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Synthesis of a [5.5.5.5]Fenestrane *via Pauson-Khand* Reaction

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Abstract. A short synthesis of a functionalized [5.5.5.5]fenestrane is described.

Despite a variety of methods, which we and others have developed for the synthesis of [5.5.5.5]fenestranes, the chemistry of such tetracyclic compounds has hardly been explored [1–4]. This is mainly due to the fact, that our procedures leading to functionalized compounds, attractive for further transformations, are low-yield processes.

We now have found that functionalized [5.5.5.5]fenestranes can be prepared in good yield by a short route with the *Pauson-Khand* cyclization as the key step. This reaction has recently been shown to provide an efficient method for the preparation of a wide variety of cyclopentenones by Co-mediated reaction of an alkyne and an alkene with CO [5]. *Schore* and *Knudsen* demonstrated the wide applicability of the intramolecular variety of this method [6], and most recently *Schreiber* and coworker have reported conditions for efficient cyclizations at room temperature [7].

A retrosynthetic analysis reveals that the bicyclo[3.3.0]octene **2** with a butinyl side chain may be an appropriate starting material for the *Pauson-Khand* reaction to give a [5.5.5.5]fenestrane of type **1**. From a simple thermochemical estimate, it can be concluded, that the formation of cyclopent-2-enone form HC≡CH, $H_2C{=}CH_2$ and CO is exothermic by *ca.* 160 kJ/mol. Further deconvolution leads to a 2,5-disubstituted cyclopentanone **3**. For the regio- and stereochemical control in the double alkylation, ethyl 2-oxocyclopentanecarboxylate (**4**) was eventually chosen as starting material.

Results

Deprotonation of **4** with NaH-BuLi in THF at –78° and reaction with 4-iodobutyne lead to alkylation in γ-position of the β-keto ester. Subsequent alkylation of **5a** with 3-bromo-2-ethoxypropenyl phosphonate gave **5b**, which was hydrolyzed to give the keto phosphonate **5c**. Cyclization under phase transfer conditions lead to the bicyclic compound **6a** as the predominant stereoisomer in an overall yield of 34%. Selective reduction of the C=O group from the *exo*-side gave, after acetylation, **7b** in 73%.

Reaction of **7b** with $Co_2(CO)_8$ for 12 h lead upon addition of *N*-methylmorpholine *N*-oxide to the desired fenestrane **8** in 35–38%.

Structure Elucidation

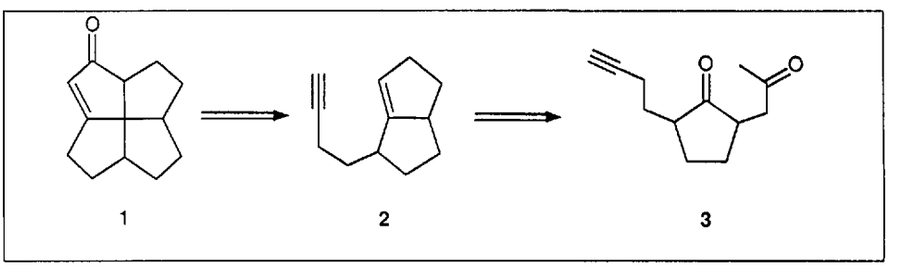
The structures of **6a,b** and **8** were established by detailed analysis of NMR spectra. The C,H and H,H correlations for the ring system and the substitutents of **6a** were obtained from COSY and hetero-COSY measurements (*Table 1*). A $^1H,^1H$-NOE analysis revealed the *cis*-relationship between H–C(4), H–C(7), and H–C(8) on the *endo*-side of the bicyclic ring system. $^{13}C,^1H$-hetero-NOE results clearly showed, that H_{exo}–C(4) and H_{exo}–C(6) are on the same side with the EtOCO group [8].

The structure of **8** was apparent from the ^{13}C- and ^1H-NMR spectra (*Table 2*). Based on the observation of a small coupling constant between H–C(4) and H–C(5) (J = 2.9 Hz) and the *cis*-relationship between H–C(5) and H_{exo}–C(6) (NOE results), it was concluded, that the AcO group is *trans* to the EtOCO group at C(7). Since NOE results reveal a *cis*-relationship between H–C(4) and H–C(10), the [5.5.5.5]fenestrane **8** belongs to the (all-*cis*)-series. The stereoisomerism in [*m.n.o.p*]fenestranes has been already discussed [9].

Discussion

Several procedures have been proposed for high-yield *Pauson-Khand* reactions [5–7]. Usually the $Co_2(CO)_6$-alkine complex is prepared prior to the thermal or amine oxide induced reaction. In our hands, thermal cyclizations with different functionalities in **6** and different solvents gave essentially no products [10] and clearly shows the superior modification found by *Schreiber* and coworkers [7].

