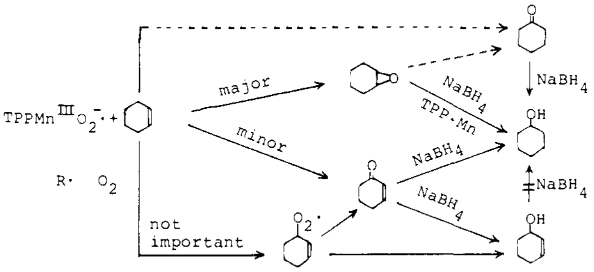
Scheme I. Pathway of the TPP·Mn–O_2–$NaBH_4$ (P-450 Type) Oxidation



that shown in Scheme I. Under conditions where cyclohexene was converted into oxygenated products in 2.5% yield,[7] yields of cyclohexanol and cyclohexenol based on O_2 used were 53 and 13%, respectively, and that based on TPP·Mn was 1530% (each TPP·Mn molecule produced 15.3 molecules of oxygenated products). Most of the $NaBH_4$ used in an excess amount was recovered unchanged after the oxygenation was over.

Pure TPP·Mn^{III}Cl treated with $NaBH_4$ in carefully purified benzene showed the characteristic electronic spectrum of TPP·Mn^{II} as shown in Figure 2. Application of dioxygen to the solution finally resulted in practically complete conversion into the corresponding Mn(III) (see Figure 2). However, neither of the individual final products, TPP·Mn^{III} nor O_2^{-}·, gave the observed oxidation products. While a mixture of both components TPP·Mn^{III} and KO_2 in the presence of 18-crown-6 gave the oxygenation products, the yields were low. Thus, the active species should be some intermediate between the two extreme states of eq 3.

$$\begin{tikzcd} \text{TPP}\cdot\text{Mn(II)} + O_2 \arrow[r] & \text{[intermediate]} \arrow[r] \arrow[d, "\text{substrate}"] & \text{TPP}\cdot\text{Mn(III)} + O_2^{-} \\ & \text{oxygenation products} & \end{tikzcd} \quad (3)$$

Careful spectroscopic investigations indicated that at least two intermediates (Mn^{IV}·O_2^{2-} (side-on complex[8]) and Mn^{III}–O_2^{-} complex) were involved in the reaction. Thus, the fact that the reducing reagent, $NaBH_4$, and one of these intermediates, possibly TPP·Mn^{III}–OO^{-}, seem to provide the real active species the fact again closely resembles the established cyt-P-450 mechanism.

Detailed studies are now underway.

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(3) (a) Sato, R.; Omura, T. In "Cytochrome P-450"; Kodansha Ltd: Tokyo, 1978. (b) Boyd, G. S.; Ullrich, V. *Biochem. Soc. Trans.* **1975,** 803. (c) Nordblom, G. D.; White, R. E.; Coon, M. J. *Arch. Biochem. Biophys.* **1976,** *175,* 524.
(4) Calculation on iron(II) porphyrin·O_2 Im (as HRP compound I model) and iron(II) porphyrin·O_2 S^{-}–Me (as P-450 model). Loew, G. H.; Kert, C. J.; Hjelmeland, L. M.; Kirchner, R. F. *J. Am. Chem. Soc.* **1977,** *99,* 3534.
(5) (a) TPP = tetraphenylporphyrin. (b) It is simply a concentration problem since initial concentration of cyclohexene was much larger than that of the product, cyclohexenol.
(6) Since the major path of cyclohexenol formation seems to be direct oxidation, this value is a considerable overestimation.
(7) Conversion was kept low in order to suppress any undesirable further oxidation.
(8) Hoffman, B. M.; Weschler, C. J.; Basolo, F. *J. Am. Chem. Soc.* **1976,** *98,* 5473.

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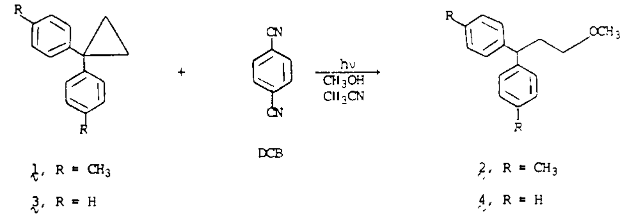
Arylcyclopropane Photochemistry. Electron-Transfer-Mediated Photochemical Addition of Methanol to Arylcyclopropanes

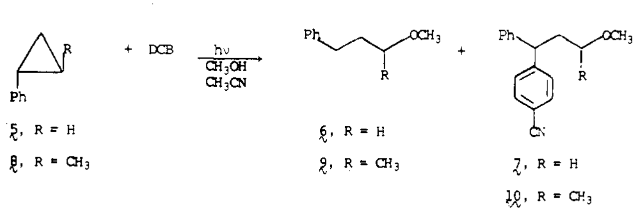
Sir:

