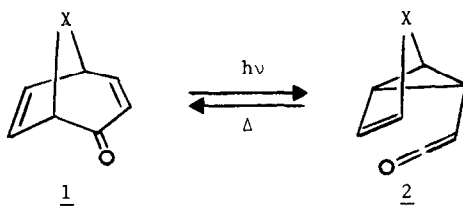


PHOTOCHEMISTRY OF BRIDGED CYCLOHEPTADIENONES  
 SUBSTITUENT EFFECT ON THE TRANSITION STATE OF INTRAMOLECULAR KETENE CYCLOADDITION

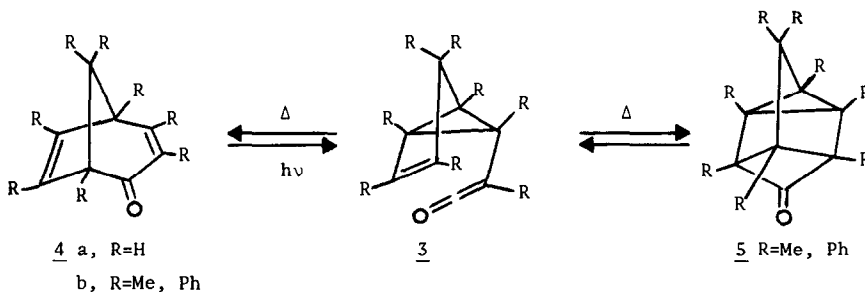
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The  $n, \pi^*$  singlet excited state photochemistry of bridged cycloheptadienones of general structure 1 involves a [3,3] sigmatropic ring opening to a homoconjugated bicyclic ketene 2, which has been directly observed by low-temperature infrared spectroscopy<sup>1</sup> These ketenes can be usually trapped by protonic nucleophiles to give the corresponding acid derivatives, or, in the absence of nucleophiles, undergo thermal recyclization to starting dienone and/or dimerization<sup>2</sup> Recently, it has been shown by Hart and Love<sup>3</sup> that highly substituted ketenes (3, R=Me, Ph) produced by the photolysis of bicyclo[3.2.1]octadienones (4b), being unreactive towards nucleophiles, substantially change the course of the thermal reaction, giving tetracyclic cyclobutanones 5 by a "normal"  $\pi_2 + \pi_2$  intramolecular cycloaddition<sup>4,5</sup>

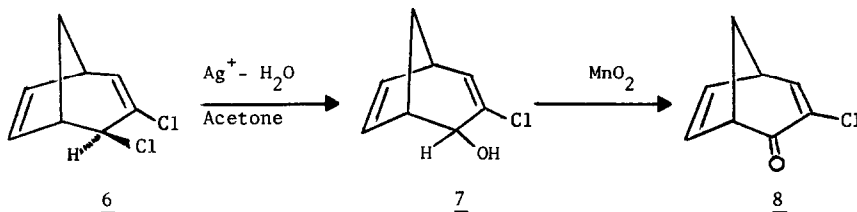


X- electron pair, CH<sub>2</sub>, CH=CH, o-C<sub>6</sub>H<sub>4</sub>, RO<sub>2</sub>CN-NCO<sub>2</sub>R

