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Competitive Reactions of Diene Cation Radicals Formed on Irradiated Metal Oxide Surfaces

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Abstract: The heterogeneous photochemical oxygenation of conjugated dienes induced by long wavelength UV irrradiation of TiO_2 powders suspended in oxygenated CH_3CN was studied. In nearly all cases, products resulting from the oxidative cleavage of the double bonds were observed, in parallel to that previously reported for monoolefins. A mechanism is proposed which involves the intermediacy of a diene cation radical generated by transfer of an electron from the adsorbed diene to a photogenerated hole localized at the surface of the excited TiO_2 particle. Non-oxidative cleavage products are also observed, and the effect of the semiconductor surface in controlling reactivity of the photogenerated cation radical is discussed. The first examples of aromatization and Diels-Alder dimerization mediated by irradiated semiconductor suspensions are presented.

INTRODUCTION

Increasing activity in the field of organic heterogeneous photocatalysis has been prompted by the development of synthetically useful functional group transformations on irradiated semiconductor powders. In particular, the semiconductor catalyzed photooxidation of substituted alkenes affords preparatively useful quantities of carbonyl products.[1] It was, thus, of interest to determine whether the efficient reaction of olefinic substrates could be generalized to conjugated dienes, and whether the surface characteristics of the semiconductor photocatalyst can control secondary chemical reactions of the intermediates formed. Such studies are not only important from a synthetic perspective but also as a means to probe important mechanistic pathways occurring on photoexcited surfaces. Reported herein are the results of the photocatalytic reactions of a series of substituted dienes in which both oxidation and cycloaddition products are observed.

RESULTS AND DISCUSSION

In a representative experiment, the semiconductor powder was suspended in an oxygenated acetonitrile solution of the diene. By sonication for a few minutes in an ultrasonicator, effective dispersion of the insoluble semiconductor particles was achieved. Heterogeneous suspensions containing 1,3-cyclohexadiene (**1**), 2,4-dimethyl-1,3-pentadiene (**2**), or α-terpinene (**3**) were illuminated in a Rayonet photochemical reactor equipped with lamps blazed at 350 nm. 1-Phenyl-1,3-cyclohexadiene (**4**), and *trans, trans*-1,4-diphenyl-1,3-butadiene (**5**), which absorb at 350 nm (ε_{350}=35,000 and 160, respectively) were irradiated at wavelengths greater than 380 nm by an appropriately filtered (basic potassium nitrite) 450 watt medium pressure mercury arc lamp.

The products resulting from the semiconductor-catalyzed photooxygenations are listed in Table 1. Structures were determined by mass spectral fragmentation patterns obtained by GC/MS as well as by spectral and chromatographic comparison with authentic samples. All dienes, with the exception of **4**, showed incorporation of oxygen or gave oxidative cleavage products upon photolysis. Aromatization constituted a major pathway in the oxidation of **3** and was the sole observable product derived from **4** under these photocatalytic conditions. In addition, Diels-Alder dimerization was observed for dienes **1** and **2**. Polymerization was a major competing side reaction in all of these photooxidations.

A plausible mechanism for the initial photochemical steps in these heterogeneous oxidations is shown in Scheme I. Band gap irradiation of TiO_2 causes the promotion of an electron into the conduction band (E_{CB}=-0.9 V vs SCE) and the production of a hole in the valence band (E_{VB}=+2.4 V vs SCE).[2] The adsorbed diene then donates an electron to the hole at the surface of the TiO_2 particle, forming the adsorbed diene cation radical. The observed oxidative peak potentials of dienes **1-5** in acetonitrile (Table 2) indicate that oxidation of an adsorbed diene to the corresponding cation radical by a photogenerated hole should be kinetically favorable on the illuminated TiO_2 surface. Such positively charged intermediates have been implicated in the TiO_2-catalyzed oxidation of olefins based on electronic effects in the decomposition of *para*-substituted diphenylethenes[3] as well as in the spectroscopic observation of cation radical intermediates formed upon flash photolysis in colloidal TiO_2 suspensions.[4]

The necessity of oxygen in these heterogeneous reactions follows from the requirement for a suitable electron acceptor for the conduction band electron of photoexcited TiO_2. In the absence of such a species the adsorbed 1,3-diene cation radical would be rapidly reduced by the photogenerated conduction band electron, thus quenching the photoinduced charge separation. Oxygen serves to inhibit unproductive back electron transfer by interfering with electron-hole recombination at the surface, producing surface-bound superoxide and allowing observable chemistry to occur.

