This deactivation of the Ru colloid by thiols toward CO_2 reduction is general, and cysteine or mercaptoethanol show similar inhibition effects. We thus conclude that thiols prevent the reduction of CO_2, and selective H_2 evolution can be accomplished. Added bipyrazine shows inhibitoric effects toward H_2 evolution as well as CO_2 reduction although the deactivation is more pronounced toward the former process. We anticipate that other ligands might show higher selectivity in the degree of deactivation of these reactions. Also, the possibility to control the selective CO_2-reduction or H_2-evolution process suggests that on the Ru colloid exist distinct and different catalytic sites for the two reactions.

Conclusions

We have discussed the novel application of Ru and Os colloids as catalysts for the photosensitized CO_2 reduction to CH_4. The fixation of CO_2 to CH_4 in aqueous solutions is accompanied by the kinetically favored H_2-evolution process. Our results emphasize that selectivity toward CO_2 reduction might be accomplished by proper design of a relay–catalyst configuration that exhibits overpotential properties toward H_2 evolution. In this respect we find that bipyrazine acts as an inhibitor that eliminates H_2 evolution. Similarly, thiols eliminate CO_2 reduction but do not affect evolution of H_2. The multielectron fixation of CO_2 to CH_4 that involves eight electrons is certainly a stepwise process that involves various intermediates. We emphasize that no other reduction products of CO_2, i.e. formate, formaldehyde, or methanol, could be detected in the photosensitized transformation. We have shown that C_2 hydrocarbons (ethane and ethylene) are also formed during the photoreduction of CO_2. The formation of these products suggests that $Ru{=}CH_2$ (or $Os{=}CH_2$) and $Ru{-}CH_3$ act as intermediates along the photoreduction of CO_2 since ethylene would be formed by the dimerization of the carbene species while ethane is anticipated to originate from dimerization of the metal–methyl intermediate. It should be noted that similar intermediates have been suggested[41] in the methanation process of CO_2.

Our study has emphasized that photoreduction of CO_2 occurs via electron transfer followed by protonation steps rather than by a hydrogenation mechanism. The control experiments that were applied to elucidate the mechanistic aspects of the photoreduction of CO_2 revealed that the photochemically generated reduced relays $Ru(bpz)_3^+$ or the bipyridinium radicals mediate the reduction of CO_2 to CH_4 in the presence of Ru or Os colloids. Since bipyridinium radicals can be produced by H_2 and heterogeneous catalysts, we might envisage routes to develop novel methanation reactions or electrocatalyzed methanation processes that proceed at ambient temperatures and atmospheric pressure via an electron-transfer pathway. Further attempts to characterize mechanistic aspects involved in the photoreduction of CO_2 to methane, development of other CO_2-reduction catalysts, and the development of the dark electron-transfer reduction processes of CO_2 are now under way in our laboratory.

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Registry No. 1, 41491-80-9; **2**, 7325-63-5; **3**, 16651-68-6; 4, 86690-04-2; TEOA, 102-71-6; CO_2, 124-38-9; $Ru(bpy)_3^{2+}$, 15158-62-0; Ru, 7440-18-8; Os, 7440-04-2; Pt, 7440-06-4; H_2, 1333-74-0; tris(bipyrazine)ruthenium(II), 75523-96-5; ethylene, 74-85-1; ethane, 74-84-0; methane, 74-82-8; dithiothreitol, 3483-12-3; 3,3′-dimethyl-4,4′-bipyridine, 4479-73-6; 1,3-propanesultone, 1120-71-4.

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Cyclobutene Photochemistry. Nonstereospecific Photochemical Ring Opening of Simple Cyclobutenes

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Abstract: The photochemistry of bicyclo[3.2.0]hept-6-ene, bicyclo[4.2.0]oct-7-ene, and *cis*- and *trans*-3,4-dimethylcyclobutene has been investigated in hydrocarbon solution with monochromatic far-ultraviolet (185 and 193 nm) light sources. All of these simple cyclobutene derivatives undergo ring opening to yield the isomeric 1,3-dienes, and the latter three open nonstereospecifically to yield mixtures of the possible geometric isomers. The isomeric 3,4-dimethylcyclobutenes yield different mixtures of the three 2,4-hexadiene isomers, and in each case the mixtures are weighted in favor of the orbital symmetry forbidden isomer(s). Attempts have been made to analyze the relative isomeric diene yields from ring opening of bicyclo[4.2.0]octene and the isomeric 3,4-dimethylcyclobutenes within the context of the purely disrotatory, adiabatic ring-opening mechanism that recent ab initio calculations suggest should be possible. While the results for the former compound are consistent with this mechanism, analysis of the relative yields of the isomeric 2,4-hexadienes from photolysis of the latter two compounds indicates that photochemical ring opening by the formally forbidden, conrotatory pathway may compete to some extent with disrotatory ring opening.

In spite of the central role that the thermal[2,3] and photochemical[3b,4,5] interconversions of cyclobutene and 1,3-butadiene play in our understanding of pericyclic reactions,[6] there are few reported examples that illustrate the photochemical electrocyclic ring-

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[1] Natural Sciences and Engineering Research Council of Canada University Research Fellow, 1983–1988.

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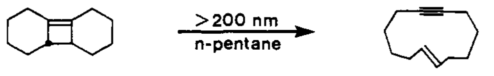
opening process in simple systems.[7] The reason for this is largely a practical one; conventional photochemical techniques require substrates that absorb at wavelengths >230 nm, and cyclobutenes which meet this requirement generally do not undergo ring opening upon photolysis.[8] For example, phenylated cyclobutenes fluoresce efficiently in hydrocarbon solvents,[8a] photosolvolyze in protic solvents,[8b] and/or undergo formal retro-($2\pi+2\pi$) cycloaddition.[8c] It appears that the only systems from which stereochemical information on the process might be obtained are those with nonconjugating substituents;[5] these systems absorb at wavelengths <210 nm and require the use of far-UV techniques for their investigation.

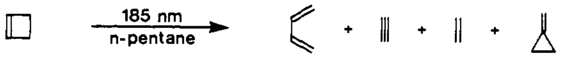
To our knowledge, there is only one published report that offers stereochemical information on the photochemical electrocyclic ring opening of cyclobutene.[5a] Saltiel and Lim reported the photochemistry of the tricyclic cyclobutene derivatives **1** and **2** (eq 1 and 2), providing results which strongly suggest that photochemical ring opening prefers the symmetry-allowed, disrotatory pathway.[5a] Disrotatory opening of **2** would yield the highly strained *cis,trans*-1,1′-bicyclohexenyl; the failure of **2** to yield the stable cis,cis isomer indicates that conrotatory photochemical opening does not occur to any significant extent.

