Photochemical Electron-Transfer Reactions of 1,1-Diarylethylenes

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Abstract: The dimerizations, nucleophilic additions, and oxygenation reactions of 1,1-diarylethylenes (**1**), induced by photoexcited cyanoanthracenes, have been investigated. 1,1-Diphenylethylene (**1a**) yields 2 + 2 and 2 + 4 cyclodimers and one dehydrodimer, whereas 1,1-dianisylethylene (**1b**) gives two dehydrodimers, and 1,1-bis(4-(dimethylamino)phenyl)ethylene (**1c**) forms no dimers. Formation of the dehydrodimers is accompanied by reduction of the cyanoanthracene sensitizer. For the dimerization of **1b**, the quantum yields and product ratios can be altered by the addition of quinones. The hydroquinone then replaces the reduced sensitizer. The reaction constant for nucleophilic addition of methanol to $\mathbf{1a}^{\bullet+}$ is 1.6×10^9 M^{-1} s^{-1}; for addition to $\mathbf{1b}^{\bullet+}$ it is $\sim 10^7$ M^{-1} s^{-1}. Methanol does not add efficiently to $\mathbf{1c}^{\bullet+}$. Photooxygenation of the diarylethylenes yields mainly the corresponding 3,3,6,6-tetraaryl-1,2-dioxane in a chain process. In the presence of methanol and oxygen, **1a** yields mainly 1-hydroperoxy-2-methoxy-1,1-diphenylethane.

Photoinduced electron-transfer photoreactions are attracting much attention in organic photochemistry. Considerable work has been done recently to define the scope of these reactions, their kinetics, and the mechanisms involved. Several reactions of olefins as electron donors sensitized by a number of electron acceptors have been identified. These include isomerizations (geometric and valence), rearrangements, dimerizations, mixed additions, acceptor-donor additions, nucleophilic additions, and oxygenations.[1]

This article deals with the dimerizations, nucleophilic additions, and oxygenation reactions of 1,1-diarylethylenes (**1**) induced by photoexcited 9,10-dicyanoanthracene (DCA)[2] or 2,6,9,10-tetracyanoanthracene (TCA).[3] Special emphasis is given to the kinetics of these reactions, the role of the geminate radical ion pair, and manipulations via secondary electron-transfer processes.

$Ar_2C{=}CH_2$ **1**

a: $Ar = C_6H_5$
b: $Ar = 4\text{-}CH_3OC_6H_4$
c: $Ar = 4\text{-}(CH_3)_2NC_6H_4$

From kinetic analyses based on quantum yields and concentration dependence of the different products, ratios of reaction constants are readily obtained. Quenching, via interception of the radical cations by compounds of low oxidation potentials, yields ratios of some of these reaction constants to that of quenching. By the proper choice of quenchers, it is safe to assume that the quenching reaction proceeds at the diffusion-controlled limit of 1.5×10^{10} M^{-1} s^{-1} in acetonitrile at room temperature. From these, the individual rate constants are obtained. The accuracy of these values is estimated to be within 30%.

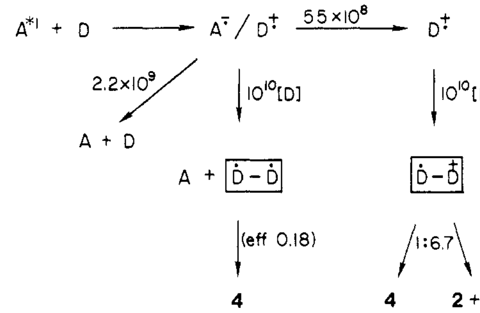
Results and Discussion

Dimerization of 1,1-Diphenylethylene (1a). The electron-transfer-photosensitized dimerization of 1,1-diphenylethylene (**1a**) to the tetrahydronaphthalene derivative **2** was first reported by Neunteufel and Arnold, who used methyl 4-cyanobenzoate as the electron-acceptor sensitizer.[4] Similar results were achieved with other sensitizers.[5,6] However, sensitization with phenothiazonium radical cation led to the dihydronaphthalene analogue **3**, the formation of which was attributed to oxidation of the dimeric radical cation by the sensitizer followed by double deprotonation.[7]

Table I. Effect of Added Quinones on the Quantum Yield of Dimerization of **1b** Sensitized by DCA

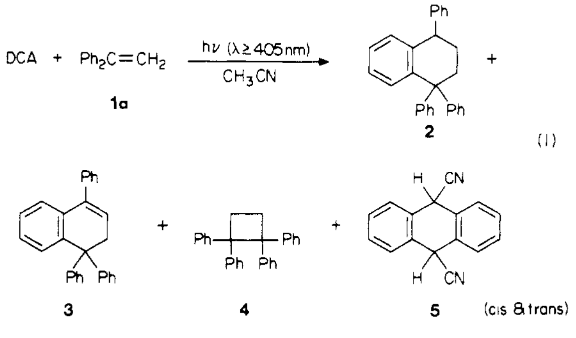
quinone (Q)	E_Q^{red} (V)	Φ_Q/Φ	9/8
none		(1)	0.5
1,4-naphthoquinone	−0.64	3.5	1.4
benzoquinone	−0.53	7.0	3.5
2,3-dichloronaphthoquinone	−0.39	7.5	2.0

Scheme I



Additional features of this dimerization reaction were encountered when we used the cyanoanthracenes as sensitizers. These include competing 2 + 2 and 2 + 4 cyclizations as well as radical cation/radical anion interactions resulting in competition between electron transfer and proton transfer, depending on the electron acceptor used.

Using DCA as a sensitizer for the dimerization of **1a** in acetonitrile, we obtained similar amounts of both **2** and **3** in addition to the 2 + 2 cyclodimer **4**[8] and the reduced sensitizer, *cis*- and *trans*-dihydrodicyanoanthracene **5** (eq 1).



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(1) Mattes, S. L.; Farid, S. In *Organic Photochemistry*; Padwa, A., Ed.; Marcel Dekker: New York, 1983; Vol. 6, p 233, and references therein.

(2) Evans, T. R.; Wake, R. W.; Jaenicke, O. In *The Exciplex*; Gordon, M.; Ware, W. R., Eds.; Academic: New York, 1975; p 345.

(3) Mattes, S. L.; Farid, S. *J. Am. Chem. Soc.* **1982**, *104*, 1454.

(4) Neunteufel, R. A.; Arnold, D. R. *J. Am. Chem. Soc.* **1973**, *95*, 4080.