Several chemical routes are then available to the adsorbed cation radicals: they can interact with other adsorbed dienes or diene cation radicals to initiate dimerization and/or polymerization, can migrate toward surface-bound oxygen or superoxide to initiate oxygenation or proton transfer, or can desorb into the bulk solution where reactions parallel to those expected for homogeneously dispersed cation radicals can be anticipated. A question of primary scientific interest to us relates to defining the influence of the surface on the partition of the photogenerated intermediate among the potential reaction paths. We consider here each of the dienes to exemplify the chemical diversity attainable.

1,3-Cyclohexadiene

The irradiation of a TiO_2 suspension containing 1,3-cyclohexadiene (**1**) afforded the Diels-Alder dimer (**6**) as a major product, along with several unidentified oxygenated products (Table 1). Formation of adduct (6) by cation radical dimerization of **1** in homogeneous solution has been demonstrated by Bauld and coworkers using tris(*p*-bromophenyl)aminium hexachlorostibnate as an electron transfer catalyst[5] and, more recently, by Gassman and Singleton upon 9,10-dicyanoanthracene-sensitized photolysis of **1**.[6] While these reactions lead to predominantly *endo* adducts (5:1),[5] less complete stereoselection was observed in the semiconductor-catalyzed reaction (endo:exo 2:1). This loss of selectivity seems to imply that the photogenerated cation radical reacts on the surface of the photocatalyst prior to desorption. Pronounced effects on the chemical reactivity for ion radicals strongly absorbed at the semiconductor-liquid interface have also been suggested in other semiconductor-catalyzed oxidations.[1,7] Adsorbed to the semiconductor surface, the orientational freedom of the cation radical is restricted, and secondary orbital interactions, conventionally credited for *endo* stereoselection, would be attenuated. The loss of *endo* selectivity has been observed also in other heterogeneous media, e.g. clays and zeolites.[5d,8]

The preference for the endo isomer is also diminished upon triplet sensitization of **1** in homogeneous solution (endo/exo <<1).[9] Since back electron transfer between surface-bound ion radical doublets is not subject to spin restrictions encountered in direct photoexcitation, recapture of an electron by a surface-bound cation radical could in principle generate either a triplet or the quenched ground state singlet. If the triplet can initiate Diels-Alder dimerization, as the sensitization experiments would imply, electron transfer sensitization to form triplets might be an alternate explanation for the observed stereochemical effects.

Several observations mitigate against this interpretation, however. First, since the solutions are air-saturated, the concentration of oxygen in bulk solution is sufficiently high to completely quench any photogenerated triplet, given a high rate of oxygen quenching and usual diene triplet lifetimes.[10] In fact, the local oxygen concentration near the adsorbed diene cation radical (and hence near the postulated triplet formed via reversible electron transfer), probably exceeds that in homogeneous solution since TiO_2 strongly adsorbs oxygen[11] and in fact acts as a storage matrix for photogenerated oxygen formed during water splitting.[12] Thus, any triplets formed by this route would more likely be quenched than activated toward dimerization. Second, the triplet state of the diene leads predominantly to [2+2] dimers, in addition to lowering the endo to exo ratio.[13] No [2+2] dimers were observable in our semiconductor mediated reactions. We therefore believe that the observed Diels-Alder dimerization occurs via a surface bound cation radical in which the effect of the surface is reflected in diminished stereoselection, rather than via an excited state formed through reversible electron transfer.

