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The palladium-catalyzed intramolecular cyclization of alkadienyl-substituted 1,3-diketones

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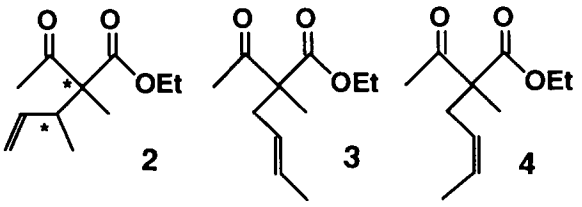
Abstract

Hydroxydeca-3,7,9-triene-2-one (prepared by metallation of acetylacetone followed by treatment with 1-bromopenta-2,4-diene) undergoes intramolecular cyclization in the presence of a [Pd(^{i}Pr$_2$PC$_2$H$_4$P^{i}Pr$_2$)] catalyst to give a mixture of cyclohexanone and cycloheptenone derivatives. The cyclohexanone 2-(1-hydroxyethyliden)-3-vinylcyclohexanone isomerizes in the presence of palladium to give the palladium-alkene complex (η^2-2-acetyl-3-ethylcyclohex-2-enone)Pd(^{i}Pr$_2$PC$_2$H$_4$P^{i}Pr$_2$) whose crystal structure has been established by X-ray diffraction. A related cyclization reaction involving the disubstituted 1,3-diketone 9-hydroxy-1,3,7,12,14-pentaene-7-one leads to the formation of a mixture of spiro compounds (mainly 5,11-divinyl-spiro[5.5]undeca-1,7-dione) whose structures have been elucidated with the help of ^{1}H- and ^{13}C-NMR spectroscopies using ^{2}D-NMR techniques.

Keywords: Palladium catalysis; Intramolecular cyclization; 1,3-diketones

1. Introduction

There is considerable current interest in transition metal-catalyzed cyclization reactions and systems involving palladium have proved to be particularly versatile [1,2]. In recent publications we reported that the selectivity of the palladium-catalyzed reaction between 1,3-dienes and active-hydrogen compounds to give 1 : 1-adducts can be significantly improved by modifying the metal with the bidentate ligand bis(diisopropylphosphino)ethane [3–5]. For example, the reaction between 1,3-butadiene and ethyl methylacetoacetate in the presence of 1 mol% of (η^2-1,3-butadiene)Pd(^{i}Pr$_2$PC$_2$H$_4$^{i}Pr$_2$) (**1**) in CH_2Cl_2 at 20°C leads within 7 h to the exclusive formation of the butene derivatives **2–4** (ratio 15 : 77 : 8) without contamination due to products resulting from the oligomerization of the butadiene.



2 **3** **4**

Here we report the extension of this class of reaction to the intramolecular cyclization of alkadienyl-substituted 1,3-diketones.

2. Results and discussion

The reaction which we have investigated in greatest detail is that of 4-hydroxydeca-3,7,9-triene-2-one (**5**). This compound has been prepared in 63% yield by reacting penta-1,4-dione (acetylacetone) with sodium amide in liq. NH_3 followed by treatment with 1-bromopenta-2,4-diene in a manner similar to that described for the preparation of nona-2,4-dione [6].

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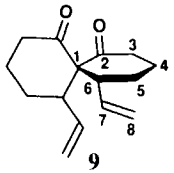
Table 1
The ^{1}H NMR spectroscopic data for **9–11** measured in $CDCl_3$ at 400.1 MHz



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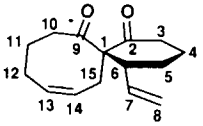

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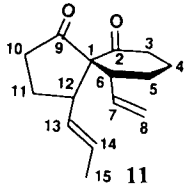
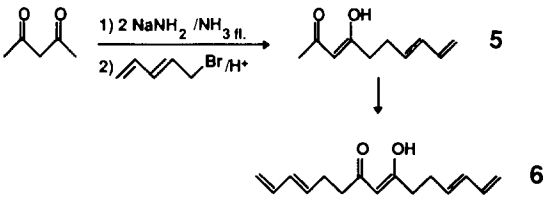