(5) Majima, T.; Pac, C.; Nakasone, A.; Sakurai, H. *J. Am. Chem. Soc.* **1981**, *103*, 4499.

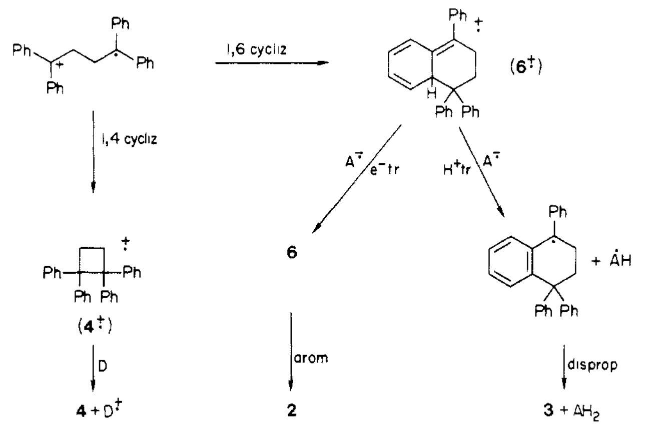
(6) Mizuno, K.; Ogawa, J.; Kamura, M.; Otsuji, Y. *Chem. Lett.* **1979**, 731.

(7) Moutet, J. C.; Reverdy, G. *Tetrahedron Lett.* **1979**, 2389.

(8) The 2 + 2 cyclodimer **4** is thermally unstable; it cleaves exclusively to **1a** with a half-lifetime $T_{1/2}$ of 47 min at 51 °C. See Experimental Section for its spectroscopic data.

0002-7863/86/1508-7356$01.50/0

Scheme II



Several kinetic data strongly support the mechanism outlined in Scheme I. Because of a high reaction constant ($\sim 10^{10}$ M^{-1} s^{-1}) for the addition of the olefin radical cation ($D^{\bullet+}$) to the neutral olefin, interception of the geminate pair ($A^{\bullet-}/D^{\bullet+}$) by D competes with the cage separation.[9] The intercepted pair gives the dimeric radical cation in cage with the acceptor radical anion ($A^{\bullet-}/D^{\bullet}-D^{+}$). Through back-electron transfer, this radical cation is reduced to the corresponding biradical ($D^{\bullet}-D^{\bullet}$), which undergoes 1,4-cyclization to give the cyclobutane **4**. The separated dimeric radical cation, however, undergoes both 1,6- and 1,4-cyclization, leading to the naphthalenes **2** and **3** and to the cyclobutane **4**, respectively.

Strong support for the proposed mechanism of interception of the geminate pair was obtained through a route circumventing this intermediate. Irradiation in the presence of biphenyl (B) results in competition between this additive and the olefin (D) for the excited acceptor (TCA). The former reaction leads to $B^{\bullet+}$, which then oxidizes D to $D^{\bullet+}$. As expected, the ratio of **4**/(**2** + **3**) decreases with increasing [B] until it approaches the value of ~1:6.7 expected from the separated dimeric radical cation.

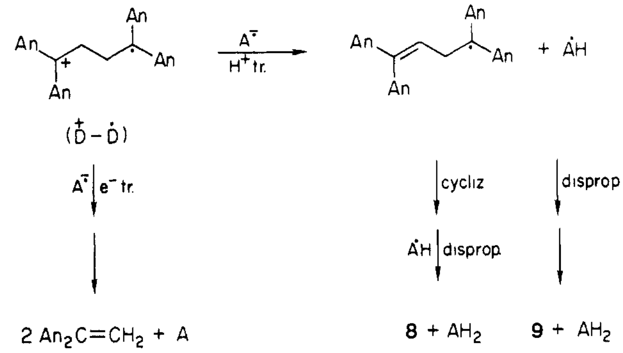
$$\begin{tikzcd}
A^{*1} + B \arrow[r] & A^{\overline{\cdot}}/B^{\dot{+}} \arrow[r] & B^{\dot{+}} \arrow[d, "D"] \\
A^{*1} + D \arrow[r] & A^{\overline{\cdot}}/D^{\dot{+}} \arrow[r] & D^{\dot{+}}
\end{tikzcd}$$

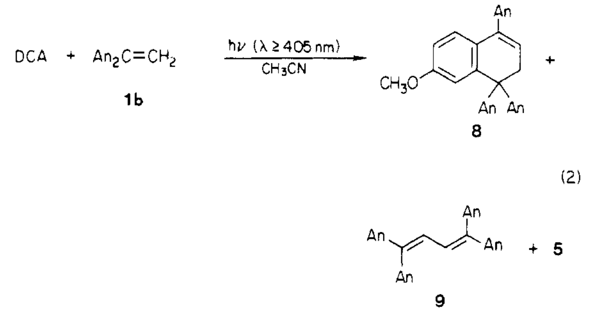
The fate of the radical cation $6^{\bullet+}$ (Scheme II) seems to depend on the acceptor used. In the studies of Neunteufel and Arnold[4] and Pac and co-workers,[5] where methyl 4-cyanobenzoate and 1,4-dicyanobenzene were the electron acceptors, only **2** was isolated. We also found that sensitization with 1,4-dicyanonaphthalene gives, besides **4**, the tetrahydronaphthalene **2**. The DCA- or TCA-sensitized dimerization yields, however, almost equal amounts of **2** and **3**.

These data suggest that the reaction of $6^{\bullet+}$ with the acceptor radical anion ($A^{\bullet-}$) can lead either to electron transfer followed by aromatization to yield **2**, as proposed by Neunteufel and Arnold,[4] or to proton transfer to give a pair of radicals that disproportionate to **3** and the dihydro derivative of the acceptor (AH_2). The radical anions of the cyanoanthracenes are likely to be stronger bases than those of the cyanobenzenes and cyanonaphthalenes, because ring protonation of the anthracene molecule is not accompanied by a large loss of aromatization energy.

Dimerization of 1,1-Dianisylethylene. We also investigated the photodimerization of 1,1-dianisylethylene (**1b**), using DCA as a sensitizing acceptor.[10] No cyclobutane was formed, and only a small amount of the tetrahydronaphthalene analogue of **2** (**7**) was obtained in this reaction. However, two dehydrodimers, the dihydronaphthalene **8** and the diene **9**,[11] were obtained besides the reduced acceptor **5**.