2,4-Dimethyl-1,3-pentadiene

To delineate the generality of Diels-Alder adduct formation observed with **1**, 2,4-dimethyl-1,3-pentadiene (**2**), which is also known to give a high yield of cation radical derived Diels-Alder dimer under homogeneous conditions,[6] was subjected to our TiO_2 photocatalytic conditions. Along with a large number of oxygenated products, the cation radical dimer **15** was formed in 4% yield. Although this yield is too low for synthetic interest, the detection of this dimer constitutes added proof that a cation radical mechanism is operative, since acid catalysis (TiO_2 having the potential to act alternatively as a Lewis acid) of **2** resulted in completely different dimeric products.[5d,6] The predominance of oxygenated products implies that this photocatalytic route will not be the best way, in general, to produce cation radical derived dimers. However, when the initial concentration of the diene is increased, the amount of dimer produced increases proportionally.

Two of the oxygenated products, **7** and **8**, result from oxidative cleavage of the terminal double bond, and in the case of **8**, subsequent oxidation of the internal double bond. Products **11** and **13** presumably result from a 1,4-addition across the *s-cis* form of the diene cation radical (Scheme II). Diene **2** is believed to exist predominantly in the *s-cis* conformation.[14] Although this endoperoxide is also formed by singlet oxygenation, no evidence has been clearly established which implicates singlet oxygen as being formed in TiO_2-mediated hydrocarbon oxidations in nonaqueous media. In fact, the possibility of its involvement has been specifically refuted in the photocatalyzed oxidation of olefins. Biradical **10**, formed from the endoperoxide, can then abstract a hydrogen atom through a 6-membered transition state to form product **11**. Geometric isomerization, assumed to be rapid on the Lewis acid-rich surface, produces two isomers ***11Z*** and ***11E*** (at approximately a 1:1 ratio), which together comprise 17% of the reaction mixture. In the next step the aldehyde moiety is further oxidized on the illuminated semiconductor surface to form the acid, the *Z*-form of which can then dehydrate to form the observed furanone **13**. The additional unidentified oxidation product **14** is not the reasonably expected *E*- isomer.

α-Terpinene

The major products observed upon irradiation of a TiO_2 suspension containing 1-isopropyl-4-methyl-1,3-cyclohexadiene (α-terpinene) were the dione **16**, (7%), *p*-cymene **17**, (21%), ascaridole **18**, (15%), and isoascaridole **19**, (9%). Standardization of the reaction was not accomplished, since the products of this reaction could not be completely removed from the TiO_2. Repeated washing with several polar solvents in addition to CH_3CN were beneficial, but a faint yellow residue on the semiconductor persisted, and total recovery of the organic materials was not possible. Dione **16** is formed by oxidative cleavage of both double bonds. Products arising from the oxidation of only one of the double bonds were not detected. Control experiments showed that formation of **17** could be attributed to simple air oxidation over TiO_2.

The other products of this reaction appear to have a more interesting origin. Several workers have investigated the oxygenation of α-terpinene. For example, Barton and coworkers established that Lewis acids initiate triplet oxygen insertion into some conjugated dienes to yield cyclic peroxides identical to those obtained by reaction of singlet oxygen with these substrates.[15] Non-transition metal Lewis acids required irradiation for maximum catalytic activity, whereas transition metal Lewis acids acted as effective thermal catalysts. Triarylaminium cation radicals bearing electronegative substituents also served as good thermal initiators for the addition of triplet oxygen to dienes. Mechanistic elaboration of these reactions by Haynes[16] revealed that this reaction probably involves an electron transfer to form the diene cation radical and the reduced Lewis acid. Further work by Tang demonstrates that the role of the Lewis acid (i.e., triarylaminium cation radical) is not that of a catalyst, but rather as the initiator for a cation radical chain reaction.[17]

We propose a mechanism for the semiconductor-mediated reaction analogous to that suggested by these previous investigators. In photoexcited semiconductor suspensions, the electrophile is the photogenerated hole. This hole accepts an electron from the adsorbed diene to form the cation radical. This intermediate can be directly oxygenated by superoxide formed by interfacial capture of a conduction band electron. Alternately, triplet oxygen can add across the 1,4-positions to form the cation radical of the endoperoxide which is then reduced to ascaridole by accepting an electron either from the conduction band of TiO_2 or from another diene molecule.[17] If the latter occurs, a cation radical chain reaction would be established so that the initial photoevent would be amplified in product formation. While singlet oxygen again produces similar chemistry upon dye sensitization of **3** in homogeneous solution, we have no data which require or support its involvement here. As was mentioned earlier the involvement of singlet oxygen in these semiconductor systems has been shown to be a minor process at best.[1,18]

