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Photoaddition of 2-(3,3-dimethylbut-1-ynyl)-cyclopent-2-enone to 2,3-dimethylbut-2-ene

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Abstract

Irradiation (350 nm) of the newly synthesized cyclopent-2-enone **6** in the presence of 2,3-dimethylbut-2-ene under standard conditions (10^{-1} M **6** and 10-fold molar excess alkene in benzene) affords a 1 : 1 : 5 mixture of **7**, **8** and **9**. The main product **9** is the head-to-tail (HT) *cis–transoid–cis* cyclodimer of **6** as established by X-ray analysis, its formation becoming negligible only at much higher dilution (10^{-3} M **6** and 50-fold molar excess alkene). Compounds **7** and **8** are [enone + alkene] adducts; the latter one isomerizes to **10** on attempted gas chromatographic separation. © 1999 Elsevier Science S.A. All rights reserved.

Keywords: 2-Alkynylcyclopent-2-enone; Cyclopentenone photodimerization; α-Cleavage; [3,3] Sigmatropic rearrangement

1. Introduction

Irradiation of 2-(3,3-dimethylbut-1-ynyl)-cyclohex-2-enone (**1a**) or 5,5-dimethyl-6-oxocyclohex-1-ene-1-carbonitrile (**1b**) in the presence of 2,3-dimethylbut-2-ene affords a tricyclic furan **2a** [1,2] or 1,2-oxazole **2b** [3,4], respectively. These reactions proceed via addition of the alkene to the unsubstituted olefinic C atom of the triplet excited enone, followed by 1,5-cyclization of the triplet biradical [5], and finally electrocyclic ring closure of the β-acylvinylcarbene or nitrene. In contrast, 4,4-dimethyl-5-oxocyclopent-1-ene-1-carbonitrile (**3**) under the same conditions reacts not to yield a tricyclic isoxazole [4] but to give a 2 : 1 mixture of bicycloheptanone **4** and alkenylcyclopentanone **5** (Scheme 1). Here we report on the photochemical behaviour of the newly synthesized title compound **6** in the presence of the same alkene.

2. Results

2-(3,3-Dimethylbut-1-ynyl)-cyclopent-2-enone (**6**) was obtained in 80% yield from 2-iodocyclopent-2-enone and 3,3-dimethylbut-1-yne via Sonogashira coupling according to [6]. Irradiation (350 nm) of a 10^{-1} M solution of **6** in benzene in the presence of a 10-fold molar excess of 2,3-dimethylbut-2-ene affords a 1 : 1 : 5 mixture (GC, increasing retention times) of **7**, **8** and **9**. From GC/MS-analysis it becomes evident that the two minor products (**7** and **8**) are [enone + alkene] adducts, while the main product is a dimer of **6**. Indeed, **9** is formed selectively on irradiation of **6** in the absence of alkene, the assignment of the head-to-tail (HT) *cis–anti–cis* structure stemming from X-ray analysis. Irradiation of a 2×10^{-3} M solution of **6** in the presence of a 50-fold molar excess of alkene affords a 4 : 4 : 1 mixture of the same products, from which **7** and **8** can be isolated by chromatography. On attempted preparative gas chromatographic isolation, adduct **8** undergoes quantitative (thermal) isomerization to **10** (Scheme 2). The assignment of the structures of these products comes from their ^{1}H NMR-, ^{13}C NMR- and mass spectra.

3. Discussion

In contrast to 2-cyclohexenones **1a** and **1b** which exhibit very similar photoreactivity patterns towards alkenes in general and 2,3-dimethylbut-2-ene in particular, cyclopentenones **6** and **3** differ in various aspects. First, there is the unprecedented ease of photodimerization of **6** to **9**, even in the presence of excess alkene. Triplet excited cyclopent-2-

