Intramolecular Cross-ring Enone–Alkene Photoannelation in 6-(ω-Alkenyl)-cyclohex-2-en-1-ones†

A. B. Lakshmi and Jampani Madhusudana Rao*

Indian Institute of Chemical Technology, Hyderabad 500 007, India

The irradiation of some 6-(ω-alkenyl)-cyclohex-2-en-1-ones in micelles gave a carbonyl bridged intramolecular photoadduct but the reaction is restricted to enones tethered to an alkene by not more than a four-carbon chain.

The generally accepted mechanism of enone–alkene photoannelation involves the formation of an exciplex[1] which collapses to a 1,4-diradical with the initial bond formation at the β-carbon atom of the enone.[2] In the intramolecular version[3] the rule of five[4] governs the regiochemistry whenever the two reaction C=C bonds are separated by not more than three carbon atoms as in non-conjugated dienes. Frostl and Margaretha[5] have found no preference for the rule of five in the intramolecular photoannelation of some alkylated cyclohex-2-en-1-ones having an allyl function at C-6. Becker *et al.*[6] in a recent study gave evidence for the intermediacy of a 1,4-diradical and noted that intramolecular photoannelation is limited to compounds in which the two reactive centres are separated by a chain of less than eight carbons.

This prompted us to study some 6-(ω-alkenyl)-cyclohex-2-en-1-ones with varying chain length separating the two C=C functions; the preliminary results are now reported. The reaction is expected to give tricyclic compounds with a carbonyl bridge, which can serve as precursors to novel carbocyclic systems with seven or more members.

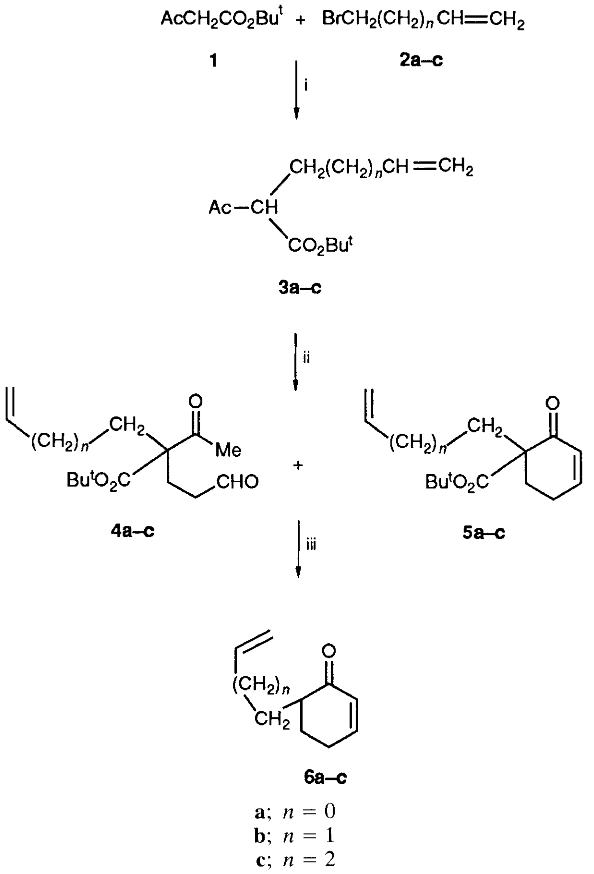
The enones **6a–c** were synthesised *via* the route shown in Scheme 1. The alkylation of t-butyl acetoacetate **1** with the 1-bromo-ω-alkene **2** to give **3** followed by Michael addition to acrolein under phase-transfer catalysis (PTC) conditions,[7,8] gave a product mixture containing predominantly **5** and some **4** which on distillation *in vacuo* in the presence of *p*-Me-$C_6H_4SO_3H$[9] gave the desired enone‡ **6**. The overall yields are in the range 36–40%.

