Scheme I

$$\mathrm{DCA} \xrightarrow{h\nu} {}^{1}\mathrm{DCA}^{*}$$

$${}^{1}\mathrm{DCA}^{*} + 1 \longrightarrow 1^{+\cdot} + \mathrm{DCA}^{-\cdot}$$

$${}^{1}\mathrm{DCA}^{*} + \mathrm{BP} \longrightarrow \mathrm{BP}^{+\cdot} + \mathrm{DCA}^{-\cdot}$$

$$\mathrm{BP}^{+\cdot} + 1 \longrightarrow 1^{+\cdot} + \mathrm{BP}$$

$$\mathrm{DCA}^{-\cdot} + O_2 \longrightarrow O_2^{-\cdot} + \mathrm{DCA}$$

$$1^{+\cdot} + O_2^{-\cdot} \longrightarrow 2$$

**2** or cleave to form **3** and the carbonyl oxide. Experiments[11] with electrochemically generated $\mathbf{1}^{+\cdot}$ have demonstrated that **3** may also result from C–O bond rupture in $\mathbf{1}^{+\cdot}$.

The catalysis of the photooxygenation of **1** by BP presents a more interesting mechanistic question. We have previously reported that the rate of DCA-sensitized photooxygenation of 2,3-bis(*p*-methoxyphenyl)-1,4-dioxene (**4**, $E^{ox}_{1/2} = 0.73$ V vs. SCE, in MeCN) was increased in the presence of 2,3-bis(*p*-methylphenyl)-1,4-dioxene (**5**, $E^{ox}_{1/2} = 0.84$ V vs. SCE, in MeCN).[2k] It was proposed that the enhanced reactivity for **4** results from an exothermic electron exchange with $\mathbf{5}^{+\cdot}$. Similar results have recently been described by Foote for the indirect photooxygenation of tetraphenylethylene in the presence of *trans*-stilbene.[13] Distinct from these two cases is the present example of cosensitization by BP and DCA. BP is more easily oxidized than epoxide **1** ($E^{ox}_{p}$ of BP = 1.85 V vs. SCE, in MeCN[14] and consequently quenches ${}^{1}\mathrm{DCA}^{*}$ more efficiently ($k_q = 3.1 \times 10^9\ \mathrm{M}^{-1}\ \mathrm{s}^{-1}$) to generate $\mathrm{BP}^{+\cdot}$. However, subsequent electron transfer from **1** to $\mathrm{BP}^{+\cdot}$ is highly *endothermic*. Nevertheless, this secondary electron transfer is the key step in the BP-catalyzed photooxygenation of **1** (Scheme I).[15] An important factor in the enhanced rate of formation of intermediate $\mathbf{1}^{+\cdot}$ is certainly the much longer lifetime for $\mathrm{BP}^{+\cdot}$ compared to ${}^{1}\mathrm{DCA}^{*}$. Additional insight into the mechanism of this reaction is obtained by considering the analogous process in the homogeneous redox catalysis of electrochemical reactions.[18] For example, direct electroreductions of aliphatic halides (RX) generally occur at very slow rates and require large overvoltages. However, electrochemically generated radical anions of aromatic hydrocarbons can be employed as catalytic agents. Electron transfer from this species to RX forms the unstable $\mathrm{RX}^{-\cdot}$ and regenerates the hydrocarbon. Although this reversible step is energetically unfavorable, it is driven by the subsequent irreversible cleavage of $\mathrm{RX}^{-\cdot}$. Similarly, we suggest that the opening of epoxide **1** to give $\mathbf{1}^{+\cdot}$ and trapping by $O_2^{-\cdot}$ to form ozonide **2** provides the driving force for the catalysis by BP of the DCA-sensitized photooxygenation of **1**.

We have found that biphenyl can be used as a cosensitizer for the photooxygenation of various epoxides that are inefficiently oxidized by DCA alone. Other types of substrates can also be photooxidized under these conditions.[19] These results will be reported shortly.

**Acknowledgment.** Support from the U.S. Army Research Office is gratefully acknowledged. We thank Professor Dennis Evans, University of Wisconsin, for helpful discussions.