Scheme III





(2)

This reaction can be explained in terms of the mechanism outlined in Scheme III. The cyclization of the dimeric radical cation ($D^{+}-D^{\bullet}$) is apparently very slow, owing to high charge delocalization. Interaction between $D^{+}-D^{\bullet}$ and $A^{\bullet-}$ can result in either electron transfer or proton transfer. Electron transfer leads to a biradical, which in this case cleaves either directly or via an unstable cyclobutane to the olefin, i.e., the net effect is an energy-wasting step. On the other hand, proton transfer gives a pair of radicals, which through disproportionation or through electron transfer followed by proton transfer gives the diene **9**. The formation of the dihydronaphthalene **8** requires cyclization of the ene-radical prior to reaction with $A^{\bullet}H$ (Scheme III).

In agreement with this scheme, the partitioning between the two competing reactions of $D^{+}-D^{\bullet}$ with $A^{\bullet-}$ could be influenced by replacing $A^{\bullet-}$ by another radical anion. Thus, irradiation in the presence of low concentrations of different quinones significantly increases product quantum yields and gives a different product distribution. Depending on the quinone used, the quantum yield increases by up to ca. 7-fold, accompanied by an increase in the **9**/**8** ratio.[12] The higher quantum yield is explained by stronger basicity of the quinone radical anion over that of DCA, thus enhancing the acid–base reaction over the competing redox reaction. As expected in these reactions, the dihydro derivative of DCA (**5**) is replaced by the hydroquinone. The 7-fold increase in the quantum yield shows that with the counterion ($A^{\bullet-}$) being $DCA^{\bullet-}$, the partition between proton and electron transfer is ca. 1:6. In agreement with this view, about a 7-fold increase in quantum yield could be achieved also by adding acids, e.g., trichloroacetic acid, at ca. 10^{-2} M to the DCA-sensitized reaction. Protonation of $DCA^{\bullet-}$ prevents the energy-wasting electron-transfer reaction.

Nucleophilic Addition. The photochemical anti-Markovnikov

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(9) Mattes, S. L.; Farid, S. *J. Am. Chem. Soc.* **1983**, *105*, 1386.

(10) With TCA as a sensitizer, the photodimerization of **1b** yielded a mixture containing 5% **9**, 60% **8**, and 30% **7**. The decrease in the formation of diene and the increase in the formation of tetrahydronaphthalene suggest that $TCA^{\bullet-}$ is less basic (i.e., more stabilized) than $DCA^{\bullet-}$. **7** and **8** were identified from an NMR spectrum of the mixture, by analogy to **2** and **3** (see Experimental Section).

(11) In an electron-transfer-sensitized photoreaction of **1b** and furan, two dimers, **8** and 1,1,4,4-tetraanisyl-1-butene, were obtained in 23% and 67% yield, respectively. Mizuno, K.; Ishii, M.; Otsuji, Y. *J. Am. Chem. Soc.* **1981**, *103*, 5570.

(12) When TCA is used as the sensitizer, the quantum yield increases by 16-fold, depending on the quinone used.

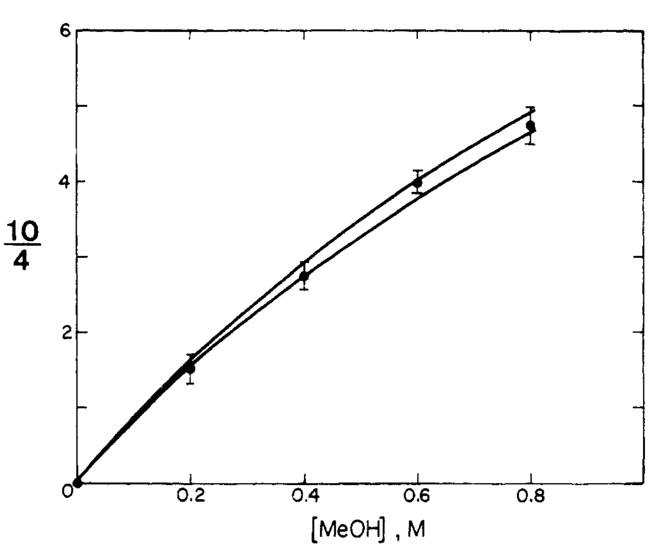
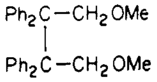


Figure 1. Product ratio from irradiation of DCA and **1a** (0.1 M) as a function of [MeOH]. The upper and lower curves are calculated on the basis of k_{ig} of 2.2×10^9 and 6×10^9 s^{-1}, respectively. See text for other reaction constants used to calculate these curves.

addition of methanol to **1a** was first reported by Neunteufel and Arnold,[4] who used methyl 4-cyanobenzoate as an electron-transfer sensitizer. Strong evidence was presented for the following sequence of reactions: addition of MeOH to the olefin radical cation, deprotonation, one-electron reduction of the resultant radical by the acceptor radical anion, and finally protonation of the anion to give the ether **10**.

Ph_2CHCH_2OMe

10



$$\begin{array}{l} Ph_2C{-}CH_2OMe \\ \quad | \\ Ph_2C{-}CH_2OMe \end{array}$$

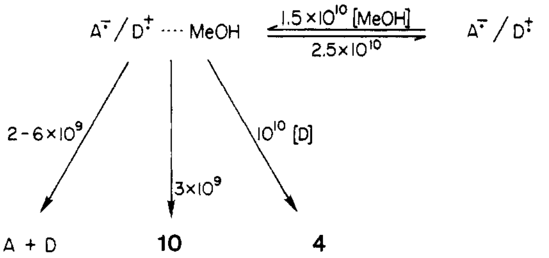
11

We studied the kinetics of the nucleophilic addition, using the cyanoanthracenes as sensitizers, by irradiating in acetonitrile containing various amounts of methanol. When TCA was used as the sensitizer, the major product was not the ether **10** but the dimeric compound **11**. Evidently the reduction of the radical $Ph_2\dot{C}CH_2OMe$ by $TCA^{\bullet -}$ is much slower than that with $DCA^{\bullet -}$, showing that the reduction potential of this radical is more negative than −0.45 V, the reduction potential of TCA. Compound **11** results from dimerization of the radical.

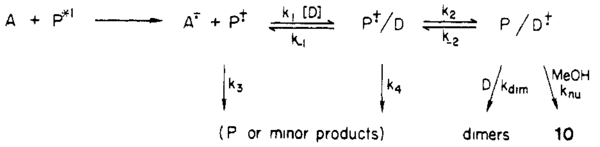
Strong quenching of the formation of the naphthalene products **2** and **3** by relatively low concentrations of methanol shows that the nucleophilic addition of MeOH to $D^{\bullet +}$ is also a fast process. Not surprisingly, the cyclobutane, which is formed mostly via the intercepted geminate pair, is less susceptible to quenching by methanol. Even in neat methanol, at 0.2 M D, the cyclobutane is formed at a quantum yield of ca. 0.02, which is only 4.5 times less than that from the corresponding reaction in acetonitrile. The quantum yield for the formation of the ether **10** in neat methanol is ca. 0.3.