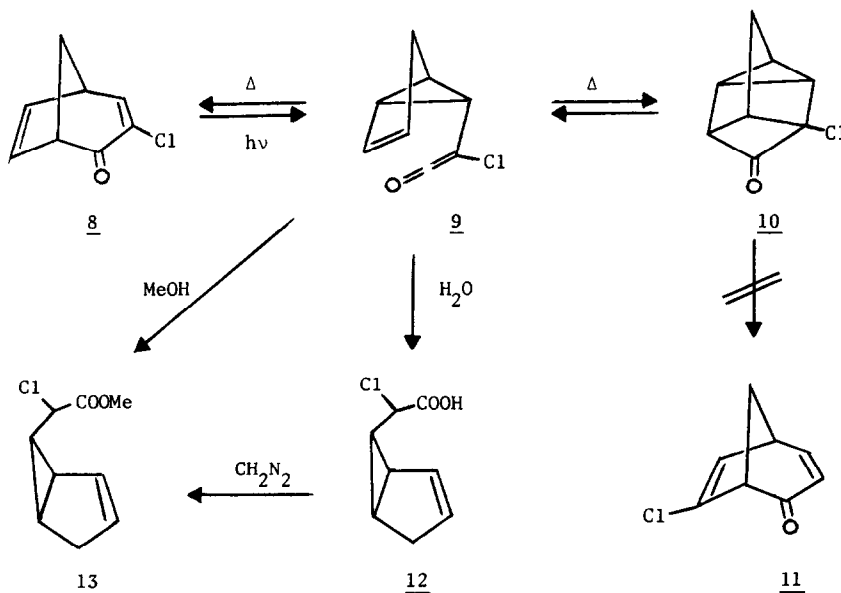


In this connection and in continuation of our earlier search for photochemical diversities of bridged cycloheptadienones,<sup>2b,6</sup> we wish to report a unique substituent effect on the reactivity of ketenes (3), which reflects the role of the ketene function in directing intramolecular cycloadditions

Thus, 3-chloro-bicyclo[3.2.1]octa-3,6-dien-2-one (8), [m p 44-45<sup>o</sup>;  $\nu_{\max}$  (chloroform) 1695  $\text{cm}^{-1}$ ,  $\lambda_{\max}$  (cyclohexane) 270 nm ( $\epsilon$  2300), 360 (90), nmr ( $\text{CDCl}_3$ )  $\delta$  2.52 (2H,m), 3.32 (1H,m) 3.56 (1H,m), 6.20 (1H,d,d,J=5.5, 3.0 Hz), 6.71 (1H,d,d,5.5,3.0), 7.41 (1H,d,7.0)] was synthesized by oxidation ("active  $\text{MnO}_2$ ")<sup>7</sup> of the mixture of chloroalcohols 7, obtained by the  $\text{Ag}^+$  promoted hydrolysis<sup>8</sup> of the readily accessible dichloride 6<sup>9</sup>



Irradiation of chloroketone 8 in ether (1% solution) using "3500Å" light,<sup>10</sup> gave a single photoproduct by glpc<sup>11</sup> which was assigned structure 10 based on its spectral data, ir ( $\text{CHCl}_3$ ) 1805  $\text{cm}^{-1}$  ( $\alpha$ -chlorocyclobutanone), nmr ( $\text{CDCl}_3$ ) shows no vinyl protons, three proton signals at  $\delta$  2.11, 2.32 and 2.82, and a complex four proton multiplet at  $\delta$  1.74. Chlorocyclobutanone 10 completely converts back to 8 on heating in chloroform (sealed tube) to 135<sup>o</sup> (ca 25hr), in perfect analogy to interconversion 5 $\leftrightarrow$ 3.<sup>3</sup> Interestingly, no isomeric chloroketone 11 has been detected.<sup>3</sup>



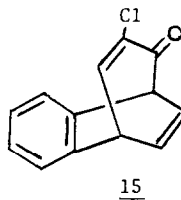
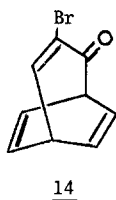
However, in sharp contrast to the behaviour of 3 (R=Me, Ph)<sup>3</sup>, irradiation <sup>10</sup> of 8 in moist ether solution afforded a mixture (ca 1:4 by nmr) of 10 and the hygroscopic chloroacid 12 [nmr (CDCl<sub>3</sub>) δ 1.62 (1H,m), 1.94 (1H,m), 2.52 (3H,m), 3.84 (d,J=11 Hz), 5.76 (2H,m)]<sup>12</sup>

Chloroacid 12 on reaction with diazomethane gave the corresponding methyl ester 13, indistinguishable from the ester obtained by photolysis of 8 in methanol solution

Clearly, the photolysis of 8 involves the formation of chloroketene 9 which, in comparable rates, can either react with nucleophiles or undergo intramolecular 2+2 cycloaddition

More remarkable, however, is the dramatic substituent effect on the direction of cyclization compared to the reaction of unsubstituted 3<sup>13</sup>. Apparently, α-chloro substitution of ketene (9) lowers the transition state energy for 2+2 cycloaddition compared with that for the competing [3,3] sigmatropic ring closure, thus leading to exclusive formation of the thermodynamically less stable 10. This enhancement in reactivity is in accord with the well known higher reactivity of α-haloketenes as compared with unsubstituted ketenes in cycloaddition reactions<sup>14</sup>

Finally, it should be noted that in addition to the substituent effect, geometrical factors play a critical role in directing the reaction. Preliminary studies of the phototransformations of 3-bromo-bicyclo[3.2.2]nonatriene (14)<sup>15</sup> and benzochloroketene 15<sup>16</sup> showed that they do not give cyclobutanones, but instead undergo rearrangements similar to that of the corresponding parent ketenes



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