

38. Photodecarbonylation of 2,5,5-Trimethyl-2-(1-propynyl)cyclopentanone. 1,5- vs. 1,4-Ring Closure of a Propargyl-Alkyl Biradical

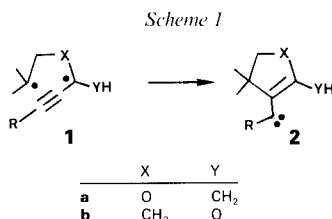
by Andreas Rudolph, Paul Margaretha*, and William C. Agosta¹⁾

Institut für Organische Chemie, Universität, D-2000 Hamburg 13

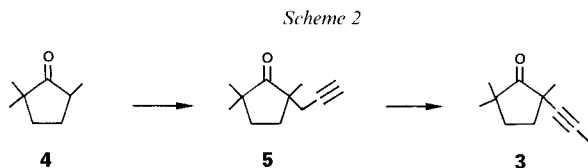
(24.XI.86)

Propargyl-alkyl biradical **12** generated by photodecarbonylation of title ketone **3** undergoes ring closure to cyclobutane **7** and to vinyl carbene **13**, this latter intermediate rearranging to the 5-ethylidenecyclopentenones **8a** and **8b**.

We have recently reported that intermediate biradical **1a** generated by photoaddition of conjugated acetylenic ketones to alkenes affords oxetans as well as furan derivatives, the five-membered cyclic ether stemming from vinyl carbene **2a** [1–4]. Similarly, the *Norrish-II* biradical **1b** formed by irradiating 2,2,8-trimethyl-3-nonyn-5-one affords, albeit in low yield, vinyl carbene **2b**, which is again further transformed according to well known reaction paths in carbene chemistry [5] (*Scheme 1*).



We were intrigued to know to what extent the O-atom vicinal to the propargyl-radical center influences such 1,5-ring closures. We, therefore, designed several model compounds which could act as precursors of all-C biradicals analogous to **1**. Herein, we report on the generation of such a species by CO extrusion from 2,5,5-trimethyl-2-(1-propynyl)cyclopentanone (**3**), synthesized by alkylation of 2,2,5-trimethylcyclopentanone (**4**) [6] with propargyl bromide (= 2-propynyl bromide) and subsequent isomerization of 2,5,5-trimethyl-2-(2-propynyl)cyclopentanone (**5**) with *t*-BuOK in DMSO [7] in 25% overall yield (*Scheme 2*). Such tetraalkylated cycloalkanones are known to photodecarbonylate with reasonable quantum yields [8].



¹⁾ Laboratories of The Rockefeller University, New York.

Table. Spectroscopic Data of Photoproducts 6–10

Compound	$^1\text{H-NMR}$ (CDCl_3) ^{a)}	MS ^{b)}
6		80 (100, M^{+}), 65 (26), 52 (11)
7	2.20 1.55 (<i>m</i> , 4 H); 1.85, 1.25, 1.17, 0.94 (4 <i>s</i> , CH_3)	136 (1, M^{+}), 121 (100), 108 (35), 93 (34), 91 (38), 80 (89)
8a	5.52 (<i>br. s</i>); 5.22 (<i>q</i> , $J = 7.4$); 2.23 (<i>br. s</i> , 2 H); 1.83 (<i>d</i> , $J = 7.4$, 3 H); 1.68 (<i>m</i> , 3 H); 1.26 (<i>s</i> , 6 H)	136 (47, M^{+}), 121 (100), 105 (37), 91 (27) ^{c)}
8b	5.58 (<i>br. s</i>); 5.07 (<i>q</i> , $J = 7.4$); 2.16 (<i>br. s</i> , 2 H); 2.04 (<i>m</i> , 3 H); 1.87 (<i>d</i> , $J = 7.4$, 3 H); 1.08 (<i>s</i> , 6 H)	
9	9.54 (<i>s</i>); 5.53 (<i>t</i> , $J = 8.0$); 2.42 (<i>d</i> , $J = 8.0$, 2 H); 2.01 (<i>s</i> , 3 H); 1.85 (<i>s</i> , 3 H); 1.08 (<i>s</i> , 6 H)	164 (3, M^{+}), 121 (68), 108 (30), 105 (33), 91 (100)
10	9.55 (<i>s</i>); 5.72 (<i>t</i> , $J = 8.0$); 2.26 (<i>d</i> , $J = 8.0$, 2 H); 1.95 (<i>s</i> , 3 H); 1.89 (<i>s</i> , 3 H); 1.09 (<i>s</i> , 6 H)	164 (3, M^{+}), 91 (100)

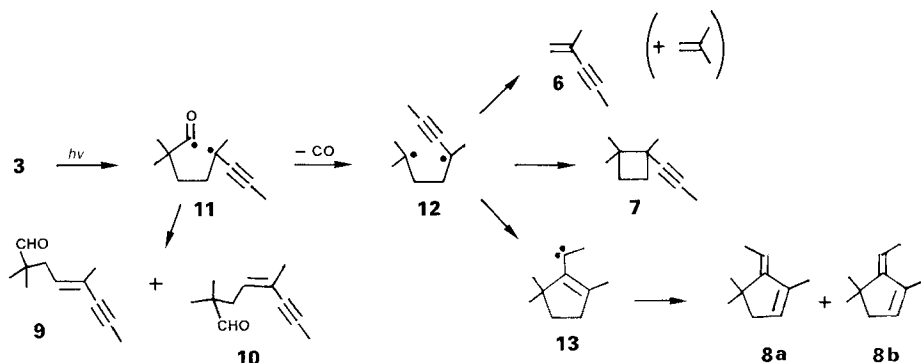
^{a)} Chemical shifts δ in ppm, coupling constants J in Hz.

