42. The Tandem *Pauson-Khand* Reaction

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Dedicated to *Hans-Dieter Scharf* on the occasion of his 65th birthday

(28.XII.95)

The conditions for the novel tandem *Pauson-Khand* reaction have been explored. The highly functionalized tetracyclic compounds **11c**, **11d**, and **16** were prepared from the ene-diynes **4c**, **4d**, and **10** by treatment with 2 equiv. of $[Co_2(CO)_8]$ and 4-methylmorpholine *N*-oxide (NMO) or Me_3NO in yields of 24, 22, and 53%, respectively (*Table*). In the presence of 1–3 equiv. of H_2O added to the NMO used for induction of the *Pauson-Khand* reaction of **6d**, a mixture of cyclopentanones **17**/**18** and cyclopentenones **12**/**13** was obtained (*Scheme 5*). The first example of a $[Co_2(CO)_6]$-induced highly stereoselective ene reaction is described. To account for these results, the formation of intermediates are proposed (*Schemes 6* and *7*) which hitherto have not been considered in the mechanistic description of the *Pauson-Khand* reaction.

Introduction. – Amongst the transition-metal-induced C–C bond-forming cyclocarbonylation reactions, the *Pauson-Khand* (*PK*) cyclization [1] plays an important role: Cyclopentenones are formed in good-to-excellent yields in intermolecular reactions between an alkyne, complexed with $[Co_2(CO)_6]$, and an olefin [2]. It is, therefore, of considerable synthetic interest [3] (for use of $CoBr_2$ in the preparation of $[Co_2(CO)_6L]$ complexes, see [4]). Usually, this transformation is initiated by heating in solution or oxidation using 4-methylmorpholine *N*-oxide (NMO), trimethylamine oxide (Me_3NO) or DMSO. In addition, special methods were described [5], *e.g.* the use of solid adsorbing materials [6] or catalysts [7]. Intramolecular cyclization-carbonylations, by which hept-1-en-6-ynes and oct-1-en-7-ynes were transformed into bicyclo[3.3.0]oct-1-en-3-ones and bicyclo[4.3.0]non-6-en-8-ones [8], could also be achieved under these conditions. The choice of the method for activating the cyclization reaction depends on the substrate. Thus, the tetracyclic [5.5.5.5]fenestrane **2** was only formed by treatment of **1** with a trialkylamine *N*-oxide like NMO or Me_3NO [9] (*Scheme 1, a*).

A very attractive approach to fenestranes is given by a tandem *Pauson-Khand* reaction of easily accessable ene-diynes. Thus, we had observed that the open-chain ene-diyne **4c** reacted with 2 equiv. of $[Co_2(CO)_8]$ in the presence of NMO *via* a tandem reaction directly to the tetracyclic diketone **11c** in an isolated yield of 9% [10] (*Scheme 1, b*). In an effort to explore the main features of this tandem reaction, by which six C–C bonds and three stereogenic centers were formed concomitantly, we investigated the influence of substituents at the tertiary center of the ene-diyne, the impact of H_2O on the NMO-induced reaction, and the stereoselectivity of these novel Co-carbonyl dependent cyclization-carbonylations. Moreover, our studies aimed at an efficient synthesis of highly functionalized [5.5.5.5]fenestranes.

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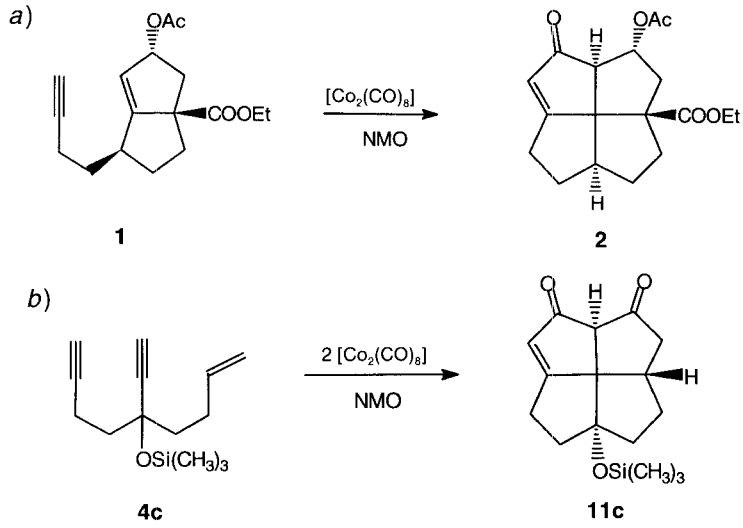
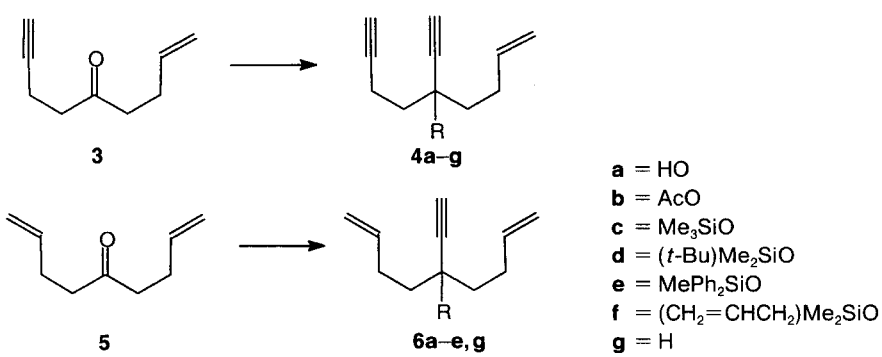
Scheme 1



Results and Discussion. – The ene-diynes **4a–g** and the dien-ynes **6a–e, g** served as substrates for a study of the influence of substituents (R) at the tertiary center on the cyclocarbonylations on the tandem *PK* reaction. In addition, the reactions of the oxy-connected ene-diyne **10** and dien-ynes **26a, b** (see below) were studied.

The key intermediates **4a** and **6a** were prepared from pent-4-ynoic and pent-4-enoic acid *via* the intermediates non-1-en-8-yn-5-one (**3**) and nona-1,8-dien-5-one (**5**), respectively, by treatment with ethynyl anions ($M^+ = Li^+$, $MgBr^+$; *Scheme 2*). Acetylation or silylation gave the ene-diynes **4b–f** and dien-ynes **6b–e**, respectively. The unsubstituted

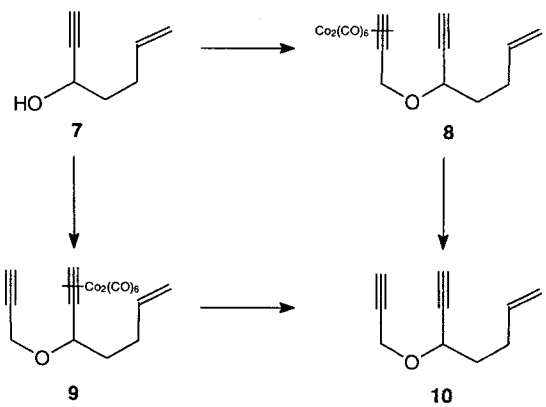
Scheme 2



hydrocarbons **4g** and **6g** were each obtained by reduction of the complexes $[Co_2(CO)_6(\mathbf{4a})]$ and $[Co_2(CO)_6(\mathbf{6a})]$ by a modified *Nicholas* reaction [11].

First, the $[Co_2(CO)_6]$ complex of the (propargyloxy)ene-diyne **8** was prepared from the $[Co_2(CO)_6]$ complex of propargylic alcohol and **7** (from pent-4-enal), whereas com-

Scheme 3

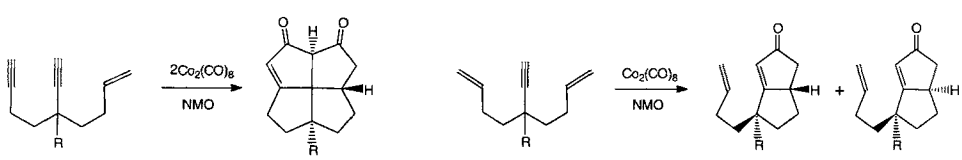


plex **9** was obtained from the $[Co_2(CO)_6(7)]$ and propargylic alcohol, both by a *Nicholas* reaction [11] (*Scheme 3*). However, when **8** and **9** were submitted to the *PK* reaction conditions, only products of higher molecular weight were obtained. Thus, **8** and **9** were each submitted to decomplexation with Ce^{4+} to give **10**.

When a solution of anhydrous NMO was added under optimized conditions to the complex $[\{Co_2(CO)_6\}_2(\mathbf{4c})]$, the yield of the fenestrenedione **11c** could be improved to an isolated yield of 24% (*cf. Table*). Similar results were obtained with **4d**, whereas **4e–g** gave poorer yields; neither bicyclic nor tetracyclic products were obtained with **4a** or **4b**. Thus, the yield of this novel tandem cyclization-carbonylation reaction strongly depends on the substituents at the tertiary center of the diyn-enes.

For comparison, the reactions of the dien-ynes **6b–e, g**, which can only undergo one cylcization step, were performed (*cf. Table*). The NMO-induced cyclization-carbonylations proceeded in good yields in the case of the complexes $[Co_2(CO)_6(\mathbf{6c})]$ and

Table. Pauson-Khand *Reaction of Ene-diynes* **4b–g** *and Dien-ynes* **6b–e,g**

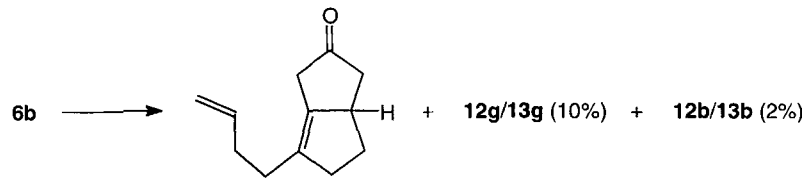


4b-g **11b-g** **6b-e,g** **12b-e,g** **13b-e,g**

Ene-diyne	Product	Yield [%]	Substituent R	Dien-yne	Products	Yield [%]	Ratio **12/13**
4b	**11b**	0	AcO	**6b**	**12b/13b**	2	1:1
4c	**11c**	24	Me_3SiO	**6c**	**12c/13c**	70	1:1
4d	**11d**	22	(*t*-Bu)Me_2SiO	**6d**	**12d/13d**	61	1:1.3
4e	**11e**	13	$MePh_2SiO$	**6e**	**12e/13e**	38	1:1.7
4f	**11f**	15	$(CH_2{=}CHCH_2)Me_2SiO$	–	–	–	–
4g	**11g**	5[a])	H	**6g**	**12g/13g**	38	1:1.5

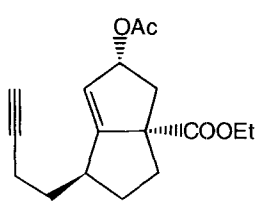
[a]) Only NMO step.

Scheme 4



$[Co_2(CO)_6(\mathbf{6d})]$, whereas **6e** and **6g** gave lower yields. The observation that the NMO-induced reaction of $[Co_2(CO)_6(\mathbf{6b})]$, which is related to that of **4b**, gave *via* reductive elimination, **14** as the major product (28%) rather than **12b/13b** (2%; *Scheme 4*) may explain why **11b** was absent in the attempted tandem reaction of **4b**. Overall, the tendency of the yields in the reactions of **6b–e, g** is in agreement with those obtained in the tandem reactions. In all cases, the stereoselectivity was rather low and in the range of 1:1 to 1:1.7.

In view of this rather modest stereoselectivity and the observation, that **15**, a stereoisomer of **1**, did not undergo the NMO-induced *PK* reaction to give a [5.5.5.5]fenestrene-dione stereoisomeric to **2**, it is apparent that the tandem reaction proceeds only *via* those bicyclic intermediates in which the peripheral butynyl group is formally in an '*exo*'-position[2]) (see below). Thus, the important 4 of the 8 stereogenic centers of the tetracyclic compounds **11c–g** are only formed with the specific configuration of an all-*cis*-fenestrane [12][3]).