Since it was unclear, whether the EtOCO group at the bridgehead position of **7b** would hamper the *Pauson-Khand* reaction, we decided to prepare **9a**. With the ester group located at the *endo*-side of the bicyclic ring system and not, as in **6a** at the *exo*-side, steric hindrance would be less during cyclization. Alkylation of **4** with 3-iodo-2-ethoxypropenyl phosphonate gave **5d** as a mixture of diastereoisomers in 27%. Further alkylation with 4-bromobutyne gave **5e** which was hydrolyzed to yield **5f**. When **5f** was submitted to the same phase-transfer



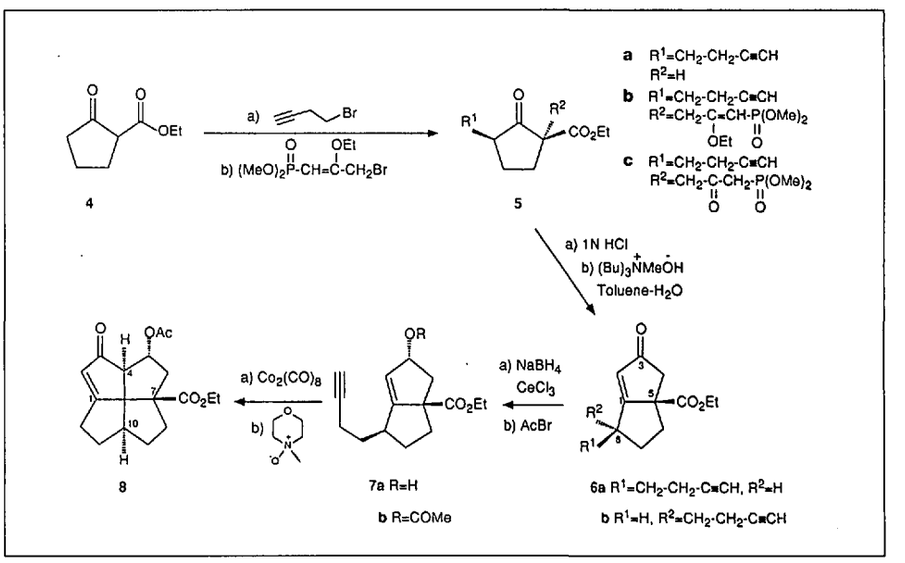


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Table 1. *NMR Data of* **6a**

Assignment	^{13}C-NMR[a]) δ [ppm]	^{1}H-NMR[b])[c]) δ [ppm]	^{1}H,^{1}H Connectivity[d])
C(1)	187.841 (*s*)	–	–
H–C(2)	127.970 (*d*)	6.10 (*d*, 1.3)	H_x–C(4), H–C(8)
C(3)	208.669 (*s*)	–	–
CH_2(4)	48.661 (*t*)	2.32 (*d*, H_n, 17.3)	H_x–C(4)
		2.74 (*d*, H_x, 17.3)	H–C(2), H_n–C(4)
C(5)	60.288 (*s*)	–	–
CH_2(6)	33.578 (*t*)	1.43 (*ddd*, Hn 12.2, 12.2, 8.5)	H_x–C(6), CH_2(7)
		2.73 (*dd*, H_x, 12.5, 7.0)	H_n–C(6), CH_2(7), H–C(8)
CH_2(7)	32.090 (*t*)	1.55–1.84 (*m*, H_x)	CH_2(6), H_n–C(7), H–C(8)
		2.23–2.34 (*m*, H_n)	CH_2(6), H_x–C(7), H–C(8)
H–C(8)	38.063 (*d*)	3.01–3.15 (*m*)	H–C(2), H_x–C(6), CH_2(7), CH_2(12)
C(9)	172.930 (*s*)	–	–
CH_2(10)	61.646 (*t*)	4.11 (*dq*, H_a, 10.7, 7.0)	H_x–C(4), H_x–C(6), CH_3(11)
		4.17 (*dq*, H_b, 10.7, 7.3)	
CH_3(11)	14.015 (*q*)	1.22 (*t*, 3 H, 7.0)	CH_2(10)
CH_2(12)	33.376 (*t*)	1.62 (*ddt*, H_a, 13.6, 8.8, 6.6)	H–C(8), CH_2(13)
		1.75 (*dtd*, H_b, 13.2, 7.4, 1.9)	
CH_2(13)	17.064 (*t*)	2.23–2.34 (*m*, 2 H)	CH_2(12), H–C(15)
C(14)	83.062 (*s*)	–	–
H–C(15)	69.426 (*d*)	2.01 (*t*, 2.6)	CH_2(13)

NOE results: H–C(2): H_n–C(7), H–C(8); H_n–C(4): H–C(2), H_x–C(4), H_n–C(6); H_n–C(6): H_n–C(4), H_x–C(6), H_n–C(7), H–C(8); H_x–C(6): H_n–C(6); H_x–C(7): H_n–C(7); H_n–C(7): H_n–C(6), H_x–C(7), H–C(8); H–C(8): H–C(2), H_n–C(6), H_n–C(7), CH_2(12); CH_2(12): H–C(8), CH_2(13).

[a]) Multiplicity determined by DEPT. [b]) Assigned according to hetero-COSY. [c]) Approximate multiplicity. [d]) COSY results; n = *endo*, x = *exo*; ^{1}H-NOE results are reported in the following way: H–C(X) irradiated [signal enhancement at H–C(Y)].

conditions used for cyclization of **5c**, a mixture **9c/9d** instead of **9a/9b** was obtained.

The structures of **9c** and **9d** were deduced from 1D- and 2D-NMR data. In **9c**, the butinyl group is assigned to the *exo*-position, because a *syn*-relationship between the *endo*-H's at C(4), C(6), C(7), and H–C(8) could be established by NOE results.