^{b)} m/z , relative intensities in % of the base peak in parentheses.

^{c)} 3:1 mixture of **8a/8b**.

Irradiation ($\lambda = 300$ nm) of a 10^{-1}M solution of **3** in pentane afforded the five products **6** (12%)²⁾, **7** (38%), **8** (11%), **9** (28%), and **10** (11%) as monitored by GC (*Scheme 2*). Combined GC/MS analysis indicated the first three products to be hydrocarbons (molecular formulas: C_6H_8 for **6** and $\text{C}_{10}\text{H}_{16}$ for **7** and **8**), the MS of **8** resembling those of several monoterpenes [9]. The other two products were isomers ($\text{C}_{11}\text{H}_{16}\text{O}$) of ketone **3**. Preparative GC allowed the isolation of **7**, **8**, of a 2:1 mixture of **9** and **3**, and finally of **10** (this latter in 75% purity). The $^1\text{H-NMR}$ spectral data summarized in the *Table* suggests **7** to be a cyclobutane, **8** to represent a 3:1 mixture of diastereoisomeric 5-ethylidenecyclopentenes – the configurational assignment for **8a** (major) and **8b** (minor) being based on comparison with reported data of 1,1-dimethyl-2-ethylidenecyclopentanes [10] [11] – and finally **9** and **10** to be diastereoisomeric γ,δ -unsaturated aldehydes. Assignment of structure **6** (2-methylpent-1-en-3-yne) to the C_6H_8 hydrocarbon is based on its MS data identical to reported ones [12] (*Scheme 3*).

Scheme 3



²⁾ In parentheses, relative composition of the product mixture.

Cyclization of **12** to **13** represents the first example of a hydrocarbon 1,4-propargyl-alkyl biradical with no O-substituents undergoing 1,5-ring closure to a vinyl carbene. The multiplicity (singlet or triplet) of biradical **12** is not yet known. Sensitized irradiations (acetone or benzene) of **3** afforded much more complex product mixtures, probably due to consecutive interactions of the primary photoproducts with the sensitizer. Further experiments with deuterium-labeled **3**, in order to establish the mechanism of formation of **8a/8b** from **13**, are in progress.

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Experimental Part

General. See [4]. Prep. GC was performed on a 2 m 10% *QF1* column. Irradiations were run in a *Rayonet RPR 100* photoreactor using 300-nm lamps.

2,5,5-Trimethyl-2-(2-propynyl)cyclopentanone (5). To a suspension of 10 g (0.26 mol) of NaNH_2 in 100 ml of THF at -30° is added a soln. of 28 g (0.22 mol) of 2,2,5-trimethylcyclopentanone (**4**) [6] in 200 ml of THF. The mixture is stirred for 5 h, the temp. rising to r.t. After cooling to 0° , a soln. of 56 g (0.47 mol) of 2-propynyl bromide in 100 ml of THF is added, the mixture stirred at r.t. for 60 h, poured on ice, acidified with 1N H_2SO_4 , and extracted with Et_2O . The org. phases are washed with sat. NaHCO_3 and NaCl solns. and dried (MgSO_4). After evaporation of the solvent, distillation affords 22.9 g (63%) of **5**, b.p. $78-81^\circ/13$ Torr. IR (film): 3300, 2130, 1740. $^1\text{H-NMR}$ (CDCl_3): 2.27–1.61 (m, 6 H); 1.91 (t, $J = 2.5$); 1.03, 1.01, 0.97 (3s, CH_3). $^{13}\text{C-NMR}$ (CDCl_3): 224; 73; 70; 48; 45; 35; 31; 27; 24; 23. MS: 164 (M^{+}), 56.

2,5,5-Trimethyl-2-(1-propynyl)cyclopentanone (3). A soln. of 10 g (0.061 mol) of **5** in 30 ml of DMSO is added to 7 g (0.062 mol) of *t*-BuOK in 160 ml of DMSO. Stirring for 1 h, workup as described in [7], and distillation afford 3.7 g (37%) of **3**, b.p. $80-83^\circ/15$ Torr. UV (Cyclohexane): 304 ($\epsilon = 110$). IR (CCl_4): 2200, 1730. $^1\text{H-NMR}$ (CDCl_3): 2.15–1.68 (m, 4 H); 1.75, 1.26, 1.15, 1.02 (4s, CH_3). $^{13}\text{C-NMR}$ (CDCl_3): 220; 80; 78; 45; 44; 35; 34; 26; 25; 23; 4. MS: 164 (M^{+}), 80.

Irradiation of 3. Ar-degassed solns. of $328 \text{ mg } (2 \cdot 10^{-3} \text{ mol})$ of **3** in 20 ml of pentane were irradiated for 72 h up to 65–70% conversion of starting material as monitored by GC. The photoproducts 1,2,2-trimethyl-1-(1-propynyl)cyclobutane (**7**), (*E*)- and (*Z*)-5-ethylidene-1,4,4-trimethyl-cyclopentene (**8a** and **8b**, resp.), and (*E*)- and (*Z*)-2,2,5-trimethyloct-4-en-6-ynal (**9** and **10**, resp.) were isolated by GC.

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