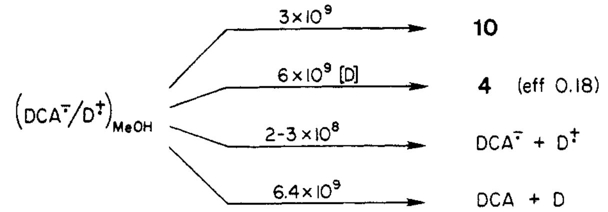
From these values, the nucleophilic addition rate constant (k_{nu}) can be estimated. The viscosities of methanol and acetonitrile at 25 °C are 0.547 and 0.345 cP, respectively. Therefore, the dimerization constant in MeOH, k_d', is expected to be 6×10^9 M^{-1} s^{-1}, i.e., proportionately lower than that in MeCN, which is 10^{10} M^{-1} s^{-1}, owing to the higher viscosity. If we assume that the efficiency of the cyclobutane formation in this process is similar in both solvents, then the rate of nucleophilic addition within the methanol-solvated cage of the radical ion pair is ca. 3×10^9 s^{-1}. Accordingly, in neat methanol, most (ca. 90%) of the ether is formed via the geminate pair, since the separation rate constant in methanol is about $2-3 \times 10^8$ s^{-1}.[13] From these rate constants and the above mentioned quantum yields, the return electron transfer constant in MeOH, k_{ig}', is ca. 6.4×10^9 s^{-1}.

Scheme IV



Scheme V





Strong support for the value of 3×10^9 s^{-1} for the rate of nucleophilic addition of MeOH in cage with $D^{\bullet +}$ is obtained from the ratio of **10**/**4** as a function of the concentration of methanol added to the acetonitrile solution. As shown in Figure 1, good agreement is obtained between the experimental data and the calculated values based on this reaction constant and those determined above from the dimerization experiments. Note that the difference between the two curves, calculated on the assumption that k_{ig} from $(DCA^{\bullet -}/D^{\bullet +}\cdots MeOH)_{CH_3CN}$ is 2.2×10^9 s^{-1} as found in $(DCA^{\bullet -}/D^{\bullet +})_{CH_3CN}$ or 6.4×10^9 s^{-1} as estimated in $(DCA^{\bullet -}/D^{\bullet +})_{MeOH}$, is very small and lies within the experimental error of the data. The calculated curves are based on the following partial scheme (Scheme IV) in which the rate constants for methanol penetration in and out of the geminate cage are the diffusion-controlled limits, i.e., 1.5×10^{10} M^{-1} s^{-1} and 2.5×10^{10} s^{-1}, respectively. The other reactions of $A^{\bullet -}/D^{\bullet +}$ are similar to those discussed in the previous section, except that the separated $D^{\bullet +}$ in these experiments leads predominantly to **10**.

From the rate constants in Scheme IV, the effective bimolecular reaction constant (k_{nu}) for the nucleophilic addition of MeOH to the radical cation of diphenylethylene can be calculated from eq 3, where k_{diff} is the diffusion rate constant (1.5×10^{10} M^{-1} s^{-1}), k_{-diff} is the rate of diffusion out of the cage (2.5×10^{10} s^{-1}), and k_r is the first-order constant for addition (3×10^9 s^{-1}). These values lead to k_{nu} of 1.6×10^9 M^{-1} s^{-1}.

$$k_{nu} = k_{diff}\frac{k_r}{k_r + k_{-diff}} \qquad (3)$$

Pac and co-workers[5] carried out a kinetic study of methanol addition to diphenylethylene (**1a**), using phenanthrene (P) as a light-absorbing primary donor and 1,4-dicyanobenzene as the electron acceptor (A). Since P has a lower oxidation potential than **1a** (D), these authors proposed that $P^{\bullet +}$ forms a π complex with the olefin as the reactive intermediate in this reaction. They interpreted the kinetic data as ruling out the endothermic electron transfer between $P^{\bullet +}$ and D and concluded that such a π complex reacts with MeOH at a rate of 7×10^5 M^{-1} s^{-1}. This very low reaction constant was attributed to weak electrophilicity of the π complex, "owing to less development of the positive charge on the side of D in the π complex". Moreover, the authors assumed a very small constant for the dimerization step, which contradicts

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(13) Weller, A. *Z. Phys. Chem. Neue Folqe* **1982**, *130*, 129.

the almost-diffusion-controlled rate we observed in our study. We propose, instead, Scheme V to interpret the data reported by Pac.

This scheme is based on the energetically feasible reversible electron transfer in the pair $P^{\bullet+}/D \rightleftharpoons P/D^{\bullet+}$. We used the values determined from our work for the dimerization and nucleophilic addition constants, k_{dim} and k_{nu}, of 10^{10} and 1.6×10^{9} M^{-1} s^{-1}, respectively, and obtained reasonably good fit to the data in ref 5 using the following reaction constants: $k_1 = 5 \times 10^{9}$ M^{-1} s^{-1}, $k_{-1} = 10^{7}$ s^{-1}, $k_2 = 10^{7}$ s^{-1}, $k_{-2} = 7 \times 10^{9}$ s^{-1}. The pseudo-first-order rate constants k_3 and k_4, which are due to impurity quenching (cf. ref 5), are assumed to be 10^{7} and 10^{6} s^{-1}, respectively. The quenching rate of $P^{\bullet+}$, $P^{\bullet+}/D$, and $P/D^{\bullet+}$ by low-oxidation-potential compounds such as triethylamine was taken as the diffusion-controlled limit of 1.5×10^{10} M^{-1} s^{-1}.

It is interesting to note that the equilibrium constant of ~500 M^{-1} for $P^{\bullet+} + D \rightleftharpoons P^{\bullet+}/D$ is in the same range as those determined for a number of radical cations of aromatic hydrocarbons interacting with their neutral counterparts.[14]

The equilibrium constant K_2 of 1.43×10^{-3}, which corresponds to an energy difference of 0.17 eV, also compares well with the difference of 0.15 V between the oxidation potentials of P and D. This phenanthrene-induced reaction is very susceptible to quenching and the presence of impurities, not because of slow nucleophilic addition but because of the slow, endothermic electron-transfer step, k_2. In the directly sensitized reactions, i.e., via an excited acceptor, where such a step is absent, quenching is inefficient.

