avoid intramolecular hydrogen abstraction reactions. This is particularly true for the benzylic ethers. For instance, the process shown in eqn 16 has a rate constant[18] of 108 sec^{-1} which makes
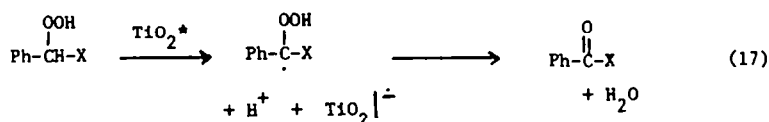

(16)

intramolecular hydrogen abstraction dominate intermolecular hydrogen abstraction even at much higher concentrations of the substrate ether than used in our experiments. If the process shown in eqn 16 indeed occured, further oxygenation and a lack of regioselectivity in these photocatalyzed oxidations would be expected. In our experiments, the observation of clean mono-oxidation suggests the peroxy radical is destroyed by some competing process before it has a chance to undergo this intramolecular hydrogen transfer.

The most likely fate of the peroxy radical is reduction by the TiO_2 conduction band electron (or by photogenerated superoxide). In contrast to the reduction of oxygen discussed above, step 8 should be very favorable since electron transfer from the conduction band of TiO_2 (-0.8V) to the HMO of the $ROO^{\cdot}/ROO\cdot^{-}$ couple (+1.44V)[14] is exothermic by about 2.2V. Back donation of the proton from the metal hydroxylate surface in step 9 then gives the hydroperoxide. Deprotonation of starting material to form the hydroperoxide and an oxidizable benzylic anion (which could then participate in chain oxygenations) is highly unlikely from relative pK_a considerations.

Relative oxidation potentials of $PhCH_2X$ and $Ph\overset{\bullet}{C}H-X$ allow us to predict that the second oxidation step shown in eqn 14 should be more favorable thermodynamically than the first and because of preferential adsorption may be kinetically favored as well. This process will give the benzylic radical (parallel to steps 1 and 5 of Scheme 1) (eqn 17). Now, however, the benzyclic radical will readily fragment because of the weak oxygen-oxygen bond to give the carbonyl group and a hydroxy radical which is reduced and protonated to form water.

$$\underset{Ph-CH-X}{\overset{OOH}{|}} \quad \xrightarrow{TiO_2{}^*} \quad \underset{\underset{\cdot}{Ph-C-X}}{\overset{OOH}{|}} \quad \longrightarrow \quad \underset{Ph-C-X}{\overset{O}{||}} \qquad (17)$$
$$+ \ H^+ \ + \ TiO_2|^{\cdot-} \qquad\qquad + \ H_2O$$

We see therefore that photocatalytic semiconductor-medited electron exchange can provide a method for highly regioselective benzyl oxidations which is useful on a preparative scale. Conventional routes to radical cation/radical anion pairs adsorbed on the surface of the irradiate semiconductor lead to a convenient mechanistic rationale for the observed ractivity. Such radical ions, by proton exchange on the metal oxide or metal hydroxide surface, also provide unique methods for the generation of the neutral radical under controlled conditions.

EXPERIMENTAL

Substrates: Benzylmethyl ether, phthalan, tetralin, diphenylmethane, and 2,3-dihydrobenzofuran were commercial samples and were distilled before use. 6-Methoxytetralin (Aldrich) has an unidentified impurity (10%) which was removed by flash chromatography (silica gel/$CHCl_3$) before distillation.
All other substrates were prepared by Williamson coupling. In a typical procedure, 4.8 g of NaH (50% oil dispersion, 0.1 mol) was washed with hexanes and then suspended in 125 mL of DMF under nitrogen. Then 0.2 g (0.1 mol) of 1-hexanol in 25 mL of DMF was added slowly and the reaction mixture was stirred at room temperature for 3 hours. Finally, 12.6 g (0.1 mol) of benzyl chloride in 25 mL of DMF was added slowly and the resulting solution was stirred at room temperature for 16 hours. The mixture was then poured into 200 mL of ice water and extracted with 200 mL of methylene chloride. The extract was washed with 50 mL of 5% NaOH and 4x100 mL of water, dried over $MgSO_4$ and concentrated to give 23.0 g of crude product which by nmr was pure ether plus a small amount of DMF.