The *endo*-position of the butinyl side chain in **9d** was also apparent from NOE data, which showed a *syn*-relationship between the *endo*-H's at C(4), C(6), and C(7) as well as between H_{exo}–C(7) and H–C(8).

The unexpected removal of the EtOCO group during the cyclization reaction in the case of **5f** but not in **5c** may be due to the different arrangement of the phosphonate and the EtOCO group after cyclization but prior to the terminating step of the *Horner-Emmons* reaction.

Model considerations reveal, that in **5c** as well as in **5f** the phosphono-enolate adds in the C=O group in such a way, that *cis*-bicyclo[3.3.0]octane structures like **10** and **11** and **12**, respectively, are formed. The *cis*-relationship of the C–O$^-$ and the C–PO(OCH$_3$)$_3$ bond necessary for the *syn*-elimination and formation of the double bond is established in **10** and **11** as well.

The excess of OH$^-$ ions, provided by phase transfer and added to the phosphonate moiety might induce the hydrolysis of the ester group in **11** and **12**. Steric crowding may prevent the interaction between the basic phopshono- and the ester group in **10**.

Given the high stability and the ready formation of lactones like **13** [11], the interaction of the two functionalities in **12** appears reasonable. Model considerations suggest, that an intramolecular reaction is also possible in **11**. Base-induced *endo*→*exo*-isomerization of the phosphono group in **12** might then lead to the γ-carboxy-substituted enone, which decarboxylates during workup to give upon preferential protonation from the *exo*-side **9d** as the major isomer.

The observation, that **14**, which was obtained in high yield by pig-liver esterase reaction of the corresponding ethyl- resp. allylester, readily decarboxylates [12], corroborates the fast decarboxylation.

Concluding Remarks

The *Pauson-Khand* reaction provides an efficient route to a [5.5.5.5]fenestrane, appropriately functionalized for further transformation and exploration of the chemistry of this class of compounds. Further work in this area of the deformation space of tetracoordinate carbon is in progress.

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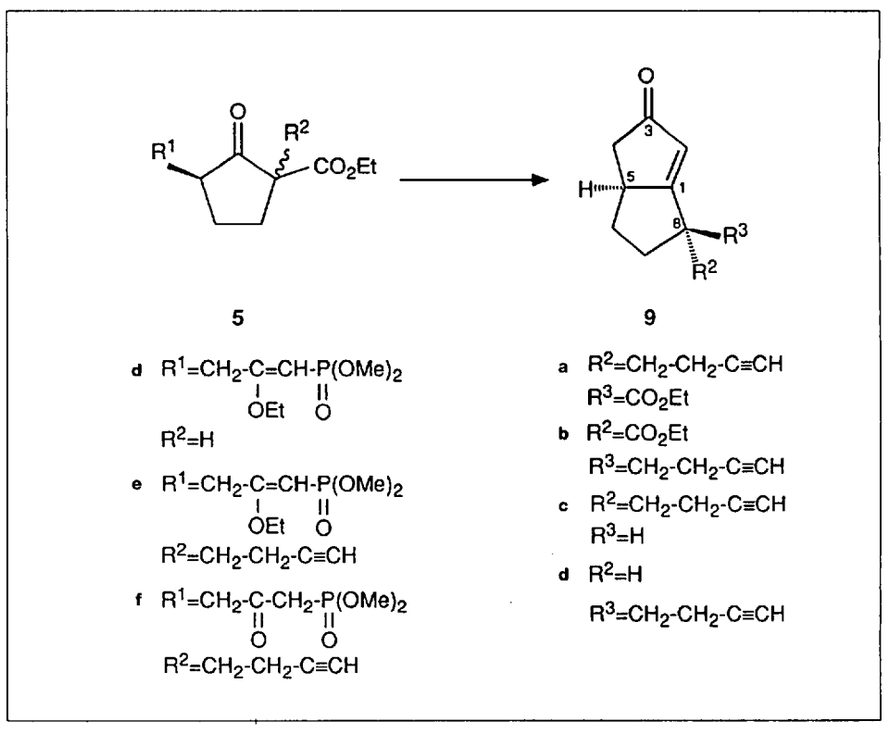
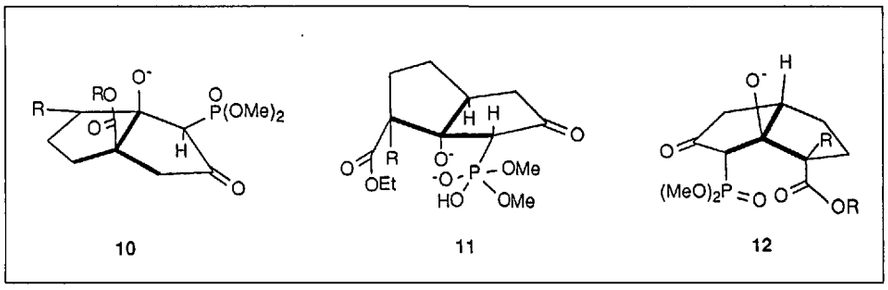