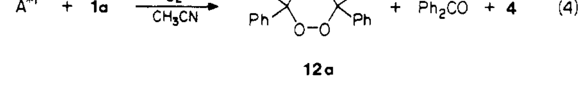
With dianisylethylene (**1b**), nucleophilic addition of MeOH to the radical cation is much slower than the corresponding rate for **1a**. From competition between the dimerization, which occurs as with **1a** at 10^{10} M^{-1} s^{-1}, and methanol addition, the latter rate constant is estimated to be 10^{7} M^{-1} s^{-1}, i.e., almost two orders of magnitude lower than that of **1a**. This is clearly due to higher delocalization of the positive charge in the methoxy-substituted compound.

In accordance with this decrease of methanol activity toward the radical cation of **1b**, the radical cation of the dimethylamino analogue **1c** seems to have an immeasurably low reactivity to methanol. As shown below, oxygenation reactions of this olefin can be carried out even in neat methanol without the formation of methanol adducts.

Oxygenation. Electron-transfer photooxygenation has attracted considerable interest in the last few years.[1] Much of the research centered around reactions of the donor radical cation with $O_2^{\bullet-}$, which is formed via secondary electron transfer from the acceptor radical anion (mostly DCA) to molecular oxygen.

It seems that the reaction constant for addition of oxygen to most olefin and acetylene radical cations is very small. Therefore, such reactions occur only if competing processes, such as the return electron transfer from the radical anion to the radical cation, are suppressed. Efficient reactions with molecular oxygen, however, may occur when preceded by other reactions of the olefin radical cation.

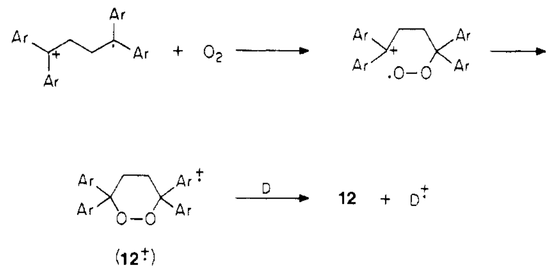
In the DCA- or TCA-sensitized reactions of **1a**, O_2 suppresses the formation of the naphthalene products, which are replaced by a higher quantum yield of the 1,2-dioxane **12a**[15] and benzophenone. However, the reaction via the intercepted geminate pair (Scheme I) yielding the cyclobutane **4** is affected only marginally, if at all, by the presence of oxygen. The data show that the cyclization of the dimeric 1,4 radical cation in this case is apparently slow enough that addition to oxygen can compete favorably with this intramolecular process. The resultant dioxane radical cation, having a higher oxidation potential than the olefin, is oxidized by the latter, thus resulting in a chain reaction (Scheme VI). On the other hand, the biradical leading to the cyclobutane seems to cyclize much faster than that being trapped by O_2 at 10^{-2} M.



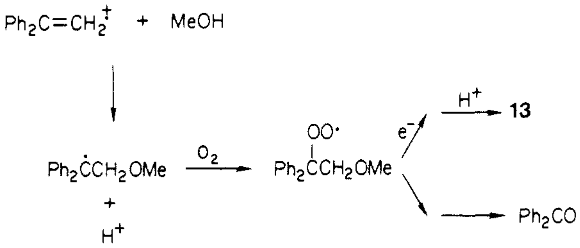
(4)

12a

Scheme VI



Scheme VII



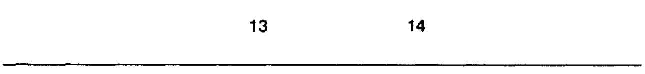
It is most unlikely that the formation of benzophenone under our reaction conditions is via reaction of $\mathbf{1a}^{\bullet+}$ with O_2, as such additions are very slow and cannot compete with the almost-diffusion-controlled addition of $\mathbf{1a}^{\bullet+}$ to the neutral olefin. It is more likely that benzophenone is formed via reaction of O_2 with the dimeric radical cation in competition with the dioxane formation.

Superoxide cannot be involved in this reaction or those discussed below, as proposed by Eriksen and Foote,[16] since the addition of the olefin radical cation to a neutral olefin is almost diffusion controlled. Even at 10^{-3} M olefin, its concentration will still be many orders of magnitude higher than that of $O_2^{\bullet-}$. Moreover, these reactions are also sensitizable with TCA, which cannot efficiently generate superoxide because of the >0.3-eV endothermicity for electron transfer from $TCA^{\bullet-}$ to O_2.

Analogous sensitized irradiations of **1b**[17] and **1c** under oxygen lead to the corresponding dioxanes **12b** and **12c** in high yields. Compound **12c**, which was previously reported[18] to be the head-to-tail 2 + 2 cyclodimer, was also obtained when **1c** was subjected to (dark) one-electron oxidation with $Cu(NO_3)_2$ in methanol.

In agreement with the very slow cyclization rate of the dimeric radical cation, D^{+}–$D^{\bullet}$, derived from **1b**, as mentioned in the previous section, traces of oxygen suppress the formation of the dimers. Dimerization will proceed only after the oxygen is consumed in the dioxane formation.

Electron-transfer-sensitized photooxygenation of **1a** in the presence of methanol yields the methoxy hydroperoxide derivative **13** and benzophenone as the major products and the methoxy alcohol **14** as a minor component. The ratio of **13**/benzophenone can be altered by irradiating in the presence of sodium methoxide (~10^{-3} M). With TCA as a sensitizer, this increases the ratio from about 1 to 4, and with DCA from about 0.1 to 1.



$$A^{*1} + \mathbf{1a} \xrightarrow[CH_3CN]{O_2,\ MeOH} Ph_2\overset{OOH}{\overset{|}{C}}CH_2OMe + Ph_2\overset{OH}{\overset{|}{C}}CH_2OMe + Ph_2CO \qquad (5)$$

13 **14**

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(14) Kira, A.; Arai, S.; Imamura, M. *J. Chem. Phys.* **1971**, *54*, 4890. Arai, S.; Kira, A.; Imamura, M. *J. Chem. Phys.* **1972**, *56*, 1777. Kira, A.; Arai, S.; Imamura, M. *J. Phys. Chem.* **1972**, *76*, 1119. Rodgers, M. A. J. *J. Chem. Soc., Faraday Trans. 1* **1972**, *68*, 1278.