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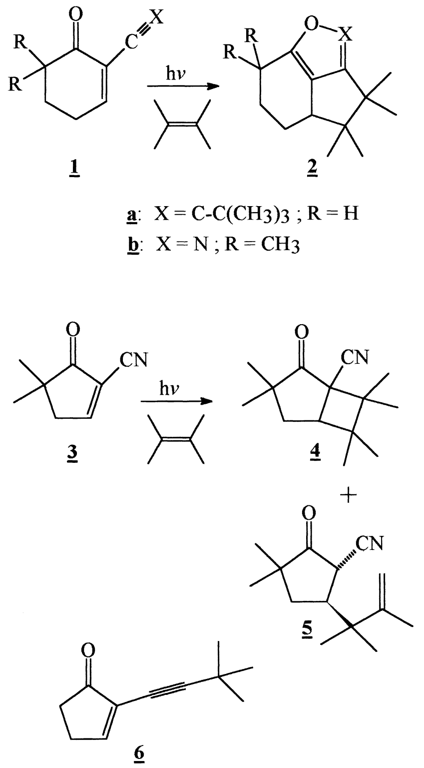
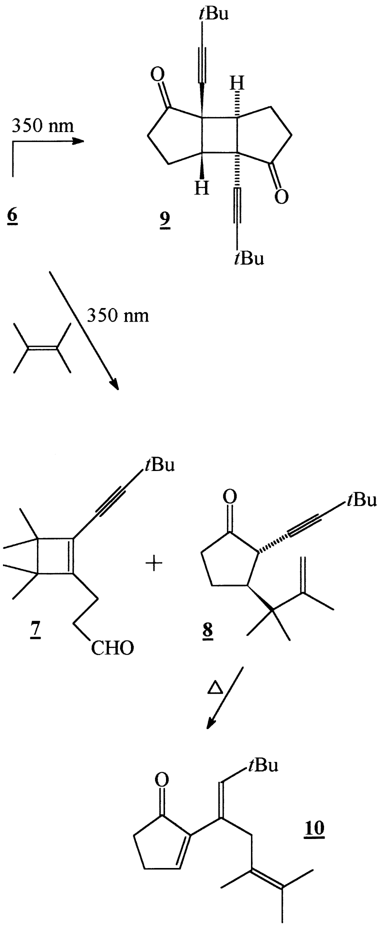


Scheme 1.

enone itself [7,8] reacts much more efficiently with alkenes than with a second enone molecule, i.e. photodimerization is *not* observed in the presence of alkene. The observed affinity of triplet excited **6** towards ground state **6** can be best interpreted by the combination of (a) the C–C double bond of (ground state) **6** being sufficiently electron rich to intercept the electrophilic enone triplet, and (b) the so formed excimer proceeding quantitatively to dimer **9**. The addition step of triplet excited **6** to 2,3-dimethylbut-2-ene corresponds to that of **3** with this same alkene affording triplet biradical **11**, which then undergoes spin inversion to singlet biradical **12**. Again, as for **3**, there is no evidence for an equilibrium between **11** and (triplet) carbene **13**, as no products deriving from this intermediate are formed. Biradical **12** undergoes a 1,5-hydrogen shift to **8** and, most probably, 1,4 cyclization to bicycloheptanone **14**. It is noteworthy that on monitoring the photoreaction by GC, aldehyde **7** is detected as a primary product, i.e., there is no indication for the formation of **14**. Apparently excitation of ketone **14** occurs readily and subsequent α-cleavage to **15** and 1,4-hydrogen shift to **7** are highly efficient, all in contrast to bicycloheptanone **4** which is (photo)stable under these conditions. Finally the formation of **10** from **8** can be best explained by an equilibrium between **8** and allene **16**, followed by an irreversible [3,3] sigmatropic rearrangement (Scheme 3). Examples of *Cope* rearrangements with involvement of allenic C–C double bonds have been reported in the literature [9].