Distillation, 102-105^0 (0.5 mm), gave the pure ether.
     Ethers prepared this way, the starting materials used and their nmr (CDCl$_3$)
spectra are as follows: benzyl t-butyl ether, t-butanol, benzyl chloride, δ 1.29
(9H, s), 4.47 (2H, s), 7.37 (5H, br.s); benzyl hexyl ether, 1-hexanol, benzyl
chloride, δ 0.7-1.0 (3H, m), 1.1-1.8 (8H, m), 3.42 (t, 2H), 4.47 (2H, s), 7.34
(5H, br.s); benzyl 3-phenyl-1-propyl ether, 3-phenyl-1-propanol, benzyl chloride,
δ 1.93 (2H, quintet), 2.72 (2H, t), 3.50 (2H, t), 4.50 (2H, s), 7.24 (5H, br.s),
7.38 (5H, br.s); 4-methoxybenzyl 3-phenyl-1-propyl ether, 3-phenylpropanol,
4-methoxybenzyl chloride, δ 1.90 (2H, quintet), 2.70 (2H, t), 3.46 (2H, t), 3.78
(3H, s), 4.42 (2H, s), 6.8-7.0 (2H, d), 7.1-7.4 (7H, m).

Photolysis Products: Methyl benzoate, ethyl benzoate, benzophenone, tetralone,
6-methoxytetralone, 7-methoxytetralone, salicyclic acid, phthalic acid and
phthalide were commercial samples. ß-Furanone; mp 96-97^0 from ethanol; nmr
(CDCl$_3$) δ 4.63 (2H, J), 7.0-7.8 (4H, m); mass spec. 175 (3), 136 (16), 134 (100),
133 (19), 120 (28), 105 (71), 104 (25), 92 (18), 78 (10), 77 (27), 76 (49), 75 (10),
74 (10), 63 (11).; was isolated as a photolysis product of 2,3-dihydrobenzofuran
by flash chromatography (silica gel/benzene).
     All other esters were prepared by reaction of the acid chloride with the
alcohol. In a typical procedure, to a solution of 9.2 g (0.1 mol) of 1-hexanol
in 100 mL of benzene and 5 mL of pyridine was added 14.0 g (0.1 mol) of benzoyl
chloride in 20 mL of benzene. The reaction mixture was stirred overnight at room
temperature. The reaction mixture was poured into 200 mL of water and the benzene
layer was washed with 50 mL of 10% HCl, 50 mL of 5% NaOH and 50 mL of water,
dried over MgSO$_4$ and concentrated to give 18.0 g of crude ester. Distillation,
107-110^0 (0.5 mm), gave the pure ester. Esters prepared this way and their nmr
(CDCl$_3$) spectra are as follows: t-butyl benzoate, δ 1.61 (9H, s), 7.3-7.8 (3H, m),
8.0-8.2 (2H, m); 1-hexyl benzoate 0.8-1.1 (3H, ,), 1.2-2.0 (8H, m), 4.33 (2H, t),
7.3-7.7 (3H, m), δ 8.0-8.3 (2H, m); 3-phenyl-1-propyl benzoate, 2.13 (2H, quintet),
2.80 (2H, t), 4.33 (2H, t), 7.1-7.7 (3H, m), 8.0-8.3 (2H, m); 3-phenyl-1-propyl
4-methoxybenzoate, δ 2.10 (2H, quintet), 2.80 (2H, t), 3.82 (3H, s), 4.32 (2H, t),
6.93 (2H, d), 7.28 (5H, br.s), 8.03 (2H, d).

Photolysis: All irradiations were with a 450 W medium-pressure Hanovia mercury
lamp. The immersion well was cooled by circulation of a solution containing 6 g of
Bi(OAc)$_3$ in 4 L of 10% HCl which has a sharp cut off at 355 nm. In a typical
reaction, 100 mg of substrate was dissolved in 30 mL of CH$_3$CN (HPLC grade)
containing 50 mg of TiO$_2$ (MCB powder dried at 110^0 for 30 hours and stored in a
vacuum desiccator). The TiO$_2$ was dispersed by ultrasonication for 5 minutes and
kept in suspension by stirring. A slow stream of oxygen was bubbled through the
reaction mixture during the photolysis. Samples were withdrawn by syringe through
a teflon tubing outlet. For product isolation, the photolysate was filtered through
a fine sintered glass funnel to remove the TiO$_2$. The solvent was evaporated and
the residue dissolved in 20 mL of CHCl$_3$. The solution was then extracted with 20 mL
of water, dried over MgSO4 and concentrated again. Products were then isolated
and compared with authentic samples.

Analytical Procedures: The progress of these photoreactions was monitored by HPCL
using a Waters reverse phase column and methanol/water mixture as eluent. For
analysis of acids formed, 0.5% H$_3$PO$_4$ was added to the eluent. Detection was by
ultraviolet absorption at either 254 or 280 nm depending on the chromophore of the
substrate and product. The response of the detector was calibrated with standards
of known concentration in all cases. Benzyl 3-phenyl-1-propyl ether and 3-phenyl-
1-propyl benzoate could not be resolved but measurement of the single peak at the
two different wavelengths gave reliable analytical results.

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