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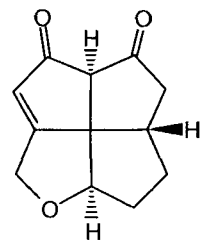

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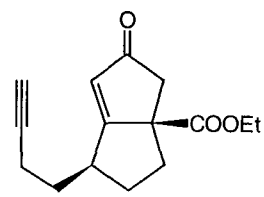

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To gain further insight into the conditions of the *PK* reaction, substrate **10** was submitted to the conditions of the tandem reaction. This (propargyloxy)ene-diyne gave the oxa[5.5.5.5]fenestrene-dione **16** with an isolated yield of 53%. This higher yield as compared to that of **11** is in accordance with the observation that replacement of CH_2 group by an oxy moiety in the propargylic position of hept-1-en-6-ynes leads to a higher proportion of '*exo*'-substituted bicyclo[3.3.0]octenones [13].

In view of the open question, whether anhydrous *N*-oxides should be used for reliable yields of *PK* products, we investigated the reaction of dien-yne **6d** with NMO to which H_2O had been added. With anhydrous NMO, the stereoisomeric bicyclic enones **12d** and

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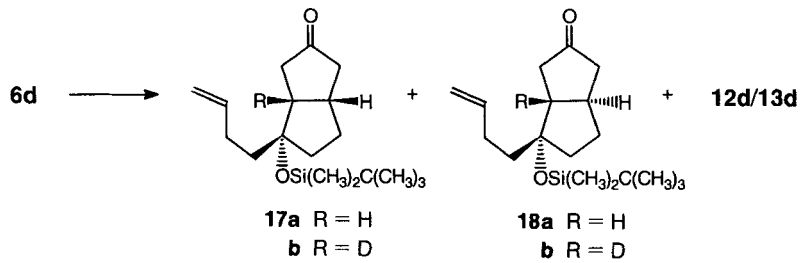
[2]) '*exo*' and '*endo*' refer to the location of substituents above or below the roof-like structure of bicyclo[3.3.0]octane and bicyclo[3.3.0]oct-1-ene, respectively.

[3]) *cis* refers to the ring fusion of the bicyclo[3.3.0]octane subunits.

13d were obtained in a yield of 61% (*cf. Table*). When the complex $[Co_2(CO)_6(\mathbf{6d})]$ was treated with NMO containing up to 3 mol-equiv. of H_2O, the amount of the saturated ketones **17a** and **18a** increased from 16 to 50% with the total yield of the stereoisomer mixture of products in the *PK* cyclization (**12d/13d** + **17a/18a**) remaining constant in the range of 58–61% (*Scheme 5*). In the presence of D_2O, the bridgehead positions of the bicyclic products **17b** and **18b**, and to a smaller extent the CH_2 group in the α-position to the carbonyl group were deuterated. When the tandem reaction of **4d** was run in the presence of hydrated NMO, the yield of **11d** decreased. The fenestrane-dione, where the C=C bond of **11d** is saturated, was not found.

Scheme 5

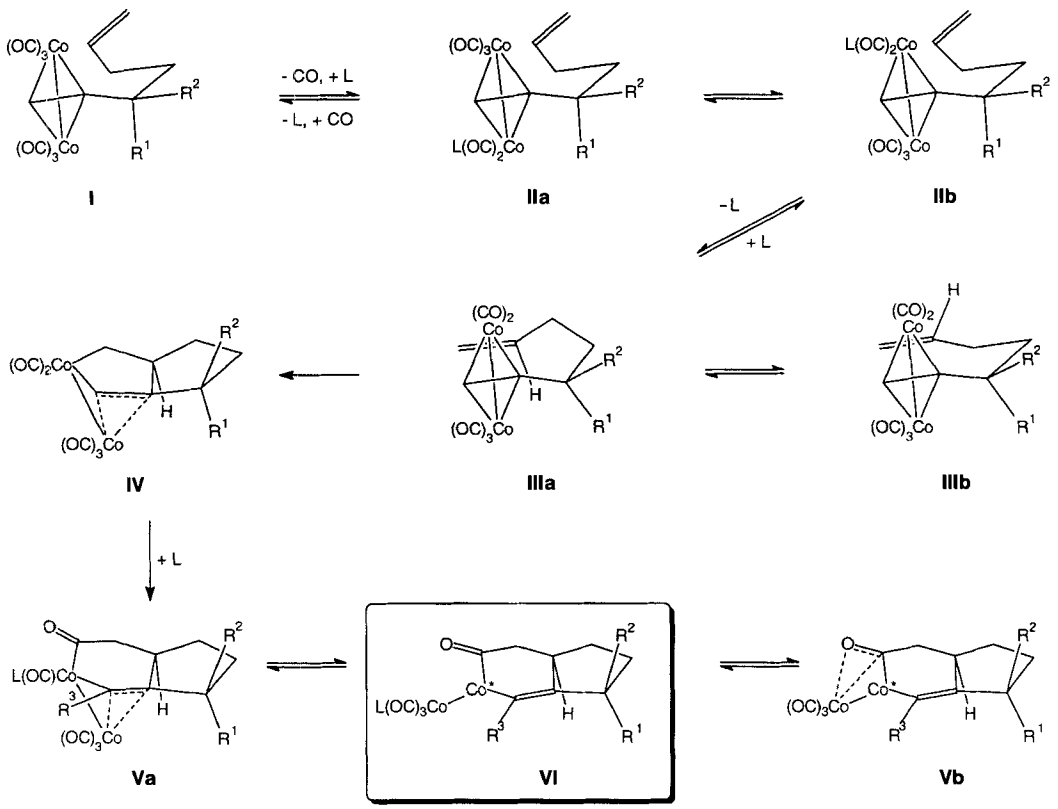


As mentioned above, reduction was also observed in the *PK* reaction of the acetoxy-diene-yne **6b**, where **14** and **12g/13g** (1:1 mixture of stereoisomers) were formed as the main products while the expected products **12b/13b** were isolated with 2% yield only (see *Scheme 4*).

Mechanistic Implications. Based on stereoselectivities, *Magnus* and *Principe* [14] have developed a mechanistic concept for the *PK* reaction which subsequently was improved by *Schore* [15] and others. It is suggested that the reaction rate is determined by the first C–C bond formation step, also controlling the stereoselection. Most recently, *Krafft et al.* [16] have studied the effect of coordinating ligands on the cyclization reaction and observed an intermediate which reacted to the product much faster than the corresponding $[Co_2(CO)_6]$ complex of the en-yne itself, indicating an early rate-determining transition state. This led to an improved mechanistic model for the *PK* reaction [15]. The study of substituent effects led to the conclusion that π-acceptor groups conjugated with the alkyne are compatible with the *PK* reaction, whereas π-acceptor groups attached to the C=C bond do not undergo the typical cyclocarbonylation reaction but may instead, react to other products [17]. This was further supported by our observation that **19** (see above) gave only high-molecular-weight products rather than a tetracyclic fenestrenedione. In addition, reduction of the C=C bond in **12d/13d** was not observed when the enone was treated with $[Co_2(CO)_8]$ and hydrated NMO.

We are thus led to a mechanistic proposition, where an intermediate **VI** with an uncomplexed C=C bond is formed, which, *prior* to its conjugation with a carbonyl group, is amenable to further reactions including the second *PK* reaction (*cf. Scheme 6*). The C≡C bond of a $[Co_2(CO)_6$(alkyne)] complex [18] **I**, conformationally stable with respect to rotation of the alkyne moiety relative to the Co–Co bond axis, resembles with a bond length of the C≡C bond of 133 pm rather than 120.2 pm and with bond angles between

Scheme 6



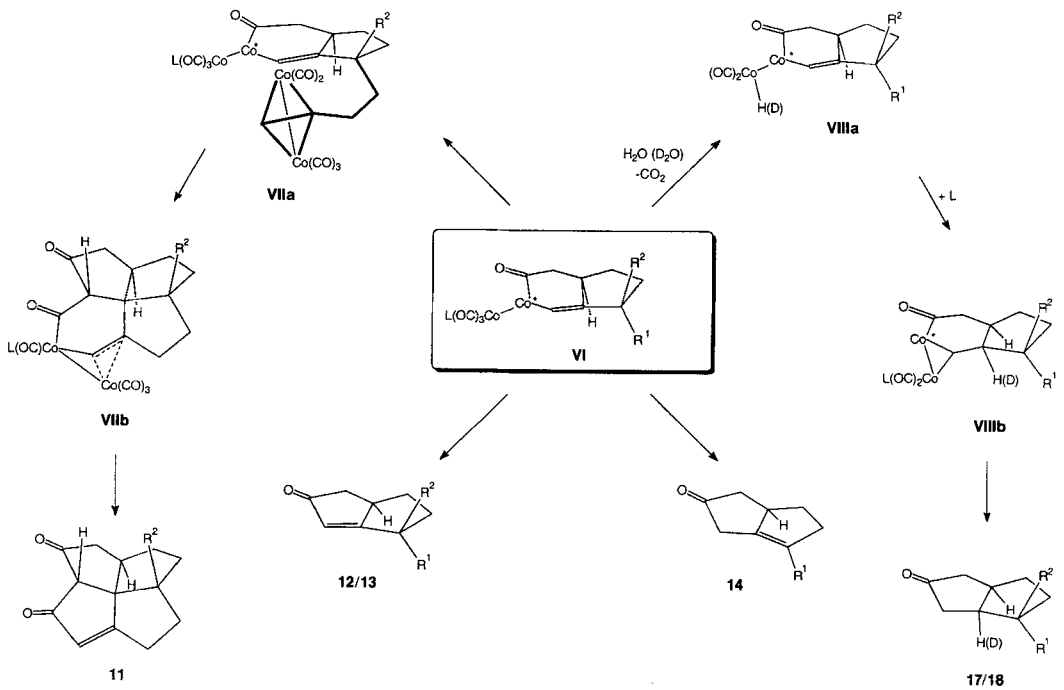
$R^1 = [Co_2(CO)_6(CH{\equiv}CCH_2CH_2)]$ or $CH{=}CHCH_2CH_2$, $R^2 = R$ (see *Table*), $R^3 = H$, Me_3Si, Co* = Co(CO)L.

136° and 145° rather than 180° [19] strongly a C=C bond. The $Co_2(CO)_6$ moiety reacts *via* exchange or removal of a CO ligand at either of the two Co centers to a coordinatively unsaturated complex where the CO groups might be highly fluxional. It can temporarily be stabilized by an exchange of L and/or CO [20] for a solvent molecule or a separate ligand at either of the 2 Co centers (**IIa** or **IIb**) [16] and may eventually react with the olefinic C=C bond to a rapidly equilibrating mixture of **IIIa** and **IIIb**. The stereoselectivity is controlled in the C–C bond-forming step leading to **IV**: due to the strongly bent C≡C bond in the complex **III**, substituents in the propargylic position with '*endo*'-orientation (R^2) interfere with substituents at the terminal C of the alkyne ($R^3 \neq H$) leading to partial $A^{1,3}$ allylic strain [21]. Since C=C bonds are elongated and pyramidalized in π-complexes with transition metals [22], it is reasonable to expect that the strain – and hence the stereoselection – is smaller than with a structure of 'full' allylic strain [23]. The cobaltacycle **IV** leads in a stereoelectronically favorable reaction to the six-membered [Co(acyl)(vinyl)] complex **Va**, where fluxional behavior and incorporation of an external ligand (CO in the thermal variant) are feasable. This complex might be in equilibrium *via*

VI with **Vb**, where the π-system of the carbonyl group stabilizes the second Co group by enhanced backbonding [24], before the cyclopentenone ring is formed *via* reductive elimination of the basal Co moiety.

For the tandem reaction to be successful, the [Co]-(acyl) complex **VI** containing an olefinic C=C bond with the basal Co as electron-donor substituent can undergo a further π-interaction with the adjacent $[Co_2(CO)_6]$ complex of the '*exo*'-but-3-ynyl side chain (R^1), leading *via* **VIIa,b** eventually to the tetracyclic system **11** (*cf. Scheme 7*). For the

Scheme 7



$R^1 = [Co_2(CO)_6(CH{\equiv}CCH_2CH_2)]$ or $CH_2{=}CHCH_2CH_2$, R^2 = R (see *Table*), Co* = Co(CO)L.