1   (1)



2   (2)

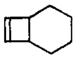
The solution-phase photochemistry of cyclobutene itself has recently been reported by Adam and co-workers.[5c] In addition to the expected fragmentation and ring-opening products, a high yield of methylenecyclopropane was obtained (eq 3). The latter product and acetylene and ethylene were postulated to arise from carbene intermediates formed by [1,2]-hydrogen and -alkyl shifts, respectively, a rather common alkene photoreaction which has been proposed to involve the π,R(3s) Rydberg state.[9]



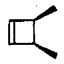
(3)

We wish to report the results of our investigation of the photochemistry of four simple cyclobutene derivatives in solution, bicyclo[3.2.0]hept-6-ene (**3**), bicyclo[4.2.0]oct-7-ene (**4**), and *cis*- and *trans*-3,4-dimethylcyclobutene (**5**). In contrast to previously reported results for **3** and **4**,[5b] our results show that monochromatic photolysis of both these compounds in hydrocarbon solution results in competitive fragmentation and ring opening. More importantly, we find that the photochemical electrocyclic ring opening of **4** and both c- and t-**5** formally proceeds nonstereospecifically, yielding mixtures of 1,3-diene geometric isomers in each case.

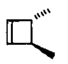
3



4



c-**5**



t-**5**

Table I. Quantum Yields from Photolysis of Bicyclo[3.2.0]hept-6-ene (**3**)[a,b]

wavelength, nm	quantum yield[c] **6**	quantum yield[c] **7**
185[d]	0.12 ± 0.01	0.14 ± 0.01
193[e]	0.09 ± 0.01	0.09 ± 0.01

[a] In isooctane, 25 °C. [b] Acetylene was identified as a product in the photolyses but its yield was not determined. [c] By cyclooctene actinometry, using a value of $\Phi = 0.32$[11b] for the quantum yield of *trans*-cyclooctene at both excitation wavelengths. Product yields were calculated from the slopes of concentration vs. time plots, and errors were calculated by using two standard deviations from these plots. [d] Filtered low-pressure Hg lamp. [e] Ar/F_2 excimer laser.

Table II. Quantum Yields from Photolysis of Bicyclo[4.2.0]oct-7-ene (**4**)[a,b]

wavelength, nm	quantum yield[c] cc-**8**	quantum yield[c] ct-**8**	quantum yield[c] **9**	quantum yield[c] **10**
185[d]	0.12 ± 0.01	0.040 ± 0.004	0.17 ± 0.01	0.009 ± 0.003
193[e]	0.08 ± 0.01	*f*	0.11 ± 0.01	*f*

[a] In pentane, 25 °C. [b] Acetylene was identified as a product in the photolyses but its yield was not determined. [c] By cyclooctene actinometry, using a value of $\Phi = 0.32$[11b] for the quantum yield of *trans*-cyclooctene at both excitation wavelengths. Product yields and errors were calculated from concentration vs. time plots. [d] Filtered low-pressure Hg lamp. [e] Ar/F_2 excimer laser. [f] Not determined.

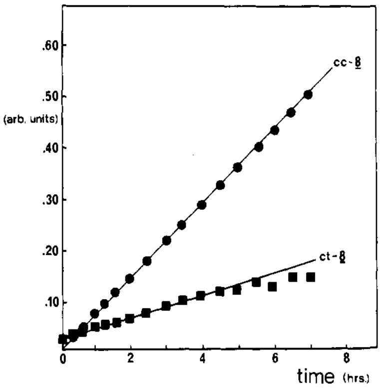
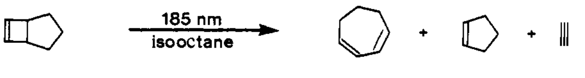


Figure 1. Concentration vs. time plot for formation of cc-**8** (●) and ct-**8** (■) from 185-nm photolysis of **4** in pentane solution to ca. 3.5% conversion. The analogous plot illustrating the formation of **9** coincides with that for cc-**8** and has been omitted for clarity.

Results

Irradiation of **3** as a deoxygenated, 0.018 M solution in isooctane with a filtered (3 × 25 mm LiF window subjected to 1.7 Mrad of radiation from a ^{60}Co source[10]), low-pressure mercury lamp (185 nm) or the pulses (193 nm, ~10 ns, 20–100 mJ) from an excimer laser produced the product mixture shown in eq 4.



3   **6**   **7**   (4)

Product yields were determined from the slopes of concentration vs. time plots constructed for **6** and **7** and were similar for both excitation wavelengths. These plots were linear over the conversion range investigated (0.1–2%; based on the amount of **3** consumed at the maximum irradiation time). The yield of acetylene was not determined, but its presence in the photolysates was confirmed

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(5) (a) Saltiel, J.; Ng Lim, L.-S. *J. Am. Chem. Soc.* **1969**, *91*, 5404. (b) Inoue, Y.; Sakae, M.; Hakushi, T. *Chem. Lett.* **1983**, 1495. (c) Adam, W.; Oppenlander, T.; Zang, G. *J. Am. Chem. Soc.* **1985**, *107*, 3921.

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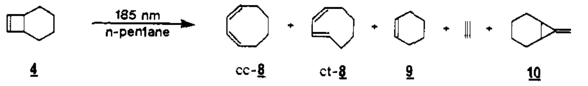
by coinjection of an authentic sample. Product quantum yields were determined at both wavelengths by cyclooctene actinometry[11] and are collected in Table I. A value of $\Phi = 0.32$ for the formation of *trans*-cyclooctene[11b] has been used for *both* excitation wavelengths. No other products in addition to those reported in eq 4 were observed in greater than ~2% yield.

Similarly, photolysis of 0.017 M deoxygenated pentane solutions of **4** yielded the product mixture shown in eq 5. Product yields



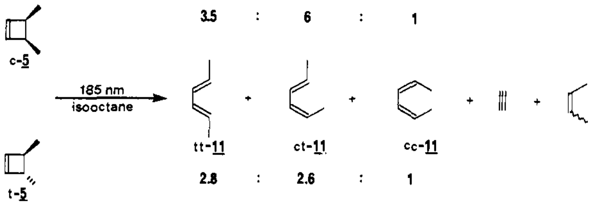
(5)

were determined in similar fashion to those from **3**, and quantum yields determined by cyclooctene actinometry are collected in Table II. Figure 1 shows concentration vs. time plots for *cis,cis*(cc)- and *cis,trans*-(ct)-**8**, constructed from data in the 0.1–3.5% conversion range.