We propose that isoascaridole **19** is formed by secondary irradiation of the primary photocatalytic product **18**. Previous work[19] has established that excitation of ascaridole at 366 nm (pyrex filter) formed isoascaridole as a major product. If isoascaridole were a secondary photolysis product in our semiconductor system shorter irradiation times should produce an increased yield of ascaridole at the expense of isoascaridole. This was indeed the case: irradiation for 16 h gave a ascaridole/isoascaridole ratio of 1.7, while irradiation for 10 h resulted in an increase in the ratio to 2.2. Control experiments established that ascaridole did not convert to isoascaridole upon stirring the former in an acetonitrile solution of the light-protected semiconductor for 16 h, although exposure of the suspension to irradiation did produce the expected isomerization.

1-Phenyl-1,3-cyclohexadiene

1-Phenyl-1,3-cyclohexadiene, **4**, shows different behavior under the heterogeneous photooxidation conditions than is observed in the first three cases. Neither oxygenation or dimerization was observed. Instead, one product, biphenyl, is formed in 65% yield. Control experiments indicate that the aromatization was, in part, photocatalytically mediated rather than the result of simple air oxidation.[20] Bubbling oxygen through a light-protected acetonitrile solution of **4** resulted in nearly quantitative recovery of the substrate after 18 hours. The conversion of starting material to biphenyl was more significant (approximately 15% after 9 hours) in irradiated oxygenated solutions lacking the semiconductor catalyst, but its efficiency is still much lower than that observed in the presence of catalyst.

A mechanism involving two successive oxidation/deprotonation steps, outlined in Scheme III, can rationalize the observed results. The oxidation of the pentadienyl radical **21** to its cationic form **22** should occur very rapidly under conditions where **4** is oxidized, so that aromatization ultimately competes very favorably with oxygenation routes. Similar two-electron oxidative pathways have been postulated in the electrooxidation of 1,4-cyclohexadiene to benzene.[21]

Cyclic voltammetric studies also provide additional evidence for the cation radical pathway proposed in Scheme III. In deaerated acetonitrile containing 0.1 M tetra-*n*-butylammonium perchlorate, cyclic voltammograms of chromatographically pure (>99.5%) **4** display two irreversible oxidation waves at +0.90 and +1.59 V vs Ag/$AgNO_3$. The first oxidation wave is assigned to the two electron oxidation, since controlled potential electrolysis of 1,3-cyclohexadiene in nonaqueous media typically yields products resulting from removal of two electrons and two protons from the parent substrate.[22,23] The initial step in the oxidative process produces the highly reactive cation radical **20** which can rapidly deprotonate in a nonnucleophilic solvent such as acetonitrile. The resulting phenylcyclohexadienyl radical **21** would be expected to lose an electron readily at the oxidation potential of the parent diene forming cation **22**.

The second oxidative wave at +1.59 V corresponds to that of biphenyl, **23**. This assignment was comfirmed by comparison with voltammograms of an authentic sample as well as with literature data.[24] In accord with Scheme III, rapid deprotonation of cation **22**, generated at +0.9 V, forms biphenyl which is subsequently detected at a more positive potential. Comparison of this electrochemical pathway with the heterogeneous systems under investigation here is reasonable in view of considerable evidence establishing cation radical intermediates in a wide array of semiconductor-mediated organic transformations.[3,4,7,18,25]

Thus, in both the electrochemical and photoelectrochemical oxidations, aromatization provides the chemical driving force for the rapid deprotonation. The second oxidation occurs before desorption of the radical or oxygenation can occur. This rapid aromatization precludes the observation of either Diels-Alder dimer or oxygenation products in conjugated cyclohexadienes. The semiconductor surface thus cannot reverse normal oxidative chemoselectivity for aryl dihydroaromatics.

