Some Observations Concerning the Thermally Induced Oxy-Ene Reaction

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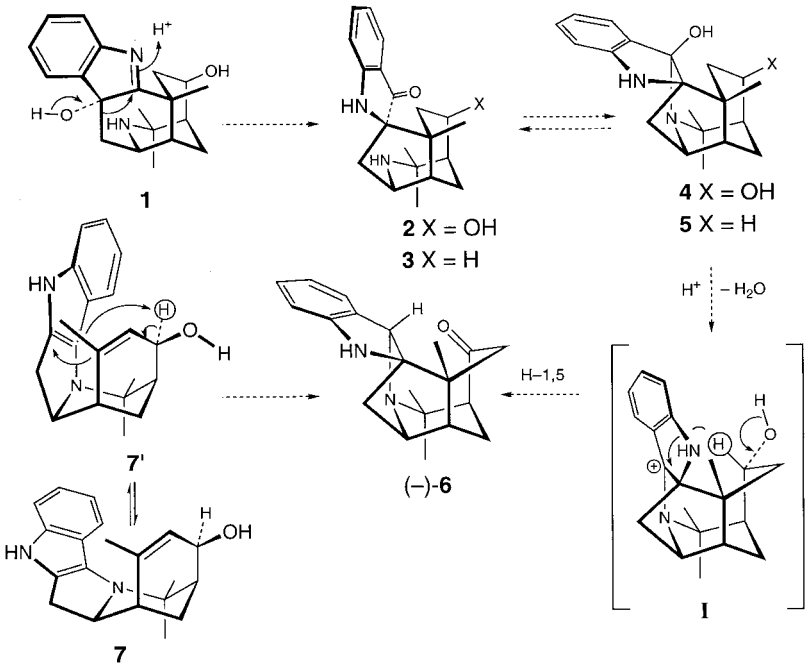
Several examples of thermally induced intramolecular oxy-ene reactions leading to six- or five-membered rings are reported. The yields vary from poor to good, depending on the thermal lability of the substrate. Considering the high temperatures required to effect these transformations (several hours at *ca.* 250°), the observed diastereoselectivities favoring the *trans*-1,2-substituted cycloalkane derivatives are excellent. In the case of product **26**, these substituents were shown to prefer a *trans*-diaxial orientation both in the solid state (X-ray evidence) and in solution, presumably to avoid the allylic strain prevailing in the *diequatorial* conformer.

1. Introduction. – In a recent review article dealing with the *Aristotelia* alkaloids, one of us speculated [1] that the biosynthesis of the hexacyclic representative aristone (**6**) (*Scheme 1*) might not follow the course invoked earlier by *Silva* and co-workers [2]. They postulated that 19-oxyserratoline (**1**) is rearranged to *exo*-19-oxyaristotelone (**2**), the hemiaminal form **4**, of which undergoes H_2O elimination to yield the carbenium ion **I**. This intermediate would then be stabilized *via* an intramolecular 1,5-hydride shift, followed by loss of the hydroxylic proton to furnish aristone (**6**). The main drawback of this hypothesis is that the lone-pair of the piperidine N-atom in **2** lies in the same plane as the C=O bond, whereas it should be orthogonal to it to form the hemiaminal **4** [3]. Indeed, in the spectra of the deoxy analogue aristotelone (**3**), no sign of the corresponding hemiaminal form **5** could be discerned [4]. As an alternative, we proposed that the crucial N–C(3) bond is formed on the tetracyclic level to yield the precursor **7**, which, in the axial conformation **7′**, could undergo an intramolecular oxy-ene reaction, or the anionic equivalent thereof, to produce aristone (**6**).

In a formal sense, the oxy-ene reaction envisaged (general representation **16** → **17**; *Scheme 2*) is situated somewhere between the well-established *Conia* reaction [5] (**8** → **9**) and the oxy-*Cope* rearrangement [6] (**10** → **11**), common aspects being the crucial intermediacy of enol forms and the intramolecular nature of these processes. A literature survey on the oxy-ene reaction revealed that this transformation is virtually unknown. The only precedent we have come across is an investigation of *Klärner et al.* in 1981 [7]. They obtained, *e.g.*, the cyclopropane derivatives **13** and **15** from the $\alpha\beta,\delta\varepsilon$-unsaturated alcohols **12** and **14** in a fashion that they called a '[1,5]-homodienyl hydrogen shift'. Generally, this reaction is viewed as belonging to the family of homosigmatropic transpositions (*cf.* [8]), but in our context, it can equally well be described as an oxy-ene reaction. In connection with the aim to synthesize aristone (**6**)

[1]) Part of the forthcoming Ph.D. thesis of *G. S.*, ETH-Zürich.