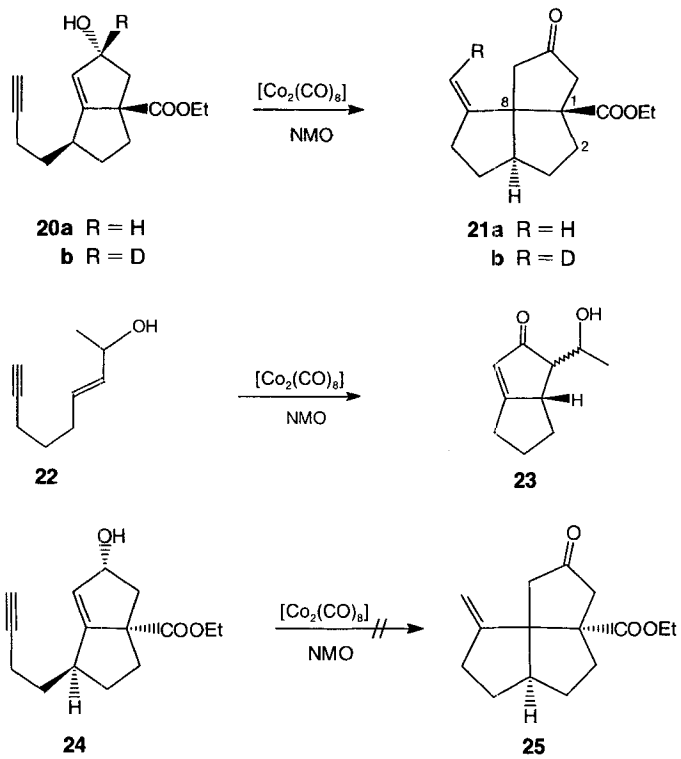
sequence of events favoring the tandem *PK* reaction, the decomposition of the peripheral $[Co_2(CO)_5L(alkyne)]$ complex must be slower than its interaction with the cobaltacycle to give **VII**. This fine tuning of events might only be possible when the cyclization-carbonylation of the Co complexes is run in the presence of NMO or Me_3NO, but not under thermal conditions or adsorbed on silica gel. Furthermore, the lack of ω-substitution at the 'inner' alkyne group (R^3 = H) seems to be critical for the success of the second *PK* reaction: with a Me_3Si group (see **Va,b**, and **VI** with $R^3 = Me_3Si$ in *Scheme 6*), no product of a tandem *PK* reaction was observed [10].

This model also allows for an interpretation of the reductive elimination in the reaction of **6b** (R^2 = R = AcO) to **14**. The leaving of AcO^- is enhanced by the low-valent

Co group, complexed to the adjacent C=C bond as in **Va**. For the formation of **17**/**18** in the *PK* reaction of **6d** ($R^2 = R = (t\text{-Bu})Me_2SiO$, $R^1 = CH_2{=}CHCH_2CH_2$) with hydrated NMO, H_2O might react with one of the CO ligands in **VI** leading of **VIIIa** with a Co–H(D) moiety [25]. Addition of Co–H(D) to the C–C bond will give *via* **VIIIb** the saturated bicyclic ketones **17**/**18**.

The involvement of a $Co_2(CO)_x$ species in H-transfer reactions is also suggested by the attempted *PK* reaction of **20a** which react in the presence of NMO to the tricyclic

Scheme 8

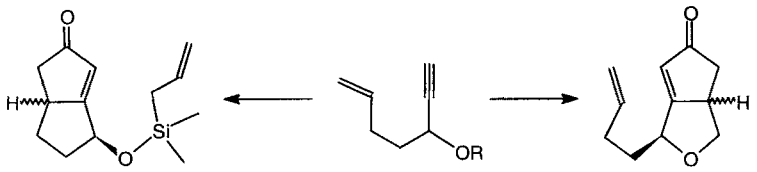


structure **21a** (*Scheme 8*). Labelling experiments showed that a D-atom is stereoselectively transferred from the 3-'*exo*' position in **20b** to the *cis*-position (rel. to the angular C(8)) of the exocyclic C=C bond in **21b**. This seems to be a special case, because control experiments with en-ynes like **22** led to the normal *PK* product **23**. En-yne **24**, stereoisomeric to **20**, gave neither a tetracyclic product nor **25**.

The enlarged mechanistic model depicted in *Schemes 6* and *7* might be useful for further investigations of the chemo-, regio-, and stereoselectivity of the *PK* reaction.

An intriguing new example for the regioselectivity in *PK* cyclocarbonylations was provided by the observation that **27** was formed from **26a**, whereas **26b** led to **28** [15] [26] (*Scheme 9*; **26a**, **b** were prepared from hept-6-en-1-yn-3-ol (7); for exper. details, see [26]).

Scheme 9



28 **26a** R = CH_2=$CHCH_2$ **27**
b R = (CH_2=$CHCH_2$)Me_2Si

Conclusions. – Particularly noteworthy is the observation that a tandem *PK* reaction is possible at all. This suggests that the decomposition of the peripheral [$Co_2(CO)_5$L(alkyne)] complex is slower than its interaction with an adjacent C=C bond in a distance suitable for preferential formation of a 5- or 6-membered ring [5] [27] and the subsequent reactions. A thermochemical estimate of the formation of cyclopent-2-enone from acetylene, ethylene, and CO clearly indicates that this formal [2 + 2 + 1] cycloaddition is exothermic by *ca.* 38 kcal/mol and thus might allow for the built-up of strain. However, it has been found that **15**, stereoisomeric to **1**, does not undergo a *PK* reaction, and, in the tandem reaction of **4c–g**, the three stereogenic centers are formed with a configuration corresponding to the most stable stereoisomeric [5.5.5.5]fenestrenedione. The systematic variation of substituents at the tertiary center of ene-diynes, the influence of heteroatoms in other positions, and the use of hydrated NMO led to a more precise concept of some mechanistic steps most likely involved in the *PK* reaction. Moreover, the synthetic goal of an efficient preparation of tetracyclic fenestrenediones is apparent from the result that the functionalized [5.5.5.5]fenestrenes **11c** and **16** can be prepared from pent-4-ynoic acid and pent-4-enal in 5 and 3 steps, respectively, with overall yields of 17 and 47%.

This work was generously supported by the *Swiss National Science Foundation* (project No. 20-37270.93) and the *Stipendienfonds der Basler Chemischen Industrie*. We are grateful to Dr. *C. Monnier*, *Ciba*, Marly, for generous supply of intermediates and thank PD Dr. *P. Bigler* for NMR analyses.

Experimental Part

1. *General.* Chemicals were purchased from commercial suppliers and used without further purification. CH_2Cl_2 was distilled over P_2O_5, THF and Et_2O were distilled over sodium benzophenone ketyl, and pentane and hexane were distilled over NaH prior to use. DMF *puriss. p.a.* over molecular sieves (*Fluka*) was used without further purification. Reactions were normally performed under Ar in standard glassware. After workup by normally pouring the reaction mixture onto ice water and extraction with Et_2O, the solns. were dried ($MgSO_4$). Flash chromatography (FC): silica gel *60* (230–400 mesh). TLC: silica-gel plates *SIL G/UV$_{254}$* (*Macherey & Nagel*): eluent *1* (hexane/Et_2O), *2* (hexane/*t*-BuOMe), *3* (hexane/AcOEt), *4* (hexane), *5* (Et_2O), *6* (AcOEt). GC: *Hewlett-Packard-HP-5890* instrument, *HP-5-Ultra* capillary column (10 m × 0.2 mm); temp. program 40–280° (6°/min). Anal. HPLC *LiChrosorb* (*SI 60*, 5 μm) column (250 × 3.2 mm). Prep. HPLC: *LiChrosorb* (*SI 60*, 5 μm) column (250 × 23 mm). M.p.: *Büchi-510* melting-point apparatus; uncorrected. IR Spectra: *Perkin-Elmer-782*-IR or FTIR-*1600* spectrophotometers; at 296 K in $CHCl_3$. NMR Spectra: *Bruker-AC-300* (^{1}H, 300 MHz; ^{13}C, 75 MHz), *-AM 400* (NOE; ^{1}H, 400 MHz; ^{13}C, 100 MHz), and *-DRX-500* (NOE, homo-COSY, and hetero-COSY; ^{1}H, 500 MHz; ^{13}C, 125 MHz) spectrometers; at 296 K in $CDCl_3$; δ in ppm rel. to internal $SiMe_4$ (= 0.00 ppm), *J*'s in Hz; stack = heavily overlapping signals. MS: *Varian-MAT-CH7A* (70 eV, EI) and *Fisons-Autospec-Q* spectrometer; in *m/z* (rel. intensity). GC/MS: *VG-Autospec* spectrometer.

2. *Ene-diynes* **4a–g**. *Non-1-en-8-yn-5-one* (**3**). To a soln. of pent-4-ynoyl chloride (prepared from 6.68 g (68.2 mmol) of pent-4-ynoic acid by treatment with PCl_3 at 50° and decanting) in 100 ml of THF was added by syringe a soln. of but-3-enyl magnesium bromide (75 mmol) in 100 ml of THF at −78° over 90 min. After warming to r.t. for 3 h, the mixture was worked up: 9.85 g (94%) of **3**. Yellow oil. GC: purity 89%. R_f (*1* 2:1) 0.47. IR: 3305, 2120, 1720, 1245, 1015. ^{1}H-NMR: 5.85–5.71 (*m*, 1 H); 5.05–4.93 (stack, 2 H); 2.65 (*t*, *J* = 6.6, 2 H); 2.52 (*t*, *J* = 7.0, 2 H); 2.46–2.39 (*m*, 2 H); 2.36–2.27 (*m*, 2 H); 1.93 (*t*, *J* = 2.6, 1 H). ^{13}C-NMR: 207.5 (*s*); 136.8 (*d*); 115.2 (*t*); 82.9 (*s*); 68.6 (*d*); 41.7 (*t*); 41.2 (*t*); 27.5 (*t*); 12.8 (*t*). MS: 136 (1, M^+), 121 (8), 117 (4), 108 (8), 107 (8), 95 (13), 94 (20), 93 (18), 83 (44), 81 (100), 79 (45), 55 (71), 53 (69).

5-(Ethynyl)non-1-en-8-yn-5-ol (**4a**). To a sat. soln. of ethyne in 180 ml of THF at 0° was slowly added a soln. of 200 mmol of EtMgCl in 100 ml of THF at −5° under a continuous flow of ethyne. After stirring for 30 min at 5–10°, 9.85 g (64.3 mmol) of **3** was added dropwise at −5°. The green-brownish mixture was stirred at r.t. for 18 h. After workup with a sat. NH_4Cl soln., the crude product was flash chromatographed (*1* 1:1): 8.18 g (74% from pent-4-ynoic acid) **4a**. Viscous, yellowish oil. GC: purity 98%. For an alternative method, see [10]. R_f (*1* 2:1) 0.34. IR: 3600, 3310, 1645, 1450, 1445, 1075. ^{1}H-NMR: 5.93–5.79 (*m*, 1 H); 5.12–4.93 (stack, 2 H); 2.59–2.39 (stack, 3 H); 2.52 (*s*, 1 H); 2.38–2.25 (stack, 2 H); 2.00 (*t*, *J* = 2.2, 1 H); 1.91 (*dd*, *J* = 7.0, 8.5, 2 H); 1.75 (*dd*, *J* = 6.8, 9.6, 2 H). ^{13}C-NMR: 138.1 (*d*); 115.1 (*t*); 85.2 (*s*); 84.1 (*s*); 73.6 (*d*); 70.7 (*s*); 69.0 (*d*); 41.1 (*t*); 40.3 (*t*); 28.6 (*t*); 13.8 (*t*). MS: 162 (3, M^+), 143 (49), 129 (80), 128 (75), 117 (50), 115 (49), 109 (82), 107 (100), 105 (73), 104 (57), 103 (58), 95 (47), 91 (71), 81 (83), 79 (82), 78 (57), 77 (98), 55 (67), 53 (92). HR-MS: 162.1038 (M^+, $C_{11}H_{14}O^+$, calc. 162.1044).

5-(Ethynyl)non-1-en-8-yn-5-yl Acetate (**4b**). Treatment of 0.2 g (1.23 mmol) of **4a** with 0.198 g (1.85 mmol) of Ac_2O in 5 ml of pyridine gave, after addition of 0.03 g (0.24 mmol) of 4-(dimethylamino)pyridine at 0° and stirring for 2 h at r.t., 0.227 g (90%) of **4b**. Yellowish oil. R_f (*1* 5:1) 0.32. IR: 3306, 1740, 1240. ^{1}H-NMR: 5.87–5.71 (*m*, 1 H); 5.08–4.93 (stack, 2 H); 2.62 (*s*, 1 H); 2.43–1.92 (stack, 9 H); 2.03 (*s*, 3 H). ^{13}C-NMR: 169.1 (*s*); 137.2 (*d*); 115.1 (*t*); 83.3 (*s*); 81.7 (*s*); 77.2 (*s*); 75.2 (*d*); 68.5 (*d*); 37.2 (*t*); 37.2 (*t*); 28.2 (*t*); 21.7 (*q*); 13.7 (*t*). MS: 204 (1, M^+), 143 (18), 129 (59), 128 (57), 123 (96), 121 (40), 115 (24), 107 (28), 103 (31), 91 (36), 77 (35), 43 (100).

