

# Photochemistry of acetone in the presence of exocyclic olefins: an unexpected competition between the photo-Conia and Paternò–Büchi reactions

Wen-Sheng Chung\* and Chia-Chin Ho

Department of Applied Chemistry, National Chiao Tung University, Hsinchu, Taiwan 30050, ROC

**When irradiated in the presence of several exocyclic olefins, acetone undergoes homoalkylation with the olefins to form a series of 4-cycloalkylbutan-2-ones (with quantum yields of  $0.14 \pm 0.01$ ) rather than exhibiting the expected Paternò–Büchi reaction; in contrast, the photolysis of perdeuteriated acetone gave both types of products.**

Carbonyl group photochemistry has been covered in many excellent reviews and books over the last four decades.<sup>1</sup> It has long been known that when irradiated in the presence of olefins, aliphatic ketones undergo the Paternò–Büchi reaction,<sup>2</sup> Norrish type I or Type II reactions,<sup>2,3</sup> the former of which gives oxetane products, and the latter, pinacols, alcohols and hydrocarbon dimers. In some rare cases they may also lead to ene-reaction products.<sup>4</sup> Results other than those described above have been reported<sup>5</sup> but the reports have long been ignored.<sup>1</sup> For example, the photochemistry of acetone with norbornene was reported<sup>5a</sup> to proceed by chain addition of acetyl radicals to norbornene, a process analogous to the addition of cyclohexanone to oct-1-ene<sup>5b</sup> and to cyclohexene.<sup>5c</sup> The same outcome, when obtained thermochemically, is known as the Conia reaction.<sup>6</sup> Thus, we shall call the latter reactions photo-Conia reactions.

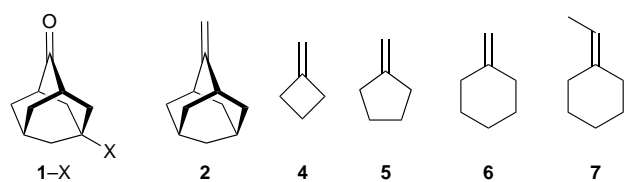
In the course of studying face selectivity in the photocycloaddition reaction of 5-substituted adamantane-2-ones **1**–**Xs**, we have used many different olefins with nitrile or alkoxy substituents and have found that they all give oxetane products in excellent yields.<sup>7</sup> It is of interest to know whether the photocycloaddition occurs when **1**–**X** is replaced with methyleneadamantane **2** and the olefin is replaced with a ketone (Scheme 1). It is also surprising to note that the photochemistry of ketones in the presence of exocyclic olefins has not been

systematically studied.<sup>1</sup> We report here the photochemistry of acetone **3a** with methyleneadamantane **2** and a series of exocyclic alkenes, *e.g.* methylenecyclobutane **4**, methylenecyclopentane **5**, methylenecyclohexane **6** and ethylidenecyclohexane **7**.

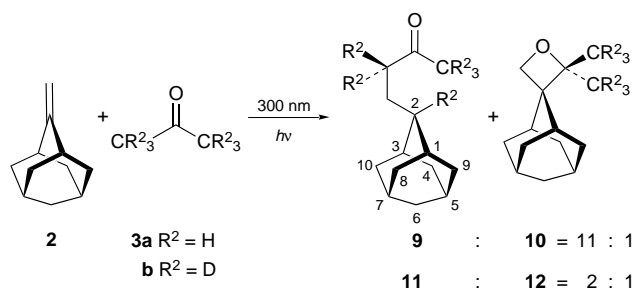
Irradiation at 300 nm of a degassed solution of 0.1 g of **2** in 20 ml spectrograde acetone **3a** at room temp. for 12 h leads to the formation of a novel photo-Conia<sup>6</sup> adduct **9** as a major product† (52% isolated yield), some oxetane **10** (5%), and many other minor reaction products (each less than 5% as determined by GC) (Scheme 2). The major product was first identified as a 1 : 1 adduct by GC–MS which indicated a molecular ion peak at *m/z* 206. If oxetane **10** were the major product, ring metathesis fragments<sup>3b,7</sup> would have been observed in the mass spectrum, *e.g.* *m/z* at 176 ( $M^+ - \text{HCOH}$ ) and 148 (**2**), however, the major peaks were observed at *m/z* 191 ( $M^+ - \text{Me}$ ), 188 ( $M^+ - \text{H}_2\text{O}$ ) and 163 ( $M^+ - \text{COMe}$ ). This observation along with information from <sup>1</sup>H and <sup>13</sup>C NMR spectra (*vide infra*) confirmed structure **9** as the major product.

