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

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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-ethylidenecyclopentenes **8a** and **8b**.

We have recently reported that intermediate biradical **1a** generated by photoaddition of conjugated acetylenic ketones to alkenes affords oxetanes 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)*.

Scheme 1

	X	Y
a	O	CH_2
b	CH_2	O

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].

Scheme 2

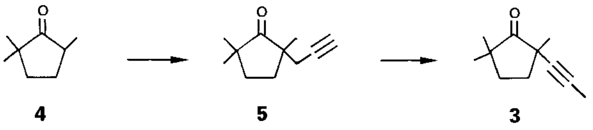

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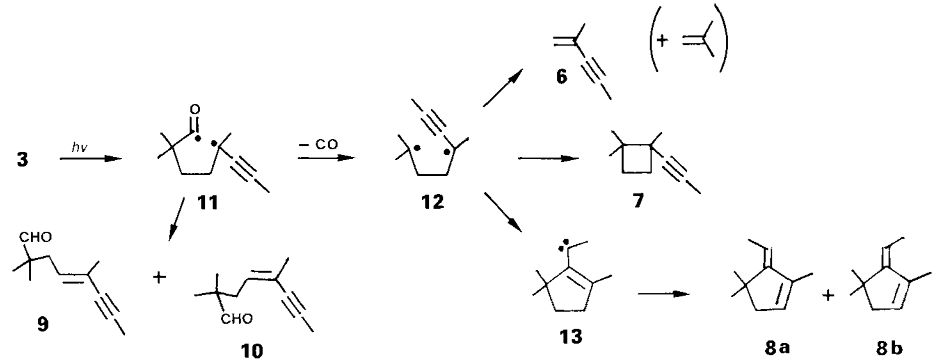
Table. *Spectroscopic Data of Photoproducts* **6–10**

Compound	^{1}H-NMR ($CDCl_3$)[a]	MS[b]
6		*80* (100, $M^{+\cdot}$), 65 (26), 52 (11)
7	2.20 1.55 (*m*, 4 H); 1.85, 1.25, 1.17, 0.94 (4*s*, CH_3)	136 (1, $M^{+\cdot}$), *121* (100), 108 (35), 93 (34), 91 (38), 80 (89)
8a	5.52 (br. *s*); 5.22 (*q*, *J* = 7.4); 2.23 (br. *s*, 2 H); 1.83 (*d*, *J* = 7.4, 3 H); 1.68 (*m*, 3 H); 1.26 (*s*, 6 H)	136 (47, $M^{+\cdot}$), *121* (100), 105 (37), 91 (27)[c]
8b	5.58 (br. *s*); 5.07 (*q*, *J* = 7.4); 2.16 (br. *s*, 2 H); 2.04 (*m*, 3 H); 1.87 (*d*, *J* = 7.4, 3 H); 1.08 (*s*, 6 H)	
9	9.54 (*s*); 5.53 (*t*, *J* = 8.0); 2.42 (*d*, *J* = 8.0, 2 H); 2.01 (*s*, 3 H); 1.85 (*s*, 3 H); 1.08 (*s*, 6 H)	164 (3, $M^{+\cdot}$), 121 (68), 108 (30), 105 (33), *91* (100)
10	9.55 (*s*); 5.72 (*t*, *J* = 8.0); 2.26 (*d*, *J* = 8.0, 2 H); 1.95 (*s*, 3 H); 1.89 (*s*, 3 H); 1.09 (*s*, 6 H)	164 (3, $M^{+\cdot}$), *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 (λ = 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 $C_{10}H_{16}$ for **7** and **8**), the MS of **8** resembling those of several monoterpenes [9]. The other two products were isomers ($C_{11}H_{16}O$) 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}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



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[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°/13 Torr. IR (film): 3300, 2130, 1740. ^{1}H-NMR ($CDCl_3$): 2.27–1.61 (*m*, 6 H); 1.91 (*t*, *J* = 2.5); 1.03, 1.01, 0.97 (3*s*, CH_3). ^{13}C-NMR ($CDCl_3$): 224; 73; 70; 48; 45; 35; 31; 27; 24; 23. MS: 164 ($M^{+\cdot}$), *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°/15 Torr. UV (Cyclohexane): 304 (ε = 110). IR (CCl_4): 2200, 1730. ^{1}H-NMR ($CDCl_3$): 2.15–1.68 (*m*, 4 H); 1.75, 1.26, 1.15, 1.02 (4*s*, CH_3). ^{13}C-NMR ($CDCl_3$): 220; 80; 78; 45; 44; 35; 34; 26; 25; 23; 4. MS: 164 ($M^{+\cdot}$), *80*.

Irradiation of **3**. Ar-degassed solns. of 328 mg ($2 \cdot 10^{-3}$ 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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