(15) Haynes, R. K.; Probert, M. K. S.; Wilmot, I. D. *Aust. J. Chem.* **1978**, *31*, 1737.

(16) Eriksen, J.; Foote, C. S. *J. Am. Chem. Soc.* **1980**, *102*, 6083.

(17) The photooxygenation of **1b** sensitized by DCA was also studied, independently, by Gollnick and Schnatterer. Gollnick, K.; Schnatterer, A. *Tetrahedron Lett.* **1984**, 185.

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The mechanism of this reaction is analogous to that we reported for 1,1-dimethylindene[3] (Scheme VII). Methanol adds to the olefin radical cation, with loss of a proton, to form a free radical that is trapped by oxygen, forming a peroxyradical. Reduction of the peroxyradical followed by protonation gives **13**. This peroxyradical is also the most likely precursor to benzophenone. Eriksen and Foote,[16] who also studied this reaction, however, proposed that benzophenone is formed via reaction of **1a**$^{\bullet+}$ with $O_2^{\bullet-}$. This route can be ruled out on a kinetic basis. We have shown above that the rate constant for methanol addition to **1a**$^{\bullet+}$ is only one-tenth of the diffusion-controlled rate. Even if the addition of $O_2^{\bullet-}$ to **1a**$^{\bullet+}$ is ten times faster, this reaction cannot compete with the methanol addition, as the concentration of this nucleophile is at least six orders of magnitude higher than that of $O_2^{\bullet-}$.

Experimental Section

Materials. Acetonitrile (HPLC grade, J. T. Baker) and methanol (HPLC grade, J. T. Baker) were used without further purification. DCA (Kodak Laboratory Chemicals) was recrystallized twice from pyridine. TCA was prepared from 2,6,9,10-tetrabromoanthracene according to the published procedure.[3] 1,1-Diphenylethylene (**1a**) (Tokyo Kasei Kogyo Co., Ltd.) was used without further purification. 1,1-Dianisylethylene (**1b**) was prepared by addition of methylmagnesium bromide (2.7 M in ether, Alfa) to 4,4′-dimethoxybenzophenone (Aldrich) (73% yield). 1,1-Bis(4-(dimethylamino)phenyl)ethylene was prepared by addition of methylmagnesium iodide to 4,4′-bis(dimethylamino)benzophenone.[19]

Photolysis Methods. Irradiations on a preparative scale were done under continuous bubbling of nitrogen or oxygen in an immersion apparatus equipped with a GWV[20] glass filter to eliminate the 366-nm line and shorter wavelengths. All of the major products, and most of the minor ones, have been accounted for by NMR and gas chromatographic analyses of the total reaction mixtures. No attempt was made to optimize the workup for product isolation. However, some of the products, particularly those which precipitate out during irradiation, are very easy to synthesize. Examples of such products are the diene **9** and the dioxanes **12a–c**. The samples for kinetic studies in the absence of oxygen were degassed by 3 freeze–pump–thaw cycles and irradiated, with stirring, on a "merry-go-round" mounted on an optical bench. The output of a PEK 200-W superhigh-pressure mercury lamp was filtered through water-cooled Corning CS 5-58 and 3-75 filters to isolate the 405- and 436-nm lines. Analytical-scale photooxygenations were carried out in 1-cm, long-necked UV cells under continuous bubbling of oxygen. All samples, preparative and analytical, contained excess solid sensitizer. The photoreaction of 9,10-phenanthrenequinone (10^{-3} M) with *trans*-stilbene (0.1 M) in benzene was used as an actinometer for irradiations at 405 and 436 nm. The quantum yield[21] for the disappearance of the quinone, which is monitored by absorption spectroscopy (λ_{max} 410 nm, ϵ 1800), is 0.065.

Analytical Methods. Gas chromatographic analyses were done on a Hewlett-Packard 7620A chromatograph equipped with an HP3380A integrator, using a 1.5% Dexsil 300 on Chromosorb W 80/100 ($^1/_8$ in. × 6 ft) glass column (column A), or on a Hewlett-Packard 5840A chromatograph, using a J&W fused-silica capillary column (SE30, 15 m × 0.25 mm i.d., 0.25 μm film thickness) (column B), splitless mode. NMR spectra were obtained on a Varian EM390 NMR spectrometer. Ultraviolet–visible spectra were obtained on a Cary 15 spectrophotometer or a Perkin-Elmer 320 spectrophotometer. Fluorescence spectra were obtained on a Spex Fluorolog. GC/MS[22] was performed on a LKB9000 combined gas chromatograph/mass spectrometer.

Dimerization of 1,1-Diphenylethylene (1a). A mixture of 4 mmol (720 mg) of 1,1-diphenylethylene and 2 mmol (456 mg) of DCA in 60 mL of acetonitrile was irradiated (HPK, GWV filter) under nitrogen for 3 h. The solution was filtered from unreacted DCA, and the solvent was distilled. The residue was digested in hexane and filtered, leaving an insoluble solid that was a mixture of DCA and *trans*- and *cis*-dihydrodicyanoanthracene (**5**). Recrystallization from cyclohexane gave one isomer of **5**. Isomer a: mp 205 °C dec; IR (KBr) 2925, 2255, 2240, 1480, 1460, 815, 767, 716, 642, 463 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 5.23 (s, 2 H), 7.42 and 7.63 (AA′BB′, 8 H, arom); ^{13}C NMR ($CDCl_3$) δ 130.5, 129.3, 127.6, 116.9, 36.5; mass spectrum, *m/e* (rel intensity) 230 (M$^+$, 100), 215 (14), 203 (40). Isomer b: ^{1}H NMR ($CDCl_3$) δ 4.93 (s, 2 H), 7.44 and 7.76 (AA′BB′, 8 H, arom); ^{13}C NMR ($CDCl_3$) δ 129.8, 129.0, 126.3, 116.9, 37.1.

Anal. Calcd for $C_{16}H_{10}N_2$: C, 83.5; H, 4.4; N, 12.2. Found: C, 83.7; H, 4.5; N, 12.1.

When analyzed by GC (column B, 180–230 °C at 5 °C/min, injection port 250 °C), isomers a and b decomposed to a mixture of 9-cyanoanthracene (4.0 min), a and b (4.2 and 4.7 min), and DCA (5.5 min).