We are not sure how to interpret the apparent wavelength dependence of the product quantum yields that are obtained from photolysis of **3** and **4** with the two light sources, since the quantum yield for cyclooctene cis,trans isomerization has not actually been determined for 193-nm laser excitation. It is possible that the actinometer quantum yield is different at the two wavelengths, although we would not have thought this to be likely a priori.[12] We have tried to rule out the possibility of sequential, two-photon excitation with the laser by determining the quantum yields at different laser fluxes, and these did not vary within experimental error. In view of the fact that the *relative* fragmentation/ring-opening yields do not vary with excitation wavelength, it may still be that the apparent wavelength dependence of the "absolute" product quantum yields is an artifact of some sort, and we assume that the quantum yields measured for 185-nm excitation are the correct ones.

To ensure that the formation of ct-**8** in the photolyses of **4** is not an artifact of secondary photolysis of the cis,cis diene isomer or results from quenching of spurious impurity triplets by cc-**8**, the following control experiment was performed. A deoxygenated pentane solution containing **3** (0.02 M) and cc-**8** (0.0002 M) was irradiated with the filtered 185-nm source under the same conditions as those used above. After ca. 3% conversion of **3**, only **3**, cc-**8**, and the products from photolysis of **3** (see eq 4) could be detected by VPC analysis of the photolysate; ct-**8** amounted to less than ca. 5% of the amount of cc-**8** present (this represents the limits of our analytical method).

Photolysis of deoxygenated, 0.02 M isooctane or pentane solutions of c- and t-**5** yielded *cis,cis*-, *cis,trans*-, and *trans,trans*-2,4-hexadiene (**11**) in the relative yields shown in eq 6. The



(6)

formation of *cis*- and/or *trans*-2-butene and acetylene was also evident in runs carried out in isooctane, but their yields were not monitored in either case. No other products could be detected in greater than 10% yield from photolysis of either isomer of **5** in either solvent. Photolysis of a deoxygenated pentane solution containing c-**5** (0.02 M) and *trans*-1,3-pentadiene (0.0002 M) was carried out to ca. 3% conversion, using the filtered 185-nm light source. *cis*-1,3-Pentadiene could not be detected in the photolysate within our detection limits, and the relative yields of tt-, ct-, and cc-**11** were indistinguishable from those reported in eq 6 for the photolysis of c-**5**.

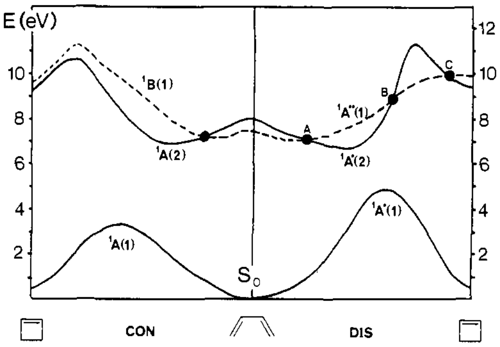


Figure 2. Calculated[15a] potential energy curves for the ground- and excited-state con- and disrotatory interconversions of cyclobutene and butadiene.

Discussion

The most recent[13a] calculated state correlation diagrams for the ground- and excited-state con- and disrotatory interconversions of cyclobutene and butadiene[13] are shown in Figure 2. These calculations are, for the most part, totally consistent with the numerous experimental examples that illustrate the course of the thermal and photochemical interconversions of these compounds.

The thermal interconversions are known to proceed in both directions almost exclusively by the conrotatory pathway.[2,3] Brauman and Archie have shown that the thermal ring opening of c-**5** proceeds with greater than 99.9% stereospecificity to ct-**11**, and from the ~0.005% yield of tt-**11** that was detected, estimated the thermal disrotatory pathway to have an activation energy about 15 kcal/mol higher than that of the allowed conrotatory process.[2d] Thermolysis of t-**5** yields tt-**11** exclusively,[2a] indicating that the formation of the other symmetry-allowed product cc-**11** is subject to a substantially higher activation energy, presumably due to the unfavorable effects of buttressing the methyl groups as ring-opening proceeds.[2d]

The photochemical cyclization of cc-**8** is very inefficient,[14b] perhaps because the two double bonds are constrained to be almost perpendicular to one another in the most stable conformation of the molecule.[15] While the π system in cc-**6** is more nearly coplanar than that in **8**, it is not clear to what extent ring closure competes with cis,trans isomerization in the excited state.[14a] In acyclic dienes, disrotatory ring closure apparently does proceed when there is a significant proportion of s-cis diene conformers present in solution.[4b,16] Thus, tt-**11** yields c-**5** upon irradiation in solution while ring closure of the ct and cc isomers is negligible.[4b,16]

Disrotatory photochemical closure of 1,3-dienes is thought to proceed by a mechanism involving an allowed crossing from S_1 ($^1A''(1)$) to the S_2 ($^1A'(2)$) potential energy surface during the intermediate stages of the reaction. As Figure 2 shows, the $^1A'(2)$ surface has a minimum at a geometry near that of the maximum in the ground-state disrotatory surface. Funneling to the ground state at this point allows disrotatory closure to proceed to completion; forcing the process to occur entirely within the $^1A''(1)$ surface is not possible because the cyclobutene excited singlet state is at least 50 kcal/mol higher in energy than that of the diene.[13c,17]

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[11] (a) Srinivasan, R.; Brown, K. H. *J. Am. Chem. Soc.* **1978**, *100*, 2589. (b) Schuchmann, H.-P.; von Sonntag, C.; Srinivasan, R. *J. Photochem.* **1981**, *15*, 159.

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[13] (a) Morihashi, D.; Kikuchi, O. *Theor. Chim. Acta* **1985**, *67*, 293. (b) Van der Lugt, W. Th. A. M.; Oosterhoff, L. J. *J. Am. Chem. Soc.* **1969**, *91*, 6042. (c) Grimbert, D.; Segal, G.; Devaquet, A. *J. Am. Chem. Soc.* **1975**, *97*, 6629. (d) Welsher, T. L.; Seitz, W. A.; Yurke, B.; Gonzales, R. A.; Matsen, F. A. *J. Am. Chem. Soc.* **1977**, *99*, 8389. (e) Morihashi, K.; Kikuchi, O.; Suzuki, K. *Chem. Phys. Lett.* **1982**, *90*, 346.

[14] (a) Inoue, Y.; Hagiwara, S.; Daino, Y.; Hakushi, T. *J. Chem. Soc., Chem. Commun.* **1985**, 1307. (b) Nebe, W. J.; Fonken, G. J. *J. Am. Chem. Soc.* **1969**, *91*, 1249.

[15] (a) MM2 calculations reveal a dihedral angle of 71° about the C_2–C_3 bond in cc-**8**. (b) Dauben, W. G.; Williams, R. G.; McKelvey, R. D. *J. Am. Chem. Soc.* **1973**, *95*, 3932.

