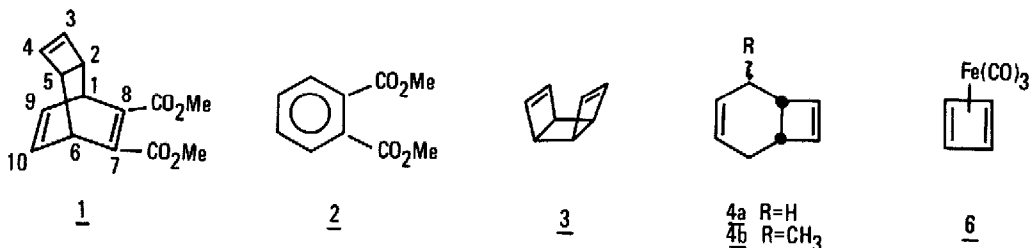


## "THE PHOTOAROMATIZATION OF SOME SUBSTITUTED BICYCLOOCTADIENE DERIVATIVES"

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We have reported that the photolysis of 1 in solution led to dimethyl phthalate 2 and syn-tricyclo[4.2.0.0<sup>2,5</sup>] octa-3,7-diene 3.<sup>1</sup> On the basis of the isolation of 3 and the formation of crossadducts such as 4 in the presence of 1,3-dienes (e.g., trans-1,3-pentadiene yields 4b), cyclobutadiene 5 was implicated as an intermediate.<sup>2</sup> While it seemed that the exclusive production of 1,4-adducts with 1,3-dienes was indicative of a Diels-Alder cycloaddition and less compatible with a stepwise dissociation of 1 (i.e., homolytic cleavage of the 1,2(5,6) bond), reaction of the diradical with the diene and subsequent fragmentation to the observed products, the possibility could not definitely be excluded at the time. We now present conclusive evidence of the intermediacy of cyclobutadiene and examine a basic structural requirement for the photoaromatization.



To eliminate radical intermediates as the immediate precursor to the crossadducts such as 4, a pair of structurally similar dienes, each a sensitive radical trap but only one of which is an effective Diels-Alder diene was needed. Cis- and trans-1,3-pentadiene (piperylenes) seemed ideal since each should be susceptible to radical addition at the unsubstituted terminus,<sup>3</sup> but the trans isomer alone is a good Diels-Alder diene.<sup>4</sup> Accordingly, the irradiation of 1 (254nm) in the presence of cis and transpiperylene produced the following results (see Table 1). When 1 is

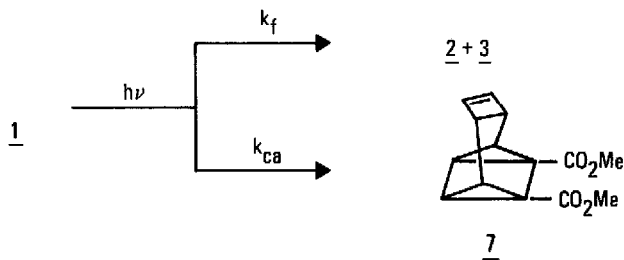
**Table 1**  
Product Yields (%)

| Diene Conc. | <u>2</u> | <u>3</u> | <u>4b</u> | % Conversion      |
|-------------|----------|----------|-----------|-------------------|
| 0           | 46       | 28       | —         | 20 <sup>a,b</sup> |
| 0.1M trans  | 45       | 21       | 8         | 22                |
| 0.1M cis    | 47       | 29       | —         | 23                |

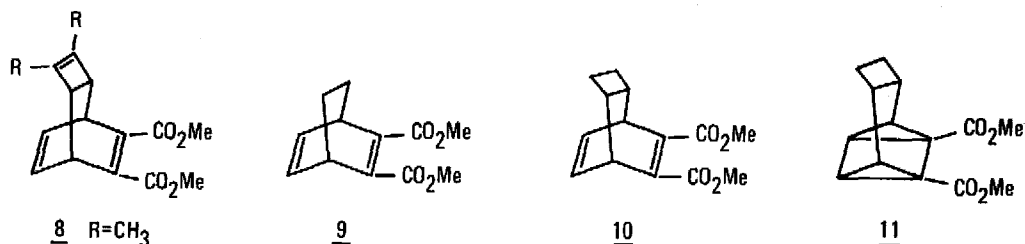
<sup>a</sup> Each tube was 0.03M in 1 (ether);<sup>b</sup> irradiation time 0.5 hr (254 nm).