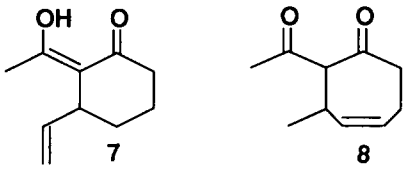
11

n	δH*n*, *J*(*n*, *n*′)	δH*n*, *J*(*n*, *n*′)	δH*n*, *J*(*n*, *n*′)	δH*n*, *J*(*n*, *n*′)	δH*n*, *J*(*n*, *n*′)	δH*n*, *J*(*n*, *n*′)
3	2.25 m, *J*(3, 3) ~ 14, 2.22 m	2.38 m	2.29 m, 2.42 m	~ 2.27 m	~ 2.25 m, *J*(3, 3) 16, 2.38 m	2.24 m, *J*(3, 3) 14, 2.86 dt
4	1.91 m, *J*(4, 5) ~ 12, 1.63 m, *J*(4, 5) ~ 4	1.85 m	1.67 m, 2.01 m	~ 1.96 m	1.71 m, 1.97 m	1.62 m, 2.04 m
5	2.41 m, *J*(5, 5) ~ 12, *J*(5, 6) ~ 12, 1.58 m	1.60 m, 2.06 m	1.59 m, 2.08 m	~ 2.35 m	1.77 m	1.46 m, *J*(5, 5) 13.7, ~ 2.18 m
6	2.47 ddd, *J*(6, 7) 8.8	3.18 dt, *J*(6, 7) 10.4	2.16 m	~ 2.46 ddd, *J*(6, 7) 9.3	3.05 m	2.60 m, *J*(6, 7) 9
7	5.96 ddd, *J*(7, 8E) 10.2, *J*(7, 8Z) 17.1	5.65 dt, *J*(7, 8E) 10.2, *J*(7, 8Z) 16.8	6.29 dt, *J*(7, 8E) 9.2, *J*(7, 8Z) 17.6	5.58 ddd, *J*(7, 8E) 0.2, *J*(7, 8Z) 16.8	5.58 m, *J*(7, 8E) 10.2, *J*(7, 8Z) 17	5.65 ddd, *J*(7, 8E) 10.2, *J*(7, 8Z) 17
8*E*	5.00 ddd, *J*(8E, 8Z) 2.2	5.08 m, *J*(8E, 8Z) 1.8	5.00 dq	5.06 dd, *J*(8E, 8Z) 1.8	5.06 dd, *J*(8E, 8Z) 1.4	5.02 dd, *J*(8E, 8Z) 1.4,
8*Z*	4.95 ddd	5.15m,	5.00 dq	5.09 m	5.03 m	5.05 dd
10		2.36 m	2.19 m, 2.33 m	~ 2.31 m	1.99 m, *J*(10, 10) 8.6, 2.43 m	~ 2.17 m, ~ 2.26 m
11		2.04 m	1.54 m, 1.66 m	1.90 m	~ 1.76 m, 1.88 m	~ 1.85 m, ~ 1.94 m
12		2.83 m, *J*(12, 13) 8.8, *J*(12, 14) 0.7, 2.15 m	1.99 m, 2.10 m	2.83 m, *J*(12, 13) 8.8, *J*(12, 14) 0.7	3.06 m, *J*(12, 13) 9	3.87 m, *J*(12, 13) 6.8, *J*(12, 14) 1.1
13		5.66 dt	5.59 m	5.75 ddq, *J*(13, 14) 15.3, *J*(13, 15) 1.7	5.33 dq, *J*(13, 14) 5.2, *J*(13, 15) 1.6	5.47 m, *J*(13, 14) 15.4 *J*(13, 15) 1.4,
14		5.55 m	5.80 m	5.49 ddq, *J*(14, 15) 6.4	5.56 m, *J*(14, 15) 6.4	5.59 m, *J*(14, 15) 6.2
15		2.10 m, 2.81 m	2.12 m	1.67 dd	1.67 dd	1.67 m

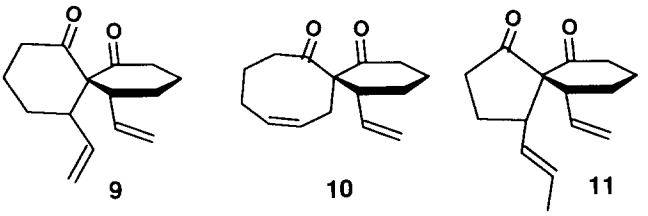


The NMR spectra of **5** indicate that the compound exists at room temperature to the extent of 91% in the enol form.

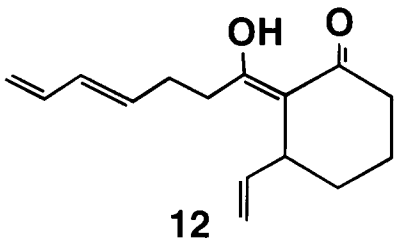
The catalytic reaction of **5** in the presence of 2 mol% of **1** at 40°C in acetone results in a quantitative conversion into the cyclohexanone derivative **7** (as a racemic mixture) as well as into lesser amounts of the cycloheptenone derivative **8** (**7**:**8** ~ 12:1).



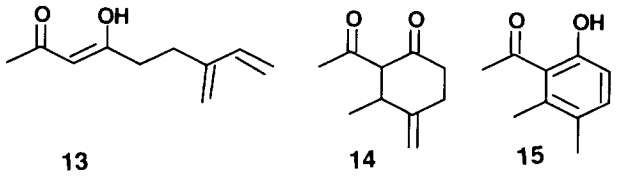
Treatment of **5** with further sodium amide and 1-bromopenta-2,4-diene results in its conversion into 7-hydroxypentadeca-1,3,7,12,14-pentaene-9-one (**6**) in 41% yield. Under the conditions described above, **6** is catalytically converted into a mixture of spiro compounds of which ca. 80% is one of three diastereomeric forms of **9** with lesser amounts of both diastereomers of **10** and of three of the four diastereomeric forms of **11**. These compounds have been separated by preparative GC and identified by the NMR spectroscopic investigations described below.



NMR spectroscopic analysis of the reaction mixture before completion indicates that the reaction is stepwise: the mixture contains **12** in addition to **9**.



A related cyclization reaction has been observed with 4-hydroxy-7-methylenenona-3,8-diene-2-one (**13**) which reacts to give mainly **14** as well as a variety of products, e.g. **15**, presumably the result of a palladium-catalyzed dehydrogenation of **14** [7].