Silylation of the Tertiary OH Group in **4a**. *General Method*. To a soln. of **4a** (1.23 mmol) and Et_3N (1.6 mmol) in 10 ml of THF were added dropwise 1.3 mol-equiv. of the corresponding silyl triflate at −10°. After stirring for 10 min at r.t., the mixture was poured onto ice water and extracted with pentane.

5-(Ethynyl)-5-(trimethylsilyloxy)non-1-en-8-yne (**4c**): Yield 93%. Colorless oil. R_f (*3* 9:1) 0.59. IR: 3310, 1250, 1100, 1000, 865, 840, 660, 640. ^{1}H-NMR: 5.87 (*ddt*, *J* = 16.9, 10.2, 6.6, 1 H); 5.04 (*ddt*, *J* = 16.9, 1.6, 1.6, 1 H); 4.97 (*ddt*, *J* = 10.2, 1.6, 0.8, 1 H); 2.50 (*s*, 1 H); 2.36 (stack, 2 H); 2.21 (stack, 2 H); 1.91 (stack, 3 H); 1.72 (stack, 2 H); 0.18 (*s*, 9 H). ^{13}C-NMR: 138.2 (*d*); 114.6 (*t*); 85.8 (*s*); 84.4 (*s*); 74.3 (*d*); 71.3 (*s*); 68.0 (*d*); 41.9 (*t*); 41.5 (*t*); 28.6 (*t*); 13.8 (*t*); 1.9 (*q*). MS: 234 (1, M^+), 233 (3), 219 (14), 195 (9), 181 (74), 179 (100), 163 (20), 145 (17), 130 (20), 129 (20), 105 (32), 83 (28), 75 (58), 73 (87), 45 (18).

5-[(tert-Butyl)dimethylsilyloxy]-5-(ethynyl)non-1-en-8-yne (**4d**): Yield 98%. Colorless oil. R_f (*1* 6:1) 0.74. IR: 3305, 2960, 2925, 1252, 1095, 838. ^{1}H-NMR: 5.92–5.76 (*m*, 1 H); 5.08–4.93 (stack, 2 H); 2.50 (*s*, 1 H); 2.41–2.34 (stack, 2 H); 2.30–2.16 (stack, 2 H); 1.97–1.88 (stack, 2 H); 1.95 (*t*, *J* = 2.5, 1 H); 1.77–1.69 (stack, 2 H); 0.88 (*s*, 9 H); 0.19 (*s*, 6 H). ^{13}C-NMR: 138.1 (*d*); 114.5 (*t*); 85.9 (*s*); 84.3 (*s*); 74.0 (*d*); 71.1 (*s*); 68.0 (*d*); 41.8 (*t*); 41.4 (*t*); 28.6 (*t*); 25.7 (*q*); 18.1 (*s*); 13.7 (*t*); −3.0 (*q*); −3.1 (*q*). MS: 263 (7, $[M - 13]^+$), 221 (39), 178 (24), 163 (15), 145 (21), 75 (100), 73 (50). HR-MS: 276.1911 (M^+, $C_{17}H_{28}OSi^+$, calc. 276.1909).

5-(Ethynyl)-5-[(methyl)diphenylsilyloxy]non-1-en-8-yne (**4e**). Prepared with $MePh_2SiCl$ and 1*H*-imidazole in DMF at r.t. Yield 85%. Colorless oil. R_f (*1* 40:1) 0.41. IR: 3305, 1111. ^{1}H-NMR: 7.65–7.60 (stack, 4 H); 7.44–7.35 (stack, 6 H); 5.84–5.70 (*m*, 1 H); 5.03–4.92 (stack, 2 H); 2.46–2.38 (stack, 2 H); 2.44 (*s*, 1 H); 2.28–2.18 (stack, 2 H); 2.09–1.95 (*m*, 2 H); 1.95 (*t*, *J* = 2.5, 1 H); 1.84–1.76 (stack, 2 H); 0.84 (*s*, 3 H). ^{13}C-NMR: 138.1 (*d*); 137.5 (*s*); 137.4 (*s*); 134.6 (*d*); 134.6 (*d*); 129.8 (*d*); 127.8 (*d*); 114.8 (*t*); 85.7 (*s*); 84.4 (*s*); 74.9 (*d*); 72.6 (*s*); 68.3 (*d*); 41.6 (*t*); 41.2 (*t*); 28.7 (*t*); 14.0 (*t*); −0.6 (*q*). MS: 358 (3, M^+), 357 (3), 343 (6). 330 (4), 317 (8), 305 (36), 304 (47), 303 (72), 267 (7), 265 (5), 239 (15), 227 (18), 225 (20), 222 (28), 207 (18), 199 (61), 198 (57), 197 (100), 181 (26), 137 (54).

5-[(Allyldimethylsilyloxy)]-5-(ethynyl)non-1-en-8-yne (**4f**). Prepared with (allyl) (chloro)dimethyl silane and 1*H*-imidazole in DMF at r.t. Yield 71%. Colorless oil. R_f (*1* 2:1) 0.67. IR: 3300, 2960, 1255, 1155, 1095, 1063, 995. ^{1}H-NMR: 5.91–5.72 (stack, 2 H); 5.08–4.83 (stack, 4 H); 2.53 (*s*, 1 H); 2.41–2.33 (stack, 2 H); 2.26–2.15 (stack, 2 H); 1.96–1.87 (stack, 3 H); 1.77–1.67 (stack, 2 H); 1.68 (*d*, *J* = 8.3, 2 H); 0.21 (*s*, 6 H). ^{13}C-NMR: 138.2 (*d*); 134.4 (*d*); 114.7 (*t*); 113.7 (*t*); 86.0 (*s*); 84.5 (*s*); 74.5 (*d*); 71.6 (*s*); 68.2 (*d*); 41.9 (*t*); 41.5 (*t*); 28.7 (*t*); 26.1 (*t*); 13.9 (*t*); −0.1 (*q*). MS: 219 (3, $[M - 41]^+$), 207 (2), 205 (3), 185 (5), 183 (7), 178 (13), 173 (8), 163 (9), 145 (11), 128 (7), 117 (6), 115 (5), 105 (5), 99 (9), 91 (10), 83 (12), 75 (100), 59 (14).

[5-(Ethynyl)non-1-en-8-yne]bis(hexacarbonyldicobalt) ([{$Co_2(CO)_6$}$_2$ (**4g**)]). A mixture of 0.4 g (2.47 mmol) of **4a** and 1.795 g (5.25 mmol) of [$Co_2(CO)_8$] in 24 ml of CH_2Cl_2 was stirred for 2.5 h at r.t. After addition of 0.78 g

(12.35 mmol) of $NaBH_3CN$ at −10°, 2.9 ml (37.8 mmol) of CF_3COOH were added dropwise during 20 min. The coagulated red mixture was poured onto ice water and stirred until the solid material had dissolved. After removal of most of the solvent, the crude product was filtered through *Celite* and silica gel to give 1.16 g (65%) of $[\{Co_2(CO)_6\}_2$ (**4g**)] as a dark red solid which decomposed in air, but was stable under Ar at –20° for several days. R_f(*4*) 0.44. IR: 2090, 2050, 2020. ^{1}H-NMR: 6.13 (*s*, 1 H); 6.03 (*s*, 1 H); 5.84 (*m*, 1 H); 5.20–5.00 (stack, 2 H); 3.03 (stack, 2 H); 2.83 (*m*, 1 H); 2.27 (stack, 2 H); 2.05–1.55 (stack, 4 H; br. signals). ^{13}C-NMR: 199.7 (*s*); 137.5 (*d*); 115.4 (*t*); 101.5 (*s*); 96.1 (*s*); 74.2 (*d*); 72.8 (*d*); 41.1 (*d*); 38.5 (*t*); 35.7 (*t*); 32.1 (*t*); 31.3 (*t*). MS: 718 (3, M^+), 690 (15), 662 (40), 550 (77), 522 (59), 494 (100), 466 (88), 438 (63), 432 (42), 410 (51), 380 (40), 378 (44), 376 (56), 320 (40), 292 (55), 264 (58), 28 (59).

3. *Dien-ynes* **6a**–**e**. *5-(Ethynyl)nona-1,8-dien-5-ol* (**6a**) was prepared from pent-4-enoic acid *via* **5** as described for **4a**, except that Li-acetylide/ethylenediamine was used.

Nona-1,8-dien-5-one (**5**): Yield 81%. Yellowish oil. R_f (*1* 7:3) 0.28. IR: 1715. ^{1}H-NMR: 5.81 (*ddt*, J = 17.3, 10.0, 6.6, 2 H); 5.02 (*ddt*, J = 17.3, 1.7, 1.5, 2 H); 4.97 (*ddt*, J = 10.0, 1.7, 1.5, 2 H); 2.51 (*t*, J = 7.0, 4 H); 2.37–2.28 (*m*, 4 H). ^{13}C-NMR: 27.7 (*t*); 41.8 (*t*); 115.2 (*t*); 137.1 (*d*); 209.3 (*s*). MS: 138 (18, M^+), 123 (11), 114 (9), 97 (12), 96 (20), 84 (37), 83 (100), 82 (22), 56 (25), 55 (96).

6a: Yield 61%, based on pent-4-enoic acid. GC: purity 91%. Colorless oil. R_f (*1* 6:1) 0.27. IR: 3600, 3308, 1643, 1452, 995, 915. ^{1}H-NMR: 5.94–5.80 (*m*, 2 H); 5.12–4.96 (stack, 4 H); 2.50 (*s*, 1 H); 2.39–2.26 (stack, 4 H); 2.22 (*s*, 1 H); 1.76 (*t*, J = 8.8, 4 H). ^{13}C-NMR: 138.4 (*d*); 115.1 (*t*); 86.2 (*s*); 73.2 (*d*); 71.1 (*s*); 41.1 (*t*); 28.8 (*t*). MS: 149 (2, $[M - 15]^+$), 131 (19), 117 (20), 109 (55), 105 (26), 95 (24), 91 (51), 83 (31), 81 (100), 79 (74), 55 (62), 53 (90). HR-MS: 164.1196 (M^+, $C_{11}H_{16}O^+$, calc. 164.1201).

5-(Ethynyl)nona-1,8-dien-5-yl Acetate (**6b**). As described for **4b**. Yield 89%. Colorless oil. R_f (*1* 3:1) 0.40. IR: 3300, 3020, 1738, 1210. ^{1}H-NMR: 5.89–5.75 (*m*, 2 H); 5.09–4.94 (stack, 4 H); 2.61 (*s*, 1 H); 2.29–2.09 (stack, 6 H); 2.04 (*s*, 3 H); 2.02–1.91 (*m*, 2 H). ^{13}C-NMR: 169.0 (*s*); 137.3 (*d*); 114.8 (*t*); 82.5 (*s*); 77.7 (*s*); 74.4 (*d*); 37.3 (*t*); 28.1 (*t*); 21.7 (*q*). MS: 206 (1, M^+), 131 (59), 123 (100), 117 (51), 109 (39), 105 (60), 104 (35), 95 (43), 93 (32), 91 (63), 81 (34), 79 (53), 77 (38), 55 (33), 43 (78). HR-MS: 206.1292 (M^+, $C_{13}H_{18}O_2^+$, calc. 206.1306).

5-(Ethynyl)-5-(trimethylsilyloxy)nona-1,8-diene (**6c**). As described for **4c**. Yield 86%. Colorless oil. R_f (*1* 1:40) 0.62. IR: 3305, 3020, 1520, 1250, 1255. ^{1}H-NMR: 5.93–5.78 (*m*, 2 H); 5.09–4.94 (stack, 4 H); 2.48 (*s*, 1 H); 2.31–2.18 (*m*, 4 H); 1.79–1.69 (*m*, 4 H); 0.20 (*s*, 9 H). ^{13}C-NMR: 138.5 (*d*); 114.3 (*t*); 86.7 (*s*); 73.7 (*d*); 71.8 (*s*); 41.9 (*t*); 28.6 (*t*); 1.9 (*q*). MS: 235 (1, $[M - 1]^+$), 183 (19), 182 (54), 181 (100), 91 (23), 83 (31), 75 (48), 73 (74), 55 (17).

