Rearrangement of the intermediate 1,4-biradicals in photocycloaddition of cyclohex-2-enones to alkenes*

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Two unusual examples of enone/alkene photocycloaddition involving a rearrangement of the intermediate 1,4-biradical are presented. The first reaction proceeds *via* the addition of one of the radical centers to a carbonyl C atom and subsequent bond cleavage, *i.e.*, with rearrangement to a 1,3-biradical, while the second reaction involves abstraction of an H atom by one of the radical centers.

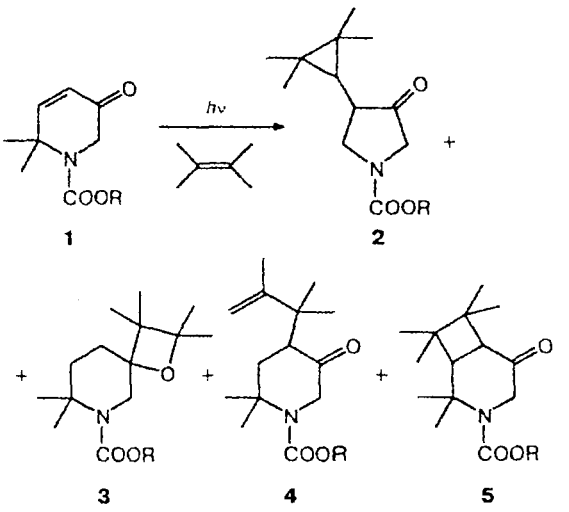
Key words: 1,4-biradicals, 1,3-biradicals, piperidine/pyrrolidine ring contraction, biradical/biradical rearrangement.

Triplet tetramethylene 1,4-biradicals are easily accessible upon the addition of an alkene (or an alkene fragment) to one of the C atoms of the C=C double bond in the triplet-excited cyclohex-2-enone.[1] The nonradiative intersystem crossing of the triplet biradical affords a singlet biradical, which either undergoes 1,4-cyclization to give cyclobutane or decomposes to give the starting compounds. The factors affecting the distribution between these two alternative reactions seem to be well understood.[2–4] Here we report on two unusual previously unknown rearrangements of these intermediates.

Photoaddition of 2,2-dimethyl-5-oxo-1,2,5,6-tetrahydropyridine-1-carboxylates (1) to 2,3-dimethylbut-2-ene

Irradiation ($\lambda > 340$ nm) of ethyl carbamate **1a** in benzene in the presence of excess 2,3-dimethylbut-2-ene unexpectedly afforded cyclopropylpyrrolidine **2a** (50%) as the main product,[5] in addition to oxetane **3a** (25%) and a mixture (1 : 1) of the expected[6] photoaddition (**4a**) and photocycloaddition (**5a**) products (25%) (Scheme 1). Methyl carbamate **1b** reacts in a similar way, giving a ring contraction product, pyrrolidine **2b** (30%), together with oxetane **3b** (28%) and a mixture of compounds **4b** and **5b** (42%) (GLC data). The structures of the products were confirmed by GLC/MS analysis and ^{1}H NMR spectroscopy. Indeed, the cyclopropane ring proton in **2b** resonates at 0.16 ppm (d, J = 10.7 Hz), and the olefinic protons in oxetane **3b** are manifested at 6.62 and 6.00 ppm (both d, J = 10.2 Hz).

Scheme 1



R = Et (**a**), Me (**b**)

We suggested[5] that the COOR group at the ring N atom increases the steric hindrance to 1,4-cyclization of biradical **6** due to the presence of two vicinal methyl groups. Therefore, **6** rearranges *via* biradical **7** to give biradical **8** and the latter cyclizes to cyclopropane **2** (Scheme 2). In our opinion, this mechanism is supported by the fact that the proportion of product **2** decreases when the ethoxycarbonyl group at the ring N atom is replaced by a smaller methoxycarbonyl group.