**Registry No.** Tetraphenyloxirane, 470-35-9; 9,10-dicyanoanthracene, 1217-45-4; biphenyl, 92-52-4.

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(13) Steichen, D. S.; Foote, C. S. *J. Am. Chem. Soc.* **1981**, *103*, 1855.

(14) Osa, T.; Yildiz, A.; Kuwana, T. *J. Am. Chem. Soc.* **1969**, *91*, 3994.

(15) Farid has suggested a similar mechanism for the cosensitization by phenanthrene and 9-cyanoanthracene of the electron-transfer dimerization of phenyl vinyl ether.[16] Alternatively, Pac has proposed the intermediacy of a $\pi$ complex in the electron-transfer photochemical addition of methanol to 1,1-diphenylethylene cosensitized by *p*-dicyanobenzene and aromatic hydrocarbons.[17]

(16) (a) Farid, S.; Hartman, S. E.; Evan, T. R. In "The Exciplex"; Gordon, M., Ware, W. R., Eds.; Academic Press: New York, 1975; p 327. (b) Mattes, S. L.; Farid, S. *Acc. Chem. Res.* **1982**, *15*, 80.

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

(18) For leading references, see: (a) Andrieux, C. P.; Blocman, C.; Dumas-Bouchiat, J. M.; M'Halla, F.; Savéant, J. M. *J. Electroanal. Chem.* **1980**, *113*, 19. (b) Savéant, J. M. *Acc. Chem. Res.* **1980**, *13*, 323. (c) Evans, D. H.; Naixian, X. *J. Electroanal. Chem.* **1982**, *133*, 367. (d) Sease, J. W.; Reed, R. C. *Tetrahedron Lett.* **1975**, 393. (e) Lund, H.; Simonet, J. *J. Electroanal. Chem.* **1975**, *65*, 205. (f) Boujlel, K.; Simonet, J. *Electrochim. Acta* **1979**, *24*, 481. (g) Britton, W. E.; Fry, A. J. *Anal. Chem.* **1975**, *47*, 95.

(19) Schaap, A. P.; Lopez, L.; Anderson, S. D.; Gagnon, S. D. *Tetrahedron Lett.* **1982**, *23*, 5493.

(20) **Note Added in Proof**: Subsequent to the submission of this paper, Ohta and co-workers reported the DCA-sensitized photooxygenation of electron-rich epoxides: Futamura, S.; Kusunose, S.; Ohta, H.; Kamiya, Y. *J. Chem. Soc., Chem. Commun.* **1982**, 1223. Tetraphenyloxirane was found to be unreactive under their conditions.

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## Symmetry of a Reactive Intermediate from Ring Expansion of Cyclobutylidenecarbene. Cyclopentyne

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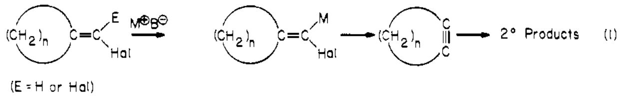
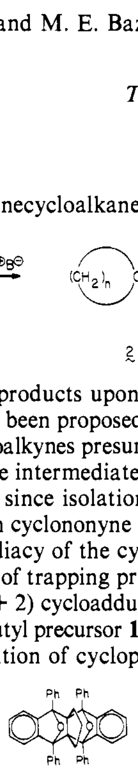
Halomethylenecycloalkanes **1** ($n$ = 2–4, 6, 7, 9, 11) yield

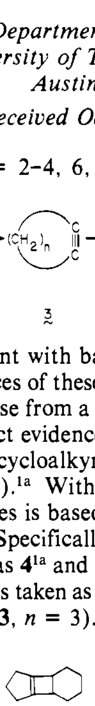


**1** **2** **3** (1)

ring-expanded products upon treatment with bases, and cycloalkynes, **3**, have been proposed as sources of these substances (eq 1).[1,2] The cycloalkynes presumably arise from a carbenic species derived from the intermediate **2**. Direct evidence for conversion of **1** to **3** exists since isolation of the cycloalkyne is sometimes possible, as with cyclononyne (**3**, $n$ = 7).[1a] With systems having $n \leq 4$, intermediacy of the cycloalkynes is based exclusively on the observation of trapping products. Specifically, generation of (2 + 4) and (2 + 2) cycloadducts such as **4**[1a] and **5**,[1c] respectively, from the cyclobutyl precursor **1** ($n$ = 3) is taken as being diagnostic for the intervention of cyclopentyne (**3**, $n$ = 3).