5-[(tert-Butyl)dimethylsilyloxy]-5-(ethynyl)nona-1,8-diene (**6d**). As described for **4d**. Yield 98%. Colorless oil. R_f (*1* 6:1) 0.54. IR: 3303, 1642, 1254, 838. ^{1}H-NMR: 5.93–5.78 (*m*, 2 H); 5.09–4.92 (stack, 4 H); 2.47 (*s*, 1 H); 2.28–2.17 (*m*, 4 H); 1.77–1.68 (*m*, 4 H); 0.89 (*s*, 9 H); 0.20 (*s*, 6 H). ^{13}C-NMR: 138.6 (*d*); 114.4 (*t*); 86.9 (*s*); 73.5 (*d*); 71.5 (*s*); 41.9 (*t*); 28.7 (*t*); 25.8 (*q*); 18.2 (*s*); −2.9 (*q*); −2.9 (*q*). MS: 263 (1, $[M - 15]$), 223 (40), 221 (39), 167 (17), 145 (29), 91 (23), 83 (29), 75 (100), 73 (70). HR-MS: 278.2056 (M^+, $C_{17}H_{30}OSi^+$, calc. 278.2065).

5-(Ethynyl)-5-[(methyl)diphenylsilyloxy]nona-1,8-diene (**6e**). As described for **4e**. Yield 92%. Colorless oil. R_f (*1* 30:1) 0.69. IR: 3305, 2121, 1640, 1428, 1118, 1064. ^{1}H-NMR: 7.73–7.67 (stack, 4 H); 7.48–7.39 (stack, 6 H); 5.93–5.76 (*m*, 2 H); 5.10–4.95 (stack, 4 H); 2.47 (*s*, 1 H); 2.37–2.27 (*m*, 4 H); 1.91–1.81 (*m*, 4 H); 0.90 (*s*, 3 H). ^{13}C-NMR: 138.4 (*d*); 137.8 (*s*); 134.6 (*d*); 129.7 (*d*); 127.7 (*d*); 114.6 (*t*); 86.6 (*s*); 74.3 (*d*); 73.1 (*s*); 41.6 (*t*); 28.8 (*t*); −0.4 (*q*). MS: 360 (2, M^+), 306 (9), 305 (31), 228 (9), 227 (35), 199 (26), 198 (29), 197 (100), 195 (12), 137 (32).

4. *Dien-yne* **10**. *Hept-6-en-1-yn-3-ol* (**7**). Acetylene, purified by conc. H_2SO_4, P_2O_5 on glass wool, and solid KOH, was bubbled through 250 ml of THF and cooled to −75°. BuLi (90 ml, 1.6M) in hexane was added during 30 min. After 15 min, 11.7 g of pent-4-enal [28] (GC purity 90%, 0.125 mol) was added at −70°. After warming to r.t. for 4 h, the mixture was worked up and distilled *in vacuo*: 13.2 g (96%) of **7**. Yellowish oil. GC: purity 99%. R_f (*1* 4:1) 0.31. B.p. 60–63°/12 Torr. IR: 3580, 3280, 1045, 1005, 910. ^{1}H-NMR: 5.83 (*ddt*, J = 17.3, 10.3, 6.6, 1 H); 5.08 (*ddt*, J = 17.3, 1.9, 1.8, 1 H); 5.00 (*ddt*, J = 10.3, 1.9, 1.1, 1 H); 4.40 (*dt*, J = 6.7, 2.2, 1 H); 2.49 (*d*, J = 2.2, 1 H); 2.46 (br. *s*, 1 H); 2.26 (*m*, 2 H); 1.82 (*m*, 2 H). ^{13}C-NMR: 137.5 (*d*); 115.3 (*t*); 84.8 (*s*); 73.2 (*d*); 61.5 (*d*); 36.6 (*t*); 29.3 (*t*). MS: 110 (2, M^+), 109 (10), 95 (18), 91 (100), 81 (18), 79 (19), 68 (32), 67 (21), 56 (13), 55 (79), 53 (19), 41 (19), 39 (23). HR-MS: 110.0731 (M^+, $C_7H_{10}O^+$, calc. 110.0731).

5-(Prop-2-ynyloxy)hept-6-en-1-yne (**10**). a) *From* **7** via **9**. To a soln. of 1.10 g (10 mmol) of **7** in 10 ml of Et_2O were added 3.6 g (10.5 mmol) of $[Co_2(CO)_8]$. After stirring for 40 min at r.t., the residue was chromatographed (*4* and *1* 4:1) to give 3.72 g (94%) of $[Co_2(CO)_6$ (**7**)] as a cherry red oil. BF_3 gas (940 ml, 0.038 mol) was added to the soln. of this complex in 40 ml of CH_2Cl_2 at −50° *via* syringe. After 15 min, 2.11 g (38 mmol) of prop-2-yn-1-ol was added. At −5°, 4 ml of Et_2O were added, and the soln. was stirred for 20 min. After workup and FC (*4* and *3* 10:1), 3.79 g (93%) **9** was obtained as a cherry red oil. After oxidation of 0.204 g (0.47 mmol) of **9** in 1 ml of acetone with 1.16 g (2.12 mmol) of $Ce(NH_4)_2(NO_3)_6$ in 2.5 ml of acetone at r.t., workup and FC (*3* 30:1) gave 68 mg (98%) of **10**.

Colorless oil. GC: purity 99%. R_f (*1* 4:1) 0.53. IR: 3315, 1645, 1455, 1337, 1082. ^{1}H-NMR: 5.82 (*m*, 1 H); 5.11–4.97 (stack, 2 H); 4.35 (*dd*, *J* = 15.8, 1.7, 1 H); 4.31 (*dt*, *J* = 6.6, 1.8, 1 H); 4.25 (*dd*, *J* = 15.8, 2.2, 1 H); 2.47 (*d*, *J* = 1.8, 1 H); 2.43 (*t*, *J* = 2.2, 1 H); 2.25 (*m*, 2 H); 1.87 (*m*, 2 H). ^{13}C-NMR: 137.4 (*d*); 115.3 (*t*); 81.7 (*s*); 79.3 (*s*); 74.6 (*d*); 67.3 (*d*); 55.7 (*t*); 34.5 (*t*); 29.2 (*t*). MS: 147 (0.1, $[M-1]^+$), 105 (11), 93 (29), 92 (12), 91 (100), 79 (20), 65 (27), 39 (30). HR-MS: 148.0888 (M^+, $C_{10}H_{12}O^+$, calc. 148.0888).

b) *From* **7** via **8**: 0.608 g (1.78 mmol) of $[Co_2(CO)_6$(prop-2-yn-1-ol)] (R_f (*3* 4:1) 0.41) in 5 ml of CH_2Cl_2/$MeNO_2$ 4:1 were treated with 180 ml (7.2 mmol) of BF_3 gas. After addition of 25 ml of Et_2O (−50°) and decanting, the precipitate was dissolved in CH_2Cl_2/$MeNO_2$, and 0.250 g (1.7 mmol) of **7** were added at −10°. After 20 min, the mixture was worked up, and subsequent FC (*3* 15:1) gave 0.594 g (76%) of **8** as a cherry red oil. Decomplexation with Ce^{IV} as reported for **9** gave **10** quantitatively.

5. *Tandem* Pauson-Khand *Cyclizations of* **4** *and* **10**. *General Procedure*. The ene-diynes **4a–g** (1 mmol in 10 ml of CH_2Cl_2) were treated with 2.12 mol-equiv. of $[Co_2(CO)_8]$ in 10 ml of THF for 3 h at r.t. A soln. of 6 mol-equiv. of anh. 4-methylmorpholine *N*-oxide in 20 ml of THF/CH_2Cl_2 1:1 was added dropwise at 15–20° during 4–6 h (exothermic, gas evolution, rapid change in colour from dark-red to dark brown and violet). Filtration over silica gel and rinsing with Et_2O gave a brownish-red filtrate, which was flash chromatographed with *1*.

all-cis-*7-(Trimethylsilyloxy)tetracyclo[5.5.1.0^{4,13}.0^{10,13}]tridec-3-ene-2,12-dione* (**11c**): Yield 24%. Colorless crystals. For data see [14]. HR-MS: 290.1343 (M^+, $C_{16}H_{22}O_3Si^+$, calc. 290.1338).

all-cis-*7-[(*tert*-Butyl)dimethylsilyloxy]tetracyclo[5.5.1.0^{4,13}.0^{10,13}]tridec-3-ene-2,12-dione* (**11d**): Yield 22%. Colorless crystals. R_f (*5*) 0.48. M.p. 137.5°. IR: 1750, 1700, 1635. ^{1}H-NMR: 5.76 (br. *s*, 1 H); 3.29 (*d*, *J* = 1.5, 1 H); 2.81–2.61 (stack, 3 H); 2.53–2.44 (*m*, 1 H); 2.34 (*ddd*, *J* = 4.5, 9.4, 13.8, 1 H); 2.23 (*ddd*, *J* = 1.8, 3.9, 18.3, 1 H); 2.11–1.95 (stack, 4 H); 1.59–1.49 (*m*, 1 H); 0.77 (*s*, 9 H); 0.05 (*s*, 6 H). ^{13}C- NMR: 208.3 (*s*); 201.4 (*s*); 189.6 (*s*); 121.9 (*d*); 87.7 (*s*); 72.6 (*s*); 63.2 (*d*); 46.2 (*t*); 42.3 (*d*); 41.2 (*t*); 39.3 (*t*); 31.0 (*t*); 26.9 (*t*); 25.5 (*q*); 17.8 (*s*); −2.7 (*q*); −2.9 (*q*). MS: 317 (2, $[M-15]^+$), 277 (10), 276 (27), 275 (100), 257 (11), 247 (14), 183 (47), 155 (15), 75 (49), 73 (28). Anal. calc. for $C_{19}H_{28}O_3Si$: C 68.63, H 8.49; found: C 68.62, H 8.52.

all-cis-*7-[(Methyl)diphenylsilyloxy]tetracyclo[5.5.1.0^{4,13}.0^{10,13}]tridec-3-ene-2,12-dione* (**11e**): Yield 13%. Colorless oil. R_f (*5*) 0.51. IR: 1750, 1700, 1632, 1180, 1118. ^{1}H-NMR: 7.50–7.46 (stack, 4 H); 7.41–7.31 (stack, 6 H); 5.80 (*t*, *J* = 1.1, 1 H); 3.53 (*d*, *J* = 1.5, 1 H); 2.73–2.61 (stack, 3 H); 2.53–2.44 (*m*, 1 H); 2.30–1.90 (stack, 6 H); 1.57–1.45 (*m*, 1 H); 0.68 (*s*, 3 H). ^{13}C-NMR: 208.2 (*s*); 201.5 (*s*); 189.5 (*s*); 136.7 (*s*); 134.1 (*d*); 134.0 (*d*); 129.9 (*d*); 128.0 (*d*); 128.0 (*d*); 122.2 (*d*); 88.9 (*s*); 72.74 (*s*); 63.5 (*d*); 46.4 (*t*); 42.7 (*d*); 41.5 (*t*); 39.8 (*t*); 31.0 (*t*); 27.1 (*t*); −0.7 (*q*). MS: 414 (12, M^+), 399 (46), 337 (23), 336 (69), 321 (19), 199 (50), 198 (21), 197 (100), 195 (17), 137 (17), 84 (16). HR-MS: 414.1647 (M^+, $C_{26}H_{26}O_3Si^+$, calc. 414.1651).