Surprisingly, and disappointingly, no catalytic products

Table 2
The ^{13}C NMR spectroscopic data for **9**–**11** measured in $CDCl_3$ at 100.6 MHz (numbering scheme shown in Table 1)

n	**9**	**10**		**11**		
	δC*n*, *J*(C, H)	δC*n*, *J*(C, H)	δC*n*, *J*(C, H)	δC*n*, *J*(C, H)	δC*n*, *J*(C, H)	δC*n*,*J*(C, H)
1	70.7	74.5	75.5	71.7	70.5	70.7
2	208.1	209.0	208.8	206.0	210.8	206.0
3	41.7, *J*(C, H) 130	41.5, *J*(C, H) 130	41.4, *J*(C, H) 130	40.4, *J*(C, H) 130	42.0, *J*(C, H) 128	39.6, *J*(C, H) 130
4	25.1, *J*(C, H) 130	23.1, *J*(C, H) 128	26.7, *J*(C, H) 134	23.4, *J*(C, H) 130	23.6, *J*(C, H) 128	24.7, *J*(C, H) 130
5	29.1, *J*(C, H) 131	29.3, *J*(C, H) 126	29.4, *J*(C, H) 131	27.9, *J*(C, H) 128	25.2, *J*(C, H) 129	28.1, *J*(C, H) 131
6	49.8, *J*(C, H) 129	47.3, *J*(C, H) 132	55.2, *J*(C, H) 129	48.3, *J*(C, H) 128	45.5, *J*(C, H) 129	48.3, *J*(C, H) 132
7	138.2, *J*(C, H) 156	136.4, *J*(C, H) 151	139.6, *J*(C, H) 158	138.3, *J*(C, H) 153	137.6, *J*(C, H) 152	138.1, *J*(C, H) 158
8	117.2, *J*(C, H) 158	117.5, *J*(C, H) 156	115.9, *J*(C, H) 157	118.0, *J*(C, H) 154/159	116.9, *J*(C, H) 154/159	116.7, *J*(C, H) 155/159
9		210.1	210.0	215.0	217.7	215.2
10		38.0, *J*(C, H) 128	40.8, *J*(C, H) 128	39.7, *J*(C, H) 131	38.4, *J*(C, H) 132	39.4, *J*(C, H) 130
11		25.1, *J*(C, H) 132	25.0, *J*(C, H) 132	27.0, *J*(C, H) 133	26.4, *J*(C, H) 132	24.6, *J*(C, H) 133
12		26.4, *J*(C, H) 130	26.4, *J*(C, H) 130	48.0, *J*(C, H) 126	45.1, *J*(C, H) 131	43.5
13		131.8, *J*(C, H) 156	130.9, *J*(C, H) 155	130.0, *J*(C, H) 152	131.6, *J*(C, H) 149	128.9, *J*(C, H) 152
14		127.5, *J*(C, H) 160	129.1, *J*(C, H) 161	128.3, *J*(C, H) 147	127.9, *J*(C, H) 148	127.9, *J*(C, H) 153
15		28.1, *J*(C, H) 130	29.8, *J*(C, H) 131	18.0, *J*(C, H) 126	17.9, *J*(C, H) 127	18.1, *J*(C, H) 126

could be isolated from the reaction of 4-hydroxyundeca-3,8,10-triene-2-one. The identification of the spiro compounds **9–11** is based upon ^{1}H- and ^{13}C-NMR spectroscopic investigations (Tables 1 and 2).

The structures were determined and the spectra assigned using (i) COSY spectra, and ^{13}C, ^{1}H chemical shifts correlated 2D spectra optimized for (ii) ^{1}J(C, H) and (iii) long range couplings ^{n}J(C, H). Unless stated, the given signal assignments are unambiguous, even though in most cases the proton NMR spectra showed considerable second order character, which complicated the interpretation of the 2D NMR spectra. The spin systems were not analyzed in detail, so that no further assignment of the geminal protons as axial or equatorial was attempted. NOESY spectra were also recorded but neither the NOE data nor the ^{13}C chemical shifts provided a reliable means of determining the relative configurations of both C-6 carbon atoms in **9** and of C-6 and C-12 in **11**.

Our investigation of the mechanism of the formation of 1 : 1-adducts between 1,3-butadiene and methanol [8,9] or ethyl methylacetoacetate [4,5] suggest that a key role is played by η^3-allyl-palladium intermediates which are formed by the protonation of an (η^2-1,3-butadiene)Pd species. The formation of **7**, for example, can be visualized as proceeding by the intramolecular transfer of a proton to the 7-position of a palladium-complexed molecule of **5** to give the η^3-allyl-palladium-species **16** which reacts further by reductive coupling (Scheme 1), which leaves it undecided whether **16** should be more correctly formulated as a close-ion-pair of the type [(η^3-allyl)Pd]$^+$X$^-$. **8** is then seen to be the product of a proton transfer to the 10-position in **5**.

In an attempt to obtain direct mechanistic evidence, we have studied the stoichiometric reaction between **1** and **5** at −25°C: a yellow, crystalline compound (**17**) is formed in 73% yield. Attempts to elucidate the structure of **17** by NMR spectroscopy were initially inconclusive, so that a crystal structure determination was carried out by X-ray diffraction. The molecular structure is shown in Fig. 1 and establishes that the compound contains a 2-acetyl-3-ethylcyclohex-2-enone molecule coordinated in an η^2-manner through the C=C double bond to a Pd(^{i}Pr$_2$PC$_2$H$_4$P^{i}Pr$_2$) fragment. The palladium atom has a planar coordination geometry. The oxygen atom of the acetyl group is directed towards the Pd atom (torsion angle O1–C9–C2–C1 30(1)°) but does not interact directly (Pd ··· O1 3.07 Å). The organic ligand can be displaced unchanged from **17** by further reaction with bis(diisopropylphosphino)ethane. The significance of these results only became apparent after we established that **17** is also the product of a palladium-induced isomerization