**4**



**5**

Mechanisms exist that do not require the originally chemically differentiated vinylic carbon atoms of **1** to become equivalent *prior* to reaction with the trapping agent, as is demanded if the cycloalkyne is an intermediate. In fact, data for the cyclobutyl system **1** ($n$ = 3, E = H, Hal = Br) indicate that the pathway for formation of 1-bromocyclopentene, the major isolated product arising from ring expansion, is *not* derived from cyclopentyne.[1a,4] Consequently, it is of paramount importance to establish that ring expansion of carbenic intermediates of the alkylidenecycloalkane variety involves species having the symmetry expected for a cy-

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(1) Erickson, K. L.; Wolinsky, J. *J. Am. Chem. Soc.* **1965**, *87*, 1142. (b) Erickson, K. L.; Vanderwaart, B. E.; Wolinsky, J. *Chem. Commun.* **1968**, 1031. (c) Fitjer, L.; Kliebisch, U.; Wehle, D.; Modoressi, S. *Tetrahedron Lett.* **1982**, *23*, 1661.

(2) Analogy for ring expansion of cyclobutylidenecarbenes is found in formation of cyclopentene as the major product of isomerization of cyclobutylcarbene(oid).[3]

(3) Paskovich, D. H.; Kwok, P. W. N. *Tetrahedron Lett.* **1967**, 2227.

(4) Erickson, K. L. *J. Org. Chem.* **1971**, *36*, 1031.

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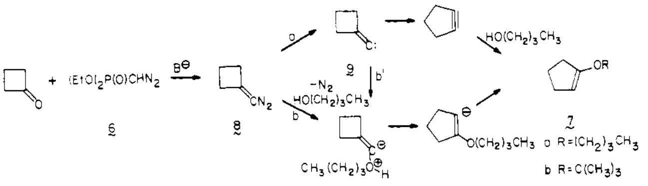


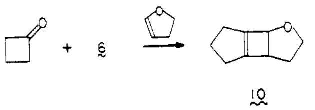
**Figure 1.** Possible mechanisms for formation of **7a**.

cloalkyne. The present communication addresses this question in the case of expansion of the four-membered to the five-membered ring.

Base-promoted reaction at 0 °C between cyclobutanone and diethyl (diazomethyl)phosphonate (**6**)[5] in 1-butanol afforded 1-(butyloxy)cyclopentene (**7a**) in 43% isolated yield (Figure 1).[6] The formation of **7a** finds close analogy in the production of enol ether **7b**, in 2–4% yield, from α-elimination of bromomethylenecyclobutane (**1**, $n = 2$, E = H, Hal = Br), with potassium *tert*-butoxide.[1a,4] For the present case, work by ourselves[7] and others[8] suggests scenarios like those outlined in Figure 1. The diazoethene **8**, a chemical relative of **2** ($n = 3$), is generated by reaction between cyclobutanone and **6** and is subsequently converted to **7a** by pathways that involve either (a) chemical equivalency of the vinylic carbon atoms in the form of cyclopentyne or (b) nonequivalency of these atoms at the time of interaction with 1-butanol.[9]

Repetition of the reaction between cyclobutanone and **6**, the latter now containing approximately 5% excess $^{13}C$ at the diazomethyl carbon atom,[10] produced **7a**, in which the label was equally distributed between atoms C-1 and C-2.[12] This is precisely as expected from a mechanism in which the vinylic carbon atoms of **7a** have become chemically equivalent before trapping by alcohol. The result can be accommodated by path b or b′ (Figure 1) with the proviso that nucleophilic attack occur with *equal* facility at both vinylic carbon atoms of **8** or **9**, but this impresses us as chemically untenable. The data are most economically rationalized by intervention of cyclopentyne as the exclusive precursor to **7a**.[14]

