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 ± 0.01) rather than exhibiting the expected Paternò–Büchi reaction; in contrast, the photolysis of perdeuteriated acetone gave both types of products.

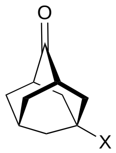
Carbonyl group photochemistry has been covered in many excellent reviews and books over the last four decades.[1] It has long been known that when irradiated in the presence of olefins, aliphatic ketones undergo the Paternò–Büchi reaction,[2] Norrish type I or Type II reactions,[2,3] the former of which 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**.

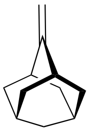
Irradiation at 300 nm of a degassed solution of 0.1 g of **2** in 20 ml spectrograde acetone **3a** at room temp. for 12 h leads to the formation of a novel photo-Conia[6] adduct **9** as a major product† (52% isolated yield), some oxetane **10** (5%), and many other minor reaction products (each less 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 ^1H 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 ^1H 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**.

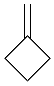
In order to determine the proton source on C-2 of product **9**, we also irradiated **2** in deuteriated [^2H]acetone **3b** for comparison. The ratio of photo-Conia product to oxetane **9**/**10** was about 11 in acetone, but about 2 (**11** : **12**) in [$^2H_6$]acetone. Comparing the ^1H NMR spectra 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



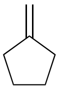
1–X



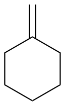
2



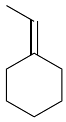
4



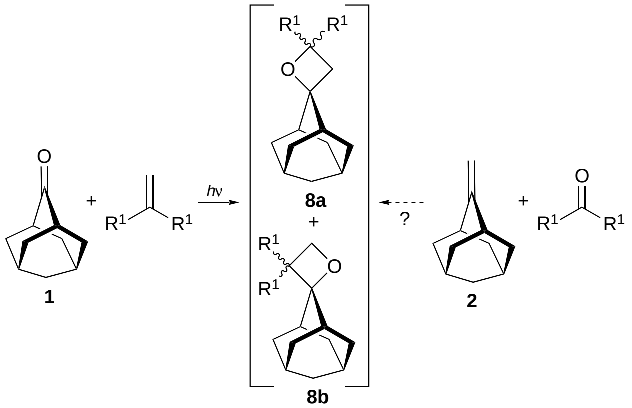
5



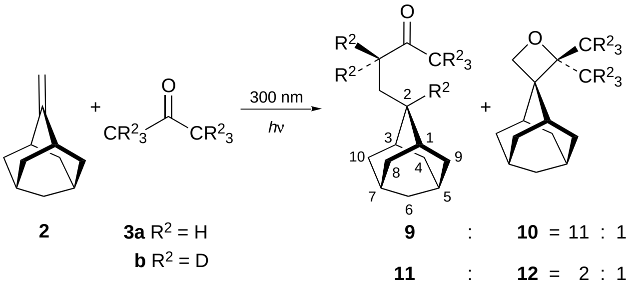
6



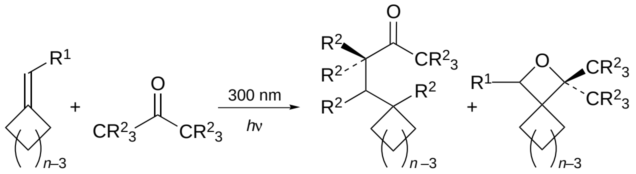
7



Scheme 1



Scheme 2



4 *n* = 4, R1 = H	**3a** R2 = H	**13** (14%)	trace
5 *n* = 5, R1 = H	**3a** R2 = H	**14** (12%)	trace
6 *n* = 6, R1 = H	**3a** R2 = H	**15** (60%)	trace
7 *n* = 6, R1 = Me	**3a** R2 = H	**16** (17%)	**17** (17%)
7 *n* = 6, R1 = Me	**3b** R2 = 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·] 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.

We thank the National Science Council of the Republic of China for its financial support (Grant No. NSC 84-2113-M-009-002).

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.