Photoisomerization of 3-(3,3-dimethylbut-1-ynyl)-4-(pent-4-enyl)cyclohex-2-enone (9)

Irradiation ($\lambda > 340$ nm) of cylohex-2-enone **9** gives at low degrees of conversion (<40%) two isomeric satu-

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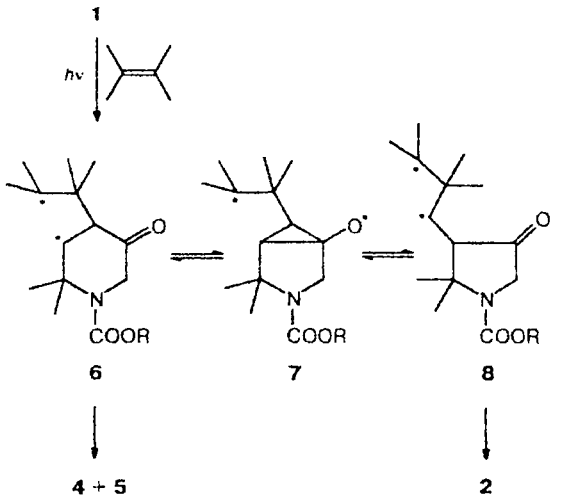
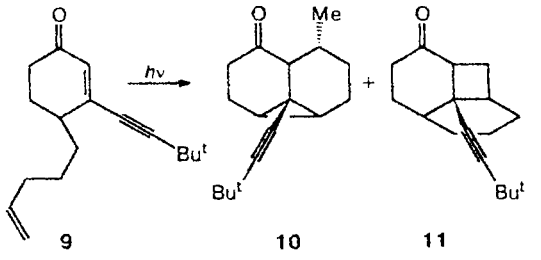
Scheme 2



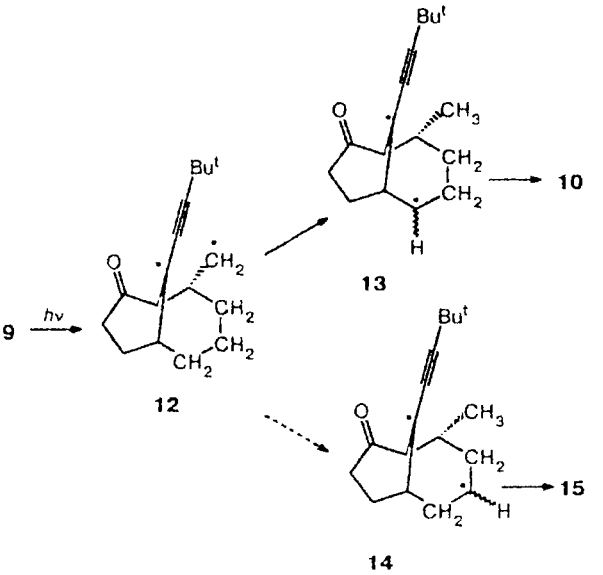
rated ketones **10** and **11**, containing intact C≡C triple bonds,[7,8] in 2.5 : 1 ratio (Scheme 3). On subsequent irradiation at the same wavelength, product **10** undergoes photodecomposition. The minor product **11** results from intramolecular [2+2]-cycloaddition, in which the terminal CH_2 group of the alkene fragment has added to the C(2) atom of the enone.[9] In the ^1H and ^{13}C NMR spectra of compound **10** (in CD_3CN), the signals of the formed methyl group (δ 1.15, d, J = 7 Hz (^1H NMR) and δ 21.8 (^{13}C NMR)) immediately attract attention. The $^1H,^{13}C$ COSY spectrum allows assignment of four CH and four CH_2 groups; however, the $^1H,^1H$ COSY spectrum cannot be fully interpreted due to the partial overlap of the proton signals in the ^1H NMR spectrum. Nevertheless, it is evident that the CH group adjacent to the methyl group is bound to the CH group that is vicinal to the carbonyl C atom.