[16] Saltiel, J.; Metts, L.; Wrighton, M. *J. Am. Chem. Soc.* **1970**, *92*, 3227.

[17] Dauben, W. G. In *Solvay Institute 13th Chemistry Conference: Reactivity of the Photoexcited Organic Molecule*; Wiley-Interscience: New York, 1967; 171.

For the conrotatory pathway, no real energy barrier is encountered until ring closure is almost complete. In this case though, funneling to the ground-state surface is less favorable, because the larger $^1A(2)$–$^1A(1)$ energy gap at the partially closed geometry affords a substantially lower probability to this transition.[13a]

On the cyclobutene side, there are substantial calculated energy barriers to ring opening in S_1 by either pathway. For the disrotatory process, however, another allowed crossing (to the $^1A''(1)$ surface at point C in Figure 2) provides a low activation energy route to ring opening that does not exist for the conrotatory process. Thus, the ab initio calculations summarized in Figure 2 afford the same prediction that the qualitative correlation diagram does: the photochemical electrocyclic ring opening of cyclobutene should proceed by the disrotatory pathway.

The reported results for **1** and **2**[5a] appear to be perfectly consistent with this prediction. Disrotatory opening proceeds upon photolysis of **1** to yield the stable cis,cis isomer of 1,1′-bicyclohexenyl. In the case of **2**, however, disrotatory opening would yield the highly strained cis,trans isomer. This relatively high energy (though formally allowed) process does not occur on photolysis of **2**; it is now known that the formation of the cis,trans diene even as a transient intermediate would have been detected as the apparent isomerization of **2** to **1**.[18] *cis,trans*-1,1′-Bicyclohexenyl has recently been detected by flash spectroscopic methods from direct or triplet-sensitized excitation of the cis,cis isomer.[18] In aprotic solvents, the transient has a lifetime of ca. 0.8 μs and decays predominantly to the cis,cis isomer, but also (ca. 3%) by thermal (conrotatory) cyclization to yield **1**. The major implication of the photochemical behavior of **2** though is that ring opening by the forbidden conrotatory pathway does not occur to any significant extent.

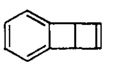
Photochemical ring opening of bicyclo[3.2.0]hept-6-ene (**3**) to yield 1,3-cycloheptadiene (**6**) proceeds with relatively high efficiency, competing effectively with the formal ($\pi 2s + \pi 2s$) cycloreversion to cyclopentene and acetylene. These results contrast with those of Inoue and co-workers, who found only the latter products from photolysis of this compound with an unfiltered low-pressure mercury lamp.[5b] The difference between our results and theirs is due solely to the difference in excitation sources; the high output of 254-nm radiation from the low-pressure mercury lamp precludes the buildup of photolabile products such as **6** that absorb strongly at this wavelength.[19] It is well-known that **6** yields **3** rather efficiently upon irradiation with 254-nm light,[4c,d] and this is now known to proceed by a pathway involving photochemical cis,trans isomerization to ct-**6**, which then undergoes rapid, thermal (conrotatory) electrocyclic ring closure to yield **3**.[14a] Recently, ct-**6** has been detected spectroscopically at low temperatures from irradiation of the cis,cis isomer.[14a]

Complete stereochemical information on the preferred ring-opening pathway for **3** cannot be obtained in this case, since the formation of ct-**6** under our conditions is undetectable by steady-state methods.[14a] It is clear though that ring opening, formally by the symmetry allowed disrotatory pathway, proceeds efficiently upon irradiation of **3** at 185 or 193 nm.

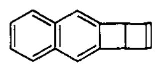
Direct photolysis of **4** yields both cc- and ct-**8** under conditions where the dienes are clearly not subject to secondary photolysis. The latter isomer is demonstrably stable at room temperature under these conditions, undergoing (conrotatory) thermal closure to regenerate **4** only at higher temperatures.[14b] The quantum yields for diene formation from 185-nm irradiation of **4** are slightly higher than the previously reported values,[5b] probably because of the absence of the long-wavelength component in the light sources used in the present study.

The apparent nonstereospecificity with which **4** undergoes photochemical ring opening may also be consistent with the disrotatory, concerted mechanism if the process occurs adiabatically to yield cc-**8** in the first excited singlet state. The theoretical calculations summarized in Figure 2 predict that the barrier encountered in proceeding from the $^1A'(2)$ minimum to the fully open S_1 diene amounts to only 5–8 kcal/mol.[13] If the calculations overestimate the height of this barrier for S_2–S_1 internal conversion (at least as it pertains to **4**), then formation of fully open diene excited singlets may effectively compete with internal conversion to the ground-state disrotatory surface at the partially open geometry. Once obtained, the excited diene should decay by cis,trans isomerization[20a,b] or disrotatory ring closure to yield its cyclobutene precursor, and the mixture of diene isomers obtained should be governed by the decay characteristics of the S_1 diene excited state. In the case of **4**, it is possible to calculate the cc/ct ratio of **8** expected in the limit of completely efficient, adiabatic ring opening from the quantum yield ratio $\Phi_{ct\rightarrow cc}/\Phi_{cc\rightarrow ct}$ measured by direct excitation of the dienes. Using the values for $\Phi_{cc\rightarrow ct}$ (=0.27) and $\phi_{ct\rightarrow cc}$ (=0.80) reported by Nebe and Fonken[14b] and allowing for an error of ca. 10% in these numbers, we obtain the ratio cc/ct = 2.9 ± 0.5. This is in excellent agreement with the ratio obtained from the direct photolysis of **4**, cc/ct = 3.0 ± 0.5.[37]

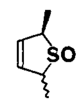
This mechanism for cyclobutene ring opening has precedent in the photochemistry of 1,4-dewarnaphthalene (**12**) and 1,4-dewaranthracene (**13**), whose photochemical ring opening has been shown to proceed adiabatically in both the excited singlet and triplet states.[21a,b] The formation of electronically excited products in these cases is evidenced by the characteristic naphthalene and anthracene emission that results from excitation of **12** and **13**, respectively. The calculated state correlation diagrams for the conversion of these rather special cyclobutene derivatives to their fully aromatic isomers are qualitatively very similar to that shown in Figure 2 for the cyclobutene–butadiene interconversions. Further analogy exists in the results of the benzene-sensitized photolyses of the 3-sulfolene derivatives (**14**).[21c] The mixtures of tt-, ct-, and cc-**11** obtained were postulated to arise by partial adiabatic ring opening of the excited triplet states of **14**.[21c]



12



13



14

Direct photolysis of *cis*- and *trans*-3,4-dimethylcyclobutene yields all three of the possible isomers of 2,4-hexadiene in each case, but in *different* relative amounts. It is important to note that in both cases, the diene mixture obtained is weighted toward the isomer(s) resulting from the *formally forbidden*, conrotatory ring-opening pathway. A simple calculation of the "expected" relative yields of the isomeric 2,4-hexadienes using the quantum yields for their direct cis,trans photoisomerization[16] and the assumption that ring opening occurs by the adiabatic, disrotatory pathway, similar to the calculation carried out above for the dienes obtained from photolysis of **4**, yields ratios which are grossly different than those actually obtained from photolysis of c- and t-**5**. This discrepancy might be attributed to the fact that cyclobutene ring opening yields the dienes initially in s-cis conformations, while the direct diene photoisomerization quantum yields report on the behavior of the s-trans diene conformers.[20,22] Since

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(18) Saltiel, J.; Marchand, G. R.; Bonneau, R. *J. Photochem.* **1985**, *28*, 367.