Irradiation of the enone **6a** or **6b** (300 ml, 2.5 × 10^{-2} mol dm^{-3}) in cyclohexane with Pyrex-filtered light using a Hanovia 450 W Hg arc lamp under Ar purging showed the formation of a mixture of new compounds (GC analysis) but in sodium dodecyl sulphate (SDS) micelles one major product

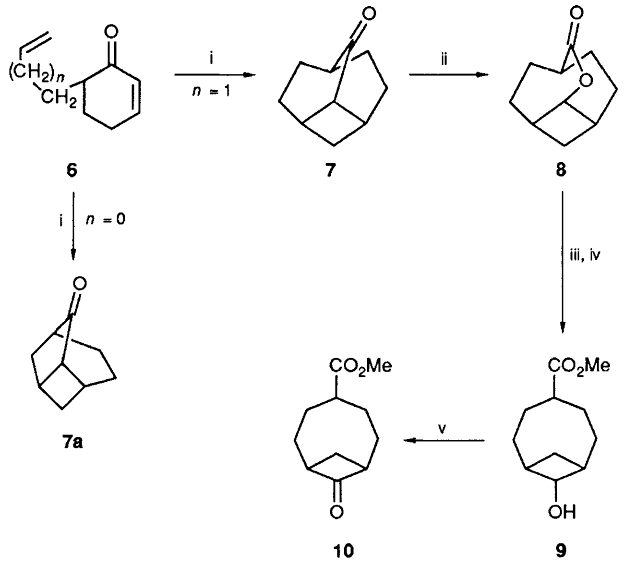
---

† IICT Communication No. 2571.

‡ All new compounds were characterised by spectral data which include exact or chemical ionisation mass spectral measurements.



Scheme 1 *Reagents and conditions*: i, NaOEt-EtOH; ii, CH_2=CHCHO, benzyltriethylammonium chloride, K_2CO_3, C_6H_6; iii, *p*-$MeC_6H_4SO_3H$, then 170 °C at 10 mmHg



Scheme 2 *Reagents and conditions*: i, *hv*, >280 nm, SDS micelle; ii, *m*-$ClC_6H_4CO_3H$; iii, KOH, MeOH; iv, CH_2N_2; v, PDC

was formed and isolated in 46–48% yield. The 6-pent-4-enyl derivative **6c** under similar conditions failed to undergo photochemical transformation and was recovered unchanged even after prolonged irradiation. The spectral data of the photoadducts did not provide clear-cut evidence in deciding the regiochemistry and hence the further transformations shown in Scheme 2 were studied. Enone **6b** gave a compound [m.p. 168–170 °C, IR ($CHCl_3$): ν_{CO} 1700 cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.85–3.0 (m, 2H), 2.45–2.6 (m, 2H), 2.2–2.35 (m, 4H), 1.9–2.2 (m, 1H), 1.5–1.65 (m, 5H)] which on Baeyer–Villiger oxidation gave a single lactone [m.p. 165–167 °C yield 73%; IR ($CHCl_3$) ν_{CO} 1705 cm^{-1}; ^1H NMR ($CDCl_3$) δ 4.96 (t, *J* 10 Hz, 1H), 3.28 (m, 1H), 2.9–3.0 (m, 2H), 1.6–2.3 (m, 10H)]. The triplet signal at δ 4.96 for the -CH-O proton in the lactone suggests that it is flanked by two methine groups and, therefore, the adduct was identified as **7b** which on oxidation gave **8**. The ^{13}C NMR spectrum of **8** gave six signals accounting for all saturated carbons at δ 75.7, 42.3, 35.3, 27.9, 25.5 and 20.5 (the carbonyl signal is masked by noise). The lactone **8** on hydrolysis followed by esterification gave compound **9** [m.p. 73 °C; yield: 72%; IR ($CHCl_3$) ν_{CO} 1710 cm^{-1}; ν_{OH} 3400 cm^{-1}] which on oxidation with pyridinium dichromate (PDC) furnished the cyclobutanone derivative **10** [colourless liquid, yield: 61%; IR ($CHCl_3$): ν_{max} 1775 and 1718 cm^{-1}, cyclobutanone and ester C=O].