Table 2. *NMR Data of* **8**

Assignment	^{13}C-NMR[a]) δ [ppm]	^{1}H-NMR[b])[c]) δ [ppm]	^{1}H,^{1}H Connectivity[d])
C(1)	187.031 (*s*)	–	–
H–C(2)	123.350 (*d*)	5.75 (*t*, 1.1)	CH_2(12)
C(3)	208.348 (*s*)	–	–
H–C(4)	66.759 (*d*)	2.92 (*d*, 2.9)	H–C(5), H_n–C(6)
H–C(5)	75.873 (*d*)	5.45 (*ddd*, 6.6, 6.9, 2.9)	H–C(4), CH_2(6)
CH_2(6)	44.413 (*t*)	1.87 (*dd*, H_n, 14.3, 6.0)	H–C(4), H–C(5), H_x–C(6)
		2.81 (*dd*, H_x, 14.3, 6.6)	H–C(5), H_n–C(6)
C(7)	63.715 (*s*)	–	–
CH_2(8)	34.679 (*t*)	1.74–1.87 (*m*, H_n)	CH_2(9), H–C(10)
		2.41–2.54 (*m*, H_x)	CH_2(9), H–C(10)
CH_2(9)	33.177 (*t*)	1.74–1.87 (*m*, H_x)	CH_2(8), H–C(10)
		2.20–2.30 (*m*, H_n)	CH_2(8), H–C(10)
H–C(10)	46.279 (*d*)	2.54–2.64 (*m*)	CH_2(8), CH_2(9), CH_2(11)
CH_2(11)	32.628 (*t*)	1.74–1.87 (*m*, H_x)	H–C(10), CH_2(12)
		2.04–2.19 (*m*, H_n)	H–C(10), CH_2(12)
CH_2(12)	28.266 (*t*)	2.41–2.57 (*m*, 2 H)	CH_2(11)
C(13)	75.430 (*s*)	–	–
C(14)	173.745 (s)	–	–
CH_2(15)	61.033 (*t*)	4.04 (*q*, 7, 2 H)	CH_3(16)
CH_3(16)	13.840 (*q*)	1.20 (*t*, 7, 3 H)	CH_2(15)
C(17)	170.099 (*s*)	–	–
CH_3(18)	21.126 (*q*)	2.065 (*s*, 3 H)	

NOE results: H–C(4): H–C(2), H–C(5), H–C(11); H–C(5): H–C(4), H_x–C(6); H_x–C(6): H–C(4), H–C(5), H_n–C(6); H–C(10): H–C(4), H_n–C(9), H_n–C(11).

[a]) Multiplicity determined by DEPT. [b]) Assigned according to hetero-COSY. [c]) Approximate multiplicity. [d]) COSY results; n = *endo*, x = *exo*; ^{1}H-NOE results are reported in the following way: H–C(X) irradiated [signal enhancement at H–C(Y)].



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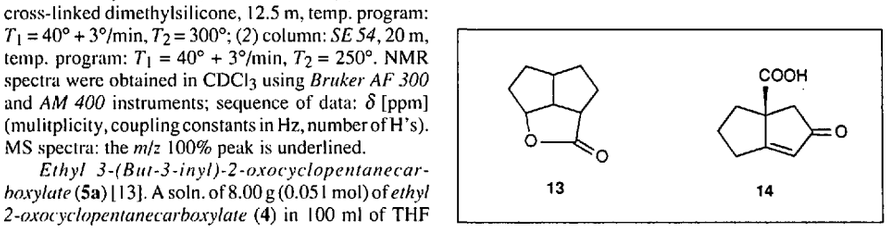
Experimental Part

General. See [1]. Workup procedure: the reaction mixture was poured onto crushed ice, if necessary neutralized, resp., acidified and extracetd 3 × with Et_2O. The Et_2O extract was dried ($MgSO_4$) and gave upon evaporation crude product. HPLC conditions: *Lichrosorb Si 60*, 7 µm, 24 cm; GC conditons: (*1*) Column: cross-linked dimethylsilicone, 12.5 m, temp. program: T_1 = 40° + 3°/min, T_2 = 300°; (*2*) column: *SE 54*, 20 m, temp. program: T_1 = 40° + 3°/min, T_2 = 250°. NMR spectra were obtained in $CDCl_3$ using *Bruker AF 300* and *AM 400* instruments; sequence of data: δ [ppm] (mulitplicity, coupling constants in Hz, number of H's). MS spectra: the *m/z* 100% peak is underlined.

Ethyl 3-(But-3-inyl)-2-oxocyclopentanecarboxylate (**5a**) [13]. A soln. of 8.00 g (0.051 mol) of *ethyl 2-oxocyclopentanecarboxylate* (**4**) in 100 ml of THF was treated with 1.23 g (0.056 mol) of NaH at 0° followed by slow addition of 23.9 ml 2.3M of BuLi in hexane (0.056 mol) at –78°. After short warming to –35°, a soln. of 9.24 g (0.053 mol) of 4-iodobut-1-yne in 10 ml of THF was added. After stirring and warming to RT. overnight, the mixture was worked up and purified by low-bar chromatography to give 6.51 g (61%) of a red oil containing **5** as mixture of diastereoisomers. R_f (AcOEt/CH_3OH 99:1) 0.71. IR: 3310, 1755, 1720. ^{1}H-NMR: 1.23–1.36 (2*t*, 3 H); 1.40–1.64 (*m*, 2 H); 1.72–2.52 (*m*, 7 H); 1.98 (*t*, 2.5, 2 H); 3.16 (*dd*, 8.3, 11.4, 0.60 H); 3.29 (*dd*, 4.4, 8.8, 0.30 H); 4.12–4.28 (*m*, 2H). MS: 208 (M^+), 207, 180, 163, 156, 134, *110*, 108.