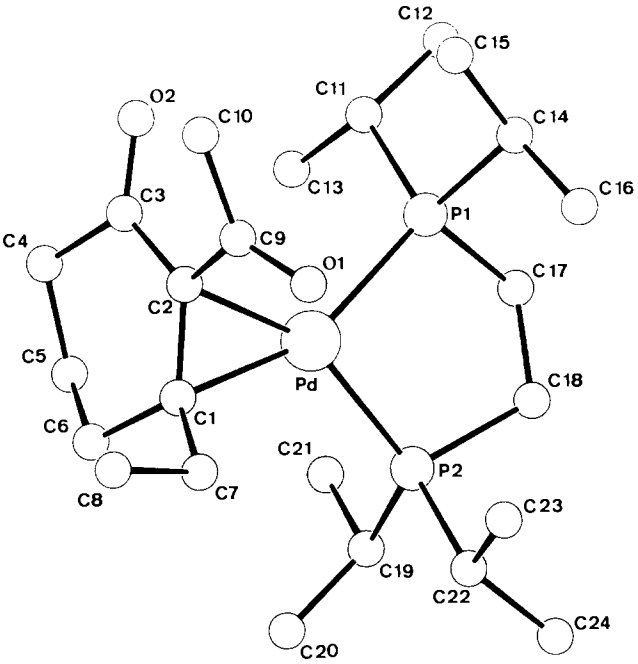
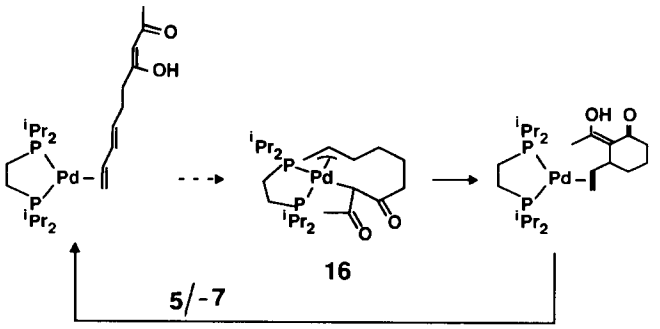
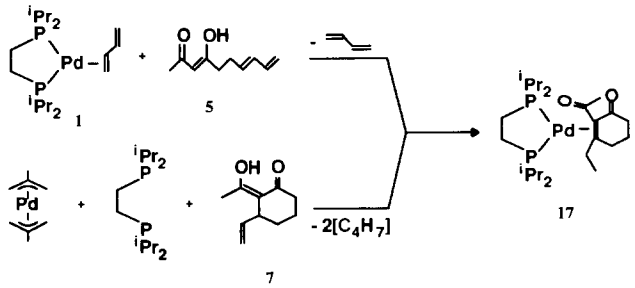


Fig. 1. The molecular structure of **17** with selected bond distances (Å) and angles (°). Bond distances (Å): Pd–C1 2.140(8); Pd–C2 2.162(8); C1–C2 1.46(1); C2–C9 1.47(1); C9–C10 1.46(2); C2–C3 1.50(1); C1–C7 1.48(1); C7–C8 1.50(2); O1–C9 1.17(1); O2–C3 1.20(1); Pd ··· O1 3.07(2); Pd–P1 2.325(2); Pd–P2 2.283(2). Bond angles (°): C2–Pd1–C1 29.6(3); C2–Pd1–P1 116.7(2); C1–Pd1–P1 156.3(2); C2–Pd1–P2 154.4(3); C1–Pd1–P2 115.1(2); P1–Pd–P2 88.6(1); C3–C2–C9 119.4(8); C6–C1–C7 110.7(7); O1–C9–C2–C1 (torsion) 30(1).



Scheme 1.



Scheme 2.

of **7** (Scheme 2) and as such it can be regarded as a secondary product of the catalytic reaction.

3. Experimental section

The organometallic compounds described below and the intermediates formed in the catalytic reactions are air-sensitive and therefore all reactions were carried out in an atmosphere of argon. The following compounds were prepared by published procedures: (η^3-2-$MeC_3H_4)_2Pd$ [10], $^iPr_2PC_2H_4P^iPr_2$ [11], (η^2-1,3-C_4H_6)$Pd(^iPr_2PC_2H_4P^iPr_2)$ [11], 1-bromopenta-2,4-diene [12], 2-bromomethylbuta-1,3-diene [13], 1-bromohexa-3,5-diene [14]. Microanalyses were performed by Dornis and Kolbe, Microanalytical Laboratory, Mülheim an der Ruhr. The NMR spectra (^1H, ^{13}C, ^{31}P) were measured on Bruker AMX-400, AMX-300, AM- and AC-200 FT-NMR spectrometers at room temperature unless otherwise stated. In the ^{13}C NMR spectra, the $^1J(C, H)$ coupling constants were estimated using gated decoupled spectra and the multiplicities were checked in DEPT spectra. The 2D NMR spectra of **9–11** were recorded on an AMX-400 using the COSY-90, HXCO and NOESYTP programs from the standard Bruker pulse program library.