Scheme 1



from the putative precursor **7**, we decided to investigate whether it is possible to construct rings larger than three-membered ones through intramolecular oxy-ene reactions and anionic versions thereof [2]).

2. Results. – As ene reactions between inactivated components usually require quite high temperatures (for reviews, see [9]), which can easily lead to undesired side-reactions in the case of allylic alcohols, compound **21** (*Scheme 3*) was chosen as the first model compound. Besides being incapable of undergoing β-eliminations, this compound shows a high degree of pre-organization towards the calculated transition state for an ene reaction [10] due to its comparatively rigid structure. The synthesis of **21** was straightforward and started with a *Suzuki* coupling [11] between (2-ethenylphenyl)boronic acid (**18**) [12] and 2-bromobenzaldehyde to furnish the biphenyl derivative **19** in high yield. A *Claisen-Schmidt* condensation of **19** with acetophenone gave (*E*)-prop-2-enone **20** as a single product, which was reduced with $NaBH_4$ at $-30°$ to give the envisaged model compound **21**. Due to atropisomerism and the presence of a chiral center, this compound was obtained as a *ca.* 1:1 mixture of two diastereoisomers, which were not separated.

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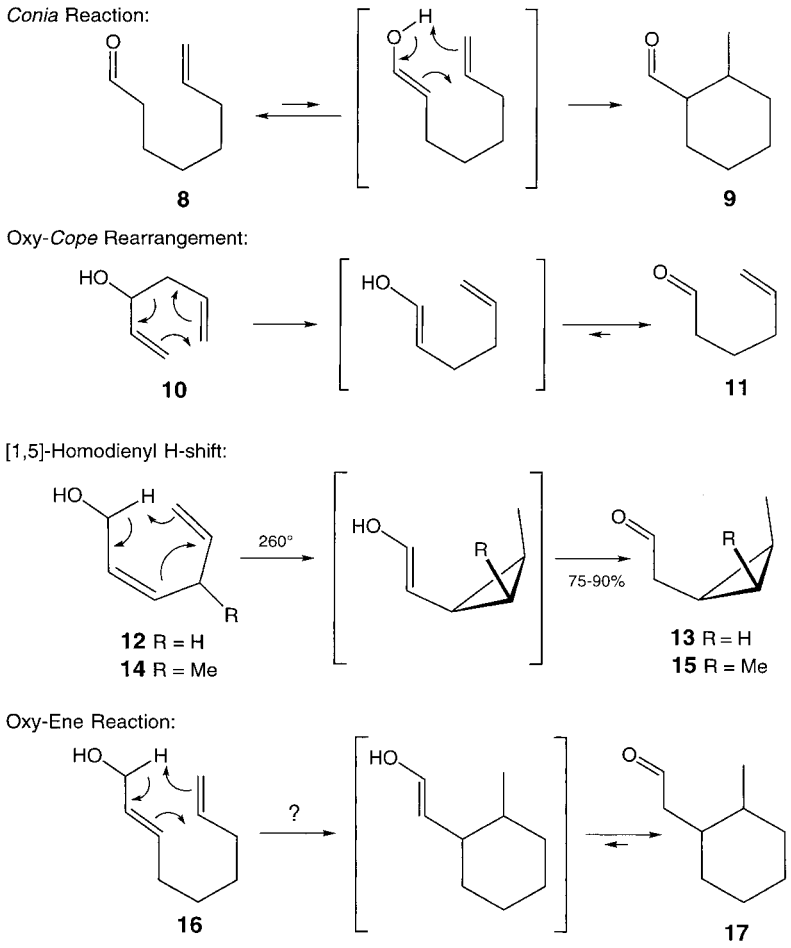
[2]) In the present paper, only the thermally induced 'oxy-ene results' of the free allylic alcohols are presented. The interesting and often complementary rearrangements of the corresponding alkoxydes will be discussed in a subsequent article in this journal.