(19) Leigh, W. J.; Srinivasan, R. *J. Am. Chem. Soc.* **1983**, *105*, 514.

(20) (a) Saltiel, J.; Charlton, J. L. In *Rearrangements in Ground and Excited States*; De Mayo, P., Ed.; Academic: New York, 1980; Vol. 3, 25 and references cited therein. (b) Saltiel, J.; D'Agostino, J.; Megarity, E. D.; Metts, L.; Neuberger, K. R.; Wrighton, M.; Zafiriou, O. U. *Org. Photochem.* **1973**, *3*, 1. (c) Stephenson, L. M.; Brauman, J. I. *Acc. Chem. Res.* **1974**, *7*, 65. (d) Recent evidence indicates that twisted diene excited singlets have appreciable zwitterionic character. See: Squillacote, M. E.; Semple, T. C. *J. Am. Chem. Soc.* **1987**, *109*, 892. This does not affect our conclusions.

(21) (a) Yang, N. C.; Carr, R. V.; Li, E.; McVey, J. K.; Rice, S. A. *J. Am. Chem. Soc.* **1974**, *96*, 2297. (b) Carr, R. V.; Kim, B.; McVey, J. K.; Yang, N. C.; Gerhartz, W.; Michl, J. *Chem. Phys. Lett.* **1976**, *39*, 57. (c) Saltiel, J.; Metts, L.; *J. Am. Chem. Soc.* **1967**, *89*, 2232.

(22) (a) Aston, J. G.; Szasz, G.; Wooley, H. W.; Brickwedde, F. G. *J. Chem. Phys.* **1946**, *14*, 67. (b) Aten, C. F.; Hedberg, L.; Hedberg, K. *J. Am. Chem. Soc.* **1968**, *90*, 2463. (c) Squillacote, M. E.; Sheridan, R. S.; Chapman, O. L.; Anet, F. A. L. *J. Am. Chem. Soc.* **1979**, *101*, 3657. (d) Squillacote, M. E.; Semple, T. C.; Mui, P. W. *J. Am. Chem. Soc.* **1985**, *107*, 6842.

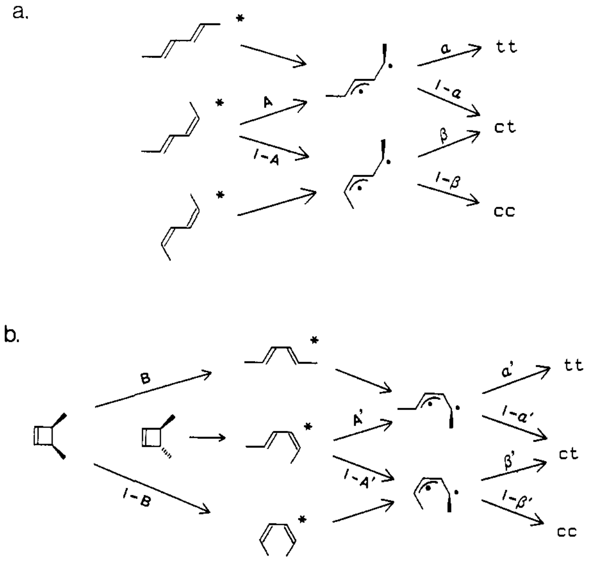

Figure 3. Allylmethylene mechanism for the direct cis,trans photoisomerization of the 2,4-hexadienes:[20a,b] (a) isomerization of s-trans diene conformers; (b) isomerization of s-cis conformers, produced by adiabatic, disrotatory ring opening of c- and t-**5**.

there is good reason to suspect that the decay characteristics of s-cis diene conformers may differ considerably from those of the s-trans conformers,[20] our results must be considered more carefully within the framework of the postulated mechanisms for direct cis,trans photoisomerization of acyclic 1,3-dienes.[16,20]

Saltiel and co-workers have analyzed the quantum yields for direct photoisomerization of the isomeric 2,4-hexadienes in terms of two alternative mechanisms.[16,20a,b] These both involve torsional relaxation of the initially "planar" diene excited singlet state about only one double bond, through relaxed, noninterconverting, diradicaloid excited states.[20d] In order to explain the fact that isomerization of any of the three diene isomers is less than 50% efficient, some component of excited-state decay that proceeds directly to the starting isomer without torsional relaxation is also required.[20b]

The allylmethylene mechanism for direct diene photoisomerization is shown in Figure 3,[20b] along with the analogous process for s-cis dienes formed by adiabatic, disrotatory ring opening of c- and t-**5**. We assume that conformational equilibration is slow compared to torsional relaxation of the s-trans and s-cis "planar" diene singlets[20,23] and allow for the possibility that in each case, the decay characteristics of s-cis and s-trans allylmethylene conformers may differ.[20a,b] This mechanism for diene excited singlet state isomerization cannot account for the fact that c- and t-**5** *each* yield diene mixtures weighted in favor of the formally forbidden isomer(s), if one assumes that ring opening proceeds only by the adiabatic, purely disrotatory pathway. This can be proven rigorously: since the reaction scheme shown in Figure 3b contains four unknown partitioning constants, and the relative isomeric diene yields from photolysis of c- and t-**5** can be expressed as four independent product ratios, it is possible to calculate the partitioning constants shown in the figure by solving the four simultaneous equations that result from expressing the diene yield ratios in terms of these parameters. The unique solution obtained is physically meaningless (i.e., values are obtained that are negative or greater than 1), and the same conclusion is obtained when any or all of the relative diene yields are allowed to vary by up to 15%. Assuming that the decay characteristics of excited diene singlets (when they are formed by adiabatic cyclobutene ring opening) should be representable by a simple twisting model such as that shown in Figure 3, the analysis indicates that disrotatory ring opening (adiabatic or not) cannot totally account for the formation of formally forbidden diene isomers in these cases.