3.1. Preparation of 4-hydroxy-3,7-trans,9-triene-2-one (5)

Penta-2,4-dione (14.6 g, 15 ml, 0.14 mol) dissolved in ether (10 ml) was added slowly at −78°C to a dark grey suspension of sodium amide in liquid ammonia prepared by reacting liq. NH_3 (200 ml) with freshly cut pieces of sodium (6.2 g, 0.27 mol) as described in ref. 6. The cooling bath was removed and the argon turned off. 1-Bromopenta-2,4-diene (17.9 g, 0.12 mol) in ether (100 ml) was added dropwise over 20 min. The reaction mixture was stirred for a further 30 min, ether (100 ml) was added, the ammonia evaporated by careful warming with a water bath and the mixture treated with ice (50 g). To the resulting solid mass was added conc. HCl (15 ml) and ice (3 g) and the organic phase was separated from the resulting solution which was also extracted with ether (3 × 25 ml). The combined organic phase was dried ($MgSO_4$) and shown by ^{13}C NMR to consist of **5** (78%), the related diketone (9%) and the *cis*-isomer 4-hydroxydeca-3,7-*cis*,9-triene-2-one (13%). Pure **5** was obtained by fractional distillation: yield 12.6 g (63%, 0.08 mol, b.p. 108°C/water pump vacuum). Anal. calc. for $C_{10}H_{14}O_2$: C, 72.26; H, 8.49. Found: C, 72.15; H, 8.55% MS: *m/e* 166 (M^+), 151, 148, 133, 123, 81. IR (film): ν(enol) 1618, 1606 cm^{-1}, ^1H NMR ($CDCl_3$, 300.1 MHz): δ 15.37 (s, HO:-4), 6.19 (dt, HC:-9, J(8, 9) 10.3), 5.98 (dd, HC:-8, J(7.8) 15.0), 5.58 (dt, HC:-7, J(6, 7) 6.5), 5.41 (s, HC:-3), 5.01 (dd, HC:-10Z, J(10Z, 9) 16.8), 4.88 (dd, HC:-10E, J(10E, 9) 10.0), 2.29 (m, CH_2-5/6), 1.94 (s, Me-1). ^{13}C NMR ($CDCl_3$, 75.5 MHz): δ 193.1 (C-2), 190.5 (C-4), 136.6 (C-9, J(C, H) 154), 132.5/131.6 (C-7/8, J(C, H) 152/151), 115.2 (C-10), 99.5 (C-3, J(C, H) 165), 37.5 (C-5, J(C, H) 130), 27.9 (C-6, J(C, H) 130), 23.3 (C-1, J(C, H) 128).

3.1.1. Deca-7-trans,9-diene,2,4-dione

^1H NMR ($CDCl_3$, 300.1 MHz): δ 3.47 (s, HC:-3), 2.11 (s, Me:-1). ^{13}C NMR ($CDCl_3$, 75.5 MHz): δ 202.8 (C-4), 201.5 (C-2), 136.5 (C-9), 132.2/131.7 (C-3/4, J(C, H) 151), 115.2 (C-10), 57.4 (C-3, J(C, H) 129), 42.6 (C-5, J(C, H) 125), 30.4 (C-1, J(C, H) 128), 25.9 (C-6, J(C, H) 128).

3.1.2. 4-Hydroxydeca-3,7-cis,9-triene-2-one

^{13}C NMR ($CDCl_3$, 75.5 MHz): δ 192.8 (C-2), 190.7 (C-4), 131.5 (C-7), 130.0/129.8 (C-8/9), 117.4 (C-10), 99.6 (C-3), 37.7 (C-5), 24.4 (C-1), 23.3 (C-6).

3.2. Preparation of 7-hydroxypentadeca-1,3-trans,7,12-trans,14-pentaene-9-one (6)

Prepared as described above by reacting **5** (16.6 g, 0.10 mol) dissolved in ether (10 ml) with sodium amide (7.8 g, 0.20 mol) in liq. NH_3 (200 ml) at −78°C followed by the addition of 1-bromo-penta-2,4-diene (14.7 g, 0.10 mol) in ether (10 ml). The reaction mixture was worked up as described above and the product isolated by crystallization from pentane at −5°C: yield 9.5 g (41% theory, 0.04 mol, m.p. 38°C). The ^{13}C NMR spectrum indicates that the compound exists as a keto-enol mixture. Anal. calc. for $C_{15}H_{20}O_2$: C, 77.55; H, 8.68. Found: C, 77.48; H, 8.66%. MS: *m/e* 232 (M^+), 151, 123, 109, 81, 67. IR; ν 1635 (enol). ^1H NMR ($CDCl_3$, 200.1 MHz): 13.72 (s, HO-7), 6.27 (dt, HC:-2), J(2, 3) 10.5), 6.06 (dd, HC:-3, J(3, 4) 15.0), 5.65 (m, HC:-4), 5.09 (dd, HC:-1E, J(1E, 2) 10.0), 4.97 (dd, HC:-1Z, J(1Z, 2) 17.0), 3.53 (s, HC:-8), 2.36 (m, CH_2-5/6). ^{13}C NMR ($CDCl_3$, 50.3 MHz): δ 192.8 (C-9), 136.5 (C-2), 132.4 (C-4), 131.6 (C-3), 115.3 (C-1), 99.0 (C-8), 37.4 (C-6), 28.0 (C-5).

3.2.1. Pentadeca-1,3-trans,7-trans,14-tetraene-7,9-dione

^{13}C NMR ($CDCl_3$, 50.3 MHz): δ 202.7 (C-7), 56.9 (C-8), 42.7 (C-6), 25.9 (C-5).