Scheme 3



The spectroscopic features mentioned above do not allow unambiguous assignment of the structure of **10**. However, it is evident that **10** is formed from biradical **12**, which isomerizes to a new biradical upon hydrogen abstraction by the primary radical center. It is well known that in flexible chains, hydrogen abstraction *via* a six-membered transition state (formation of biradical **13**) occurs faster than that *via* a five-membered transition state (formation of biradical **14**); therefore, in our opinion, the pathway leading to a cyclopropane ring closure (product **10**) is preferred over the alternative pathway that would afford tricyclo[7.1.1.$0^{5,9}$]undecan-4-one (**15**) (Scheme 4).

Scheme 4



Experimental

Photolysis was performed in a Rayonet RPR-100 photoreactor equipped with a 350-nm lamp using an additional light filter (λ < 340 nm). Analytical GLC was carried out on a 30-m long capillary column with SE-30 as the stationary phase. UV spectra were recorded on a Perkin Elmer Lambda 20 spectrophotometer. NMR spectra were run on a Bruker DRX-500 spectrometer (500 MHz for ^1H and 100.62 MHz for ^{13}C) in $CDCl_3$; chemical shifts were referred to internal tetramethylsilane. The positions of signals, whose multiplicity is not given, were derived from analysis of $^1H,^1H$ and $^1H,^{13}C$ COSY spectra.

Methyl 2,2-dimethyl-5-oxo-1,2,5,6-tetrahydropyridine-1-carboxylate (1b) was synthesized from methyl 2-[*N*-(1,1-dimethyl-2-oxopropyl)amino]ethanoate as reported previously[5] for **1a** (four steps; overall yield 12%), m.p. 45 °C. UV (C_6H_{12}), λ/nm (log ε): 340 (1.821) and 242 (3.643). ^1H NMR, δ: 1.64 (s, 6 H, CH_3), 3.73 (s, 3 H, OCH_3), 4.10 (s, 2 H, CH_2), 6.63 and 6.01 (AB system, 2 H, J = 10.7 Hz). ^{13}C NMR ($CDCl_3$), δ: 24.0 (q, CH_3), 49.0 (t, CH_2), 52.0 (q, CH_3O), 55.0 (s, C-Me_2), 122.0 (s, α-C=), 156.0 (s, COO), 157.0 (s, β-C=), 192.0 (s, CO).

3-(3,3-Dimethylbut-1-ynyl)-4-(pent-4-enyl)cyclohex-2-enone (9). 3-Methoxycyclohex-2-enone (12.6 g, 0.1 mol) was first converted into 3-methoxy-6-(pent-4-enyl)cyclohex-2-enone by low-temperature alkylation with 5-iodopent-1-ene

in the presence of LDA/HMPA. Then the product was treated with 3,3-dimethylbut-1-ynylmagnesium bromide followed by acidification and purification by chromatography (SiO_2, hexane—EtOAc, 2 : 1) to give compound **9** (in 31% yield over 2 steps) as a colorless oil, R_f = 0.70. UV (C_6H_{12}), λ/nm (log ε): 340 (1.863). ^{1}H NMR, δ: 6.10 (d, 1 H, CH=, J = 1.5 Hz). ^{13}C NMR ($CDCl_3$), δ: 26.0 (t, CH_2), 27.0 (t, CH_2), 28.0 (s, CMe_3), 30.0 (q, CH_3), 32.0 (t, CH_2), 34.0 (t, CH_2), 35.0 (t, CH_2), 39.0 (d, ring C(4)), 78.0 (s, C(1)≡), 111.0 (s, C(2)≡), 115.0 (t, side-chain C(5)), 132.0 (d, side-chain C(4)), 138.0 (d, ring C(2)), 149.0 (s, ring C(3)), 199.0 (s, CO).

Irradiation of compound 1b. An argon-degassed solution of **1b** (18.3 mg, 0.1 mmol) and 2,3-dimethylbut-2-ene (168 mg, 2 mmol) in 5 mL of benzene was irradiated for 2 h. The products were analyzed by GLC, GLC/MS, and ^{1}H NMR.