1,4-Diphenyl-1,3-butadiene

Diene **5** undergoes oxidative cleavage in competition with ring closure to a fused aromatic system on irradiated TiO_2 powders. We consider first the oxidative cleavage. The observed cleavage requires the presence of oxygen: deaerated solutions irradiated in a parallel manner do not yield oxygenated products. Thus, oxygen or a species derived from it must function as the effective source of oxygen atoms. While the potential of the conduction band of TiO_2 allows the generation of superoxide from triplet oxygen ($E_{p,c}$ = -0.9 V vs SCE)[2] the attack of superoxide on homogeneously dispersed diene is apparently negligible, since the reaction of diene **5** with solubilized potassium superoxide in a control experiment gave quantitative recovery of starting materials after 24 h.

The reaction of **5** with singlet oxygen, generated by reverse electron transfer from superoxide, is also improbable based on the contrasting products observed in these photocatalytic reactions as compared to those isolated from dye-sensitized photooxidations. Oxidation of **5** with singlet oxygen formed in homogeneous solution via photosensitization with methylene blue affords the corresponding endoperoxide in 75% yield.[26] The capture of olefinic cation radicals by triplet oxygen, most likely in a stepwise manner, has been established in both experimental [27,28] and theoretical[29] studies. Such reactions lead to dioxetanes which would cleave readily[30] under the photocatalytic conditions to precursors of the observed products. It is likely, then, that triplet oxygen or superoxide intercepts the adsorbed photogenerated cation radical **24** leading to the formation of dioxetane cation radical **25** or its reduced, neutral analogue (Scheme IV). Cleavage of the dioxetane forms 3-phenyl-2-propenal (**26**) and benzaldehyde (**27**), both of which are further oxidized to the observed product, benzoic acid, under the reaction conditions. The detection of small quantities (5-10%) of both **26** and **27** in the photolysis mixture provides evidence for this pathway.

The photocatalyzed cyclization to 1-phenylnaphthalene may also proceed via a surface-bound cation radical. The photochemical formation of 1-phenylnaphthalene upon direct irradiation of diene **5** has been demonstrated both in solution[31] and in the gas phase.[32] Although mechanistic details of this reaction were uncertain, population of the singlet excited state of the diene was thought to be critical in the ring closure.[32] Oxygen was believed to effect the aromatization of the dihydronaphthalene, yielding the observed product 1-phenylnaphthalene, since reduced yields were observed in deaerated samples.[31] Direct photoexcitation of **5** under our reaction conditions, however, is unlikely. The filtered irradiation used in these experiments precludes efficient formation of the singlet state of **5**, and, indeed, control photolyses in the absence of semiconductor catalyst demonstrated poor conversion of starting material (Table 3). Furthermore, back electron transfer in the surface-bound cation radical-superoxide pair is insufficiently exothermic to populate the excited singlet state by this indirect route. It is more probable that the observed ring closure is derived from a cation radical pathway and does not involve an electronically excited state of the diene. Arnold and coworkers have shown that cyclization does indeed ensue upon electron transfer photosensitization in homogeneous solution.[33] The relative yields of cyclized and oxygenated products show that these processes are competitive when the intermediate is adsorbed on the metal oxide surface, unlike that observed in homogeneous solution.

1-Methoxy-1,3-cyclohexadiene

The oxidation of 1-methoxy-1,3-cyclohexadiene on irradiated TiO_2 powders gave poor mass balance. The major observed product was anisole. Significant polymerization was observed, but no dimers could be detected. It is known that Diels-Alder dimerization of this compound is particularly sensitive to acid.[5] Thus, traces of water which are undoubtedly present on the TiO_2 surface will inhibit dimerization. Since only small amounts of a wide array of products was attained, the reaction mixture was not quantitatively analyzed nor were the products rigorously identified. No particular advantage in using a heterogeneous sensitizer compared with a homogeneous single electron acceptor was obvious, similar difficulties having been encountered in handling this cation radical either in solution or on irradiated surfaces.