3.3. Preparation of 4-hydroxy-7-methylenenona-3,8-diene-2-one (13).

Prepared as described above by reaction of penta-1,4-dione (8.4 g, 8.6 ml, 0.8 mol) in ether (7 ml) with sodium amide (6.0 g, 0.15 mol) in liq. NH_3 (170 ml) at −78°C followed by treatment with 2-bromomethylbuta-1,3-diene (10.2 g, 0.07 mol) in ether (7 ml). The reaction mixture was worked up as described above

and the compound isolated by distillation: yield 4.6 g (43% theory, 0.03 mol, b.p. 100–115°C/15 bar). The ^{13}C NMR spectrum indicates that the compound exists as a keto–enol mixture. Anal. calc. for $C_{10}H_{14}O_2$: C, 72.26; H, 8.49. Found: C, 71.60; H, 8.91%. MS: *m/e* 166 (M^+), 151, 148, 85. ^1H NMR ($CDCl_3$, 200.1 MHz): δ 13.73 (s, HO:-4), 6.32 (dd, HC:-8), 5.45 (s, HC:-3), 5.20 (m, HC:-9Z, *J*(8, 9Z) 17.7), 5.03 (m, HC:-9E, *J*(8, 9E) 10.8), 5.00 (m, H_2C:-7), 2.44 (m, CH_2-5/6), 1.99 (Me-1). ^{13}C NMR ($CDCl_3$, 50.3 MHz): δ 193.4 (C-2), 190.4 (C-4), 144.4 (C-7), 137.9 (C-8), 115.8 (C-9), 113.2 (CH_2:-3), 99.4 (C-3), 36.5 (C-5), 26.5 (C-6), 24.3 (C-1).

3.3.1. 7-Methylenenona-8-ene-2,4-dione

^1H NMR ($CDCl_3$, 200.1 MHz): δ 6.30 (dd, HC:-8), 5.17 (m, HC:-9Z, *J*(8, 9Z) 17.7), 3.53 (CH_2-3).

3.4. Preparation of 4-hydroxyundeca-3,8-trans,10-triene-2-one.

Prepared as described above by reacting penta-1,4-dione (17.4 g, 17.9 ml, 0.17 mol) in ether (15 ml) with sodium amide (13.6 g, 0.35 mol) in liq. NH_3 (300 ml) at −78°C followed by treatment with 1-bromohexa-3,5-diene (27.9 g, 0.17 mol) in ether (15 ml). The reaction mixture was worked up as described above and the compound isolated by distillation: yield 3.1 g (12% theory, 0.02 mol, b.p. 100°C/oil pump vacuum). The ^{13}C NMR spectrum indicates that the compound exists almost exclusively in the enol form. Anal. calc. for $C_{11}H_{16}O_2$: C, 73.30; H, 8.95. found: C, 72.60; H, 9.08%. MS: *m/e* 180 (M^+), 162, 147, 100,85. IR (film): ν 1616 (enol). ^1H NMR ($CDCl_3$, 200.1 MHz): δ 13.6 (s, HO:-4), 6.24 (dt, HC:-10, *J*(9, 10) 10.0), 6.00 (m, HC:-9, *J*(8, 9) 15.0), 5.60 (dt, HC:-8, *J*(7, 8) 7.0), 5.43 (s, HC:-3), 5.04 (ddd, HC:-11Z, *J*(10, 11Z) 16.8, *J*(11Z, 11E) 2.0), 4.91 (ddd, HC:-11E, *J*(10, 11E) 10.0), 2.20 (m, CH_2-5), 2.06 (q, CH_2-7, *J*(7, 8) + J(6, 7) 7.1), 1.98 (s, Me-1), 1.65 (m, CH_2-6, *J*(6, 7) + *J*(5, 6) 7.4). ^{13}C NMR ($CDCl_3$, 50.3 MHz): δ 193.5 (C-2), 190.8 (C-4), 136.6 (C-10), 133.4 (C-8), 131.4 (C-9), 114.7 (C-11), 99.4 (C-3), 37.1 (C-5), 31.4 (C-7), 24.6 (C-6), 24.3 (Me-1).

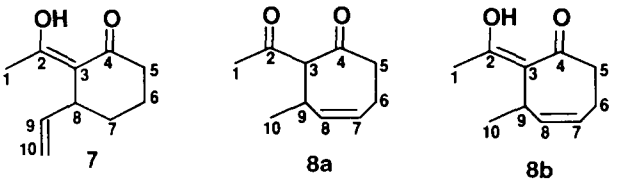
No catalytic cyclization reaction was observed upon reacting this compound in the presence of (η^2-1,3-C_4H_6)Pd($^iPr_2PC_2H_4P^iPr_2$).

3.5. Catalytic cyclization of 4-hydroxydeca-3,7,9-triene-2-one (5).

In a typical experiment **5** (1.5078 g, 9.1 mmol) and (η^2-1,3-C_4H_6)Pd($^iPr_2PC_2H_4P^iPr_2$) (0.075 g, 0.2 mmol) were stirred in CH_2Cl_2 (5 ml) at 40°C and the reaction followed by GC. The reaction was terminated after 24 h by adding elemental sulfur. The volatile components were distilled off and shown by NMR spectroscopy to consist to the extent of 60% of 2-(1-hydroxyethyliden)-3-vinylcyclohexanone (**7**) and of 5% of 2-acetyl-3-methylcyclohept-4-enone (**8**) and the corresponding enol. The components were separated by preparative GC using a 5 m × 14 mm Volaspher A 4 (60–80 mesh) column coated with 20% SE 54/SE 30 at 170°C.