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Ethyl 8-exo-(But-3-inyl)bicyclo[3.3.0]oct-1-ene-5-carboxylate (**6**). To a suspension of 0.53 g (0.013 mol) of NaH in 130 ml of THF was slowly added a soln. of 2.4 g (0.012 mol) of **5a** in 20 ml of THF, followed by addition of 4.1 g (0.015 mol) of dimethyl-3-bromo-2-ethoxypropenyl phosphonate [14] in 20 ml of THF. After stirring for 12 h at RT., the mixture was worked up and extracted with AcOEt to give 5.7 g of **5b** as an orange oil. Crude **5c**, obtained after treatment of **5b** with 9 ml of 1N HCl in 250 ml of acetone for 90 min and appropriate workup, was dissolved in 140 ml of toluene/H_2O 1:1 and stirred with 6.5 ml (0.012 mol) of $Bu_3N^+CH_3$ OH^- for 12 h. The oily crude material obtained after separation of the aq. phase and removal of the solvent, was chromatographed (hexane/Et_2O 3:2) to give 1.47 g (52%) of **6a** and **6b** (85:15). This mixture was separated by HPLC (hexane/*t*-BuOMe 9:1). Pure **6a** was obtained by recrystallization from *t*-BuOMe **6a**.

6a: m.p. 40.5°; R_f (hexane/Et_2O 4:6) 0.46. HPLC: *k'* = 11.61. GC (1): 43.15 min. IR: 3310, 1720, 1640, 1265, 1170. ^{1}H- and ^{13}C-NMR: see *Table 1*. MS: 246 (M^+), 218, 217, 174, 173, *145*, 144, 133, 117. Anal.calc. for $C_{15}H_{18}O_3$ (246.31): C 73.15, H 7.37; found: C 73.13, H 7.10.

6b: R_f (hexane/Et_2O 4:6) 0.46. HPLC: *k'* = 13.44. GC (1): 44.05 min. IR: 3310, 1725, 1710, 1630. ^{1}H-NMR: 1.23 (*t*, 8.4, 3 H); 1.45–1.72 (*m*, 3 H); 1.95–2.10 (*m*, 1 H); 2.01 (*t*, 2.1, 1 H); 2.23–2.52 (*m*, 3 H); 2.31 (*d*, 18.2, 1 H); 2.66 (*dd*, 12.1, 7.1, 1 H); 2.92 (*d*, 18.2, 1 H); 2.98–3.11 (*m*, 1 H); 4.16 (*dq*, 10.1, 8.4, 2 H); 5.97 (*d*, 0.5, 1 H). ^{13}C-NMR: 14.02 (*q*); 17.09 (*t*); 30.56 (*t*); 31.80 (*t*); 32.39 (*t*); 37.37 (*d*); 48.11 (*t*); 60.16 (*s*); 61.73 (*t*); 69.27 (*d*); 83.19 (*s*); 124.65 (*d*); 172.97 (*s*); 189.21 (*s*); 208.53 (*s*). MS: 246, 218, 189, 179, *173*, 145, 144, 133, 131, 129.

Ethyl 3-endo-Hydroxy-8-exo-(but-3-inyl)bicyclo-[3.3.0]oct-1-ene-5-exo-carboxylate (**7a**). To a soln. of 3.072 g (8.25 mmol) of $CeCl_3 \cdot 7H_2O$ in 80 ml of CH_3OH were added 2.00 g (8.13 mmol) of **6a** and 0.33 g (8.67 mmol) of $NaBH_4$ [15]. Workup gave 2.8 g of a yellowish oil, which was purified by low-bar chromatography (hexane/*t*-BuOMe 1:1) to give 1.81 g (90%) of **7a** as an oil. R_f (hexane/Et_2O 1:1) 0.29. IR: 3620, 3600, 3410, 1722, 1182, 1025. ^{1}H-NMR: 1.24 (*t*, 7, 3 H); 1.33–1.48 (*m*, 1 H); 1.4–1.58 (*m*, 2 H); 1.54 (*dd*, 12.5, 7.36, 1 H); 1.60–1.77 (*m*, 1 H); 1.77 (1 H); 1.94 (*t*, 2.6, 1 H); 2.15–2.28 (*m*, 3 H); 2.43–2.51 (*dd*, 12.1, 7.35, 1 H); 2.7–2.84 (*m*, 1 H); 2.80 (*dd*, 12.5, 6.25, 1 H); 4.11 (*dq*, 2 H); 5.38 (*m*, 1 H); 5.61 (*dd*, 1 H). ^{13}C-NMR: 155.3 (*s*, C(1)); 128.15 (*s*, C(2)); 82.54 (*d*, (C(3)); 49.7 (*t*, (C(4)); 64.6 (*s*, C(5)); 35.68 (*t*, C(6)); 33.59 (*t*, C(7)); 36.16 (*d*, C(8)); 175.7 (*s*, C(1')); 60.8 (*t*, C(2')); 14.14 (*q*, C(3')); 33.92 (*t*, C(1")); 17.01 (*t*, C(2")); 84.01 (*s*, C(3")); 68.60 (*d*, C(4")). MS: 248 (M^+), 176, *175*, 174, 146, 145, 133, 132, 131.