It has been reported<sup>7,8</sup> that hydrogen on the carbon  $\alpha$  to the oxygen of an oxetane ring has a chemical shift of  $\delta$  4–5, whereas hydrogen on the  $\beta$ -carbon atom has a chemical shift of  $\delta$  2.5–3.6. The <sup>1</sup>H NMR spectrum of **9** had a triplet at  $\delta$  2.38 for hydrogens  $\alpha$  to carbonyl and a singlet at  $\delta$  2.12 for Me, which is incompatible with an oxetane structure. One expects to see only singlet oxetane ring protons no matter whether the oxetane is **8a** or **10**. The <sup>13</sup>C NMR and DEPT signals of the major product included 7 lines for adamantane and one methyl at  $\delta$  29.80, two methylene carbons at  $\delta$  26.57 and 42.04 due to the 3,4-carbons of adamant-4-ylbutan-2-one, and a quaternary carbon at  $\delta$  209.63 due to carbonyl carbon, which provide further evidence for the photo-Conia product **9**.

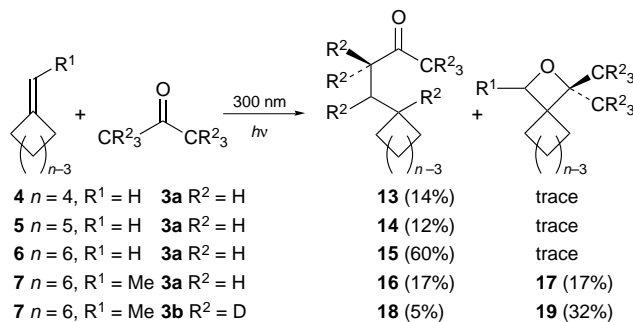
In order to determine the proton source on C-2 of product **9**, we also irradiated **2** in deuteriated [<sup>2</sup>H]acetone to oxetane **9/10** for comparison. The ratio of photo-Conia product to oxetane **9/10** was about 11 in acetone, but about 2 (**11** : **12**) in [<sup>2</sup>H<sub>6</sub>]acetone. Comparing the <sup>1</sup>H NMR spectra of **11** with **9**, three dramatic changes are observed: (i) the triplet at  $\delta$  2.38 for hydrogens  $\alpha$ -to carbonyl, (ii) the singlet at  $\delta$  2.12 for Me, and (iii) the multiplet at  $\delta$  1.55 for proton at C-2 had all disappeared. These deuteriated acetone **3b** results indicate that the proton at C-2 was abstracted from acetone. Note that oxetane **12** has now been isolated in good yield, but was only trace when acetone **3a** was used. The large deuterium isotope effect observed implies that



Scheme 1



Scheme 2



Scheme 3

a C–H bond cleavage was involved in the transition state of this novel photo-Conia reaction.

Note that the photo-Conia reaction of **2** occurs only in neat acetone and deuteriated acetone, but not in other organic solvents such as acetonitrile, benzene and cyclohexane. Compound **2** would also neither react photochemically in dilute acetone solutions ( $\leq 1 \text{ mol dm}^{-3}$  in organic solvents), nor would it react with acetone in the dark. In order to explore the scope of this photo-Conia reaction, we also photolysed **2** in acetophenone, benzophenone and butan-2-one for 24 h. No reaction was found in the aryl ketones. Although the photo reaction in butan-2-one revealed evidence of formation of some Conia-type products under GC–MS analysis, they were too complex to be isolated.

We then turned our attention to the variation of **2** into a series of exocyclic olefins **4–7**. The photolysis of methylenecyclobutane **4**, methylenecyclopentane **5** and methylenecyclohexane **6** in acetone gives photo-Conia products **13–15** as the only isolable products (Scheme 3).<sup>†</sup> Due to many possible secondary photochemical reactions, the yields from methylenecyclobutane **4** and methylenecyclopentane **5** are poor. Nevertheless, methylenecyclohexane **6** gave the homo-alkylation product **15** as the major product in 60% yield. The expected oxetane product from the Paternò–Büchi reaction was detected in trace by GC–MS but was not isolated. On the other hand, when a trisubstituted olefin such as **7** was photolysed in acetone, adducts **16** and **17** were obtained as a 1 : 1 mixture. The Paternò–Büchi reaction product **19** became dominant when **7** was photolysed in deuteriated acetone **3b**. The quantum yields for the photo-Conia reaction products of **2** and **6** in acetone (*i.e.*  $\Phi$  for **9** and **15**) were determined<sup>‡</sup> to be 0.15 and 0.13, respectively.