3.5.1. 2-(1-Hydroxyethyliden)-3-vinylcyclohexanone (7)

^1H NMR ($CDCl_3$, 300.1 MHz): δ 16.16 (sbr, HO:-2), 5.66 (ddd, HC:-9, *J*(9, 10E) 1.6, *J*(9, 10Z) 16.0), 4.90 (dt, HC:-10E, *J*(10E, 10Z) 1.6), 4.69 (dt, HC:-10Z), ca. 3.07 (m, HC-8, *J*(8, 9) 5.7, *J*(8, 10E) 1, 5, *J*(8, 10Z) 1.6), ca. 2.08 (m, CH_2-5), 1.87 (s, Me-1), ca. 1.45 (m, CH_2-6/7) ^{13}C NMR ($CDCl_3$, 75.5 MHz): δ 199.0 (C-4), 183.1 (C-2), 141.2 (C-9, *J*(C, H) 153), 115.1 (C-10, *J*(C, H) 154/158), 107.6 (C-3), 36.9 (C-8, *J*(C, H) 129), 30.5 (C-5), 28.0 (C-7, *J*(C, H) 128), 23.8 (C-1, *J*(C, H) 127), 16.2 (C-6, *J*(C, H) 128); numbering scheme shown below.



7 8a 8b

3.5.2. 2-Acetyl-3-methylcyclohept-4-enone (8a)

^{13}C NMR (d_8-THF, 300.1 MHz): 206.8/202.8//208.9/203.8 (C-2/4//2′/4′), 135.6/136.2 (C-8/8′, *J*(C, H) 158/160), 128.5/127.9 (C-7/7′), 74.4/67.6 (C-3/3′, *J*(C, H) 133), 41.6 (C-5/5′, *J*(C, H) 130/126), 32.5 (C-9/9′, *J*(C, H) 132), 30.2 (C-1/1′, *J*(C, H) 128/128), 25.5 (C-6/6′, *J*(C, H) 129), 20.5/22.6 (C-10/10′, *J*(C, H) 128); the compound consists of a mixture of diastereomers and the numbering scheme is shown above.

3.5.3. 2(1-Hydroxyethyliden)-3-vinylcyclohept-4-enone (8b)

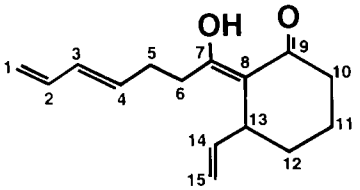
^{13}C NMR (d_8-THF, 300.1 MHz): δ 195.4 (C-4), 190.5 (C-2), 133.5 (C-8, *J*(C, H) 160), 128.2 (C-7), 114.5 (C-3), 38.4 (C-5, *J*(C, H) 130), 33.2 (C-9, *J*(C, H) 124), 24.3 (C-6), 22.4 (C-1), 18.4 (C-2); numbering scheme shown above.

3.6. Catalytic cyclization of 7-hydroxypentadeca-1,3,7,12,14-pentaene-9-one (6).

The reaction was carried out as described above. The products were separated from the catalyst by filtration through a short florisil column and separated by preparative GC using an 8 m × 14 mm Chrom P (60–80 mesh) column coated with 20% SE[54] at 220°C. The spiro compounds **9–11** were identified by NMR

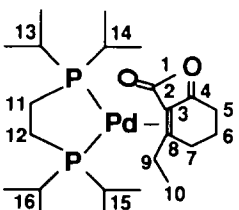
spectroscopy (Tables 1 and 2 and accompanying discussion).

Termination of the reaction after 24 h and ^{13}C NMR analysis of the product mixture indicated that it consisted to the extent of 55% of **9** and of 30% of **12**; ^{13}C NMR ($CDCl_3$): 201.1 (C-9), 182.7 (C-7), 141.5 (C-14), 136.7 (C-2), 133.3 (C-3), 131.4 (C-4), 115.7 (C-1), 115.1 (C-15), 107.7 (C-8), 36.5 (C-13), 35.4 (C-6), 30.6 (C-10), 28.2 (C-12), 27.0 (C-5), 16.3 (C-11); numbering scheme shown below.



3.7. Preparation of (η^2-2-acetyl-3-ethylcyclohex-2-enone)Pd(^{i}Pr$_2$PC$_2$H$_4$P^{i}Pr$_2$) (17).

(η^2-1,3-C_4H_6)Pd(^{i}Pr$_2$PC$_2$H$_4$P^{i}Pr$_2$) (1.023 g, 2.4 mmol) and 4-hydroxydeca-3,7,9-triene-2-one (0.402 g, 2.4 mmol) were stirred in acetone (5 ml) at −30°C for 5 h. Diethyl ether (5 ml) was added to the resulting yellow solution which was stored at −25°C for a month. The compound was deposited as yellow crystals: yield 0.9 g (73% theory, 1.8 mmol, m.p. ca. 80°C dec.). Anal. calc. for $C_{24}H_{46}O_2P_2Pd$: C, 53.88; H, 8.67; P, 11.58; Pd, 19.89. Found: C, 53.95; H, 8.68; P, 11.50; Pd, 19.96%, MS: *m/e* 534 (M^+), 368. ^1H NMR (d_8-THF, 193 K, 400.1 MHz): δ 3.1–0.8 m. ^{13}C NMR (d_8-THF, 193 K, 100.6 MHz): δ 204.3/196.1 (C-2/4, *J*(P, C) 66.8), 88.2/83.9 (C-3/8, *J*(P, C) 6.7/3.8, 15.2/41.0), 34.2/30.7 (C-5/6/7), 27.3 (C-16, *J*(P, C) 14), 26.2 (C-15, *J*(P, C) 14), 24.7 (C-14, *J*(P, C) 10), 24.5 (C-13, *J*(P, C) 17), 22.9 (C-11/12). ^{31}P NMR (d_8-THF, 193 K, 81.0 MHz): δ 59.5, 53.9, *J*(P, P) 21.9; numbering scheme shown below. The compound may also be prepared by reacting (η^3-2-MeC_3H_4)$_2$Pd, ^{i}Pr$_2$PC$_2$H$_4$P^{i}Pr$_2$ and **7** in diethyl ether for one week.