Irradiation of compound 9. An argon-degassed solution of **9** (244 mg, 1 mmol) in 10 mL of benzene was irradiated for 1 h to give a mixture of compounds **9** (65%), **10** (25%), and **11** (10%). Chromatography (SiO_2, hexane—EtOAc, 2:1) gave compound **9** and then the mixture of **10** and **11** (R_f 0.40). This second fraction was separated either by flash chromatography or by spinning-disk chromatography (hexane—EtOAc, 20 : 1, as the eluent). This gave 25 mg of 10-*exo*-(3,3-dimethylbut-1-ynyl)-6-*endo*-methyltricyclo[7.1.0.0^{5,10}]decan-4-one (**10**) as a colorless oil and 9 mg of 10-(3,3-dimethylbut-1-ynyl)tricyclo[7.1.1.0^{5,10}]undecan-2-one (**11**).

Compound **10**. ^{1}H NMR (CD_3CN), δ: 1.15 (d, 3 H, CH_3, J = 7 Hz), 1.20 (s, 9 H, Bu^t), 1.64 (HCH), 1.75 (HCH), 1.89 (HCH), 1.93 (CH), 1.95 (HCH), 1.97 (HCH), 2.07 (HCH), 2.15 (1 H, HCH), 2.26 (1 H, CH), 2.31 (1 H, CH), 2.42 (1 H, CH), 2.56 (1 H, HCH). ^{13}C NMR (CD_3CN), δ: 21.0 (q, CH_3), 24.0 (t, CH_2), 27.0 (s, CMe_3), 29.0 (t, CH_2), 30.0 (t, CH_2), 31.0 (q, CH_3), 34.0 (t, CH_2), 35.0 (d, CH), 42.0 (s, CC≡), 43.0 (d, CH), 54.0 (d, CH), 56.0 (d, CH), 85.0 (s, C(1)≡), 90.0 (s, C(2)≡), 211.0 (s, CO).

Compound **11**. ^{1}H NMR (C_6D_6), δ: 1.19 (s, 9 H, Bu^t), 1.35—1.20 (m, 5 H), 1.46 (m, 1 H), 1.57 (m, 1 H), 1.93 (2 H), 2.05 (1 H, HCH), 2.37 (1 H, HCH), 2.75 (1 H, HCH), 3.06 (dd, H(1), J = 9, 10 Hz). ^{13}C NMR (C_6D_6), δ: 15.0 (t, CH_2), 24.0 (t, CH_2), 25.0 (t, CH_2), 25.5 (t, CH_2), 26.0 (s, CMe_3), 27.0 (t, CH_2), 30.0 (q, CH_3), 35.0 (s, CC≡), 36.0 (d, CH), 37.0 (t, CH_2), 38.0 (d, CH), 48.0 (d, CH), 85.0 (s, C(1)≡), 88.0 (s, C(2)≡), 207.0 (s, CO).

References

1. M. T. Crimmins and T. L. Reinhold, *Org. React.*, 1993, **44**, 297.
2. J. C. Scaiano, E. A. Lissi, and M. V. Encina, *Rev. Chem. Intermed.*, 1978, **2**, 139.
3. R. Marshall Wilson, *Org. Photochem.*, 1985, **7**, 339.
4. R. A. Caldwell, D. C. Hrncir, T. Muñoz, Jr., and D. J. Unett, *J. Am. Chem. Soc.*, 1996, **118**, 8741.
5. C. Jeandon, R. Constien, V. Sinnwell, and P. Margaretha, *Helv. Chim. Acta*, 1998, **81**, 303.
6. G. Cruciani, C. Semisch, and P. Margaretha, *J. Photochem. Photobiol., A (Chem.)*, 1988, **44**, 219.
7. W. C. Agosta and P. Margaretha, *Acc. Chem. Res.*, 1996, **29**, 179.
8. B. Kisilowski, W. C. Agosta, and P. Margaretha, *J. Chem. Soc., Chem. Commun.*, 1996, 2065.
9. S. Andresen, B. Kisilowski, and P. Margaretha, *J. Inf. Recording*, 1996, **23**, 13.

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