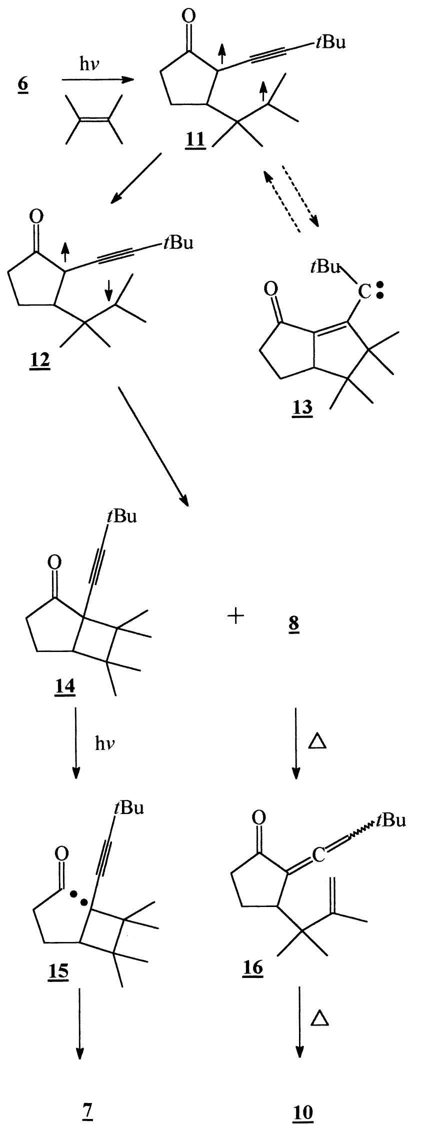
Scheme 2.

4. Experimental

^{1}H NMR (500 MHz), ^{13}C NMR (125.77 MHz) and mass (MS, 70 eV) spectra were obtained using Bruker DRK 500 and Varian MAT 311A spectrometers. The X-ray analysis of **9** was performed on an Enraf-Nonius-CAD4 four circle diffractometer at 293 K with Cu Kα radiation ($\lambda = 1.54178$ Å). Photolyses were run in a Rayonet RPR-100 photoreactor equipped with 350 nm lamps. Chromatography was achieved on silica gel (0.040–0.063 m), analytical GC on a 50 m 5% SE 30 capillary column, and preparative GC on a 2 m column (5% SE 30 on Chromosorb W-AW).

*4.1. Synthesis of 2-(3,3-dimethylbut-1-ynyl)-cyclopent-2-enone (**6**)*

According to [6] a solution of 2-iodocyclopent-2-enone (2.08 g, 10^{-2} mol), 3,3-dimethylbut-1-yne (820 mg, 10^{-2} mol), $PdCl_2(PPh_3)_2$, CuI and diisopropylamine in THF is stirred at 0° for 45 min. After evaporation the residue is purified by chromatography (SiO_2, pentane/diethyl ether 4 : 1) to afford 1.3 g (80%) **6**, $R_f = 0.25$, mp 37°. ^{1}H NMR ($CDCl_3$) δ: 1.30 (s, 9H), 2.40–2.44 (m, 2H), 2.64–2.71 (m,



Scheme 3.

2H), 7.68 (t, $J = 3$ Hz). ^{13}C NMR ($CDCl_3$) δ: 27 (t), 28 (s), 31 (q), 34 (t), 70 (s), 105 (s), 130 (s), 164 (d), 206 (s). MS (*m/z*): 162 (M^+, 64%), 105 (100%).

4.2. Photodimerization of **6**

An argon degassed solution of **6** (162 mg, 10^{-3} mol) in benzene (5 ml) is irradiated for 48 h. After evaporation of the solvent, hexane (10 ml) is added and the solution cooled to −15°. The precipitate is filtered and recrystallized from hexane to afford 80 mg (50%) (1α,2β,6β,7α)-1,6-bis(3,3-dimethylbut-1-ynyl)-tricyclo[5,3,0,$0^{2,6}$]decan-3,8-dione (**9**), mp 174°. ^1H NMR ($CDCl_3$) δ: 1.23 (s, 18H), 1.83 (dddd, $J = 8, 9, 13, 13.5$ Hz, 2H), 2.39 (dd, $J = 9, 13$ Hz, 2H), 2.45 (dd, $J = 8, 18$ Hz, 2H), 2.72 (d, $J = 8$ Hz, 2H), 2.90 (ddd, $J = 8, 13, 18$ Hz, 2H). ^{13}C NMR ($CDCl_3$) δ: 23 (t), 28 (s), 31 (q), 36 (t), 46 (s), 49 (d), 73 (s), 215 (s). MS (*m/z*): 324 (M^+, 30%), 309 (100%).