all-cis-*7-[(Allyl)dimethylsilyloxy]tetracyclo[5.5.1.0^{4,13}.0^{10,13}]tridec-3-ene-2,12-dione* (**11f**): Yield 15%. Colorless crystals. R_f (*5*) 0.34. M.p. 38–39°. IR: 1752, 1700, 1632. ^{1}H-NMR: 5.72 (*d*, *J* = 1.5, 1 H); 5.69–5.60 (*m*, 1 H); 4.82–4.77 (stack, 2 H); 3.29 (*d*, *J* = 1.9, 1 H); 2.76 (*ddd*, *J* = 3.4, 8.4, 16.3, 1 H); 2.70–2.61 (stack, 2 H); 2.48–2.42 (*m*, 1 H); 2.33 (*ddd*, *J* = 3.4, 10.2, 13.6, 1 H); 2.22 (*ddd*, *J* = 2.0, 4.6, 18.4, 1 H); 2.08–1.97 (stack, 4 H); 1.56–1.49 (*m*, 1 H); 1.51 (*dt*, *J* = 1.2, 8.1, 2 H); 0.10 (*s*, 3 H); 0.09 (*s*, 3 H). ^{13}C-NMR: 208.4 (*s*); 201.6 (*s*); 189.3 (*s*); 133.6 (*d*); 121.8 (*d*); 114.0 (*t*); 88.0 (*s*); 72.4 (*s*); 63.4 (*d*); 46.4 (*t*); 42.8 (*d*); 41.8 (*t*); 39.8 (*t*); 31.0 (*t*); 27.2 (*t*); 26.0 (*t*); 0.0 (*q*); −0.1 (*q*). MS: 316 (5, M^+), 301 (19), 276 (19), 275 (100), 257 (6), 247 (13), 183 (28), 155 (8), 115 (7), 91 (8), 75 (53).

all-cis-*Tetracyclo[5.5.1.0^{4,13}.0^{10,13}]tridec-3-ene-2,12-dione* (**11g**): Yield 5%. Colorless oil. R_f (*3* 1:1) 0.31. IR: 1755, 1700, 1633. ^{1}H-NMR: 5.80 (*t*, *J* = 1.1, 1 H); 3.05 (*d*, *J* = 1.5, 1 H); 2.71–2.44 (stack, 5 H); 2.28–2.01 (stack, 4 H); 1.90–1.79 (*m*, 1 H); 1.66–1.55 (*m*, 1 H); 1.49–1.37 (*m*, 1 H). ^{13}C-NMR: 208.7 (*s*); 201.6 (*s*); 192.2 (*s*); 121.6 (*d*); 68.7 (*s*); 67.9 (*d*); 45.8 (*d*); 45.2 (*d*); 44.8 (*t*); 34.3 (*t*); 34.3 (*t*); 33.1 (*t*); 27.4 (*t*). MS: 202 (71, M^+), 174 (29), 160 (51), 159 (11), 131 (26), 120 (19), 119 (18), 117 (25), 91 (42), 28 (65), 18 (100). HR-MS: 202.0997 (M^+, $C_{13}H_{14}O_2^+$, calc. 202.0994).

all-cis-*2-Oxatetracyclo[5.5.1.0^{4,13}.0^{10,13}]tridec-4-ene-6,8-dione* (**16**). At r.t., 2.16 g (5 mmol) of **9** were stirred with 1.88 g (5.5 mmol) of $[Co_2(CO)_8]$ for 40 min. The residue was chromatographed (hexane, *1* 10:1) to give 3.31 g (92%) of $[\{Co_2(CO)_6\}_2$ (**10**)] which was dissolved in 46 ml of THF and cooled to 5°. After slow addition of $Me_3NO \cdot 2\,H_2O$ (7.35 g, 66.2 mmol) and stirring at r.t. for 3 h, the residue was filtrated through *Celite* and silica gel with AcOEt and chromatographed (*3* 5:1→1:1): 0.517 g (53%) of **16**. Colorless crystals. GC: purity 96%. R_f (*6*) 0.40. M.p. 116–117°. IR: 1755, 1712, 1648, 1135, 1100. ^{1}H-NMR: 5.94 (br. *s*, 1 H); 4.75 (*dd*, *J* = 16.0, 1.6, 1 H); 4.69 (*d*, *J* = 6.0, 1 H); 4.43 (*d*, *J* = 3.3, 1 H); 3.29 (br. *s*, 1 H); 2.88–2.65 (stack, 2 H); 2.40–2.16 (stack, 3 H); 2.04 (*m*, 1 H); 1.67 (*m*, 1 H). ^{13}C-NMR: 207.1 (*s*); 199.5 (*s*); 185.9 (*s*); 121.2 (*d*); 86.7 (*d*); 69.7 (*s*); 66.3 (*t*); 65.1 (*d*); 47.1 (*t*); 44.1 (*d*); 33.1 (*t*); 31.9 (*t*). MS: 204 (7, M^+), 121 (5), 73 (100), 57 (38), 43 (27), 41 (23). HR-MS: 204.0783 (M^+, $C_{12}H_{12}O_3^+$, calc. 204.0786).

6. Pauson-Khand *Cyclizations of* **6a, c–e, g**. The $[Co_2(CO)_6]$ complex prepared from 0.165 g (1 mmol) of **6a** and 0.36 g (1.05 mmol) of $[Co_2(CO)_8]$ as described for **9** (see **10** from **7** *via* **9**) was dissolved in 10 ml of pentane, and 4.3 g of silica gel, pretreated with 0.43 g of H_2O were added. After evaporation, the powder was heated to 55° for 1.5 h. The grey material was extracted with AcOEt and the residue obtained chromatographed (*3* 4:1→1:1) to give 0.108 g (56%) of **12a**/**13a** 1.6:1 which could not be separated. Treatment of this mixture with $CF_3SO_3SiMe_3$ under the conditions described for **4c,d** gave **12c**/**13c** 1.5:1 and a combiend yield of 84%.

For **6c–e**, the procedure of the tandem-*PK* reaction (see *General Procedure* in *Sect. 5*) was followed, except that 1.05 equiv. of $[Co_2(CO)_8]$ and anh. NMO were used. For **12g**/**13g**, the $[Co_2(CO)_6$(**6g**)] was prepared as described for **4g** from 0.250 g (1.52 mmol) of **6a**, except that 1.05 equiv. of $[Co_2(CO)_8]$ were used: 0.404 g (61%) of $[Co_2(CO)_6$(**6g**)] which was submitted to the *PK* reaction conditions with anh. NMO. The stereochemical assignments were determined by NOE experiments. Yields are listed in the *Table*.

*rel-(5*R*,8*R*)-8-(But-3-enyl)-8-(trimethylsilyloxy)bicyclo[3.3.0]oct-1-en-3-one* (**12c**): Colorless oil. R_f (*2* 7:2) 0.29. IR: 3020, 2962, 1701, 1634, 1253, 1062, 843. ^{1}H-NMR: 5.97 (*d*, *J* = 2.2, 1 H); 5.87–5.73 (*m*, 1 H); 5.03–4.91 (stack, 2 H); 2.97–2.86 (*m*, 1 H); 2.65 (*dd*, *J* = 18.0, 6.2, 1 H); 2.31–1.95 (stack, 6 H); 1.86–1.64 (stack, 2 H); 1.52–1.37 (*m*, 1 H); 0.10 (*s*, 9 H). ^{13}C-NMR: 210.0 (*s*); 194.1 (*s*); 138.0 (*d*); 124.8 (*d*); 114.5 (*t*); 80.3 (*s*); 43.5 (*t*); 41.9 (*d*); 41.0 (*t*); 40.6 (*t*); 28.7 (*t*); 28.4 (*t*); 2.1 (*q*). MS: 264 (15, M^+), 236 (63), 221 (40), 210 (38), 209 (100), 208 (31), 207 (34), 195 (39), 167 (55), 75 (53), 73 (78). HR-MS: 264.1554 (M^+, $C_{15}H_{24}O_2Si^+$, calc. 264.1546).

*rel-(5*R*,8*S*)-8-(But-3-enyl)-8-(trimethylsilyloxy)bicyclo[3.3.0]oct-1-en-3-one* (**13c**): Colorless oil. R_f (*2* 7:2) 0.36. IR: 2960, 1700, 1642, 1635, 1252, 1143, 1075, 1038, 1020, 875, 842. ^{1}H-NMR: 5.92 (*d*, *J* = 2.2, 1 H); 5.86–5.74 (*m*, 1 H); 5.05–4.91 (stack, 2 H); 3.28–3.17 (*m*, 1 H); 2.65 (*dd*, *J* = 18.2, 6.3, 1 H); 2.31–2.13 (*m*, 1 H); 2.12–2.01 (stack, 5 H); 2.00–1.89 (*m*, 1 H); 1.68–1.58 (*m*, 1 H); 1.15–1.05 (*m*, 1 H); 0.07 (*s*, 9 H). ^{13}C-NMR: 210.7 (*s*); 190.9 (*s*); 138.2 (*d*); 124.0 (*d*); 114.6 (*t*); 77.9 (*s*); 43.7 (*d*); 43.1 (*t*); 41.6 (*t*); 38.7 (*t*); 28.6 (*t*); 28.3 (*t*); 1.9 (*q*). MS: 264 (12, M^+), 249 (14), 237 (8), 236 (39), 211 (14), 210 (18), 209 (100), 208 (22), 207 (25), 195 (29), 167 (35), 75 (37), 73 (73). HR-MS: 264.1540 (M^+, $C_{15}H_{24}O_2Si^+$, calc. 264.1546).

*rel-(5*R*,8*R*)-8-(But-3-enyl)-8-[(*tert*-butyl)dimethylsilyloxy]bicyclo[3.3.0]oct-1-en-3-one* (**12d**): Colorless oil. R_f (*1* 11:3) 0.26. IR: 1703, 1635, 1260, 1175, 1108, 1062, 835. ^{1}H-NMR: 6.00 (*d*, *J* = 2.2, 1 H); 5.87–5.73 (*m*, 1 H); 5.04–4.91 (stack, 2 H); 2.99–2.88 (*m*, 1 H); 2.65 (*dd*, *J* = 18.0, 6.2, 1 H); 2.35–2.20 (*m*, 1 H); 2.19–1.94 (stack, 5 H); 1.88–1.67 (stack, 2 H); 1.38–1.52 (*m*, 1 H); 0.88 (*s*, 9 H); 0.10 (*s*, 3 H); 0.04 (*s*, 3 H). ^{13}C-NMR: 210.1 (*s*); 194.4 (*s*); 138.2 (*d*); 124.9 (*d*); 114.7 (*t*); 80.4 (*s*); 43.8 (*t*); 42.0 (*d*); 41.5 (*t*); 40.7 (*t*); 28.9 (*t*); 28.7 (*t*); 25.8 (*q*); 18.3 (*s*); −2.3 (*q*); −2.4 (*q*). MS: 306 (1, M^+), 251 (31), 250 (31), 249 (100), 231 (11), 221 (11), 157 (35), 142 (9), 133 (10), 131 (13), 129 (37), 117 (26), 75 (74), 73 (80), 28 (29). HR-MS: 306.2000 (M^+, $C_{18}H_{30}O_2Si^+$, calc. 306.2002).

*rel-(5*R*,8*S*)-8-(But-3-enyl)-8-[(*tert*-butyl)dimethylsilyloxy]bicyclo[3.3.0]oct-1-en-3-one* (**13d**; containing **17a**): Colorless oil. R_f (*1* 3:1) 0.34. ^{1}H-NMR: 5.93 (*d*, *J* = 2.6, 1 H); 5.89–5.73 (*m*, 1 H); 5.07–4.91 (stack, 2 H); 3.27–3.16 (*m*, 1 H); 2.67 (*dd*, *J* = 18.0, 6.2, 1 H); 2.33–1.87 (stack, 7 H); 1.58–1.69 (*m*, 1 H); 1.16–1.02 (*m*, 1 H); 0.85 (*s*, 9 H); 0.07 (*s*, 3 H); 0.01 (*s*, 3 H). ^{13}C-NMR: 211.4 (*s*); 191.1 (*s*); 138.1 (*d*); 124.0 (*d*); 114.6 (*t*); 77.6 (*s*); 43.9 (*d*); 43.0 (*t*); 41.4 (*t*); 38.9 (*t*); 28.5 (*t*); 28.3 (*t*); 25.6 (*q*); 18.1 (*s*); −2.8 (*q*); −3.0 (*q*).

*rel-(5*R*,8*R*)-8-(But-3-enyl)-8-[(methyl)diphenylsilyloxy]bicyclo[3.3.0]oct-1-en-3-one* (**12e**; containing **13e**): Colorless oil. R_f (*2* 3:1) 0.38. ^{1}H-NMR: 7.67–7.53 (stack, 4 H); 7.44–7.33 (stack, 6 H); 5.85–5.71 (*m*, 1 H); 5.79 (*d*, *J* = 2.2, 1 H); 5.04–4.94 (stack, 2 H); 2.84–2.70 (*m*, 1 H); 2.50–1.91 (stack, 6 H); 2.45 (*dd*, *J* = 18.4, 6.2, 1 H); 1.70–1.57 (stack, 2 H); 1.11–0.94 (*m*, 1 H); 0.69 (*s*, 3 H). ^{13}C-NMR: 210.7 (*s*); 190.1 (*s*); 138.0 (*d*); 136.9 (*s*); 134.4 (*d*); 134.3 (*d*); 129.8 (*d*); 127.7 (*d*); 127.6 (*d*); 124.4 (*d*); 114.7 (*t*); 78.5 (*s*); 43.8 (*d*); 42.8 (*t*); 41.6 (*t*); 39.0 (*t*); 28.5 (*t*); 28.3 (*t*); −0.9 (*q*).

