

## Intramolecular Trapping of an Oxacarbene Intermediate in the Photochemical Ring Expansion of a Cyclopentanone

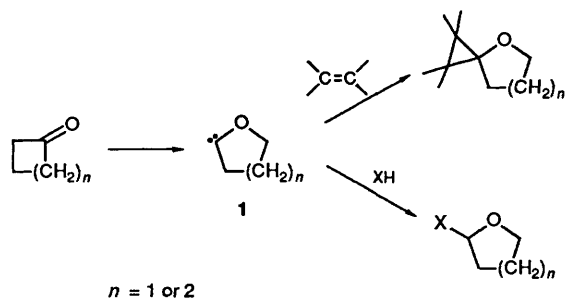
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Ultraviolet irradiation of *syn*-5-hydroxymethyl-4, *anti*-5-dimethyltricyclo[2.2.1.0<sup>2,6</sup>]heptan-3-one **4** in benzene or methanol gives the ring-expanded cyclic acetal **5** in high yield, establishing that the reaction proceeds *via* an oxacarbene intermediate.

Examples of the photochemical ring expansion of cyclopentanones to tetrahydropyran derivatives are rare,<sup>1</sup> while those of cyclobutanones to tetrahydrofuran derivatives are many.<sup>2</sup> Both types of reaction have found use in synthesis.<sup>3</sup>

Both processes have been postulated to involve the intermediacy of oxacarbenes of type **1** (Scheme 1). Two interpre-



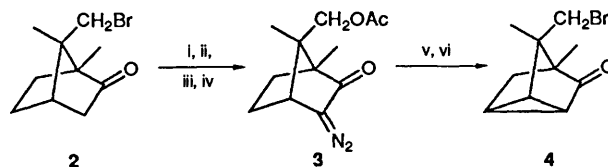
Scheme 1

tations of the difference between cyclobutanones and cyclopentanones have been proposed. First, that the reactions involve 'strained' systems and occur only with cyclopentanones that are unusually strained.<sup>4</sup> Second, that five- (or six-) membered cyclic ketones undergo the reaction only when substituents stabilize **1** and/or disfavour common competing reactions such as ketene and enal formation; *i.e.*, the reaction, which is normally unfavourable, occurs *faute de mieux*.<sup>1,5</sup>

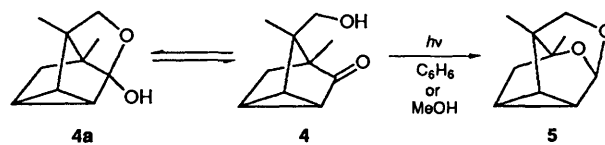
The latter interpretation requires that it be fully established that the reactions of four- and five-membered cyclic ketones follow the same chemical pathway. Plentiful evidence is available for the intermediacy of **1** in the cyclobutanone case from intermolecular<sup>2,6</sup> and intramolecular<sup>7</sup> trapping experiments and from spectroscopy.<sup>2b,4b</sup> In the cyclopentanone case intermolecular trapping evidence is scantier;<sup>1,3b</sup> a single instance of intramolecular trapping has been reported, but the primary product could not be isolated.\*<sup>8</sup> We report now the first example of intramolecular trapping of an oxacarbene from a cyclopentanone in which the primary product has been isolated.

As shown in Scheme 2, 8-bromocamphor **2**<sup>10</sup> was converted into the  $\alpha$ -diazo ketone **3**<sup>11</sup> and this in turn was converted<sup>12</sup> into the hydroxy ketone **4**; its <sup>13</sup>C NMR spectrum in C<sub>6</sub>D<sub>6</sub> showed signals attributable to both **4** and its tautomer **4a**. It was not expected that this tautomerization would affect the photochemistry since **4b** would not absorb radiation of the wavelength used.

Ultraviolet irradiation of **4** (0.5%) in benzene gave the intramolecular trapping product **5**. The efficiency of this



Scheme 2 Reagents: i, KOAc-HMPA; 140–150 °C; ii, SeO<sub>2</sub>-C<sub>6</sub>H<sub>5</sub>Br; 130 °C; iii, *p*-MeC<sub>6</sub>H<sub>4</sub>SO<sub>2</sub>NHNH<sub>2</sub>-HOAc; iv, basic Al<sub>2</sub>O<sub>3</sub>-CH<sub>2</sub>Cl<sub>2</sub>; v, AgBF<sub>4</sub>-THF; vi, K<sub>2</sub>CO<sub>3</sub>-H<sub>2</sub>O-THF



Scheme 3

trapping is demonstrated by the fact that irradiation of **4** in methanol gave only **5**, with no spectroscopic evidence for the formation of the intermolecular trapping product with methanol.

These results confirm that the photochemical ring expansion of cyclopentanones and cyclobutanones both proceed *via* oxacarbenes and, in combination with the evidence we have adduced previously,<sup>1</sup> that 'strain' is not the critical factor in the photochemical conversion of cyclic ketones into oxacarbenes. It appears more likely that a photophysical factor—the multiplicity of the excited state—accounts for the proclivity of cyclobutanones to undergo the reaction.<sup>2b,13</sup>

### Experimental

**Compound 4.**— $\nu_{\max}$ (KBr)/cm<sup>-1</sup> 3431 and 1747;  $\delta_{\text{H}}\dagger$ (CDCl<sub>3</sub>) 3.37 (d, *J* 10.5, 1 H), 3.4 (concentration dependent; br s, 1 H), 3.21 (d, *J* 10.5, 1 H), 2.0 (m, 1 H), 2.8 (m, 2 H), 1.57 (d, *J* 10.2, 1 H), 1.36 (t, *J* 5.3, 1 H), 0.90 (s, 3 H) and 0.69 (s, 3 H) (Found:  $M^+$ , 166.0991. C<sub>10</sub>H<sub>14</sub>O<sub>2</sub> requires  $M$ , 166.0993).

**Ultraviolet Irradiation of 4.**—A 0.5% solution of **4** in benzene was irradiated for 5 h with a Rayonet reactor equipped with 300 nm lamps to give the intramolecular trapping product **5**, C<sub>10</sub>H<sub>14</sub>O<sub>2</sub>, m.p. 93–94 °C, in 95% yield;  $\nu_{\max}$ /cm<sup>-1</sup> no OH or C=O stretching peaks;  $\delta_{\text{H}}\dagger$ (CDCl<sub>3</sub>) 5.10 (d, *J* 3.7, 1 H), 3.55 (d, *J* 8.8, 1 H), 3.45 (d, *J* 8.8, 1 H), 1.70 (dd, *J* 2.4, 11.9, 1 H), 1.50 (d, *J* 11.9, 1 H), 1.55–1.45 (m, 2 H), 1.20 (dd, *J* 5.4, 8.2, 1 H), 1.03 (s, 3 H) and 0.77 (s, 3 H);  $\delta_{\text{C}}\ddagger$ (CDCl<sub>3</sub>) 92.3 (o), 82.5 (e), 64.2 (e), 40.9

\* *Cf.*, also the observation of the formation, in an N<sub>2</sub> matrix at 20 K, of a cleavage product of an intermediate oxacarbene.<sup>9</sup>

† *J* Values are given in Hz.

‡ o (odd) and e (even) refer to the number of directly attached H's.

(e), 35.4 (e), 20.6 (o), 18.6 (o), 18.0 (o), 17.9 (o) and 15.6 (o) (Found: C, 71.95; H, 8.45.  $C_{10}H_{14}O_2$  requires C, 72.26; H, 8.49%).

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