Scheme 2



Thermal treatment of a benzene solution of **21** (19 h at 210° in a stainless-steel autoclave with copper fittings) furnished a mixture from which the main component was isolated in 74% yield by chromatography (*Table 1*). A closer examination of the NMR spectra of this component showed it to be a 23:1 mixture of two diastereoisomers, from which the major component could be obtained in pure state by recrystallization from cyclohexane. The structure of this compound was shown to be represented by formula **26** through X-ray crystallography[3]) (see *Figs. 1* and *2*, and *Table 2*). Interestingly, the methyl and the phenacyl substituents of the cyclohexadiene unit occupy *pseudoaxial* positions, presumably to avoid $A^{1,3}$ strain interactions that would prevail in a *diequatorial* arrangement of the two substituents [13]. As the vicinal

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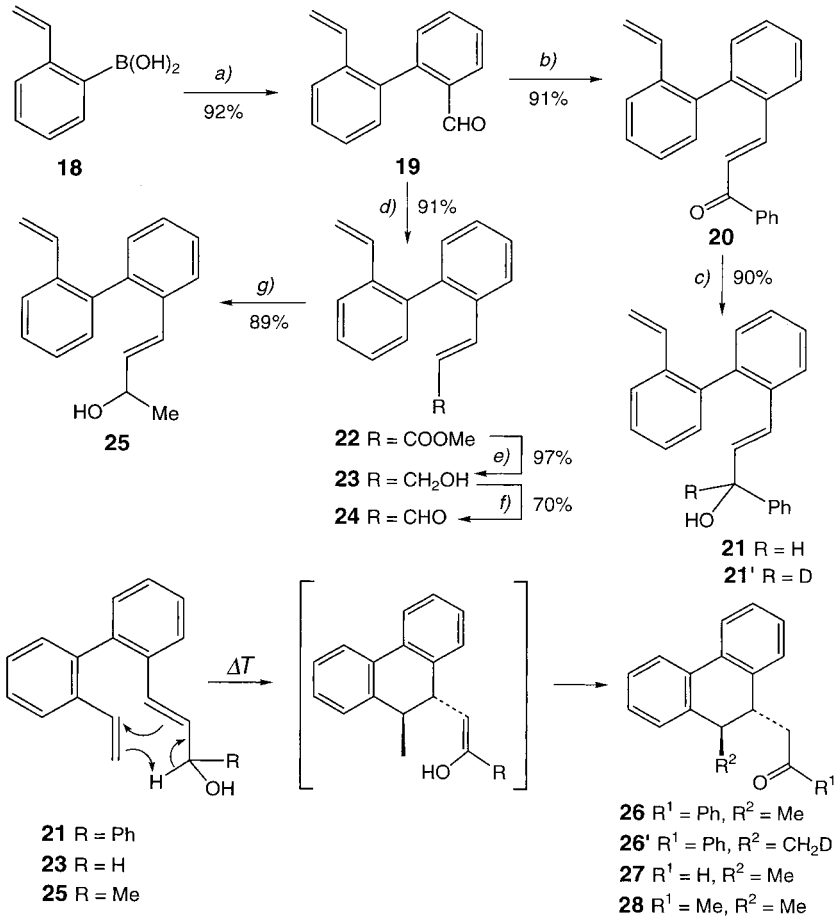
[3]) We thank Dr. *B. Schweizer*, Laboratory for Organic Chemistry, ETH-Zürich, for the determination of this X-ray crystal structure.

Scheme 3



a) $Pd(PPh_3)_4$, 2-Bromobenzaldehyde, Na_2CO_3, DME/EtOH/H_2O, 16 h reflux. *b*) Acetophenone, 2M NaOH, EtOH, 23 h, 25°. *c*) $NaBH_4$, 30 min, −30°; 30 min, 25°. *d*) $(MeO)_2P(O)CH_2COOMe$, *t*-BuOK, THF, 30 min, 25°. *e*) $(i\text{-}Bu)_2AlH$ (DIBAH), 1 h, −78°. *f*) 5 equiv. PCC, NaOAc, CH_2Cl_2, 1 h, 0°. *g*) MeLi, THF, 5 min 0°.