Conclusion

Semiconductor-sensitized cation radical formation represents the initial step in the photocatalytic reaction of dienes on irradiated TiO_2 powders. It is not likely that this oxidation process will offer synthetic utility since the number of observed oxidation products is large. The [4+1] cation radical cyclization, hitherto observed only in homogeneous solutions, is an important reaction pathway in semiconductor-sensitized photolyses, but the necessity of oxygen saturation for effective electron-hole separation on irradiated TiO_2 makes this heterogeneous process more complex, since oxygenation and oxidative cleavage products are also competitively formed.

Cycloaddition or oxidation are not observed in the heterogeneous photolysis of 1-phenyl-1,3-cyclohexadiene, since a rapid two-electron oxidation resulting in aromatization of the parent diene occurs. Although precedent for such a reaction is available from electrochemical studies, similar pathways had not been documented previously in excited semiconductor colloidal suspensions. This work, thus, provides a mechanistically significant characterization of the competing reaction pathways accessible to 1,3-diene cation radicals formed on the surface of irradiated heterogeneous semiconductor suspensions.

Experimental

Instrumentation. ^{1}H NMR were obtained at ambient probe temperature on a Varian EM-390 90 MHz spectrometer with chemical shifts reported in parts per million downfield from tetramethylsilane as an internal standard. Gas chromatography-mass spectrometry (GC/MS) analyses were performed on a Finnigan Model 4023 automated GCMS with an INCOS data system using a 50 meter DB-1 capillary column. High pressure liquid chromatography (HPLC) was performed using a Waters 6000A solvent delivery system equipped with a R401 differential refractometer detector or a Model 440 absorbance detector and a µ-Porasil 27477 analytical column or a Porasil semipreparative column. Gas-liquid chromatographic (GLC) analyses were obtained with a Varian Aerograph 1400 instrument equipped with a flame ionization detector and a 40 m SGE BP-1 capillary column unless otherwise noted. Peak intensities were monitored with a Hewlett-Packard 3390A integrator. Quantitative analyses by GLC were conducted using biphenyl or pentamethylbenzene as internal standards. When suitable internal standards could not be found, standard curves were used. UV absorption spectra were obtained on a Cary 17 spectrophotometer.

Irradiations were conducted in a Rayonet photochemical reactor (Southern New England Ultraviolet Company) equipped with a cooling fan and lamps emitting maximally at 350 nm or with a Hanovia 450 W medium pressure mercury lamp immersed in a Pyrex reaction vessel, cooled by circulation of chilled water or a chemical filter solution.

Cyclic voltammetry was conducted with a Bioanalytical Systems BAS-100 Electrochemical Analyzer equipped with a Houston Instruments DMP-40 digital plotter. A one-compartment cell was used. The acetonitrile solutions contained 0.1 M tetra-*n*-butylammonium perchlorate as the supporting electrolyte and were deaerated and kept under a positive pressure of argon during each run. Silver-silver nitrate (0.1 M in acetonitrile) served as the reference electrode and a platinum disk and wire coil were the working and counter electrodes, respectively. Positive feedback for IR compensation was utilized in all runs to minimize the effects of solution resistance between the working and reference electrodes. The supporting electrolyte-acetonitrile solutions were scanned over the solvent window prior to the addition of substrate to ensure the absence of electroactive impurities. The formal potential of the ferrocene/ferrocenium couple is +0.307 V vs. aqueous SCE compared with +0.075 V vs. our $Ag/AgNO_3$ electrode.

Solvents and Reagents. Titanium dioxide (TiO_2, MCB technical grade, anatase powder) was dried overnight at temperatures greater than 100°C before use. Oxygen gas was dried by passage through a drying tube containing dry calcium chloride. EM Reagents 250-400 mesh silica gel was used in flash column chromatography separations. Acetonitrile (Aldrich, 99%) was stored over 3A molecular sieves in an inert atmosphere prior to use.