3.8. Reaction of 17 with ^{i}Pr$_2$PC$_2$H$_4$P^{i}Pr$_2$

17 (0.1124 g, 0.2 mmol) was reacted with ^{i}Pr$_2$P-C$_2$H$_4$P^{i}Pr$_2$ (0.049 g, 0.2 mmol) in diethyl ether for one week. The volatile components were distilled under high vacuum and the organic product shown to consist mainly of 2-acetyl-3-ethylcyclohex-2-enone. ^{13}C NMR (d_8-THF): δ 202.06/196.07 (C-2/4), 163.56/139.32 (C-3/8), 37.51/29.37 (C-5/7), 30.87 (C-1), 28.37 (C-9), 22.25 (C-6), 12.18 (C-10); numbering scheme shown above.

Table 3
Atomic coordinates and equivalent isotropic thermal parameters (Å^2) for **17** with standard deviations in parentheses [a]

Atom	*x*	*y*	*z*	U_{eq}
Pd	0.1828(1)	0.1238(1)	0.0119(1)	0.039
P1	0.2128(2)	0.1831(1)	0.1088(2)	0.046
P2	0.2790(2)	0.0958(1)	0.1548(2)	0.051
O1	−0.0212(6)	0.1188(3)	0.0257(8)	0.111
O2	0.1002(6)	0.1836(2)	−0.2496(8)	0.104
C1	0.1203(6)	0.0849(2)	−0.1212(7)	0.045
C2	0.0832(6)	0.1233(3)	−0.1392(7)	0.047
C3	0.1194(7)	0.1500(3)	−0.2412(9)	0.062
C4	0.1906(8)	0.1341(4)	−0.3344(9)	0.083
C5	0.2436(8)	0.1011(4)	−0.2843(9)	0.078
C6	0.1853(7)	0.0697(3)	−0.2265(9)	0.065
C7	0.0682(8)	0.0529(3)	−0.0652(9)	0.071
C8	−0.0032(9)	0.0380(3)	−0.153(1)	0.093
C9	0.0016(7)	0.1339(3)	−0.070(1)	0.065
C10	−0.0567(9)	0.1616(4)	−0.134(1)	0.117
C11	0.2525(9)	0.2211(3)	0.0020(9)	0.075
C12	0.284(1)	0.2582(3)	0.065(1)	0.102
C13	0.3283(9)	0.2042(3)	−0.082(1)	0.096
C14	0.1312(7)	0.2096(3)	0.207(1)	0.065
C15	0.0583(9)	0.2248(4)	0.129(1)	0.109
C16	0.0937(9)	0.1832(4)	0.312(1)	0.107
C17	0.3059(7)	0.1737(3)	0.2212(9)	0.061
C18	0.3096(8)	0.1339(3)	0.2716(9)	0.080
C19	0.3844(7)	0.0760(3)	0.1036(9)	0.070
C20	0.3748(9)	0.0382(4)	0.034(1)	0.098
C21	0.4348(9)	0.1046(5)	0.024(1)	0.115
C22	0.2329(8)	0.0569(3)	0.259(1)	0.078
C23	0.1421(9)	0.0660(4)	0.304(1)	0.101
C24	0.2956(9)	0.0455(4)	0.374(1)	0.107

[a] $U_{eq} = 1/3\Sigma_i\Sigma_j U_{ij} a_i^* a_j^* \bar{a}_i \cdot \bar{a}_j$

3.9. Single crystal X-ray structure analysis of 17

Crystals suitable for an X-ray structural determination [15] were grown from acetone/diethyl ether: molecular formula $C_{24}H_{46}O_2P_2Pd$, molecular weight 535.0 g mol^{-1}, crystal colour yellow-green, crystal size 0.53 × 0.56 × 0.28 mm, a = 15.110(3), b = 10.281(1), c = 34.634(3) Å; V = 5380.2 Å^3, T = 293 K, d_{cal} = 1.32 g cm^{-3}, μ = 69.60 cm^{-1}, Z = 8, orthorhombic, space group *Pbca* [No. 61], Enraf-Nonius CAD4 diffractometer, λ = 1.54178 Å, scan mode $\omega - 2\Theta$, 11484 measured reflections (±h, +k, +l), $[(\sin\Theta/\lambda)]_{max}$ 0.63 Å^{-1}, analytical absorption correction [max: 0.998; min: 0.756], 5533 independent reflection, 4444 observed reflections [$I > 2\sigma(I)$] for 262 refined parameters, structure solved by heavy atom method, H atom positions calculated (U_H = 0.05 Å^2), R = 0.072, R_w = 0.075, residual electron density 1.36 eÅ^{-3}. Atomic positional

parameters and equivalent isotropic thermal parameters are given in Table 3.

Supplementary material available

Tables of crystallographic data, listings of H atom positional parameters, anisotropic thermal parameters, distances and angles.

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