Table 1. *Reaction Conditions and Yields of the Oxy-Ene Reactions Studied*

Starting material	Product	T (± 10°)	Time [h]	Yield [%]	ds [%]
21	**26**	210°	19	74	96
21′	**26′**	240°	21	31	94.5
23	**27**	250°	30	71	92
25	**28**	250°	27	62	96
33	**36**	250°	28	81	89
35	**37**	230°	6	23	92
41	**42**	250°	27	35	96

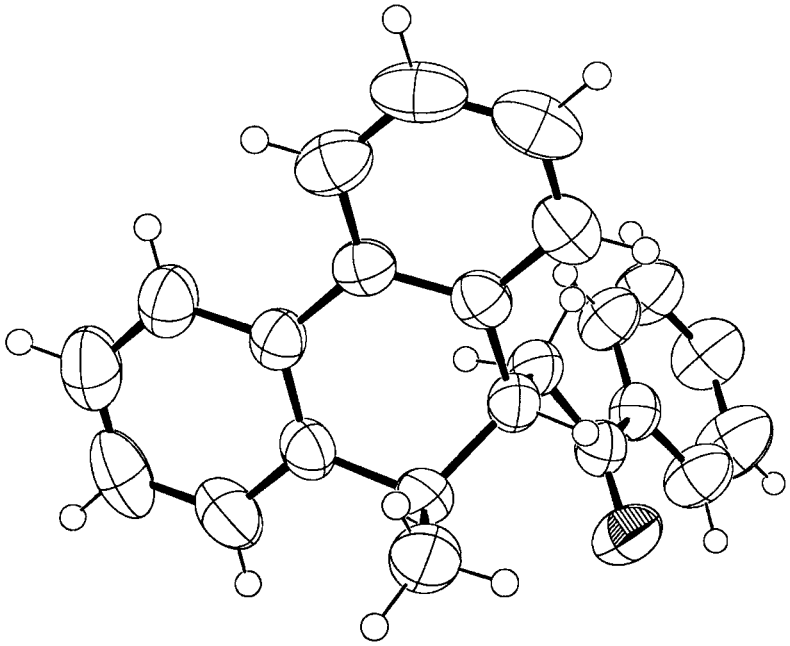


Fig. 1. *ORTEP View of* **26**. The thermal ellipsoids are scaled at the 30% level.

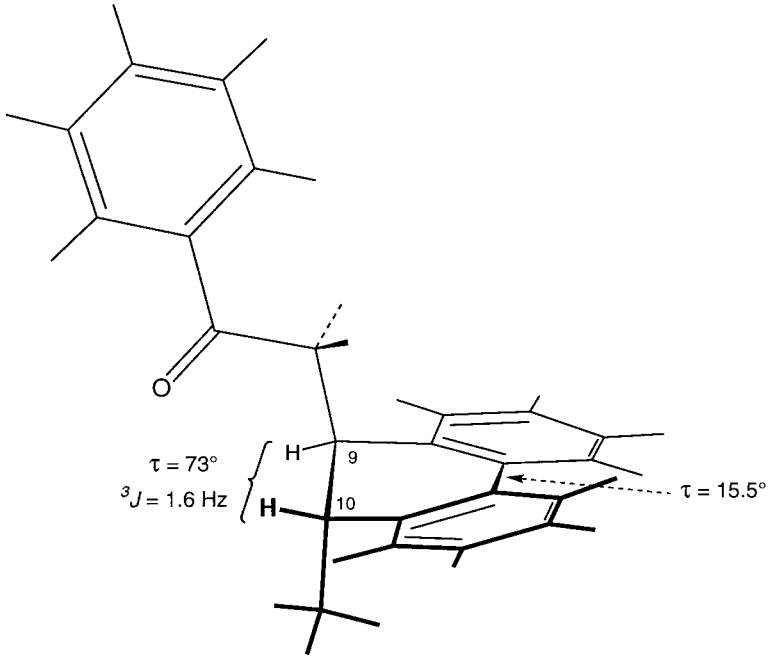


Fig. 2. *View of* **26** *based on its crystal structure.* Unlabelled substituents represent H-atoms.

Table 2. *Crystallographic Data of* rac-**26**

Empirical formula	$C_{23}H_{20}O$
Formula weight	312.39
Temp.	293(2) K
Wavelength	0.71069 Å
Crystal system	Monoclinic
Space group	*Cc*
Unit cell dimensions	$a = 18.111(18)$ Å $\alpha = 90$ deg.
	$b = 10.92(2)$ Å $\beta = 107.96(6)$ deg.
	$c = 9.304(6)$ Å $\gamma = 90$ deg.
V	1750(4) Å^3
Z	4
Density (calc.)	1.185 Mg/m^3
Absorption coefficient	0.071 mm^{-1}
$F(000)$	664
Crystal size	$0.40 \times 0.40 \times 0.25$ mm
θ Range	2.21 to 26.95 deg.
Index ranges	$0 \leq h \leq 23$, $0 \leq k \leq 13$, $-11 \leq l \leq 11$
Reflections collected	2948
Independent reflections	1958 [R(int) = 0.109]
Max/min. transmission	0.9825 and 0.9723
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	1436/2/217
Goodness-of-fit on F^2	1.447
Final R indices [$I > 3\sigma(I)$]	$R1 = 0.0569$, $wR2 = 0.1520$
R indices (all data)	$R1 = 0.0748$, $wR2 = 0.1611$
$\Delta\rho$ (max; min)	0.271 and -0.256 e · A^{-3}