The question of whether cyclopentyne is formed under reaction conditions that yield cycloadducts has also been addressed. Execution of the base-promoted reaction between cyclobutanone and **6** in the presence of dihydrofuran gave the tricyclic adduct **10**[1c] in 28% yield (eq 2). Statistical analysis of the integrated $^{13}C$ NMR spectrum of **10** derived from $^{13}C$-enriched **6** showed that the excess label again was equally distributed between the vinylic carbon atoms.[12] This result also clearly implicates cyclopentyne



(2)

as the reactive intermediate responsible for formation of the cycloadduct **10**. Consequently it is concluded that the products resulting from ring expansion of cyclobutylidenecarbene (**9**, Figure 1) in both protic and aprotic media arise from the cycloalkyne.

**Acknowledgments.** This research received support from the Robert A. Welch Foundation and the National Institute of General Medical Sciences. We thank Dr. Upali Weerasooriya for executing preliminary experiments and Dr. Ben Shoulders for assistance in the analysis of the $^{13}C$ spectral data.

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[5] Seyferth, D.; Marmar, R. M.; Hilbert, P. H. *J. Org. Chem.* **1971**, *36*, 1379.

[6] **7a**: $^1H$ NMR ($CCl_4$) δ 0.93 (3 H, t, $J = 6$ Hz), 1.23–2.10 (6 H, m), 2.27 (4 H, m), 3.63 (2 H, t, $J = 6$ Hz), 4.28 (1 H, m); $^{13}C$ NMR (neat) δ 18.34, 20.23, 28.03, 30.44, 30.83, 67.57, 91.44, 159.33; IR ($CCl_4$) 1650 $cm^{-1}$ (C=C); molecular ion, $m/e$ 140.1203 (calcd for $C_9H_{16}O$, 140.1201. Treatment of **7a** with 2,4-dinitrophenylhydrazine reagent afforded a 2,4-DNP derivative identical (mixture mp) with that from cyclopentanone.

[7] Gilbert, J. C.; Weerasooriya, U. *J. Org. Chem.* **1982**, *47*, 1837 and references cited therein.

[8] Lahti, P.; Berson, J. *J. Am. Chem. Soc.* **1981**, *103*, 7011.

[9] Paths b and b′ are only two of several that predict nonequivalency of the key carbon atoms.

[10] Labeled (diazomethyl)phosphonate **6** was prepared[5] by using formaldehyde having ca. 5% isotopic enrichment. Mass spectral analysis of the $CO_2$ derived from combustion of enriched **6** indicated 4.3% excess $^{13}C$ in the sample.[11]

[11] We thank Professor P. L. Parker and Dr. Lee Entzeroth (UT Marine Sciences Institute) for this analysis.

[12] Error in the integrated $^{13}C$ spectrum is estimated at ±6%. The spectral data were obtained with a Bruker WH-90 spectrometer on a 40:60 (v:v) solution of benzene-$d_6$ and **7a** or **10** (microcell). The solutions were 0.1 M in $Cr(acac)_2$ to enhance relaxation.[13]

[13] Shoolery, J. N. *Prog. NMR Spectrosc.* **1977**, *11*, 79.

[14] A referee has suggested that **7a** may arise from attack on **9** following prior equilibration with cyclopentyne. Although consistent with our labeling data, calculations (MINDO/3 and MNDO) render such a mechanism questionable as the ring expansion is predicted to be *exothermic* by 4.7 (MINDO/3) and 1.6 (MNDO) kcal/mol (J. C. Gilbert, unpublished results). In any event, the equilibration still posits the cycloalkyne to achieve chemical equivalency of the vinylic carbon atoms.