irradiated in the presence of cis-piperlyene, no detectible amount of C<sub>9</sub> adduct is produced at low conversions. Also noteworthy, is the observation that neither diene has any significant effect on either the rate of disappearance of 1 nor the appearance of dimethyl phthalate 2. As expected from the absence of a C<sub>9</sub> adduct, the cis-piperlyene similarly does not alter the rate of formation of the syn dimer 3. Further corroborative evidence for the intermediacy of cyclobutadiene in the photolysis of 1 comes from the oxidation of cyclobutadiene irontricarboxyl 6, a reagent known to produce free cyclobutadiene,<sup>5</sup> in the presence of the isomeric dienes. When 6 is decomposed in acetone solution (0°) containing trans-piperlyene (4M), the major volatile products were 3 (5.1%) and 4 (15%). The C<sub>9</sub> adduct isolated in this case<sup>6</sup> was chromatographically and spectrally identical to that isolated from the photolysis of 1 in the presence of trans-piperlyene. Consistently, the oxidation of 6 under the same conditions in the presence of cis-piperlyene (4M) produced the syn dimer 3 but no significant amount of C<sub>9</sub> adduct.

The overall photochemistry of 1 is more complicated than the photoaromatization implies. For example, Nelson and Gillespie<sup>7</sup> have shown that irradiation of 1 at low temperature (-50°) produces predominately the thermally unstable cycloadduct 7.<sup>8</sup> We have determined the ratio of the rate constants for cycloaddition ( $k_{ca}$ ) to fragmentation ( $k_f$ ) in Et<sub>2</sub>O<sub>d</sub><sub>10</sub> at -50° to be 9-11 by a combination of low temperature NMR analysis (-20°) of 7 and subsequent warm up prior to glpc analysis of the dimethyl phthalate 2 and the remaining starting material 1. This ratio was invariant beyond experimental error over the modest irradiation temperature range (-22° to -50°) examined. However, it did show a curious wavelength dependence, and irradiation through Pyrex at 300nm<sup>9</sup> caused a substantial increase in the value of  $k_{ca}/k_f$  to >100.<sup>10</sup> It seems that the extensive photofragmentation of 1 observed at room temperature<sup>1</sup> was due to a fortuitous combination of the short wavelength excitation source and the thermal and perhaps photochemical reversibility<sup>11</sup> of 7 under the reaction conditions.



In an effort to discover the structural features necessary for the photoaromatization, a number of related bicyclooctadienes 8-10 were synthesized and investigated. The dimethyl derivative 8<sup>12</sup> was prepared by reaction of dimethylacetylene dicarboxylate with 1,2-dimethyl cyclooctatetraene.<sup>13</sup> Irradiation of 9 (0.014M, Et<sub>2</sub>O) for 8hr (254nm) produced dimethyl phthalate 2 (60%) and a complex mixture of volatile materials in low yield. However, the rate of fragmentation of 8 was slower than 1 under comparable conditions by at least a factor of two. Surprisingly the unsubstituted derivative 9 was stable to fragmentation under the conditions (254nm) and was recovered (>90%) after 10 hr. irradiation. Similarly, a simple structural change such as the saturation of cyclobutene ring to produce 10<sup>14</sup> renders the material stable to photoelimination and 10 is almost quantitatively recovered after 10 hr (254nm).<sup>15</sup> It should be noted that this fragmentation stability of 9 and 10 relative to 1 and 8 contrasts sharply with their thermal lability. For example, under the conditions used to quantitatively analyze 1 and 8 by glpc (170°), 9 and 10 were decomposed into dimethyl phthalate 2 to a significant extent.