*rel-(5*R*,8*S*)-8-(But-3-enyl)-8-[(methyl)diphenylsilyloxy]bicyclo[3.3.0]oct-1-en-3-one* (**13e**): Colorless oil. R_f (*2* 3:1) 0.40. IR: 1700, 1634, 1115. ^{1}H-NMR: 7.58–7.54 (stack, 4 H); 7.42–7.32 (stack, 6 H); 6.11 (*d*, *J* = 2.2, 1 H); 5.85–5.72 (*m*, 1 H); 5.03–4.92 (stack, 2 H); 2.94–2.82 (*m*, 1 H); 2.60 (*dd*, *J* = 17.9, 6.4, 1 H); 2.44–2.29 (*m*, 1 H); 2.23–1.85 (stack, 6 H); 1.80–1.66 (*m*, 1 H); 1.05–0.90 (*m*, 1 H); 0.68 (*s*, 3 H). ^{13}C-NMR: 210.1 (*s*); 193.2 (*s*); 138.5 (*d*); 137.1 (*s*); 134.4 (*d*); 134.3 (*d*); 129.8 (*d*); 127.9 (*d*); 125.4 (*d*); 114.8 (*t*); 81.3 (*s*); 43.5 (*t*); 42.4 (*d*); 41.6 (*t*); 41.2 (*t*); 28.8 (*t*); 28.7 (*t*); −0.4 (*q*). MS: 388 (5, M^+), 334 (11), 333 (40), 199 (59), 198 (21), 197 (100), 137 (21). HR-MS: 388.1859 (M^+, $C_{25}H_{28}O_2Si^+$, calc. 388.1859).

*rel-(5*R*,8*S*)-8-(But-3-enyl)bicyclo[3.3.0]oct-1-en-3-one* (**12g**): Colorless oil. R_f (*2* 1:1) 0.43. ^{1}H-NMR: 5.91–5.74 (stack, 2 H); 5.07–4.96 (stack, 2 H); 3.01–2.89 (*m*, 1 H); 2.85–2.74 (*m*, 1 H); 2.60 (*dd*, *J* = 18.0, 6.2, 1 H); 2.30–2.02 (stack, 5 H); 1.67–1.53 (stack, 3 H); 1.21–1.06 (*m*, 1 H). ^{13}C-NMR: 211.1 (*s*); 194.1 (*s*); 137.8 (*d*); 125.1 (*d*); 115.3 (*t*); 45.6 (*d*); 42.3 (*t*); 38.7 (*d*); 34.3 (*t*); 33.4 (*t*); 31.9 (*t*); 30.9 (*t*). IR: 1700, 1625. MS: 177 (5, $[M+1]^+$), 176 (33), 148 (38), 134 (67), 133 (57), 122 (76), 121 (41), 120 (45), 119 (68), 107 (42), 106 (72), 105 (44), 94 (48), 93 (60), 92 (49), 91 (100), 80 (43), 79 (63), 77 (53). HR-MS: 176.1201 (M^+, $C_{12}H_{16}O^+$, calc. 176.1201).

rel-(5R,8R)-8-(But-3-enyl)bicyclo[3.3.0]oct-1-en-3-one (**13g**; contaminated with **12g**): Colorless oil. R_f (*2* 1:1) 0.43. ^{13}C-NMR: 210.7 (*s*); 194.9 (*s*); 137.6 (*d*); 123.2 (*d*); 115.1 (*t*); 46.0 (*d*); 42.5 (*t*); 38.0 (*d*); 32.7 (*t*); 32.0 (*t*); 31.5 (*t*); 31.4 (*t*). GC-MS: 177 (3, $[M + 1]^+$), 176 (21), 134 (48), 106 (46), 94 (40), 93 (69), 92 (41), 91 (100), 80 (45), 79 (73), 77 (69), 41 (54), 39 (64).

7. *Reductive* Pauson-Khand *Cyclization of* **6d**. For this cyclization, NMO containing various amounts of H_2O were used. A mixture of **17a**/**18a** and **12d**/**13d** was obtained. Isomers **18a** (R^1 = H) and **18b** (R^1 = D) were isolated in pure form by HPLC, whereas the '*exo*' isomers **17a,b** were contaminated with **12d**. The yields are listed in the *Table*.

*rel-(1R,5S,6R)-6-(But-3-enyl)-6-[(*tert*-butyl)dimethylsilyloxy]bicyclo[3.3.0]octan-3-one* (**17a**): Colorless oil. R_f (*1* 3:1) 0.36. ^{1}H-NMR: 5.87–5.72 (*m*, 1 H); 5.05–4.92 (stack, 2 H); 2.82–2.68 (*m*, 1 H); 2.58–2.41 (stack, 3 H); 2.27–1.53 (stack, 10 H); 0.85 (*s*, 9 H); 0.12 (*s*, 3 H); 0.10 (*s*, 3 H). ^{13}C-NMR: 221.2 (*s*); 138.5 (*d*); 114.5 (*t*); 85.1 (*s*); 48.7 (*d*); 46.2 (*t*); 40.5 (*t*); 39.70 (*t*); 39.1 (*t*); 38.4 (*d*); 31.6 (*t*); 29.0 (*t*); 26.0 (*q*); 18.5 (*s*); –2.1 (*q*); –2.2 (*q*). MS: 308 (2, M^+), 253 (56), 252 (61), 251 (100), 225 (11), 210 (10), 209 (37), 169 (10), 159 (52), 133 (15), 131 (32), 119 (51), 117 (34), 105 (17), 91 (34), 75 (45), 73 (38).

*rel-(1R,5S,6S)-6-(But-3-enyl)-6-[(*tert*-butyl)dimethylsilyloxy]bicyclo[3.3.0]octan-3-one* (**18a**): Colorless oil. R_f (*1* 3:1) 0.39. IR: 1732, 1080. ^{1}H-NMR: 5.88–5.72 (*m*, 1 H); 5.06–4.90 (stack, 2 H); 3.08–2.95 (*m*, 1 H); 2.63–2.51 (*m*, 1 H); 2.51–2.00 (stack, 6 H); 1.85–1.61 (stack, 4 H); 1.60–1.47 (*m*, 1 H); 1.36–1.22 (*m*, 1 H); 0.89 (*s*, 9 H); 0.12 (*s*, 6 H). ^{13}C-NMR: 220.0 (*s*); 138.6 (*d*); 114.4 (*t*); 87.7 (*s*); 51.6 (*d*); 45.7 (*t*); 40.2 (*t*); 38.2 (*d*); 37.4 (*t*); 37.3 (*t*); 30.2 (*t*); 28.9 (*t*); 25.8 (*q*); 18.4 (*s*); –2.5 (*q*); –2.7 (*q*). MS: 308 (1, M^+), 253 (21), 252 (29), 251 (100), 209 (19), 159 (52), 131 (23), 119 (52), 117 (30), 105 (16), 91 (35), 75 (76), 73 (51). HR-MS: 308.2173 (M^+, $C_{18}H_{32}O_2Si^+$, calc. 308.2172).

*rel-(1R,5S,6S)-6-(But-3-enyl)-6-[(*tert*-butyl)dimethylsilyloxy](5-$^2H_1$)bicyclo[3.3.0]octan-3-one* (**18b**): Colorless oil. R_f (*1* 3:1) 0.39. ^{1}H-NMR: 5.88–5.72 (*m*, 1 H); 5.06–4.90 (stack, 2 H); 3.08–2.95 (*m*, 1 H); 2.50–2.40 (stack, 2 H); 2.38–2.02 (stack, 4 H); 1.85–1.61 (stack, 4 H); 1.60–1.47 (*m*, 1 H); 1.36–1.22 (*m*, 1 H); 0.89 (*s*, 9 H); 0.12 (*s*, 6 H); 2.63–2.51 (10% of **18a**). ^{13}C-NMR: due to interaction with D–C(5), the intensity of the signals at 220.1, 87.8, 51.7, 40.3, and 38.3 are changed. MS: 310 (5, M^+), 309 (8), 308 (2), 295 (40), 294 (55), 253 (34), 252 (41), 211 (5), 210 (6), 160 (12), 120 (21), 119 (23), 91 (17), 75 (100), 73 (56).

8. Pauson-Khand *Cyclization of* **6b**. The *PK* reaction of **6b** was carried out under the same conditions as described for **6c** (see *Sect. 6*).

6-(But-3-enyl)bicyclo[3.3.0]oct-5-en-3-one (**14**): Yield 28%. Colorless oil. R_f (*2* 5:1) 0.51. IR: 1704. ^{1}H-NMR: 5.84–5.71 (*m*, 1 H); 5.06–4.91 (stack, 2 H); 3.20–3.06 (*m*, 1 H); 2.89 (*d*, *J* = 21.7, 1 H); 2.67 (*d*, *J* = 21.7, 1 H); 2.62 (*dd*, *J* = 18.7, 8.1, 1 H); 2.62–2.51 (*m*, 1 H); 2.33 (*dd*, *J* = 18.7, 7.0, 1 H); 2.38–2.27 (*m*, 1 H); 2.21–2.13 (stack, 3 H); 2.01–1.82 (stack, 2 H); 1.54–1.40 (*m*, 1 H). ^{13}C-NMR: 218.7 (*s*); 138.2 (*d*); 136.7 (*s*); 134.6 (*s*); 114.7 (*t*); 48.0 (*t*); 47.4 (*d*); 38.9 (*t*); 37.5 (*t*); 32.9 (*t*); 32.0 (*t*); 29.0 (*t*). MS: 177 (7, $[M + 1]^+$), 176 (54), 148 (20), 135 (44), 134 (47), 133 (51), 119 (65), 118 (54), 106 (51), 105 (52), 93 (100), 92 (43), 91 (83), 79 (50). HR-MS: 176.1200 (M^+, $C_{12}H_{16}O^+$, calc. 176.1201).

rel-(5R/S,8S)-8-(Acetoxy)-8-(but-3-enyl)bicyclo[3.3.0]oct-1-en-3-one (**12b**/**13b**): Combined yield 2%. R_f (*2* 3:1) 0.16 and 0.18. GC/MS (less polar isomer): 234 (1, M^+), 192 (4), 174 (17), 164 (4), 151 (14), 146 (14), 138 (10), 133 (46), 132 (39), 131 (23), 117 (29), 105 (30), 91 (33), 79 (23), 77 (19), 43 (100). GC/MS (more polar isomer): 234 (1, M^+), 193 (22), 192 (12), 174 (11), 164 (4), 151 (30), 149 (8), 146 (10), 137 (9), 133 (17), 132 (10), 131 (10), 117 (10), 105 (20), 95 (12), 91 (22), 79 (18), 77 (13), 55 (20), 43 (100).

rel-(5R/S,8R)-8-(But-3-enyl)bicyclo[3.3.0]oct-1-en-3-one (**12g**/**13g**): Combined yield 10%. Identified by comparison of GC/MS with the products obtained from **6g** (see above).

9. *Attempted* Pauson-Khand *Cyclization of* **20**. *Ethyl rel-(1R,3R,6R)-6-(But-3-ynyl)-3-hydroxy(3-$^2H_1$)-bicyclo[3.3.0]oct-4-ene-1-carboxylate* (**20b**). Prepared as described for **20a** [9]. To a soln. of 0.307 g (0.83 mmol) of $CeCl_3 \cdot 7\,H_2O$ in 8 ml of MeOH were added 0.20 g (0.81 mmol) of **19** followed by portions of 0.036 g (0.87 mmol) of $NaBD_4$ to give, after workup, 0.200 g (99%) of **20b**. Colorless oil. R_f (*1* 1:2) 0.24. IR: 3600, 3310, 1720, 1305, 1270, 1180, 1100. ^{1}H-NMR: 5.59 (*s*, 1 H); 4.11 (*q*, *J* = 6.8, 2 H); 2.82–2.72 (stack, 2 H); 2.48 (*dd*, *J* = 12.0, 6.1, 1 H); 2.27–2.17 (stack, 2 H); 1.95 (*t*, *J* = 3.0, 1 H); 1.89–1.84 (*m*, 1 H); 1.75–1.62 (*m*, 1 H); 1.59–1.38 (stack, 3 H); 1.24 (*t*, *J* = 6.8, 3 H). ^{13}C-NMR: 175.7 (*s*); 155.5 (*s*); 128.0; 84.0 (*s*); 68.6 (*d*); 64.7; 60.8; 49.7 (*t*); 36.2 (*d*); 35.7 (*t*); 33.9 (*t*); 33.6 (*t*); 17.0 (*t*); 14.2 (*q*). MS: 231 (22, $[M - 18]^+$), 220 (23), 207 (70), 202 (85), 176 (100), 158 (35), 147 (42), 133 (70), 118 (44), 105 (47), 91 (67), 77 (47), 67 (19), 53 (28), 41 (31), 29 (62).