References

1 For reviews on the Paternò–Büchi reaction see: D. R. Arnold, *Adv. Photochem.*, 1968, **6**, 301; J. C. Dalton and N. J. Turro, *Ann. Rev. Phys. Chem.*, 1970, **21**, 499; N. J. Turro, J. C. Dalton, K. Dawes, G. Farrington, R. Hautala, D. Morton, M. Niemczyk and N. Schore, *Acc. Chem. Res.*, 1972, **5**, 92; N. J. Turro, *Modern Molecular Photochemistry*, Benjamin, Menlo Park, 1978, ch. 10 and 11; G. Jones, II, in *Organic Photochemistry*, ed. A. Padwa, Wiley, New York, 1981, vol. 5. pp. 1–122; S. W. Schreiber, *Science*, 1985, **227**, 858; H. A. J. Carless, in *Synthetic Organic Photochemistry*, ed. W. M. Horspool, Plenum, New York, 1984, pp. 425–487; M. Demuth and G. Mikhail, *Synthesis*, 1989, 145; A. G. Griesbeck, in *Organic Photochemistry and Photobiology*, ed. W. M. Horspool and P.-S. Song, CRC, New York, 1994, p. 522; p. 550.

2 L. Paternò and G. Chieffi, *Gazz. Chim. Ital.*, 1909, **39**, 341; G. Büchi, C. G. Inman and E. S. Lipinsky, *J. Am. Chem. Soc.*, 1954, **76**, 4327.

3 (*a*) R. G. W. Norrish and C. H. Bamford, *Nature*, 1936, **138**, 1016; (*b*) J. S. Bradshaw, *J. Org. Chem.*, 1966, **31**, 237; (*c*) W. M. Nau, F. L. Cozens and J. C. Scaiano, *J. Am. Chem. Soc.*, 1996, **118**, 2275.

4 E. H. Gold and D. Ginsburg, *Angew. Chem., Int. Ed. Eng.*, 1966, **5**, 246; To compare a thermal ene reaction see: F.-G. Klärner, B. M. J. Dogan, O. Ermer, W. v. E. Doering and M. P. Cohen, *Angew. Chem., Int. Ed. Eng.*, 1986, **25**, 108.

5 (*a*) W. Reusch, *J. Org. Chem.*, 1962, **27**, 1882; (*b*) M. S. Kharasch, J. Kuderna and W. Nudenberg, *J. Org. Chem.*, 1953, **18**, 1225; (*c*) P. de Mayo, J. B. Stothers and W. Templeton, *Can. J. Chem.*, 1961, **39**, 488.

6 For reviews on Conia reactions and ene reactions see: J. M. Conia and P. le Perchec, *Synthesis*, 1975, 1; W. Oppolzer and V. Snieckus, *Angew. Chem., Int. Ed. Eng.*, 1978, **17**, 476; B. B. Snider, *Acc. Chem. Res.*, 1980, **13**, 426.

7 W.-S. Chung, N. J. Turro, S. Srivastava, H. Li and W. J. le Noble, *J. Am. Chem. Soc.*, 1988, **110**, 7882; W.-S. Chung, N. J. Turro, S. Srivastava and W. J. le Noble, *J. Org. Chem.*, 1991, **56**, 5020; W.-S. Chung, N.-J. Wang, Y.-D. Liu, Y.-J. Leu and M. Y. Chiang, *J. Chem. Soc., Perkin Trans. 2*, 1995, 307; W.-S. Chung, Y.-D. Liu and N. J. Wang, *J. Chem. Soc. Perkin Trans. 2*, 1995, 581.

8 D. R. Arnold, R. L. Hinman and A. H. Glick, *Tetrahedron Lett.*, 1964, 1425.

9 M. S. Kharasch, W. H. Urry and B. M. Kuderna, *J. Org. Chem.*, 1949, **14**, 248.

10 T.-I. Ho, T.-M. Su and T.-C. Hwang, *J. Photochem. Photobiol. A. Chem.*, 1988, **41**, 293.

11 For other homoalkylation methods by metal oxides or organic peroxides see: Von A. Rieche, E. Schmitz and E. Gründemann, *Z. Chem.*, 1964, **4**, 177; E. I. Heiba and R. M. Dessau, *J. Am. Chem. Soc.*, 1971, **93**, 524; A. Citterio, F. Ferrario and S. Bernardinis, *J. Chem. Res.* (*S*), 1983, 310, see ref. 6.

Received, 31st October 1996; Com. 6/07415D