The second postulated mechanism[16,20a,b] for the direct cis,trans photoisomerization of dienes involves partial 1,3-bonding[24] to yield cyclopropylcarbinyl diradicaloid intermediates, which lead to one-bond isomerization as a result of free rotation about the exocyclic cyclopropyl–methylene C–C bond before reopening to diene. Interconversion of the s-trans conformers of the three 2,4-hexadiene isomers requires two such intermediates, while interconversion of the s-cis conformers requires two different ones; this mechanism is therefore operationally equivalent to the allylmethylene mechanism and is similarly incapable of accounting for the present results within the context of purely disrotatory, adiabatic cyclobutene ring opening.[20d]

The present results show that, in general, photochemical cyclobutene ring opening does not occur stereospecifically in simple, unconstrained systems, although it is clear from the reported behavior of **1** and **2** that stereospecific, nonadiabatic disrotatory ring opening can occur in some cases. Our analysis of the relative isomeric diene yields from photolysis of **4** and **5** show that the nonstereospecificity which is observed in general may be due partly to competition from an adiabatic component of disrotatory opening, but other pathways for the formation of formally forbidden diene isomers must also compete if excited diene singlets when formed via adiabatic cyclobutene ring opening isomerize by the simple twisting mechanism considered in Figure 3. Given the unsatisfactory fit of our data for **5** with the adiabatic disrotatory ring-opening mechanism, it may be that the excellent fit observed for **4** is coincidental.[37] While a few possible mechanisms for the formation of formally forbidden diene isomers are considered below, further work in this area is clearly necessary before precise conclusions can be derived.

If ring opening does occur by the purely disrotatory, adiabatic pathway, then the observed diene mixtures from **5** could be obtained if the decay of s-cis singlets (unlike the s-trans conformers[20]) is governed by torsional momentum effects.[25a] This explanation is the least attractive, because while the possibility of torsional momentum effects in alkene and diene photoisomerizations has been derived theoretically,[25a] experimental support appears to be confined to charged[25b] or complexed[25c] systems.

A second possibility is that ring opening proceeds partially by the disrotatory route (adiabatically or nonadiabatically), in competition with radiationless decay to a "hot" cyclobutene ground state which undergoes ring opening by the thermally allowed conrotatory pathway.

Finally, our results may indicate that photochemical cyclobutene ring opening can occur by both the dis- and conrotatory pathways in some cases, with the obvious implication that the ab initio calculations reported to date for the parent molecule may not accurately reflect the behavior of the substituted systems that have now been studied experimentally, if ring opening proceeds entirely from the π,π^* excited state. It is interesting that the calculated barrier to conrotatory S_1 ring opening is in fact smaller than that for disrotatory S_1 ring opening (by ~15 kcal/mol; see Figure 2); it is only the presence of the surface crossing to S_2 ($^1A''(1)$; at point C in the figure) that suggests that disrotatory opening should proceed at all. It is also possible that π,R(3s) Rydberg state excitation may contribute to some extent to ring opening in these systems. Since the π,R(3s)–π,π^* singlet energy gap should be much larger in **1** and **2** (with the Rydberg state the lowest in energy) than in **5**[9,26] however, the difference in the behavior of these compounds is explainable if the cyclobutene Rydberg state[27]

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(23) Dauben, W. G.; McInnis, E. L.; Michno, D. M. *Rearrangements in Ground and Excited States*; De Mayo, P., Ed.; Academic: New York, 1980; Vol. 3, 91.

(24) We consider the 1,3-bond in this diradicaloid species to be only partial, because of the necessity for it to reopen to diene only by the reverse of the pathway by which it was formed. If it did not, then with free rotation about the exocyclic methylene–carbon bond, some degree of formal two-bond diene isomerization would result.

(25) (a) Weiss, R. M.; Warshel, A. *J. Am. Chem. Soc.* **1979**, *101*, 6131. (b) Doukas, A. G.; Junnarkar, M. R.; Alfano, R. R.; Callender, R. H.; Kakitani, T.; Honig, B. *Proc. Natl. Acad. Sci. U.S.A.* **1984**, *81*, 4790. (c) Lewis, F. D.; Howard, D. K.; Barancyk, S. V.; Oxman, J. D. *J. Am. Chem. Soc.* **1986**, *108*, 3016.

(26) Robin, M. B. *Higher Excited States of Polyatomic Molecules*; Academic: New York, 1975; Vol. II, Chapter IV.

opens stereospecifically (disrotatory) while the π,π^* state opens nonstereospecifically. This possibility may be a plausible one, to the extent that the cyclobutene Rydberg state possesses radical cation character;[9] cyclobutene radical cations, generated in the gas phase, *do* undergo ring opening,[31] although the stereochemistry of the process is unknown. It should be noted, however, that the radical cations of phenylated cyclobutenes do not undergo ring opening to yield the corresponding 1,3-dienes in solution.[32]

Conclusions

Direct photolysis of simple bi- and monocyclic cyclobutene derivatives in solution with far-UV light results in nonstereospecific electrocyclic ring opening to yield the isomeric 1,3-dienes. The results cannot be fully explained within the context of the most recent ab initio theoretical calculations for the cyclobutene/butadiene interconversions, which predict that excited-state cyclobutene ring opening should proceed by the disrotatory pathway and suggest that an adiabatic route should be possible. While adiabatic ring opening could, in principle, yield mixtures of formally allowed and forbidden diene isomers as a result of secondary cis,trans isomerization of the initially formed, excited s-cis diene singlets, it has been shown that purely disrotatory opening (adiabatic or not) cannot account in all cases for the compositions of the diene mixtures obtained from cyclobutene photolysis. Further work in this area is in progress.

Experimental Section

^{1}H NMR spectra were recorded on a Varian 390 spectrometer in deuteriochloroform solution, using tetramethylsilane as an internal reference. Mass spectra were recorded on a Hewlett-Packard HP-5995 gas chromatograph/mass spectrometer fitted with a 60 m × 0.25 mm DB-1 fused-silica capillary column or on a VG7070 mass spectrometer interfaced with a Varian 3700 gas chromatograph equipped with a 60 m × 0.25 mm OV-17 fused-silica capillary column. Ultraviolet absorption spectra were recorded in pentane or cyclohexane solution with a Perkin-Elmer Lambda 9 spectrometer equipped with a Model 3600 Data Station.