Cyclization of **20**. Treatment of **20a,b** with $[Co_2(CO)_8]$ and NMO under the *PK* cyclization conditions as described for **6c** (see *Sect. 6*) gave **21a,b**.

Ethyl rel-(1R,4R)-7-Methylidene-10-oxotricyclo[6.3.0.0^{4,8}]undecane-1-carboxylate (**21a**): Yield 81%. Colorless oil. R_f (*3* 2:3) 0.64. M.p. 53°. IR: 1740, 1280, 1270, 1250, 1180, 1150, 1100. ^{1}H-NMR: 5.03 (*d*, *J* = 2.0, 1 H); 4.76 (*d*, *J* = 2.6, 1 H, CH_2=C, *cis* to C(8), according to smaller ^3J(H,C(8) [29])); 4.16–4.01 (*m*, 2 H); 3.00 (*d*, *J* = 21, 1 H); 2.81 (*d*, *J* = 21.0, 1 H); 2.50–2.36 (stack, 5 H); 2.37 (*d*, *J* = 21.0, 1 H); 2.19 (*d*, *J* = 21.0, 1 H); 2.13–2.02 (*m*, 1 H); 1.85–1.56 (stack, 4 H); 1.26 (*t*, *J* = 6.0, 3 H). ^{13}C-NMR: 216.3 (*s*); 154.9 (*s*); 106.9 (*t*); 73.9 (*s*); 63.9 (*s*); 62.6 (*s*); 60.8 (*t*); 52.6 (*d*); 51.0 (*t*); 48.0 (*t*); 35.2 (*t*); 34.9 (*t*); 31.6 (*t*); 31.3 (*t*); 14.1 (*q*). MS: 248 (90, M^+), 202 (78), 175 (89), 146 (84), 132 (63), 117 (36), 107 (100), 91 (77), 79 (46), 65 (12). HR-MS: 248.1412 (M^+, $C_{15}H_{20}O_3^+$, calc. 248.1412).

Ethyl rel-(1R,4R)-7-($^2H_1$*)Methylidene-10-oxotricyclo[6.3.0.0^{4,8}]undecane-1-carboxylate* (**21b**): Yield 58%. Colorless oil. R_f (*3* 2:3) 0.64. ^{1}H-NMR: 5.03 (br. *s*, 1 H); 4.18–4.01 (*m*, 2 H); 3.00 (*d*, *J* = 21.0, 1 H); 2.81 (*d*, *J* = 21.0, 1 H); 2.54–2.36 (stack, 5 H); 2.37 (*d*, *J* = 21.0, 1 H); 2.19 (*d*, *J* = 21.0, 1 H); 2.12–2.02 (*m*, 1 H); 1.85–1.58 (stack, 4 H); 1.26 (*t*, 3 H); trace signal for **21a** at 4.76 (*d*, 0.01 H). ^{13}C-NMR: 216.3 (*s*); 174.0 (*s*); 154.8; 106.7; 63.9 (*s*); 62.6 (*s*); 60.6 (*t*); 52.6 (*d*); 51.05 (*t*); 48.0 (*t*); 35.2 (*t*); 34.9 (*t*); 31.6 (*t*); 31.4 (*t*); 14.1 (*q*); trace signal for **21a** at 106.9 (*t*). GC/MS: 249 (56, M^+), 203 (42), 192 (17), 176 (62), 147 (55), 133 (57), 118 (22), 108 (100), 92 (62), 80 (37), 65 (15).

REFERENCES

[1] I. U. Khand, P. L. Pauson, *J. Chem. Soc.* **1974,** 379; P. L. Pauson, in 'Organometallics in Organic Synthesis', Eds. A. de Meijere and H. tom Dieck, Springer, Berlin 1987, p. 233; W. Oppolzer, *Angew. Chem.* **1989,** *101,* 39; *ibid. Int. Ed.* **1989,** *28,* 38; C. Rousset, D. R. Swanson, F. Lamaty, E. Negishi, *Tetrahedron Lett.* **1989,** *30,* 5105; E. Negishi, *Acc. Chem. Res.* **1994,** *27,* 124; C. D. J. Boden, G. Pattenden, *Contemporary Org. Synth.* **1994,** *1,* 433; B. M. Trost, *Angew. Chem.* **1995,** *107,* 285; *ibid. Int. Ed.* **1995,** *45,* 259.

[2] N. E. Schore, in 'Organic Reactions', Ed. L. A. Paquette, Wiley, New York, 1991, Vol. 40, p. 2; *Chem. Rev.* **1988,** *88,* 1081.

[3] M. E. Krafft, X. Chirico, *Tetrahedron Lett.* **1994,** *35,* 4511; J. Marco-Contelles, *ibid.* **1994,** *35,* 5059; D. L. J. Clive, D. C. Cole, Yong Tao, *J. Org. Chem.* **1994,** *59,* 1396; S. Yoo, S. Lee, N. Jeong, I. Cho, *Tetrahedron Lett.* **1993,** *34,* 3435; N. Jeong, B. Y. Lee, S. M. Lee, Y. K. Chung, S. Lee, *ibid.* **1993,** *34,* 4023; E. G. Rowley, N. R. Schore, *J. Org. Chem.* **1992,** *57,* 6853; A. S. Gybin, W. Smit, R. Caple, A. L. Veretenov, A. S. Shashkov, L. G. Vorontsova, M. G. Kurella, V. S. Chertkov, A. A. Carapetyan, A. Y. Kosnikov, M. S. Alexanyhan, S. V. Lindeman, V. N. Panov, A. V. Maleev, Y. T. Struchkov, S. M. Sharpe, *J. Am. Chem. Soc.* **1992,** *114,* 5555; A. Stolle, H. Becker, J. Salaün, A. de Meijere, *Tetrahedron Lett.* **1994,** *35,* 3517; A. L. Veretenov, D. O. Koltun, W. A. Smit, Y. A. Strelenko, in preparation.

[4] M. Periasamy, M. R. Reddy, A. Devasagayaraj, *Tetrahedron* **1994,** *50,* 6955.

[5] S. Shambayati, W. E. Crowe, S. L. Schreiber, *Tetrahedron Lett.* **1990,** *31,* 5289; N. Jeong, Y. K. Chung, B. Y. Lee, S. H. Lee, S.-E. Yoo, *Synlett* **1991,** 204; Y. K. Chung, B. Y. Lee, N. Jeong M. Hudecek, P. L. Pauson, *Organometallics* **1993,** *12,* 220.

[6] S. O. Simonyan, W. A. Smit, A. S. Gybin, A. S., Shashkov, A. S. Mikaelian, V. A. Tarasov, I. I. Ibragimov, R. Caple, D. E. Froen, *Tetrahedron Lett.* **1986,** *27* 1245.

[7] V. Rautenstrauch, P. Mégard, J. Conesa, W. Küster, *Angew. Chem.* **1990,** *102,* 1441; *ibid. Int. Ed.* **1990,** *29,* 1413; N. Jeong, S. H. Hwang, Y. Lee, *J. Am. Chem. Soc.* **1994,** *116,* 3159.

[8] M. J. Knudsen, N. E. Schore, *J. Org. Chem.* **1984,** *49,* 5025.

[9] M. Thommen, P. Gerber, R. Keese, *Chimia* **1991,** *45,* 21.

[10] A. v. d. Waals, R. Keese *J. Chem. Soc., Chem. Commun.* **1992,** 570.

[11] K. M. Nicholas, R. Pettit, *Tetrahedron Lett.* **1971,** 3475; K. M. Siegel, J. Siegel, *J. Am. Chem. Soc.* **1985,** *107,* 4999; K. M. Nicholas, *Acc. Chem. Res.* **1987,** *20,* 207.

[12] W. Luef, R. Keese, 'Advances in Strain in Organic Chemistry', Ed. B. Halton, JAI Press, 1993, Vol. 3, p. 229–267.

[13] N. Jeong, B. Y. Lee, S. M. Lee, Y. K. Chung, S.-G. Lee, *Tetrahedron Lett.* **1993,** *34,* 4023.

[14] P. Magnus, L. M. Principe, *Tetrahedron Lett.* **1985,** 4851.

[15] N. E. Schore, in 'Comprehensive Organic Synthesis', Eds. B. M. Trost and I. Fleming, Ed. L. A. Paquette, Pergamon Press, Oxford, 1991, Vol. 5, p. 1037; J. A. Casalnuovo, R. W. Scott, E. A. Harwood, N. E. Schore, *Tetrahedron Lett.* **1994,** *35,* 1153.

[16] M. E. Krafft, I. L. Scott, R. H. Romero, S. Feibelmann, C. E. Van Pelt, *J. Am. Chem. Soc.* **1993,** *115,* 7199.

[17] P. L. Pauson, *Tetrahedron* **1985,** *41,* 5855; see, however, M. E. Krafft, R. H. Romera, I. L. Scott, *J. Org. Chem.*

1992, *20,* 57; A. L. Veretenov, W. A. Smit, M. G. Vorontsova, M. G. Kurella, R. Caple, A. S. Gybin, *Tetrahedron Lett.* **1991,** *32,* 2109; T. R. Hoye, J. A. Suriano, *J. Org. Chem.* **1993,** *58,* 1659.

[18] D. M. Hoffman, R. Hoffmann, C. R. Fiesel, *J. Am. Chem. Soc.* **1982,** *104,* 3858.

[19] Y. Rubin, C. B. Knobler, F. Diederich, *J. Am. Chem. Soc.* **1990,** *112,* 4966; P. Magnus, P. A. Carter, *ibid.* **1988,** *110,* 1626; P. Magnus, R. T. Lewis, J. C. Huffman, *ibid.* **1988,** *110,* 6921; Ed. L. E. Sutton, 'Tables of Interatomic Distances and Configuration in Molecules and Ions', Suppl. 1956–1959, Chem. Society, London, 1965.

[20] B. F. G. Johnson, 'Transition Metal Clusters', Wiley-Interscience, New York, 1980.

[21] F. Johnson, *Chem. Rev.* **1968,** *68,* 375; R. W. Hoffmann, *ibid.* **1989,** *89.* 1841; B. Giese, W. Damm, R. Batra, *Chem. Tracts. Org. Chem.* **1994,** *7,* 335.

[22] E. Stamm, K. B. Becker, P. Engel, O. Ermer, R. Keese, *Angew. Chem.* **1979,** *91,* 746; *ibid. Int. Ed.* **1979,** *18,* 685.

[23] A. Stolle, H. Becker, J. Salaün, A. de Meijere, *Tetrahedron Lett.* **1994,** *35,* 3521.

[24] a) T. T. Tsou, J. C. Huffman, J. K. Kochi, *Inorg. Chem.* **1979,** *18,* 2311; b) D. Seiferth, C. M. Archer, D. Ruschke, *Organometallics* **1991,** *10,* 3363.

[25] D. J. Darensbourg, M. Y. Darensbourg, N. Walker, J. A. Froelich, *Inorg. Chem.* **1979,** *18,* 1401.

[26] M. Thommen, part of the Ph. D. Thesis, University of Bern, 1995.

[27] W. A. Smit, S. M. Buhanjuk, S. O. Simonyan, A. S. Shashkov, Y. T. Struchkov, A. I. Yanovsky, R. Caple, A. S. Gybin, L. G. Anderson, J. A. Whiteford, *Tetrahedron Lett.* **1991,** *32,* 2105.

[28] M. S. Chada, C. S. Subramanian, *J. Chem. Soc., Perkin Trans. 1* **1979,** 2346.

[29] J. K. M. Sanders, B. K. Hunter, 'Modern NMR Spectroscopy', Oxford University Press, 1990.