4.2.1. X-ray analysis of **9**

Transparent blocks, 0.5 mm × 0.5 mm × 0.3 mm, were obtained by recrystallization from hexane. Crystal data: $C_{22}H_{28}O_2$, $M_r = 324.4$, monoclinic, space group $P2_1/c$, $a = 12.432(1)$, $b = 7.186(1)$, $c = 11.460(1)$ Å, $\beta = 93.62(1)$, $V = 1021.8(2)$ Å^3, $Z = 2$, $D_x = 1.055$ g· cm^{-3}, $F(000) = 352$, $\mu = 0.51$ cm^{-1}. The cell parameters were determined by least-squares refinement against the setting angle of 25 reflections, $\theta = 41.3$–$44.5°$. Of the 2141 independent reflections ($\theta_{max} = 76.5°$), 1848 were considered to be observed [$I > 2\sigma(I)$]. Final R value for the significant reflections $R = 0.0789$ ($wR_2 = 0.2262$)[2]

4.3. Photoaddition of **6** to 2,3-dimethylbut-2-ene

An argon degassed solution of **6** (32.4 mg, 0.2 mmol) and 2,3-dimethylbut-2-ene (840 mg, 10 mmol) in benzene (100 ml) is irradiated for 60 h. After evaporation of the solvent the residue is subject to chromatographic work-up on SiO_2 (10 g) using a 49 : 1 mixture of dichloromethane/acetone as eluent. First we obtained 3-[2-(3,3-dimethylbut-1-ynyl)-3,3,4,4-tetramethylcyclobutenyl]-propanal (**7**), $R_f = 0.5$, 12.6 mg (25%), colourless oil. ^1H NMR ($CDCl_3$) δ: 1.03 (s, 9H), 1.25 (s, 12H), 2.32 (t, $J = 7$ Hz, 2H), 2.79 (dt, $J = 1, 7$ Hz, 2H), 9.84 (t, $J = 1$ Hz). MS (*m/z*): 246 (M^+, 30%), 105 (100%). Then we collected dimer **9**, 3 mg (10%). Finally we obtained *trans*-2-(3,3-dimethylbut-1-ynyl)-3-(2,3-dimethylbut-3-en-yl)-cyclopentanone (**8**), $R_f = 0.4$, 12.4 mg (25%), colourless oil. ^1H NMR ($CDCl_3$) δ: 1.10 (s, 3H), 1.19 (s, 9H), 1.23 (s, 3H), 1.80 (s, 3H), 2.20–2.40 (m, 5H), 2.77 (d, $J = 11$ Hz), 4.72 (s), 4.80 (s). MS (*m/z*): 246 (M^+, 50%), 147 (100%). Preparative gas chromatographic separation of the reaction mixture at 150° affords as first fraction **7** and as second fraction 2-(2-2,3,7,7-tetramethylocta-2,5-dien-5-yl)-cyclopent-2-enone (**10**), colourless oil. ^1H NMR ($CDCl_3$) δ: 0.97 (s, 9H), 1.48 (s, 3H), 1.57 (s, 3H), 1.63 (s, 3H), 2.40 (m, 2H), 2.57 (m, 2H), 2.75 (d, $J = 1$ Hz, 2H), 5.47 (t, $J = 1$ Hz), 7.09 (t, $J = 3$ Hz). ^{13}C NMR ($CDCl_3$) δ: 18 (q), 20 (q), 21 (q), 27 (t), 29 (s), 31 (q), 34 (t), 44 (t), 123 (s), 125 (s), 126 (s), 128 (s), 140 (d), 159 (d), 206 (s). MS (*m/z*): 246 (M^+, 30%), 147 (100%).

Acknowledgements

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