The enone **6a** gave an adduct [m.p. 132 °C; IR ($CHCl_3$) ν_{CO} 1700 cm^{-1}; ^1H NMR ($CDCl_3$) δ unresolved m at *ca.* 2.85 (1H), *ca.* 2.72 (1H) and in the range 2.4–2.65 (3H), 1.8–2.1 (4H), and 1.4–1.7 (3H); ^{13}C NMR ($CDCl_3$ δ 219.5 (CO); CH, 51.4, 43.1, 39.6 and 34.5; CH_2, 34.8, 31.4, 29.9, and 18.5]. Baeyer–Villiger oxidation gave a mixture of two inseparable lactones. The ^1H NMR spectrum of the mixture gave a triplet and a multiplet for the -CH-O protons at δ 4.94 and 4.72 respectively. This suggests that the structure **7a** is most probable for the photoadduct formed from enone **6a**. Frostl and Margaretha[5] observed the formation of two regioisomers in the intramolecular photoannelation of alkylated 2-cyclohex-2-en-1-ones having an allyl function at C-6. Although we observed the formation of several products in hexane, in micellar media a single regioisomer was obtained both from **6a** and **6b** as revealed by GC analysis.

Dreiding models of enones **6a–c** in which all the ring carbon atoms except C-5 are in one plane[10] showed that the two reactive C=C bonds come in close proximity to each other when the alkenyl side chain is in an axial position. This is not the favoured conformation, particularly for a bulky substituent, and the failure of **6c** to undergo cross-ring photoannelation may be attributed to this. Also the two C=C bonds in enone **6c** are separated by a chain of five atoms and this requires the initial formation of a seven membered or larger ring. It is further possible that the excitation energy may be lost in *cis–trans*-isomerization of the double bond in the side chain. Also the reversible formation of an oxetane or collapse of the intermediate diradical to the starting material cannot be excluded. From literature[3,5] evidence and our own work it may be concluded that cross-ring photoannelation in 6-(ω-alkenyl)-cyclohex-2-en-1-ones occurs when the two reacting C=C bonds are separated by not more than four carbon atoms.

One of us (A. B. L.) thanks CSIR, New Delhi for a research fellowship.

Received, 8th November 1990; Com. 0/05023G

References

1 R. O. Loutfy and P. de Mayo, *J. Am. Chem. Soc.*, 1977, **99**, 3559; P. De Mayo, *Acc. Chem. Res.*, 1971, **4**, 41.
2 D. I. Schuster, M. M. Greenberg, I. M. Nunez and P. C. Tucker, *J. Org. Chem.*, 1983, **48**, 2615.
3 M. T. Crimmins, *Chem. Rev.*, 1988, **88**, 1453.
4 R. Srinivasan and K. H. Carlough, *J. Am. Chem. Soc.*, 1967, **89**, 4932; R. S. H. Liu and G. S. Hammond, *J. Am. Chem. Soc.*, 1967, **89**, 4936.
5 W. Frostl and P. M. Margaretha, *Helv. Chim. Acta*, 1976, **59**, 2244.
6 D. Becker, N. Haddad and Y. Sahali, *Tetrahedron Lett.*, 1989, **30**, 2661.
7 S. O. Lawesson, S. Gronwall and M. Andersson, *Ark. Kemi*, 1961, **17**, 457; *cf. Chem. Abstr.*, 1962, **57**, 2059.
8 S. O. Lawesson, E. A. Larsen and H. J. Jakobson, *Recl. Trav. Chim., Pay-Bas*, 1964, **83**, 464.
9 G. V. Kryshtal, V. V. Kulganek, V. F. Kucherov and L. A. Yanovskaya, *Synthesis*, 1979, 107.
10 S. A. Manley and J. K. Tyler, *Chem. Commun.*, 1970, 382.