Ethyl 3-endo-Acetoxy-8-exo-(but-3-inyl)bicyclo-[3.3.0]oct-1-ene-5-exo-carboxylate (**7b**). Freshly distilled CH_3COBr (2.45 g, 19.96 mmol) was added to a soln. of 1.65 g (6.65 mmol) of **7a** in 90 ml ether and 1.58 g (19.96 mmol) of pyridine at 0°. After stirring for 14 h, the reaction mixture was worked up and gave after low-bar chromatography 1.58 g (82%) of **7b** as viscous oil, which solidifies at *ca.* –15°. R_f (hexane/Et_2O 1:1) 0.73. IR: 3310, 1725, 1375. ^{1}H-NMR: 1.24 (*t*, 7.0, 3 H); 1.34–1.62 (*m*, 3 H); 1.71 (*dd*, 12.9, 7.4, 1 H); 1.62–1.79 (*m*, 1 H); 1.95 (*t*, 2.7, 1 H); 2.05 (*s*, 3 H); 2.17–2.31 (*m*, 3 H); 2.48–2.54 (*ddd*, 13, 12, 7.35, 1 H); 2.73–2.86 (*m*, 1 H); 2.80 (*dd*, 12.9, 6.3, 1 H); 4.10 (*dq*, 10, 7, 1 H); 4.15 (*dd*, 10, 7, 1 H); 5.59 (*dd*, 1 H); 6.13 (*ddd*, 7.4, 6.2, 1 H). MS: 290 (M^+), 248, 217, 216, 203, 202, 175, *174*, 157, 146, 142, 132.

Pauson-Khand *Reaction of* **7b**. A mixture of 0.462 g (1.6 mmol) **7** and 0.653 g (1.72 mmol) of $Co_2(CO)_8$ was stirred in 30 ml of CH_2Cl_2 for 14 h to give a red soln. Upon addition of 1.23 g (10.5 mmol) of *N*-methylmorpholino *N*-oxide the soln., which turned brownish-violet, was stirred for 24 h at RT. After addition of 50 ml of Et_2O, the soln. was centrifuged and concentrated. Low-bar chromatography with hexane/AcOEt 2:1 gave

0.192 g (34%) of a yellowish oil, from which crystals could be obtained in petroleum ether. Recrystallization gave white crystals of **8**. M.p. 77°. R_f (hexane/AcOEt 2:1) 0.49. IR: 1740, 1725, 1239. ^{1}H- and ^{13}C-NMR: *cf. Table 2*. MS: 318 (58, M^+), 276 (32), 275 (82), 259 (34), 258 (100), 230 (91), 201 (54), 184 (50), 157 (54). Anal. calc. for $C_{18}H_{22}O_5$ (318.37): C 67.91, H 6.97; found: C 68.14, H 7.08.

Ethyl 3-[2-Ethoxy-3-(dimethylphosphono)prop-2-enyl]-2-oxocyclopentanecarboxylate (**5d**). To a soln. of 0.065 mol of LDA, prepared from 31.0 ml of 2.095M BuLi in hexane and 6.58 g (0.065 mol) of (i-Pr)$_2$NH was added a soln. of 5 g (32 mmol) of 2-ethoxycarbonylcyclopentanone **4** in 10 ml of THF at –70°. After warming and stirring at 0° for 1 h, the mixture was cooled to –70°, and a soln. of 8.8 g (0.032 mol) of dimethyl (3-bromo-2-ethoxypropenyl)phosphonate [14] was added. Stirring for 30 min at –70° and for 12 h at RT. and workup with AcOEt gave an oil, which was purified by flash chromatography (AcOEt/CH_3OH 20:1) to give 2.51 g (27%) of **5d** as a 2.3:1 mixture of diastereoisomers. *Major isomer*: R_f (AcOEt/CH_3OH 20:1) 0.21. IR: 1755, 1725, 1612. ^{1}H-NMR: 1.26–1.38 (2*t*, 7.0, 7.4, 6 H); 1.59–1.76 (*m*, 1 H); 2.08–2.28 (*m*, 2 H); 2.28–2.40 (*m*, 1 H); 2.51–2.68 (*m*, 1 H); 2.81 (*ddd*, 14.3, 8.5, 1.5, 1 H); 3.03 (*ddd*, 14.2, 5.2, 1.5, 1 H); 3.19 (*dd*, 10.7, 8.1, 1 H); 3.7 (*dd*, 11.4, 1.8, 6 H); 3.82 (*q*, 7.0, 2 H); 4.22 (*q*, 7.4, 2 H); 4.48 (*d*, 5.9, 1 H). ^{13}C-NMR: 13.5 (*q*); 13.8 (*q*); 24.6 (*t*); 25.9 (*t*); 31.9 (*t*); 46.4 (*d*); 51.61 (*q*); 51.64 (*q*); 54.2 (*d*); 60.8 (*t*); 63.5 (*t*); 82.9 (*dd*, 206.7); 169.1 (*d*); 172.1 (*sd*, 22.9); 211.1 (*s*). MS: 348 (M^+), 302, 273, 229, 220, 193, 165, 151, 137. *83. Minor isomer*: ^{13}C-NMR: 13.5 (*q*); 13.7 (*q*); 24.4 (*q*); 26.4 (*t*); 32.2 (*t*); 46.2 (*d*); 51.48 (*q*); 51.50 (*q*); 53.4 (*t*); 54.2 (*t*); 63.47 (*t*); 83.6 (*dd*, 205.6); 168.6 (*s*); 172.2 (*sd*, 22.9).