The hexane filtrate from the above reaction was chromatographed on silica gel. Unreacted **1a** was eluted first, followed by a mixture of **2** and **3** (identified by comparison of their spectra to published values[4,7]) and finally **4**. 1,1,2,2-Tetraphenylcyclobutane **4** (waxy, white solid): mp 108–110 °C dec; IR (KBr) 3082, 3056, 3045, 3025, 2982, 2949, 1495, 1443, 1386, 764, 758, 753, 699, 578, 546 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 3.20 (s, 4 H, CH_2CH_2), 6.74–7.14 (br s, 20 H, arom); ^{13}C NMR ($CDCl_3$) δ 147.2, 129.0, 127.2, 125.3, 61.5, 34.8.

Dimerization of 1,1-Dianisylethylene (1b). A mixture of 960 mg (4 mmol) of **1b** and 228 mg (1 mmol) of DCA in 120 mL of acetonitrile was irradiated (HPK, GWV filter) under nitrogen for 16 h. The solution was filtered from an insoluble solid that was a mixture of DCA and 1,1,4,4-tetraanisylbutadiene **9**. The diene was recrystallized from CH_3CN with charcoal treatment: mp 202–203 °C (lit.[23] mp 206–207 °C); IR (KBr) 3030, 2950, 2930, 2900, 2840, 1605, 1510, 1462, 1282, 1250, 1175, 1031, 835, 583 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 3.73 (s, 6 H, OCH_3), 3.82 (s, 6 H, OCH_3), 6.90 (AA′BB′, J_{AB} = 9 Hz, 4 H, arom), 7.02 (AA′BB′, J_{AB} = 9 Hz, 4 H, arom); ^{13}C NMR ($CDCl_3$) 159.1, 159.0, 142.2, 135.8, 132.7, 131.9, 128.9, 124.7, 113.6, 55.3; mass spectrum, *m/e* (rel intensity) 478 (M$^+$, 100), 239 (14), 227 (17), 211 (7), 185 (10).

Anal. Calcd for $C_{32}H_{30}O_4$: C, 80.3; H, 6.3. Found: C, 79.3; H, 6.3.

A mixture of 480 mg (2 mmol) of **1b** and 139 mg (0.5 mmol) of TCA in 120 mL of acetonitrile was irradiated (HPK, GWV filter) under nitrogen for 48 h. The solution was filtered from excess TCA and evaporated to dryness. The residue was triturated with $CDCl_3$. The $CDCl_3$ solution, which contained a mixture of **7** and **8**, was analyzed by GC (column A)[10] and NMR. **7**: ^{1}H NMR ($CDCl_3$) δ 1.50–2.10 (m, 2 H), 2.40–2.65 (m, 2 H), 3.54–3.85 (s, 12 H, OCH_3), 3.97–4.18 (m, 1 H), 6.21 (d, 1 H, arom), 6.50–7.27 (m, 14 H, arom). **8**: ^{1}H NMR ($CDCl_3$) δ 3.13 (d, 2 H), 3.54–3.85 (s, 12 H, OCH_3), 5.72 (t, 1 H), 6.34 (d, 1 H, arom), 6.50–7.27 (m, 14 H, arom).

Irradiation of 1a in Methanol. A mixture of 720 mg (4 mmol) of **1a** and 100 mg of DCA in 120 mL of methanol was irradiated (HPK, GWV filter) under nitrogen for 7 h. The solution was filtered from excess DCA, and the solvent was distilled, leaving almost pure 2,2-diphenylethyl methyl ether (**10**), which was identified by comparison of its spectra with published values.[24]

In a similar reaction, a mixture of 1 g (5.6 mmol) of **1a** and excess TCA in 60 mL of methanol was irradiated (HPK, GWV filter) under nitrogen for 40 h. The solution was filtered from a light brown solid that was a mixture of TCA and the diether **11**: IR (KBr) 3055, 2980, 2920, 2890, 2812, 1602, 1495, 1448, 1442, 1106, 1082 [illegible] 733, 696, 638, 620 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 3.18 (s, 6 H, OCH_3), [illegible] s, 4 H, CH_2), 7.07 (br s, 20 H, arom); ^{13}C NMR ($CDCl_3$) δ 142.7, 1[illegible]26.9, 126.3, 78.0, 60.6, 58.4.

Photooxygenation of 1a in Acetonitrile. A m.xt [illegible] 0.90 g (5 mmol) of **1a** and excess sensitizer (DCA or TCA) in 50 [illegible] acetonitrile was irradiated (HPK, GWV filter) under oxygen for [illegible] The solution was filtered from an insoluble solid that was a mixtur[illegible] excess sensitizer and 3,3,6,6-tetraphenyl-1,2-dioxane (**12a**). The acetonitrile filtrate contained unreacted **1a** and benzophenone. The dioxane was recrystallized from acetonitrile with charcoal treatment. **12a**: mp 242–244 °C (lit.[14] mp 256–257.5 °C from THF); IR (KBr) 3082, 3058, 3030, 3022, 2978, 2948, 1492, 1447, 1385, 1005, 767, 748 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 2.57 (br s, 4 H, CH_2CH_2), 7.00–7.48 (m, 20 H, arom); ^{13}C NMR ($CDCl_3$) δ 144.3, 128.2, 127.3, 126.9, 86.0, 30.8.

Anal. Calcd for $C_{28}H_{24}O_2$: C, 85.7; H, 6.1. Found: C, 85.7; H, 6.1.

Photooxygenation of 1b. A mixture of 240 mg (1 mmol) of **1b** and 50 mg of TCA in 50 mL of acetonitrile was irradiated (HPK, GWV filter) under oxygen for 2 h. The solvent was distilled, leaving 3,3,6,6-tetraanisyl-1,2-dioxane (**12b**) contaminated with TCA. **12b** was recrystallized from acetonitrile with charcoal treatment: mp 206.5–209 °C (lit.[15] mp 217–220 °C from THF); IR (KBr) 3018, 2995, 2970, 2950, 2930, 2908, 2832, 1609, 1510, 1463, 1440, 1305, 1254, 1175, 1029, 993, 816, 608 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 2.47 (br s, 4 H, CH_2CH_2), 3.75 (s, 12 H, OCH_3), 6.60–6.89 and 6.90–7.35 (m, 16 H, arom); ^{13}C NMR ($CDCl_3$) δ 158.8, 135.8, 128.4, 113.5, 85.6, 55.2, 31.0; mass spectrum, *m/e* (rel intensity) 512 (M$^+$, 100), 480 (12.5), 388 (15), 242 (14).

Anal. Calcd for $C_{32}H_{32}O_6$: C, 75.0; H, 6.3. Found: C, 75.0; H, 6.3.