1,3-Cyclohexadiene, 2,4-dimethyl-1,3-pentadiene, *trans,trans*-1,4-diphenyl-1,3-butadiene and α-terpinene (Aldrich) were used without further purification.

Tetra-*n*-butylammonium perchlorate (Southwestern Analytical Chemicals, electrometric grade) was recrystallized three times from ethyl acetate : hexane and was dried for 24 h under vacuum prior to use.

General Procedure for Semiconductor-Mediated Photooxidations. In general, a 0.01-0.025 M solution of the diene in acetonitrile was prepared, and approximately 10 mg of TiO_2 was added per 100 mL of solution. These mixtures were sonicated in an ultrasonic bath while bubbling with oxygen for 30-60 minutes. The mixtures were then irradiated for 16-48 h without further oxygenation. A chromatographable sample of the product mixture was obtained by vacuum filtration of the catalyst and rotary evaporation to concentrate the products. Product identification was accomplished either by isolation and comparison of spectral properties with known materials or coinjection, and by comparison of mass spectral fragmentation patterns with authentic samples. Identified products and yields are listed in Table 1.

Both 1-phenyl-1,3-cyclohexadiene and *trans,trans*-1,4-diphenyl-1,3-butadiene absorb light at 350 nm; thus, passing the incident light through a filter solution of 0.1 M KNO_2 (λ>380 nm) adjusted to pH 10 by addition of NaOH assured the absence of direct substrate excitation by the Hanovia 450 W medium pressure mercury lamp. Due to the thermal instability of 1,3-cyclohexadienes, all of the semiconductor photolysis reactions were cooled to 15-20° C to minimize polymerization.

Preparation of 2,4-Dimethyl-1,3-pentadiene dimers. The Lewis acid catalyzed Diels-Alder dimer was prepared by stirring a 0.021 M dichloromethane solution of the diene over Fe(III)-exchanged montmorillonite (50 mL solution/1g clay) for 2 h. The clay was filtered and the solvent removed under rotary evaporation to give the Lewis acid dimer in quantitative yield.

The cation radical dimer was prepared by irradiating a 0.125 M acetonitrile solution of the diene containing 25 mole percent 1,4-dicyanobenzene (Aldrich) for 15 h. using a 450 W medium pressure Hanovia (pyrex filter). The solution was concentrated and the product extracted with hexanes. The dimer was then purified by vacuum distillation. Product formation was cleaner when dicyanobenzene was recrystallized prior to use. The endo/exo ratio was determined by relative peak areas by GLPC.

Preparation of ascaridole and isoascaridole. Ascaridole was prepared using 100 g α-terpinene and 190 mg eosin Y in 3000 ml ethanol. The solution was irradiated using a Hanovia lamp for 10 h.[34] Isoascaridole was prepared as described previously.[19]

Preparation of 1-phenyl-1,3-cyclohexadiene. 1-Phenyl-1,3-cyclohexadiene was prepared by reacting *trans*-1-butadienyltriphenyl-phosphine[34] with the enolate anion of acetophenone.[35] Formation of the desired product was confirmed by MS and NMR.[20]

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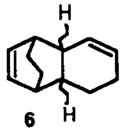
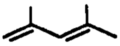
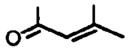
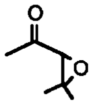
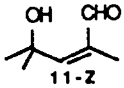
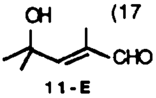
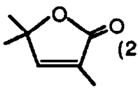
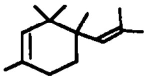
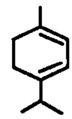
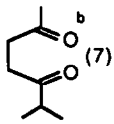
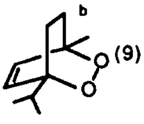
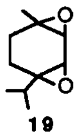
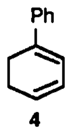
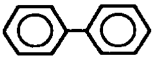
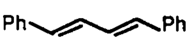
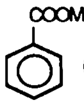
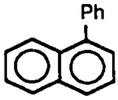
Table I. Major Products from the Photocatalyzed (UV-Irradiated Titanium Dioxide) Oxidation of Some 1,3-Dienes

substrate	products (percent yield)[a]
 1	 6 (20) (endo:exo 2:1) + $C_6H_8O_2$ isomers
 2	 7 (3)  8 (15)  11-Z  11-E (17 total)  13 (22) $C_7H_{12}O_3$ 14 (23)  15 (4)
 3	 16 (7)[b]  17 (21)[b]  18 (9)[b]  19 (15)[b]
 4	 23 (65)
 5	 28 (22)[c]  29 (34)

a. Products were determined using GC/MS and yields were calculated against an internal standard using GLC. b. GLC yield only. c. Product obtained following esterification with acidic methanol.