It seems clear that the presence of the unsaturation of the cyclobutene ring is essential for photofragmentation to occur. At this point, it is not obvious whether this functions via the general weakening of the 1,2(5,6) carbon-carbon single bonds by virtue of their allylic nature or whether the involvement of the cyclobutene double bond in the electronic transition is an essential ingredient. In this respect, it should be noted that the ultraviolet spectrum of 1 shows an unusual long wavelength maximum at  $\lambda_{\text{max}}$  (Et<sub>2</sub>O) 246nm ( $\epsilon=2137$ ) which is absent in 9 and 10 (no maximum  $\lambda > 225\text{nm}$ ). This absorption is also present in the dimethyl derivative 8 but is still further red shifted to 260nm ( $\epsilon=1645$ ).

## REFERENCES

1. R. D. Miller and E. Hedaya, *J. Am. Chem. Soc.* 91, 5401 (1969).
2. For other photochemical precursors to cyclobutadiene see: G. Maier, *Angew. Chemie, Int. Ed.* 13, 425 (1974); O. L. Chapman, *Pure and Applied Chem.* 40, 511 (1974) and references cited therein.
3. W. A. Pryor, "Free Radicals," McGraw-Hill Book Co., New York, N.Y. 1966, p. 223.
4. J. Sauer, *Angew. Chem. Int. Ed.* 6, 16 (1967).
5. A. L. Watts, J. D. Fitzpatrick and R. Pettit, *J. Am. Chem. Soc.* 87, 3253 (1965); b. E. K. G. Schmidt, *Angew. Chemie, Int. Ed.* 12, 777 (1973); c. R. H. Grubbs, and R. A. Grey, *J. Am. Chem. Soc.* 95, 5765 (1973).
6. Predominately, a single isomer was isolated in each case. The stereochemistry of the adduct is not known with certainty but is assumed to have the methyl group trans to the ring juncture protons by analogy with the reaction of trans-piperylene with cyclic dienophiles; D. Craig, *J. Am. Chem. Soc.* 72, 1678 (1950).
7. S. F. Nelsen and J. P. Gillespe, *Tet. Lett.*, 5059 (1969).
8. Similar cycloadditions of substituted bicyclooctadienes have been reported: H. Prinzbach, W. Ebenbach and G. Philipposian, *Angew. Chem., Int. Ed.* 7, 887 (1968); R. S. Liu, *Tet. Lett.*, 1409 (1969). We have found the half-life for the cycloreversion of 7 to 1 at 16° to be 16 minutes in ether.
9. The irradiation source was a Rayonet reactor (RPR-100) from Southern New England Ultraviolet with 300nm lamps.
10. One particularly intriguing possibility for this increase could be a small activation energy for fragmentation which is surmounted by the short wavelength light.
11. At 254nm (-50°) the ratio of 7/1 initially increases with increasing irradiation time until it finally reaches a constant value of ca. 1:1.
12. Spectral data for 8 mp 65-66°;  $^1\text{H}_{\text{nmr}}$  (CCl<sub>4</sub>)  $\tau$  4.0(m, 2H), 6.36 (singlet superimposed on multiplet, 8H), 7.61 (m, 2H) and 8.53 (s, 6H).
13. A. C. Cope and H. G. Campbell, *J. Am. Chem. Soc.* 73, 3536 (1951).
14. A. C. Cope, A. C. Haven, Jr., T. L. Ramp and E. R. Trumbull, *J. Am. Chem. Soc.* 74, 4867 (1952).
15. At -50°, 10 is converted to the thermally unstable cycloadduct 11 which cleanly reverts to 10 upon standing: 11,  $^1\text{H}_{\text{nmr}}$  (CDCl<sub>3</sub>)  $\tau$  6.39(s, 6H) 7.2-8.5(complex multiplet, 10H);  $\tau_{1/2}^{18}$  (CDCl<sub>3</sub>)=51 min.