Kharasch<sup>5b,9</sup> suggested that in the reaction of aldehydes with terminal olefins to form ketones, it is the acyl radical  $[R(O)C\cdot]$  that attacks the olefin. Acetone<sup>5a</sup> or cyclohexanone<sup>5b,c</sup> undergoing Type I cleavage would not, however, explain the observed photo-Conia products. Our results may be explained as follows: the rate-determining step involves an  $\alpha$ -hydrogen abstraction of acetone by another excited acetone to give an  $\alpha$ -keto radical,<sup>5c</sup> which is then added further to a molecule of exocyclic olefin. In deuteriated acetone **3b**, the C–D bond cleavage step is hampered with respect to that of a C–H bond, thus the Paternò–Büchi reaction is comparable. Although the mechanism of this photo-Conia reaction is still unclear at present, it provides a novel and good-yield method for homoalkylation,<sup>11</sup> which has long been neglected in carbonyl photochemistry.

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### Footnotes

<sup>†</sup> Satisfactory spectral data were obtained for all products. *Selected data for 9*: colourless oil; <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>),  $\delta$  2.38 (2 H, t, *J* 8.7 Hz), 2.12

(3 H, s) and 1.85–1.44 (17 H, m); <sup>13</sup>C NMR (75.4 MHz, CDCl<sub>3</sub>),  $\delta$  209.63 (C=O), 43.96 (CH), 42.04 (CH<sub>2</sub>), 39.06 (CH<sub>2</sub>), 38.25 (CH<sub>2</sub>), 31.66 (CH), 31.43 (CH<sub>2</sub>), 29.80 (Me), 28.17 (CH), 27.93 (CH) and 26.57 (CH<sub>2</sub>); *m/z* 206 (M<sup>+</sup>, 2), 191 (5), 188 (24), 163 (20), 148 (100%), 106 (36) and 92 (52); (Found: M<sup>+</sup> 206.1674. C<sub>14</sub>H<sub>22</sub>O requires 206.1671). For **11**: colourless oil; <sup>1</sup>H NMR,  $\delta$  1.88–1.81 (6 H, m), 1.72–1.65 (8 H, m) and 1.52–1.48 (2 H, m); <sup>13</sup>C NMR,  $\delta$  210.04 (C=O), 43.95 (CD), 38.98 (CH<sub>2</sub>), 38.27 (CH<sub>2</sub>), 31.60 (CH), 31.45 (CH<sub>2</sub>), 31.33 (CH<sub>2</sub>), 28.18 (CH), 27.97 (CH) and 26.48 (CH<sub>2</sub>); *m/z* 212 (M<sup>+</sup>, 3), 194 (22), 192 (5), 166 (10), 148 (100%), 92 (48) and 80 (40); (Found: M<sup>+</sup> 212.2054. C<sub>14</sub>H<sub>16</sub>OD<sub>6</sub> requires 212.2047). For **12**: colourless oil; <sup>1</sup>H NMR,  $\delta$  4.19 (2 H, s), 2.30 (2 H, br s) and 1.82–1.60 (12 H, m); <sup>13</sup>C NMR,  $\delta$  87.87 (C<sub>q</sub>), 75.59 (CH<sub>2</sub>), 49.52 (C<sub>q</sub>), 37.07 (CH<sub>2</sub>), 34.65 (CH<sub>2</sub>), 34.35 (CH<sub>2</sub>), 32.07 (CH), 26.79 (CH) and 26.55 (CH); *m/z* 212 (M<sup>+</sup>, 31), 194 (100%), 182 (95), 148 (7), 135 (28) and 65 (36). For **15**: colourless oil; <sup>1</sup>H NMR,  $\delta$  2.44 (2 H, t, *J* 7.8 Hz), 2.14 (3 H, s), 1.71–1.63 (5 H, m), 1.50–1.43 (2 H, m), 1.26–1.15 (4 H, m) and 0.93–0.86 (2 H, m); <sup>13</sup>C NMR,  $\delta$  209.58 (C=O), 41.26 (CH<sub>2</sub>), 37.12 (CH), 32.99 (CH<sub>2</sub>), 31.10 (CH<sub>2</sub>), 29.73 (Me), 26.42 (CH<sub>2</sub>) and 26.13 (CH<sub>2</sub>); *m/z* 154 (M<sup>+</sup>, 15), 136 (11), 96 (77), 81 (65) and 55 (100%); (Found: M<sup>+</sup> 154.1361. C<sub>10</sub>H<sub>18</sub>O requires 154.1358).  
<sup>‡</sup> We used *trans*-stilbene as an actinometer when taking the quantum yield for its *trans* to *cis* isomerization as 0.32 at 300 nm light and measured the quantum yield for **9** and **15**. For the use of this actinometer see ref. 10.

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