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Photooxygenation of 1c. A mixture of 200 mg of **1c** and 60 mg of TCA in 50 mL of acetonitrile was irradiated (HPK, GWV filter) under oxygen for 40 min. The solution was filtered from an insoluble solid that was a mixture of TCA and the 1,2-dioxane **12c**. **12c** was recrystallized from benzene/acetonitrile with charcoal treatment: mp 189–191 °C dec; IR (KBr) 2940, 2880, 2794, 1615, 1522, 1445, 1353, 1200, 945, 809, 557 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 2.47 (br s, 4 H, CH$_2$CH$_2$), 2.90 (s, 24 H, N(CH$_3$)$_2$), 6.43–6.72 and 6.90–7.30 (m, 16 H, arom); ^{13}C NMR (CDCl$_3$) δ 149.6, 132.0, 128.2, 112.1, 85.6, 40.6, 30.8.

Anal. Calcd for $C_{36}H_{44}N_4O_2$: C, 76.6; H, 7.8; N, 9.9. Found: C, 76.5; H, 7.7; N, 9.8.

By the procedure of Ledwith and co-workers,[18] ~10 mg of Cu(NO$_3$)$_2$·5H$_2$O (Kodak) was added to a stirred solution of 266 mg (1 mmol) of **1c** in 100 mL of methanol in a flask open to the air. The solution immediately turned dark blue, and a white precipitate formed. After 1 h, the solid was collected by filtration; it was identical in all respects with the 1,2-dioxane **12c** prepared by photooxygenation.

Photooxygenation of 1a in the Presence of Methanol. A mixture of 180 mg (1 mmol) of **1a**, excess TCA, 10^{-3} M sodium methoxide, and 1 M methanol in 50 mL of acetonitrile was irradiated (HPK, GWV filter) under oxygen for 1 h. The solution was filtered from excess TCA, and the solvent was distilled. By NMR analysis, the residue contained unreacted **1a** and a 6:3:1 mixture of 1-hydroperoxy-2-methoxy-1,1-diphenylethane[16] (**13**), benzophenone, and 1-hydroxy-2-methoxy-1,1-diphenylethane (**14**). **13**: ^{1}H NMR (CDCl$_3$) δ 3.35 (s, 3 H, OCH$_3$), 4.23 (s, 2 H, CH$_2$), 7.23 (br s, 10 H, arom).

The product mixture was reduced with excess lithium aluminum hydride in ether, which converted benzophenone to benzhydrol and **13** to **14**. This mixture was then treated with trifluoroacetic anhydride, to give the trifluoroacetate of **14**: ^{1}H NMR (CDCl$_3$/(CF$_3$CO)$_2$O) δ 3.37 (s, 3 H, OCH$_3$), 4.05 (s, 2 H, CH$_2$), 7.00–7.50 (m, 10 H, arom).

Registry No. 1a, 530-48-3; **1a**$^{\bullet+}$, 36195-39-8; **1b**, 4356-69-8; **1b**$^{\bullet+}$, 63464-03-9; **1c**, 7478-69-5; **1c**$^{\bullet+}$, 104267-21-2; **2**, 41977-31-5; **3**, 72805-46-0; **4**, 84537-61-1; (*trans*)-**5**, 104267-15-4; (*cis*)-**5**, 104267-16-5; **7**, 104267-17-6; **8**, 104267-18-7; **9**, 54655-89-9; **10**, 41976-80-1; **11**, 104291-11-4; **12a**, 68313-22-4; **12b**, 68313-25-7; **12c**, 93584-77-1; **13**, 104267-19-8; **14**, 14704-09-7; **14** (trifluoroacetate), 104267-20-1; DCA, 1217-45-4; TCA, 80721-78-4; biphenyl, 92-52-4; methanol, 67-56-1; benzophenone, 119-61-9; benzhydrol, 91-01-0.

Cobalt Carbonyl Catalyzed Reactions of Esters and Lactones with Hydrosilane and Carbon Monoxide. A Novel Synthetic Method for the Introduction of the Siloxymethylidene Group[1]

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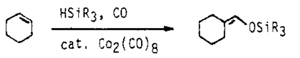
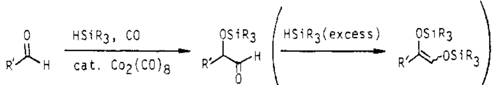
Abstract: The catalytic reactions of esters and lactones with hydrosilane and carbon monoxide in the presence of Co$_2$(CO)$_8$ have been studied in detail with the emphasis being focused on their utility in organic synthesis. The catalytic reaction of secondary alkyl acetates underwent clean incorporation of carbon monoxide to give (siloxymethylidene)alkanes (enol silyl ethers). Lactones of secondary alkyl ester type reacted similarly. The siloxymethylidenation products were converted to aldehydes. Primary alkyl acetates gave several products in a nonselective manner. In the case of tertiary alkyl esters, no incorporation of carbon monoxide took place except for bridgehead alkyl acetates. The mechanism of the catalytic reaction has been proposed, and the importance of the silylcobalt carbonyl, R$_3$SiCo(CO)$_4$, as the key catalyst species has been suggested. The high affinity of the silicon in R$_3$SiCo(CO)$_4$ toward the oxygen atom in the ester is suggested to be the driving force for the formation of alkylcobalt carbonyls as the intermediates. This step illustrates a new methodology for the formation of a carbon–transition metal bond.

Carbonyl complexes of transition metals are widely involved as the catalysts in a variety of catalytic reactions in which carbon monoxide is incorporated into an organic substrate. Some of the most commonly used metal complexes may be those containing cobalt. Numerous studies have been done on the cobalt-catalyzed reactions not only because of their role in the commercially important hydroformylation process but also because of their ability to catalyze various types of carbonylation reactions.[2] Mechanistically, migratory insertion of carbon monoxide into a carbon–cobalt bond is the essential step in these reactions.[2] The required carbon–cobalt bond is generally formed by the interaction of a given substrate with HCo(CO)$_n$, the "quintessential catalyst"[3] in the H$_2$/CO/Co$_2$(CO)$_8$ system.

On the other hand, two types of catalyst species seem to be important in the new HSiR$_3$/CO/Co$_2$(CO)$_8$ system. The reactions of olefins[4] (eq 1) or oxygen-containing compounds such as aldehydes[5] (eq 2) and cyclic ethers[6] (eq 3) with hydrosilane (HSiR$_3$)



(1)



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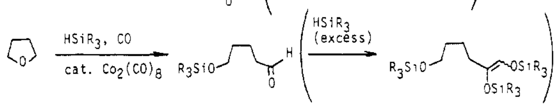

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