Ethyl 1-(But-3-inyl)-3-[2-ethoxy-3-(dimethylphosphono)prop-2-enyl]-2-oxocyclopentanecarboxylate (**5e**). The solid K^+ salt, prepared from 2.0 g (5.8 mmol) of **5d** and 0.36 g of 82% KH (7.4 mmol) in 40 ml of THF was after removal of the solvent dissolved in 40 ml of DMSO, treated with 1.080 g (6 mmol) of 4-iodobut-1-yne and stirred for 24 h. After workup and low-bar chromatography 0.94 g of **5d** and 0.59 g (49% based on turnover of **5d**) of **5e** as a 3:1 mixture of diastereoisomers were obtained. *Major isomer*: R_f (AcOEt/CH_3OH 20:1) 0.38. IR: 3310, 1750, 1725, 1620. ^{1}H-NMR: 1.25–1.34 (2*t*, 7.0, 6 H); 1.27–1.36 (*m*, 1 H); 1.80–1.93 (*m*, 2 H); 1.97 (*m*, 1 H); 2.04–2.20 (*m*, 2 H); 2.20–2.28 (*m*, 1 H); 2.28–2.40 (*m*, 1 H); 2.40–2.54 (*m*, 1 H); 2.54–2.67 (*m*, 1 H); 2.77 (*dd*, 8.8, 1.0, 1 H); 2.94 (*ddd*, 14.0, 4.1, 1.5, 1 H); 3.70 (*dd*, 11.4, 1.8, 6 H); 3.81 (*q*, 7.0, 2 H); 4.20 (*q*, 7.0, 2 H); 4.46 (*d*, 6.3, 1 H). ^{13}C-NMR: 14.0 (*q*); 14.1 (*q*); 14.4 (*t*); 26.3 (*t*); 33.4 (*t*); 32.1 (*t*); 33.5 (*t*); 47.1 (*d*); 51.9 (*q*); 52.1 (*q*); 59.8 (*s*); 61.6 (*t*); 63.8 (*t*); 68.9 (*d*); 83.1 (*dd*, 207.4); 83.4 (*s*); 170.5 (*s*); 172.8 (*sd*, 22.5); 214.0 (*s*). MS: 400 (M^+), 281, 165, 151, 137, 84, *83. Minor isomer*: ^{13}C-NMR: 14.0 (*q*); 14.1 (*q*); 14.4 (*t*); 25.0 (*t*); 30.5 (*t*); 32.6 (*t*); 32.1 (*t*); 46.5 (*d*); 52.0 (*q*); 59.6 (*d*); 61.5 (*t*); 68.9 (*d*); 83.3 (*dd*, 207.4); 83.4 (*s*); 170.9 (*q*); 172.8 (*sd*, 22.5); 213.4 (*s*).

Ethyl 2-(But-3-inyl)-2-oxo-3-[2-oxo-3-(dimethylphosphono)propyl]cyclopentanecarboxylate (**5f**). A soln. of 0.60 g (1.5 mmol) of **5e** in 10 ml of CH_2Cl_2 and 20 ml of 70% CF_3COOH was refluxed for 45 min. After treatment with sat. $NaHCO_3$ soln. and evaporation of CH_2Cl_2 the crude product was purified by low-bar chromatography (AcOEt/CH_3OH 20:1) to give 0.45 g (81%) of **5f** as a 1.1:1 mixture of diastereoisomers.

Isomer **a**: R_f (AcOEt/CH_3OH 20:1) 0.25. IR: 3310, 1750, 1725. ^{1}H-NMR: 1.26 (*t*, 7.0, 3 H); 1.62 (*ddd*, 12.5, 5.2, 1.2, 1 H); 1.80–1.94 (*m*, 1 H); 1.98 (*t*, 2.2, 1 H); 2.0–2.37 (*m*, 5 H); 2.55 (*dd*, 12.9, 6.3, 1 H); 2.62–2.92 (*m*, 2 H); 3.12 (*d*, 22.8, 2 H); 3.05–3.18 (*m*, 1 H); 3.79 (*dt*, 11.4, 2.2, 6 H); 4.18 (*q*, 7.0, 2 H). ^{13}C-NMR: 14.1 (*q*); 14.3 (*t*); 26.7 (*t*); 31.4 (*t*); 33.4 (*t*); 41.5 (*td*, 127.8); 44.5 (*d*); 44.8 (*t*); 53.1 (*q*); 53.2 (*q*); 59.7 (*s*); 61.6 (*t*); 69.1 (*d*); 83.2 (*s*); 170.3 (*s*); 199.4 (*s*); 214.3 (*s*); MS: 372 (M^+), 320, 153, 151, 124, 87, 85, *83*.