Analytical VPC separations were carried out on a Varian 3700 gas chromatograph (injector temperature = 100 °C) equipped with a flame ionization detector, a Varian CDS101 or Hewlett-Packard HP-3393a integrator, and one of the following columns: (a) 3.8% UC W982 on 80/100 Supelcoport (24 ft × $^1/_8$ in, stainless steel); (b) 20% tris(cyanoethoxy)propane (TCEP) on 80/100 Chromosorb PNAW (12 ft × $^1/_4$ in, (0.2-mm i.d.) glass); (c) 1.0-μm SPB-1 wide-bore capillary (30 m × 0.75 mm i.d. borosilicate); (d) 0.25-μm HPOV-1 wide-bore capillary (25 m × 0.31 mm i.d. fused silica). The detector response was calibrated for each photoproduct relative to an internal hydrocarbon standard by construction of working curves from a few standard solutions. Semipreparative VPC separations employed a Hewlett-Packard 5750B gas chromatograph equipped with thermal conductivity detectors (TC detector temperature = 100 °C) and one of the following stainless steel columns: (e) 3.8% UC W982 on 80/100 Supelcoport (24 ft × $^1/_4$ in.); (f) 20% oxybis(propionitrile) (ODPN) on 80/100 Chromosorb PNAW (20 ft × $^1/_4$ in.).

Pentane (Baker Photrex), methylcyclohexane (BDH Omnisolv), and 2,2,4-trimethylpentane (isooctane, Baker Photrex) were used as received. 1,3-Cycloheptadiene, 1,3-cyclooctadiene, *trans*-1,3-pentadiene, cyclopentene, and cyclohexene were all used as received from Aldrich Chemical Co. *cis*-Cyclooctene (Aldrich) was purified by VPC using column e.

Bicyclo[3.2.0]hept-6-ene (3) was synthesized by photolysis of a deoxygenated pentane (100 mL) solution of 1,3-cycloheptadiene (1.0 g, 0.011 mol) with a low-pressure Hg lamp through a Vycor filter for 4 h.[4c] Concentration of the photolysate by distillation left a slightly yellow liquid, which was distilled in vacuo to yield a colorless liquid, from which **3** was isolated by semipreparative VPC (column e). Three further VPC purifications (alternating between columns e and f) afforded **3** in >99.5% purity. The material exhibited spectral characteristics similar to those previously reported.[4c]

Bicyclo[4.2.0]oct-7-ene (4) was synthesized in similar fashion by photolysis of a pentane solution of 1,3-cyclooctadiene in a Rayonet reactor fitted with 254-nm lamps. Irradiation of a 0.1 M solution of cc-**8** for 9 days yielded a mixture of 4, cc-**8**, and ct-**8**. The latter was identified by coinjection of an authentic sample, prepared by the method of Liu.[33] Compound 4 was separated from the other two components by semipreparative VPC (column e, detector temperature = 150 °C) after concentration of the photolysate by distillation. A sample of 4 in >99.5% purity was obtained by three further purifications by semipreparative VPC (column e) and exhibited spectral characteristics similar to those previously reported.[34]

***cis*- and *trans*-3,4-Dimethylcyclobutene (c-5 and t-5).** Acetophenone (8.0 g, 0.067 mol) and maleic anhydride (47 g, 0.48 mol) were dissolved in ethyl acetate (400 mL). The solution was placed in a Pyrex immersion well apparatus, and the solution was deoxygenated with N_2 gas at room temperature. The solution was cooled to −78 °C with an external dry ice/2-propanol bath, saturated with *cis*-2-butene (C.L.A.) and irradiated at −78 °C with a medium-pressure mercury lamp. After 24 h of irradiation, NMR analysis of the photolysate revealed the disappearance of maleic anhydride to be >90% complete. The solution was allowed to warm to room temperature, and the solvent was removed on the rotary evaporator to yield a yellow oil, from which acetophenone and unreacted maleic anhydride were removed by further distillation at ca. 0.2 mmHg. Portions (10 g) of the brown oil (45 g) which remained were stirred in 10% aqueous hydrochloric acid (50 mL) for 12 h at room temperature and then extracted with ether (3 × 50 mL). The extracts were washed with water (50 mL) and dried over anhydrous sodium sulfate, and the solvent was distilled to yield a yellow oil (9 g). The NMR spectrum of this material showed resonances at δ = 1.10 (m, 6 H), 2.80 (m, 2 H), 3.68 (d, 2 H), and 9.07 (s, 2 H). The oil was dissolved in dry pyridine (50 mL, distilled from barium oxide), the mixture was placed in a 100-mL, two-neck round-bottom flask fitted with a gas inlet and a reflux condenser connected to two sequential dry ice/acetone traps, and the solution was saturated with oxygen. Lead tetraacetate (15 g, 0.034 mol) was added, a slight positive pressure of dry nitrogen was applied, and the mixture was placed in a 70 °C oil bath, where it was stirred for 24 h. The colorless liquid which had collected in the traps was dissolved in pentane (10 mL), washed with 5% aqueous HCl and water, dried over anhydrous sodium sulfate, filtered, and concentrated by slow distillation. VPC analysis of the mixture (column e) showed it to contain three products. The two major products (ca. 1:1 ratio) were collected by semipreparative VPC (column e, injector temperature = 120 °C, detector temperature = 150 °C, oven temperature = 40 °C). c-**5** and t-**5** were obtained in >99% purity by further purification by semipreparative VPC on columns e and f.

t-**5**: ^{1}H NMR δ 1.08 (d, 6 H), 2.30 (q, 2 H), 6.03 (s, 2 H); MS *m/e* (*I*) 82 (14), 70 (40), 67 (84), 55 (43), 43 (82), 42 (100), 41 (70). c-**5**: ^{1}H NMR δ = 0.96 (d, 6 H), 2.90 (m, 2 H), 6.03 (s, 2 H); MS *m/e* (*I*) 82 (20), 67 (100), 53 (38), 41 (100), 39 (93). c-**5** was identical with a sample synthesized by the method of Brauman and Archie.[2d]

***cis,trans*-Cycloocta-1,3-diene (ct-8)** was synthesized according to the published method.[33] Its spectral features (IR, NMR, GC/MS) agreed satisfactorily with those previously reported.[34,35]

7-Methylenebicyclo[4.1.0]heptane (10) was synthesized according to the published method[36] and purified by preparative VPC (column e). Its

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(27) It has been pointed out that π,R(3s) Rydberg state excitation may provide an alternative route to the formal ($\pi 2s + \pi 2s$) cycloreversion products from photolysis of alkylcyclobutenes.[5b,c] In cyclobutene, decay of the Rydberg state by [1,2]-alkyl migration (ring contraction) and [1,2]-H migration would yield cyclopropylmethylene and cyclobutylidene, respectively. Cyclopropylmethylenes undergo fragmentation to the corresponding alkene and alkyne when they are generated from diazo precursors,[28] and cyclobutylidenes undergo ring contraction to yield methylenecyclopropane derivatives.[28a,29] Thus the intermediacy of cyclobutylidene could explain the high yield of methylenecyclopropane that has been obtained from photolysis of cyclobutene.[5c] However, we observe no methylenecyclopropane products in greater than 5% yield from photolysis of **3**, c-**5**, or t-**5**, and only a minor amount of **10** from photolysis of **4**.[30]

(28) (a) Friedman, L.; Shechter, H. *J. Am. Chem. Soc.* **1960**, *82*, 1002. (b) Shevlin, P. B.; Wolf, A. P. *J. Am. Chem. Soc.* **1966**, *88*, 4735. (c) Smith, J. A.; Shechter, H.; Bayless, J.; Friedman, L. *J. Am. Chem. Soc.* **1965**, *87*, 659.

