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

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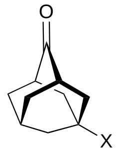
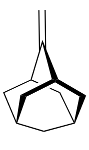
When irradiated in the presence of several exocyclic olefins, acetone undergoes homoalkylation with the olefins to form a series of 4-cycloalkylbutan-2-ones (with quantum yields of 0.14 ± 0.01) rather than exhibiting the expected Paternò–Büchi reaction; in contrast, the photolysis of perdeuteriated acetone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

Carbonyl group photochemistry has been covered in many excellent reviews and books over the last four decades.[1] It has long been known that when irradiated in the presence of olefins, aliphatic ketones undergo the Paternò–Büchi reaction,[2] Norrish type I or Type II reactions,[2,3] 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.[4] Results other than those described above have been reported[5] but the reports have long been ignored.[1] For example, the photochemistry of acetone with norbornene was reported[5a] to proceed by chain addition of acetonyl radicals to norbornene, a process analogous to the addition of cyclohexanone to oct-1-ene[5b] and to cyclohexene.[5c] The same outcome, when obtained thermochemically, is known as the Conia reaction.[6] Thus, we shall call the latter reactions photo-Conia reactions.

In the course of studying face selectivity in the photocycloaddition reaction of 5-substituted adamantan-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.[7] 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.[1] 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**.


1–X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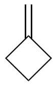
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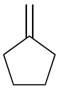
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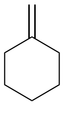
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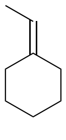
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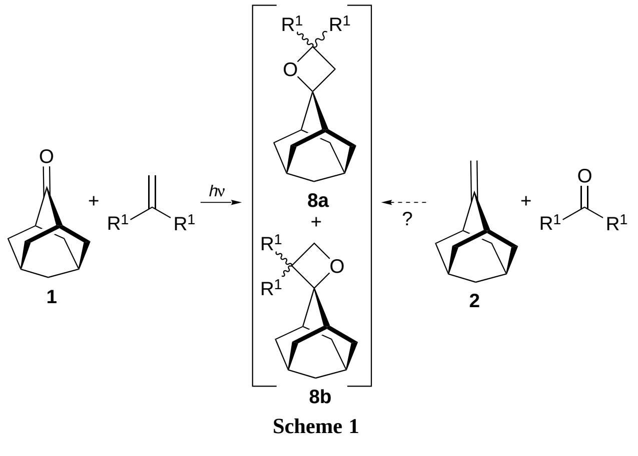
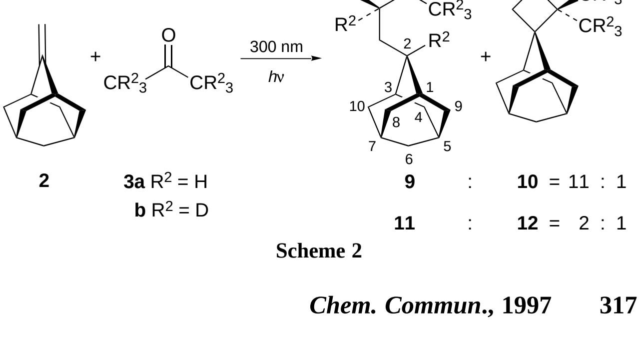


Scheme 1

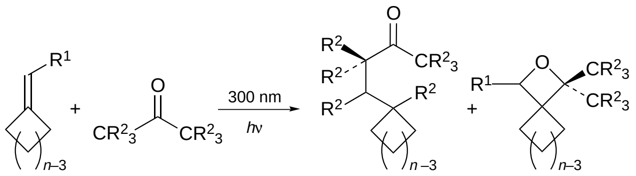
Irradiation at 300 nm of a degassed solution of 0.1 g of **2** in 20 ml spectrograde acetone **3a** at room temp. for 12 h leads to the formation of a novel photo-Conia[6] adduct **9** as a major product† (52% isolated yield), some oxetane **10** (5%), and many other minor reaction products (each less 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[3b,7] would have been observed in the mass spectrum, *e.g. m/z* at 176 ($M^+ - HCOH$) and 148 (**2**), however, the major peaks were observed at *m/z* 191 ($M^+ - Me$), 188 ($M^+ - H_2O$) and 163 ($M^+ - COMe$). This observation along with information from ^{1}H and ^{13}C NMR spectra (*vide infra*) confirmed structure **9** as the major product.

