Photochemical Formation and Dimerization of a 2,3-Cycloheptadien-1-one

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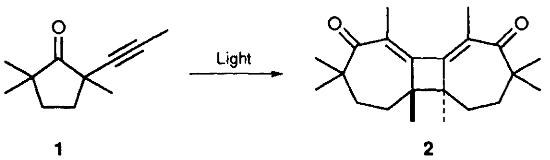
Irradiation of 2-(1-propynyl)-2,5,5-trimethylcyclopentanone **1** leads to the isomeric allenic cycloheptadienone **4**, which dimerizes spontaneously at the β,γ double bond to yield the *trans* head-to-head dimer **2**.

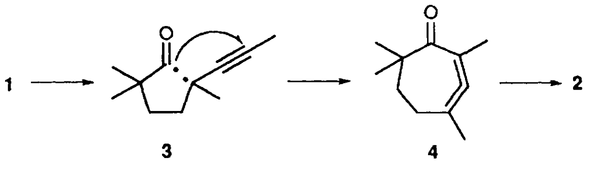
Irradiation ($\lambda > 280$ nm) of an argon-degassed 0.15 mol dm^{-3} solution of 2-(prop-1-ynyl)-2,5,5-trimethylcyclopentanone **1** in pentane furnishes a highly crystalline compound (m.p. 175–176 °C, 40% yield) not formed from this ketone on irradiation in more dilute solution.[1] The molecular mass [MS m/z 328.2375 (M^+)] of this new compound and its ^{1}H and ^{13}C NMR spectra, which contain only half the expected number of signals, indicate that it is a symmetrical dimer of **1**. Its NMR, IR, and UV spectra† and its probable origin, which is discussed below, suggested structure **2**, apart from stereochemistry. X-Ray crystallographic analysis (Fig. 1) has confirmed this structure and stereochemistry for **2**.‡ According to molecular mechanics calculations,[2] **2** is *ca.* 18 kcal mol^{-1} (1 cal = 4.184 J) more stable than the unobserved *cis* isomer of the dimer.

The simplest pathway to **2** is α-cleavage of **1** to **3** followed by closure to cycloheptadienone **4**, which then dimerizes. Although there is no direct evidence to disprove concerted rearrangement of **1** to **4**, previously observed photoproducts



1 **2**

Scheme 1



3 **4**

Scheme 2

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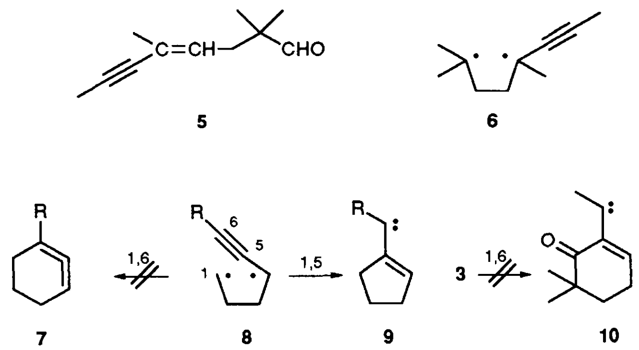
† IR: KBr, 1671 cm^{-1}; UV: λ_{max} (pentane) 281 nm (ε 7706), 288 (8676); ^{1}H NMR: CDCl$_3$, (300 MHz) δ 1.150 (s, 3 H), 1.159 (s, 3 H), 1.196 (s, 3 H), 1.290 (ddd, J 2.4, 6.0, 14.1 Hz, 1 H), 1.600 (ddd, J 6.0, 7.5, 14.5 Hz, 1 H), 1.810 (m, 1 H), 1.869 (s, 3 H), 2.233 (m, 1 H); ^{13}C NMR δ 19.672 (q), 22.450 (q), 25.144 (q), 26.206 (q), 28.231 (t), 36.073 (t), 47.611 (s), 49.724 (s), 131.049 (s), 144.336 (s), 212.413 (s).

‡ *Crystal data*: monoclinic, $P2_1/n$, a = 11.782(1), b = 16.575(1), c = 10.378(1) Å, β = 105.86(1)°, Z = 4, Cu-Kα radiation. One of the 7-membered rings is disordered. R = 0.057, R_w = 0.080. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.



Scheme 3

from **1** require formation of **3** followed either by hydrogen transfer to *E*- and *Z*-**5** or by decarbonylation to biradical **6**, which then undergoes further reactions.[1] It is likely then that formation of **4** simply implies that **3** also closes on the triple bond in an overall 1,3-shift. There is precedent for this process in β,γ acetylenic ketones.[3] Thermal $[_{\pi}2_s + _{\pi}2_a]$ head-to-head dimerization of **4** at the β,γ double bond then furnishes **2**. There is precedent for this head-to-head dimerization of an allene in the spontaneous self-addition of 1,2-cycloheptadiene to yield only the parent tricyclic diene analogous to **2**.[4] Dimerization of **4** specifically at the β,γ double bond is noteworthy, as we know of no previous example of the dimerization of a conjugated allenic ketone.

These observations are good evidence for the formation and mode of dimerization of a 2,3-cycloheptadien-1-one. The 1,7 closure of **3** is significant, because alkyl propynyl 1,4-biradicals, as **8**, close in a different fashion. These 1,4 biradicals cyclize 1,5 to vinyl carbenes,[5] as is shown formally in the conversion of **8** to **9**. Competitive 1, 6 cyclization to **7** is not observed, although 1,2-cyclohexadienes are capable of existence.[6] In contrast to the behaviour of **8**, **3** affords no products that require its 1,6 cyclization to the acyl-substituted vinyl carbene **10**. The mechanistic basis of this difference in the behaviour of **3** and **8** is not yet certain, but a reasonable possibility is a difference in spin state of the cyclizing biradicals.

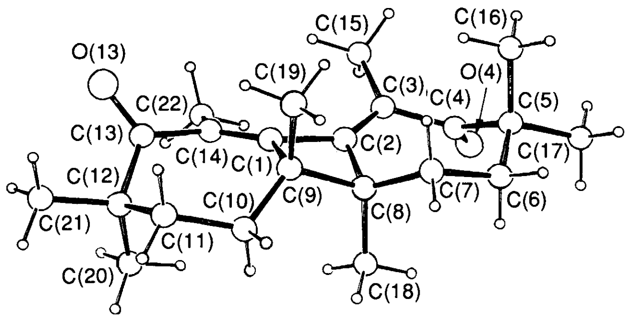


Fig. 1 ORTEP drawing of major (85%) conformation of **2** determined by X-ray crystallography. The minor conformation differs in the conformation at C(10) and C(11).

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