(29) Brinker, U. H.; Schenker, G. *J. Chem. Soc., Chem. Commun.* **1982**, *679*.

(30) We have recently obtained direct evidence for the intermediacy of cyclopropylmethylenes in the photolysis of alkylcyclobutenes: Leigh, W. J.; Clark, K. B., unpublished results.

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(32) (a) De Mayo, P.; Wenska, G. *J. Chem. Soc., Chem. Commun.* **1986**, 1626. (b) Kawamura, Y. K.; Thurnauer, M.; Schuster, G. B. *Tetrahedron* **1986**, *42*, 6195. (c) Brauer, B.-E.; Thurnauer, M. C. *Chem. Phys. Lett.* **1987**, *133*, 207.

(33) Liu, R. S. H. *J. Am. Chem. Soc.* **1967**, *89*, 112.

(34) Evans, M. V.; Lord, R. C. *J. Am. Chem. Soc.* **1961**, *83*, 3411.

(35) Cope, A. C.; Baumgardner, C. L. *J. Am. Chem. Soc.* **1956**, *78*, 2812.

spectral features (^{1}H NMR, IR, MS) agreed satisfactorily with those previously reported.[36]

Photochemical experiments employed a 10-W Osram HNS 10W/U OZ low-pressure mercury lamp or the pulses (193 nm, ~10 ns, 20–100 mJ, 0.5-Hz repetition rate) from a Lumonics TE-861M excimer laser filled with an argon/fluorine/helium mixture. The low-pressure Hg lamp was surrounded by a metal case which incorporated a 1-in. port to contain the sample cell and filter. The filter consisted of a 25 × 3 mm LiF disk (Harshaw VUV grade) which had been irradiated with ca. 1.7 Mrad of γ-radiation from a ^{60}Co source.[10] The transmittance spectrum of the filter was monitored quite closely during photolysis experiments, as the transmittance at 254 nm tends to increase slowly after prolonged exposure to (185 + 254)-nm light.[10] A freshly prepared filter typically has an optical density of ~0.5 at 185 nm and ~5 at 254 nm.[10c] The lamp was given a 20-min warmup period before each photolysis and cooled with a stream of nitrogen.

Photolyses were carried out in 10 × 25 mm cylindrical Suprasil quartz UV cells (Hellma) or in rectangular cells constructed from 10 × 20 mm rectangular Suprasil quartz tubing (Vitro Dynamics) at ambient temperature (ca. 23 °C). In the lamp runs, the sample was agitated with a small magnetic stirrer, while in the laser runs, the sample cell was contained in a mechanical shaker which provided constant, gentle agitation of the solution between laser pulses. Solutions were deoxygenated by bubbling dry nitrogen through the cooled (to ~0 °C) solutions for 5–15 min. The products obtained from photolysis of **3** and **4** were identified by coinjection with authentic samples on at least two VPC columns. Quantum yield determinations were carried out by cyclooctene actinometry, using approximately matched cells and alternately irradiating the substrate and actinometer solutions for identical, short periods of time.

Photolyses were generally carried to $<2\%$ conversion, with aliquots being withdrawn at suitable time intervals for VPC analysis. Product yields were determined relative to reacted starting material from the slopes of concentration vs. time plots constructed for all components of the mixtures relative to internal standard. Typical concentration vs. time plots, obtained from the photolysis (185 nm) of **4** in pentane, are shown in Figure 1. Quantum yields were obtained in similar fashion, after calculating the light flux from a concentration vs. time plot for the formation of *trans*-cyclooctene from the cis isomer. A value of 0.32 was employed for the actinometric quantum yield.[11b]

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(36) Salomon, G.; Sinha, A.; Salomon, M. F. *J. Am. Chem. Soc.* **1978**, *100*, 520.

(37) (a) **Note Added in Proof**: The cc/ct-**8** ratio obtained from photolysis of **4** at 193 nm is significantly *smaller* (cc/ct-**8** = 1.4 ± 0.2)[37b] than that obtained with 185-nm excitation. Complete wavelength dependence studies will be reported in a forthcoming publication. (b) Clark, K. B.; Leigh, W. J., unpublished results.

Carbon Acidity. 72. Ion Pair Acidities of Phenyl Alkyl Ketones. Aggregation Effects in Ion Pair Acidities

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Abstract: Equilibrium cesium ion pair acidities of acetophenone, propiophenone, isobutyrophenone, and *o*-methoxyacetophenone and the lithium ion pair acidity of *o*-methoxyacetophenone in tetrahydrofuran have been determined by an indicator method. For all of these compounds, the observed pK_a values decrease as the equilibrium enolate concentration is increased. It is proposed that this concentration dependence is a consequence of the aggregation of the enolates, and a method is described whereby average aggregation numbers can be determined from the acidity data. The results indicate that the extent of aggregation of enolate ions is influenced by both electronic and steric factors. In addition, internal solvation is found to be important for the lithium, but not the cesium enolate of *o*-methoxyacetophenone.

It is well established that alkyl- and aryllithium compounds form molecular aggregates in ethereal solvents.[1] Over the past several years, evidence has accumulated to indicate that many alkali-metal derivatives of ketones, esters, nitriles, and other carbon derivatives may exist as aggregates in solution.[2] Interpretations of reaction mechanisms of such derivatives must ultimately address the issue of whether monomers or aggregates are involved. Although many mechanistic hypotheses have been advanced to rationalize the regio- and stereochemical outcome of enolate ion reactions, these theories usually regard the monomeric ion (or ion pair) as the sole active nucleophile.[3] While it is probably true that monomeric enolate ions are the active species in solvents of high ionizing power (e.g., Me$_2$SO),[4] the role that aggregates play in carbanion reactions conducted in solvents of low polarity, such as ethers, is not well understood. From the above discussion, it is clear that a more complete knowledge of the state of aggregation of enolate ions in ethereal solution is needed; however, relatively few such studies are available. This paucity of data undoubtedly reflects the fact that the classical techniques for determining molecular association are difficult to apply to the highly air- and moisture-sensitive solutions of enolate ions. Despite such experimental difficulties, several workers have successfully applied the techniques of ebulioscopy,[5-7] osmometry,[8,9] and cryoscopy[10,11]

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