The photosensitized cis–trans isomerization of 1,2-diphenylcyclopropane with naphthalene derivatives as sensitizers has been suggested to proceed via formation of a singlet exciplex.[1] It has been shown that charge transfer from the cyclopropane to the excited singlet naphthalene sensitizer is important in formation and/or reaction of this exciplex.[2] We presently report the 1,4-dicyanobenzene (DCB)-sensitized photolysis of several phenylcyclopropane derivatives in methanol–acetonitrile. In most cases a novel "anti-Markownikoff" addition of methanol to the cyclopropane ring results. The reactions observed are best rationalized as proceeding via initial electron transfer from the cyclopropanes to the excited DCB to give the phenylcyclopropane radical cations.[3]

Several phenylcyclopropanes have been studied to date. In a typical reaction a solution of 1.4 mmol of 1,1-bis(*p*-tolyl)-cyclopropane (**1**), 0.7 mmol of DCB, and 1.0 mL of methanol in 12.0 mL of acetonitrile in a Vycor reaction vessel was purged with nitrogen and then irradiated at 45 °C with the 300-nm lamps of a Rayonet photochemical reactor. Progress of the reaction was monitored by gas chromatography. After 10 h (70% reaction of **1**), the solvent was removed and the photolysate was separated by preparative TLC (silica gel plates with benzene eluant) to give 3-methoxy-1,1-bis(*p*-tolyl)propane[4] (**2**, 71%) together with recovered cyclopropane **1** (7%) and DCB (88%). No other products were detected by GC, TLC, or NMR analysis of the reaction mixture. 1,1-Diphenylcyclopropane (**3**) reacted similarly to give ether **4** (30% yield at 92% conversion of **3**).



Phenylcyclopropane (**5**) and 1-methyl-2-phenylcyclopropane (**8**) afforded similar methanol adducts; however, in both cases a new product was isolated. Thus, DCB-sensitized photolysis of **5** gave 41% ether **6** and, in addition, 17% diaryl product **7** (84% conversion of **5**). Likewise, *trans*-**8** (containing ~3% of the cis isomer) yielded, at 85% conversion of **8**, 32% ether **9** and 16% **10**. Interestingly, little, if any, isomerization of *trans*-**8** to its cis isomer occurred during the photolysis.

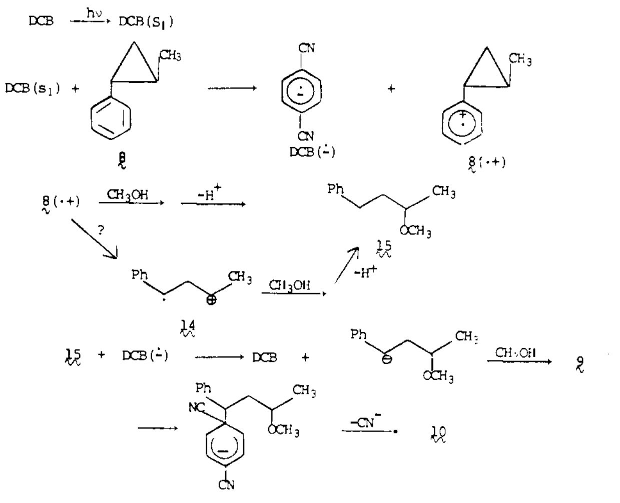


The DCB-sensitized photolysis of *trans*-1-methyl-2-phenylcyclopropane (**8**) in acetonitrile in the absence of methanol afforded no detectable new products. Slow loss of the reactants was noted, as well as a very small amount (~1%) of trans to cis isomerization.[5] (Photolysis of **8** in the absence of DCB under otherwise similar reaction conditions resulted in more efficient (but still slow) trans–cis isomerization.)[6]

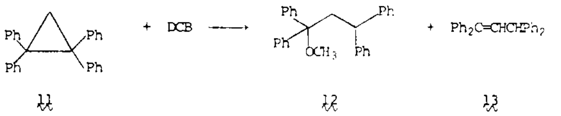
The sensitized photolysis of 1,1,2,2-tetraphenylcyclopropane (**11**) took a different course. Only traces of a methanol adduct (presumably **12**) could be detected by NMR and GC.

0002-7863/79/1501-6458$01.00/0

Scheme I



Instead, the major product was 1,1,3,3-tetraphenylpropene (**13**, yield not determined).[7]



Scheme I outlines a reasonable mechanism for reaction of the cyclopropanes, using *trans*-1-methyl-2-phenylcyclopropane (**8**) as an example. Excitation of DCB (under the reaction conditions DCB absorbs nearly all of the incident light) is followed by electron transfer from **8** to give a DCB radical anion-phenylcyclopropane radical cation pair. Attack by methanol on the cyclopropane radical cation $\mathbf{8}^{+\cdot}$ followed by proton loss affords benzylic radical **15**. Reduction of **15** by DCB$^{-\cdot}$ leads to **9** while coupling of **15** with DCB$^{-\cdot}$ gives **10**.[8,9]