Isomer **b**: ^{13}C-NMR: 14.0 (*q*); 14.4 (*t*); 25.3 (*t*); 30.9 (*t*); 32.2 (*t*); 41.4 (*dd*, 127.8); 43.7 (*t*); 44.5 (*d*); 53.0 (*q*); 53.1 (*q*); 59.1 (*s*); 61.6 (*d*); 68.8 (*d*); 83.7 (*s*); 171.0 (*s*); 199.4 (*s*); 213.6 (*s*).

8-(But-3-inyl)bicyclo[3.3.0]oct-1-en-3-one (**9c, d**). A mixture of 0.635 g (1.71 mmol) of **5f** and 2ml of 40% $(Bu)_4N^+OH^-$ (3.0 mmol) in 40 ml of toluene/H_2O 1:1 was vigorously stirred at RT. for 18 h. After neutralization with 2N HCl and extraction with CH_2Cl_2, the crude product was purified by low-bar chromatography (pentane/Et_2O 5:2) to give 0.16 g (54%) of **9c** and **9d** as a 1:9 mixture of diastereoisomers. Preparative GC (*Carbowax* 20%, 43 cm, 160°) provided **9c** and **9d** in pure form.

9c: R_f (pentane/Et_2O 5:2) 0.22. GC (2): 36.95 min. IR: 3310, 1710, 1650. ^{1}H-NMR: 1.13–1.35 (*m*, 2 H); 1.48–1.62 (*m*, 2 H); 1.65–1.75 (*m*, 1 H); 1.88–2.0 (*m*, 1 H); 2.0 (*t*, 2.8, 1 H); 2.08 (*dd*, 18.0, 3.3, 1 H); 2.14–2.22 (*m*, 1 H); 2.24–2.37 (*m*, 2 H); 2.62 (*ddd*, 18.0, 6.6, 0.8, 1 H); 2.89–3.08 (*m*, 2 H); 5.90 (*t*, 2.0, 1 H). ^{13}C-NMR: 17.1 (*t*); 29.5 (*t*); 31.4 (*t*); 32.2 (*t*); 37.7 (*d*); 42.6 (*t*); 46.1 (*d*); 69.1 (*d*); 83.4 (*s*); 123.5 (*d*); 194.1 (*s*); 210.8 (*s*). MS: 174 (M^+), 146, 132, 131, 118, 117, 105, 104, *91*.

9d: R_f (pentane/Et_2O 5:2) 0.17. GC (2): 35.98 min. IR: 3310, 1700, 1650. ^{1}H-NMR: 1.18 (*ddd*, 12.2, 7.7, 1 H); 1.58–1.69 (*m*, 1 H); 1.69–1.86 (*m*, 2 H); 2.02 (*t*, 2.6, 1 H); 2.11 (*ddd*, 17.6, 2.9, 1.5, 1 H); 2.20 (*dd*, 12.1, 6.6, 1 H); 2.29–2.36 (*m*, 3 H); 2.62 (*dd*, 17.6, 6.3, 1 H); 2.89–3.0 (*m*, 1 H); 3.01 (*p*, 7.7, 1 H); 5.9 (*t*, 1.8, 1 H). ^{13}C-NMR: 17.0 (*t*); 30.9 (*t*); 33.2 (*t*); 33.5 (*t*); 38.1 (*d*); 42.4 (*t*); 45.6 (*d*); 69.2 (*d*); 83.3 (*s*); 125 (*d*); 192.9 (*s*); 211.0 (*s*). MS: 174 (M^+), 146, 133, 131, 118, 117, 105, 104, 91.

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Synthese und Abfangen eines hochgespannten Cyclopropens**

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Abstract. Two synthetic sequences towards tricyclo[3.2.1.0^{2,4}]octa-2(4),6-diene (**12**) have been investigated starting with 1,1,2-tribromo-2-(trimethylsilyl)cyclopropane (**13**) (*Schemes 1* and *2*). F^--induced elimination **13**→**14a** and reaction with cyclopentadiene gives tricyclic dibromo precursor **15a** in a 87% yield. Subsequent reaction of **15a** with *t*-BuLi produces the highly strained cyclopropene **12** which has been trapped by [4+2] cycloaddition with diphenylisobenzofuran (40% yield). NMR-spectroscopic evidence of 2,4-disubstituted tricyclo[3.2.1.0^{2,4}]oct-6-enes **15a**, **15b**, and **16** (*Table*) is briefly discussed.

Einleitung

Gespannte Moleküle haben den organischen Chemiker seit langem fasziniert. Cyclopropene zählen zu den einfachsten Molekülen, welche eine beträchtliche Ringspannung aufweisen. Sie sind deshalb sowohl bindungstheoretisch wie spektroskopisch von erheblichem Interesse, jedoch als einfache reaktive C_3-Synthesebausteine auch synthetisch attraktiv [2]. Leider werden synthetische Anwendungen und spektroskopische Untersuchungen durch die hohe thermische Instabilität der unsubstituierten Cyclopropene eingeschränkt. Bicyclische Cyclopropene mit aussergewöhnlichen Bindungsverhältnissen gewinnt man formal beim Ersatz der beiden Vinyl-H-Atome durch eine kurze Alkyl-Kette. Theoretische Berechnungen zeigen nämlich, dass die olefinischen Substituenten der Bicyclen **1–4** nicht in einer Ebene liegen [3]. Dies lässt auf eine hohe Reaktivität der zentralen (C=C)-Bindung schliessen. Tat-

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