Table 2. Oxidation Peak Potentials of 1,3-Dienes.

substrate	Ep_a^{a} (V vs SCE)
1	1.58
2	1.44
3	1.08
4	1.13
5	1.07

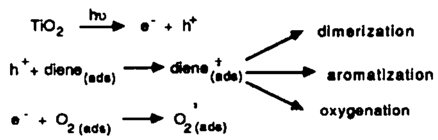
a. Obtained in CH_3CN containing 0.1 M tetra-*n*-butyl ammonium perchlorate as supporting electrolyte. All waves are irreversible.

Table 3. Control Experiments for the Photocatalytic Oxidation of 5.[a]

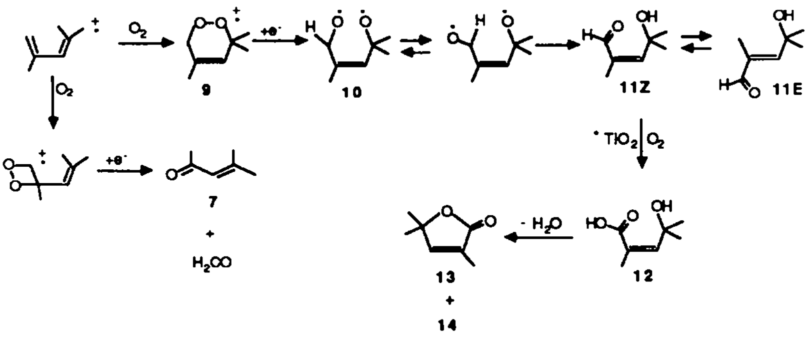
Control	Reaction Time (h)	Percent conversion[b]
TiO_2, light, $^{c}O_2$	48	95
TiO_2, dark, O_2	24	0
TiO_2, light, Ar	48	10
light, O_2	6	10
TiO_2, light, O_2	6	32

a. Concentration of substrate was 0.002 M. b. Determinations made by gas chromatography. c. Irradiations with wavelengths greater than 380nm.

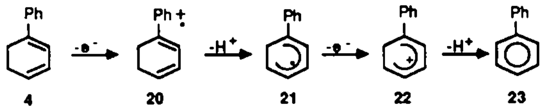
Scheme I. Initial Steps in Semiconductor Photooxidations.



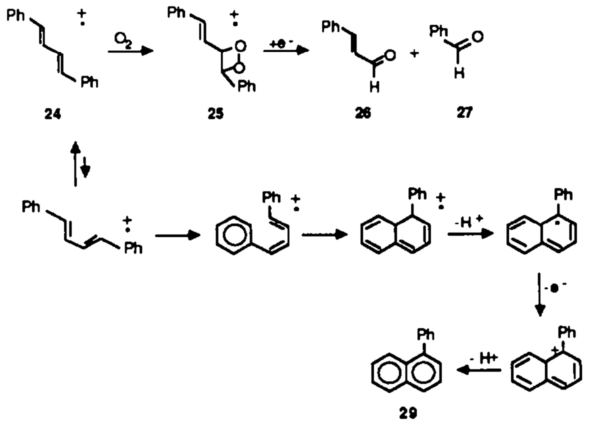
Scheme II. Propose Mechanism for 2,4-Dimethyl-1,3-pentadiene Photooxidation on TiO_2.



Scheme III. Oxidation Mechanism for 1-Phenyl-1,3-cyclohexadiene.



Scheme IV. Proposed Mechanistic Pathway for Photocatalytic Oxidation of Diene 5.



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