

## Organic Photochemistry with 6.7 eV Photons: Tetracyclo[3.2.0.0<sup>2,7</sup>.0<sup>4,6</sup>]heptane (Quadricyclene)

Ra. Srinivasan,<sup>a</sup> Thomas Baum,<sup>a</sup> and Gary Epling<sup>b</sup>

<sup>a</sup> IBM Thomas J. Watson Research Center, Yorktown Heights, NY 10598, U.S.A.

<sup>b</sup> Chemistry Department, University of Connecticut, Storrs, CT 06208, U.S.A.

Irradiation of quadricyclene in solution leads to isomeric products in addition to bicyclo[2.2.1]hepta-2,5-diene, which reduces its usefulness in solar energy storage.

The reversible system shown in equation (1) has attracted considerable interest ever since its discovery in 1961.<sup>1,2</sup> Recent work has focused on the use of photosensitizers<sup>3,4</sup> and photolysis of charge-transfer complexes<sup>5</sup> of quadricyclene to bring about the reverse reaction and the application of this system for the storage of solar energy.

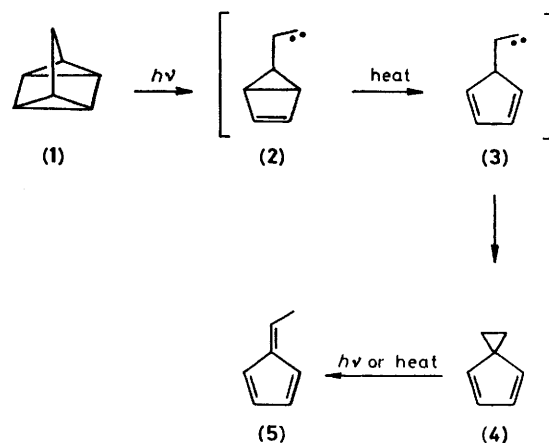
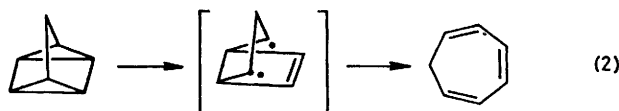
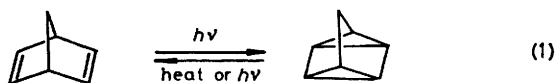
The photochemistry of quadricyclene (1) in its first absorption region has received scant attention. We report here that irradiation of quadricyclene with 185 nm light gives rise to novel products in addition to bicyclo[2.2.1]heptadiene.

The u.v. spectrum of quadricyclene shows moderately strong absorption commencing only at 230 nm. The extinction coefficient (in pentane as solvent) at 187 nm is *ca.* 1700 l mol<sup>-1</sup> cm<sup>-1</sup> which is similar to that of other alkyl-substituted cyclopropanes.<sup>6</sup> Irradiation of a 10<sup>-2</sup> M solution of quadricyclene (pentane) with 185 nm light<sup>7</sup> gave bicycloheptadiene (76%), cyclohepta-1,3,5-triene (12%), and a yellow isomeric product (10%). This last compound was identified as 6-methylfulvene (5) by a comparison of its spectral properties<sup>8,9</sup> and gas chromatographic retention times with those of an authentic sample.<sup>9</sup> The yields quoted are at low conversions (<1.5%) because the primary products absorbed the incident radiation strongly and were partially destroyed even at 15% conversion.

Cyclohepta-1,3,5-triene which was a primary product<sup>10</sup> is probably formed in a manner, equation (2), which resembles the thermal opening of the 3-oxa- and 3-aza-quadricyclene systems.<sup>11</sup> Such an opening of the carbocyclic system (*i.e.* quadricyclene itself) is unknown in its ground state.

Scheme 1 suggests a route to the formation of 6-methylfulvene. The initial 2-bond cleavage of a cyclopropane is well exemplified<sup>6,12</sup> and is the preferred mode of cleavage of alkylcyclopropanes at 185 nm. The intermediate (2) can thermally isomerize to (3).<sup>13</sup> The rearrangement of (3) to 6-methylfulvene may proceed in two steps, with (4) being a logical intermediate. The transformation of (4) to 6-methylfulvene (5) is known as being both a thermal<sup>9</sup> and a photochemical<sup>14</sup> reaction. A minor component of the reaction mixture was identified as (4) by comparison with an authentic sample.<sup>15</sup> Therefore, Scheme 1 is a reasonable route to 6-methylfulvene, the final step (4)→(5) probably being a photochemical step.

Two significant points emerge from this study. The first concerns the 2-bond cleavage of alkylcyclopropanes in the far-u.v. The present example is the first one in which a carbene



Scheme 1

intermediate can be proposed with great certainty since it has undergone an internal insertion reaction,<sup>16</sup> the product of which has been identified. The quantum yield for all of the products was 0.22.† Therefore, the 2-bond cleavage accounts for only about 0.02 of the absorbed photons. This is the lowest value that has been observed for the quantum yield of a 2-bond cleavage in a cyclopropane at 185 nm. It may be due to the reversibility of the initial opening of the molecule so that the starting material is regenerated. One other rigid, polycyclic cyclopropane, *viz.*, nortricyclene also shows extraordinary stability to 185 nm radiation,<sup>17</sup> probably for a similar reason.

A second point concerns the applicability of this system to solar energy storage. It is obvious that the formation of cyclohepta-1,3,5-triene and 6-methylfulvene detract from the reversibility of the system. Even at longer wavelengths (254 nm, direct irradiation or 300–320 nm, acetophenone as sensitizer) these side products are observable by g.c./mass spectrometry at yields of 5% (direct irradiation) to 0.1–0.5% (sensitization). This points to a need to re-examine the use of this system in solar energy storage.

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† This was based on a value of 0.35 for the quantum yield for the *cis*→*trans* isomerization of cyclo-octene under the same conditions.

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