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## Metal-Metal-Bonded Zirconium-Ruthenium and Zirconium-Iron Complexes

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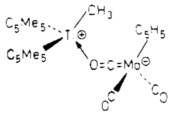
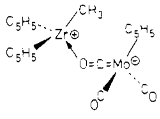
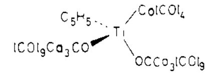
Current interest in heterobimetallic complexes incorporating both early and late transition metals stems from their potential importance in catalysis[1] and organic synthesis.[2] Among group 4 heterobimetallic complexes reported to date are complexes containing two different metal fragments linked by a bridging ligand,[3] complexes in which the group 4 metal bonds to a carbonyl oxygen of a second organometallic fragment[4–6] such as **1**-Ti[4a] and



**1**-Ti



**1**-Zr



**2**

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[1] (a) Demitras, G. C.; Muetterties, E. L. *J. Am. Chem. Soc.* **1977**, *99*, 2796. (b) Muetterties, E. L. *Bull. Soc. Chim. Belg.* **1975**, *84*, 959. (c) Muetterties, E. L. *Ibid.* **1976**, *85*, 451. (d) Masters, C. *Adv. Organomet. Chem.* **1979**, *17*, 61. (e) Wong, K. S.; Labinger, J. A. *J. Am. Chem. Soc.* **1980**, *102*, 3652. (f) Labinger, J. A.; Wong, K. S.; Scheidt, W. R. *Ibid.* **1978**, *100*, 3254.

[2] For applications of pairs of early and late metal mononuclear complexes in organic synthesis see: (a) Schwartz, J.; Loots, M. J.; Kosugi, H. *J. Am. Chem. Soc.* **1980**, *102*, 1333. (b) Negishi, E.; Okukado, N.; King, A. O.; Van Horn, D. E.; Spiegel, B. I. *Ibid.* **1978**, *100*, 2254. (c) Negishi, E.; Van Horn, D. J. *Ibid.* **1977**, *99*, 3168.

[3] (a) Schore, N. E.; Hope, H. *J. Am. Chem. Soc.* **1980**, *102*, 4251. (b) Schore, N. E. *Ibid.* **1979**, *101*, 7410. (c) Threlkel, R. S.; Bercaw, J. E. *Ibid.* **1981**, *103*, 2650. (d) Wolczanski, P. T.; Threlkel, R. S.; Bercaw, J. E. *Ibid.* **1979**, *101*, 218. (e) Marsella, J. A.; Folting, K.; Huffman, J. C.; Caulton, K. G. *Ibid.* **1981**, *103*, 5596. (f) Marsella, J. A.; Caulton, K. G. *Ibid.* **1980**, *102*, 1747.

[4] (a) $(C_5Me_5)_2Ti(CH_3)OCMo(CO)_2Cp$: Hamilton, D. M., Jr.; Willis, W. S.; Stucky, G. D. *J. Am. Chem. Soc.* **1981**, *103*, 4255. (b) $Cp_2Zr(R)$-$OCMo(CO)_2Cp$: Marsella, J. A.; Huffman, J. C.; Caulton, K. G.; Longato, B.; Norton, J. R. *Ibid.* **1982**, *104*, 6360. (c) $Cp_2Ti(Cl)OCCo_3(CO)_9$: Schmid, G.; Batzel, V.; Stutte, B. *J. Organomet. Chem.* **1976**, *113*, 67. (d) $Cp_2Ti$-$[OCCo_3(CO)_9]_2$: Stutte, B.; Batzel, V.; Boese, R.; Schmid, G. *Chem. Ber.* **1978**, *111*, 1603. (e) For a related vanadium complex see: Haustein, H. J.; Schwarzhans, K. E. *Z. Naturforsch. B* **1978**, *33B*, 1108.

[5] $CpTi[OCCo_3(CO)_9]_2Co(CO)_4$: Schmid, G.; Stutte, B.; Boese, R. *Chem. Ber.* **1978**, *111*, 1239.

[6] A complex in which Zr bonds to the oxygens of two carbonyl ligands that have coupled to form a C–C bond has been reported: Berry, D. H.; Bercaw, J. E.; Jircitano, A. J.; Mertes, K. B. *J. Am. Chem. Soc.* **1982**, *104*, 4712.

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