It is conceivable that methanol does not attack $\mathbf{8}^{+\cdot}$ directly, but instead $\mathbf{8}^{+\cdot}$ is first converted into a ring-opened species such as **14**. The fact that attack occurs at the more substituted carbon of **8** indicates that C-1 does acquire significant positive charge during reaction. However, our finding that only a very small amount of trans-cis isomerization occurs when *trans*-**8** is reacted in the absence of methanol is not readily accommodated by this scheme; for reduction of **14** by DCB$^{-\cdot}$ to a 1,3 diradical which would close to a mixture of cis and trans cyclopropanes is expected to be a facile process. Most likely the radical cation of **8** undergoing attack by methanol has a significantly weakened yet not broken C-1–C-2 bond; the radical cations of cyclopropanes **1**, **3**, and **8** probably have similarly bonded structures. We are investigating the electron-transfer-mediated addition of other nucleophiles to arylcyclopropanes as well as the reactions of other arylcyclopropane radical cations.

Acknowledgment. We thank the National Science Foundation for support of this research.

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(4) Reaction product structures were derived from analysis of their NMR and mass spectra.

(5) In the presence of methanol and DCB after 10 h of irradiation, 85% of **8** was consumed to form 32% **9** and 21% **10**. In the absence of methanol, but under otherwise similar conditions, only 18% of **8** disappeared after 11 h of irradiation. During this time the percentage of cis isomer increased from ~2.9 to 3.9%.

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(7) Ether **12** is essentially stable under the conditions of this experiment.

(8) Cyanide ion formation in the reactions of **5** and **7** is assumed.

(9) Both steric and electronic factors may account for the lack of formation of products analogous to **7** and **10** from the diarylcyclopropanes **1** and **3**.

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Hydridic Reactivity of $HMn(CO)_5$
Stabilization of a Nearly Coordinatively Unsaturated Metal Carbonyl Cation in HO_3SCF_3

Sir:

Although it is well known that $HMn(CO)_5$ ($pK_a = 7$) behaves as a weak acid,[1] the hydridic character of the hydrogen attached to the metal is still to be established. If it proved possible to abstract hydride from this compound with a "noncoordinating" acid, then one might prepare solutions of metal carbonyl complexes whose properties approach those expected for a coordinatively unsaturated species.[2]

A recent synthesis[3] of $HMn(CO)_5$ employed the reaction

$$[Mn(CO)_5]^- + HO_3SCF_3 \xrightarrow{THF} [O_3SCF_3]^- + HMn(CO)_5 \tag{1}$$

Neat HO_3SCF_3 is a considerably stronger acid medium than is its THF solution and we find that the subsequent reaction[4]

$$HMn(CO)_5 + HO_3SCF_3 \xrightarrow{HO_3SCF_3} H_2 + [Mn(CO)_5](O_3SCF_3) \tag{2}$$

can occur when $(PPN)[Mn(CO)_5]$[5] is allowed to react with pure HO_3SCF_3. The stoichiometry of reaction 2 has been confirmed by Toepler pumping of the evolved gas (1.03 ± 0.05 mol of gas/mol of $HMn(CO)_5$) and its identity as H_2 has been verified by combustion over copper oxide, as well as by mass spectroscopy. Quantitative Fourier transform IR spectroscopy of the gas fails to reveal the presence of CO and sets a limit on CO loss at <5%, if any. The IR spectrum of the deep yellow solution exhibits weak absorptions at 2164 and 2117 cm^{-1}, as well as a strong band at 2083 cm^{-1}, and one of medium intensity at 2042 cm^{-1}. An identical spectrum is obtained when $[Mn(CO)_5py]BF_4$[6] is dissolved in HO_3SCF_3. In this case the reaction

$$[Mn(CO)_5py]^+ + HO_3SCF_3 \rightarrow Hpy^+ + [Mn(CO)_5]^+[O_3SCF_3]^- \tag{3}$$

goes to completion in 1.5 h at room temperature. The IR bands are assigned, respectively, to the $A_1^{(2)}$, B_1, E, and $A_1^{(1)}$ carbon-oxygen stretching modes of $[Mn(CO)_5]^+$. A C_{4v} or distorted C_{4v} structure seems likely, by analogy to $[Mn(CO)_5NCCH_3]^+$, which displays $A_1^{(2)}$, E, and $A_1^{(1)}$ frequencies of 2161, 2060, and 2030 cm^{-1}.[6] The weak B_1 stretch was not reported for $[Mn(CO)_5NCCH_3]^+$.[6] Although $[O_3SCF_3]^-$ probably occupies the vacant coordination site of $[Mn(CO)_5]^+$, several experiments show that the association is extremely weak.

Substitution reactions of octahedral Mn(I) carbonyls are generally slow.[7] Trifluoromethanesulfonic acid solutions of $[Mn(CO)_5]^+$, however, react immediately (<10 s) with gas-