It has been reported[7,8] that hydrogen on the carbon α to the oxygen of an oxetane ring has a chemical shift of δ 4–5, whereas hydrogen on the β-carbon atom has a chemical shift of δ 2.5–3.6. The ^{1}H NMR spectrum of **9** had a triplet at δ 2.38 for hydrogens α to carbonyl and a singlet at δ 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 ^{13}C NMR and DEPT signals of the major product included 7 lines for adamantane and one methyl at δ 29.80, two methylene carbons at δ 26.57 and 42.04 due to the 3,4-carbons of adamant-4-ylbutan-2-one, and a quaternary carbon at δ 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 [^{2}H]acetone **3b** for comparison. The ratio of photo-Conia product to oxetane **9**/**10** was about 11 in acetone, but about 2 (**11** : **12**) in [$^2H_6$]acetone. Comparing the ^{1}H NMR spectra of **11** with **9**, three dramatic changes are observed: (i) the triplet at δ 2.38 for hydrogens α-to carbonyl, (ii) the singlet at δ 2.12 for Me, and (iii) the multiplet at δ 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 2



4 n = 4, R^1 = H	**3a** R^2 = H	**13** (14%)	trace
5 n = 5, R^1 = H	**3a** R^2 = H	**14** (12%)	trace
6 n = 6, R^1 = H	**3a** R^2 = H	**15** (60%)	trace
7 n = 6, R^1 = Me	**3a** R^2 = H	**16** (17%)	**17** (17%)
7 n = 6, R^1 = Me	**3b** R^2 = D	**18** (5%)	**19** (32%)

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 ($\leqslant$1 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).† 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.* Φ for **9** and **15**) were determined‡ to be 0.15 and 0.13, respectively.

Kharasch[5b,9] suggested that in the reaction of aldehydes with terminal olefins to form ketones, it is the acyl radical [R(O=)C$^\bullet$] that attacks the olefin. Acetone[5a] or cyclohexanone[5b,c] 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 α-hydrogen abstraction of acetone by another excited acetone to give an α-keto radical,[5c] 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 homo-alkylation,[11] which has long been neglected in carbonyl photochemistry.

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Footnotes

† Satisfactory spectral data were obtained for all products. *Selected data* for **9**: colourless oil; ^{1}H NMR (300 MHz, $CDCl_3$), δ 2.38 (2 H, t, *J* 8.7 Hz), 2.12 (3 H, s) and 1.85–1.44 (17 H, m); ^{13}C NMR (75.4 MHz, $CDCl_3$), δ 209.63 (C=O), 43.96 (CH), 42.04 (CH_2), 39.06 (CH_2), 38.25 (CH_2), 31.66 (CH), 31.43 (CH_2), 29.80 (Me), 28.17 (CH), 27.93 (CH) and 26.57 (CH_2); *m/z* 206 (M^+, 2), 191 (5), 188 (24), 163 (20), 148 (100%), 106 (36) and 92 (52); (Found: M^+ 206.1674. $C_{14}H_{22}O$ requires 206.1671). For **11**: colourless oil; ^{1}H NMR, δ 1.88–1.81 (6 H, m), 1.72–1.65 (8 H, m) and 1.52–1.48 (2 H, m); ^{13}C NMR, δ 210.04 (C=O), 43.95 (CD), 38.98 (CH_2), 38.27 (CH_2), 31.60 (CH), 31.45 (CH_2), 31.33 (CH_2), 28.18 (CH), 27.97 (CH) and 26.48 (CH_2); *m/z* 212 (M^+, 3), 194 (22), 192 (5), 166 (10), 148 (100%), 92 (48) and 80 (40); (Found: M^+ 212.2054. $C_{14}H_{16}OD_6$ requires 212.2047). For **12**: colourless oil, ^{1}H NMR, δ 4.19 (2 H, s), 2.30 (2 H, br s) and 1.82–1.60 (12 H, m); ^{13}C NMR, δ 87.87 (C_q), 75.59 (CH_2), 49.52 (C_q), 37.07 (CH_2), 34.65 (CH_2), 34.35 (CH_2), 32.07 (CH), 26.79 (CH) and 26.55 (CH); *m/z* 212 (M^+, 31), 194 (100%), 182 (95), 148 (7), 135 (28) and 65 (36). For **15**: colourless oil; ^{1}H NMR, δ 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); ^{13}C NMR, δ 209.58 (C=O), 41.26 (CH_2), 37.12 (CH), 32.99 (CH_2), 31.10 (CH_2), 29.73 (Me), 26.42 (CH_2) and 26.13 (CH_2); *m/z* 154 (M^+, 15), 136 (11), 96 (77), 81 (65) and 55 (100%); (Found: M^+ 154.1361. $C_{10}H_{18}O$ requires 154.1358).

‡ 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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