coupling constant between the corresponding H-atoms amounts to only 1.6 Hz, the predominant conformation in solution must be very similar to that in the solid state (*Fig. 2*). As a confirmation, semi-empirical calculations at the PM3 level revealed a ΔH_f° of 2.0 kcal/mol in favor of the *transdiaxial* conformer. The minor component of the above 23:1-mixture is probably the *cis*-isomer of **26**, because its Me group resonates at 15.1 ppm (*vs.* 21.7 ppm for the *trans*-isomer **26**) in the ^{13}C-NMR spectrum (C_6D_6, 125 MHz).

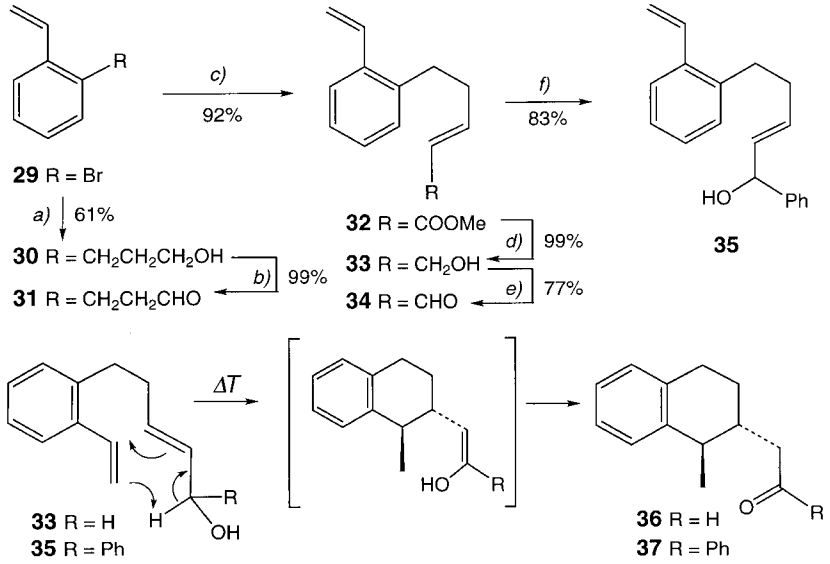
To corroborate the proposed oxy-ene mechanism, the deuterated analogue **21′** was subjected to similar reaction conditions. Due to a substantial primary isotope effect, this substrate reacted considerably more slowly than the undeuterated compound **21**, and the yield of the monodeuterated product **26′** was distinctly lower than in the former case (*Table 1*). In the purified product, the ^{2}H label showed up exclusively in the Me group, *i.e.*, in the expected position. This finding was established by an analysis of the ^{1}H- and ^{13}C-NMR spectra, as well as of the EI mass spectrum of **26′**. Whereas the mass spectra of the compounds **26**, **27**, and **28** are dominated by a *McLafferty* process leading to the radical cation of 9-methylphenanthrene (*m*/*z* 192) as the base peak in all cases, the deuterated compound **26′** shows a corresponding base peak at *m*/*z* 193.

Next, we investigated the fate of model compound **23**, readily available from aldehyde **19** in two high-yielding steps. The major change resides in the removal of the activating Ph group, which reduces the bond strength of the migrating benzylic H-atom in **21** as compared to the primary allylic substrate **23** [14]. Not surprisingly, therefore, a

longer reaction time and higher temperatures were needed to reach roughly the same yield of the corresponding rearrangement product **27** (*Table 1*). The same was found to be true in the model compound **25**, which still furnished a surprisingly good yield of **28**, considering the possibility that the major pathway for this secondary allylic alcohol could have been the competitive β-elimination of H_2O.

We then increased the conformational freedom of the chain connecting the two interacting olefinic moieties by preparing the model compounds **33** and **35** (*Scheme 4*). Whereas the yield of the expected rearrangement product fell to a disappointing 23% in the case of the reaction **35** → **37**, the primary substrate **33** furnished the desired aldehyde **36** in 81% yield.

Scheme 4

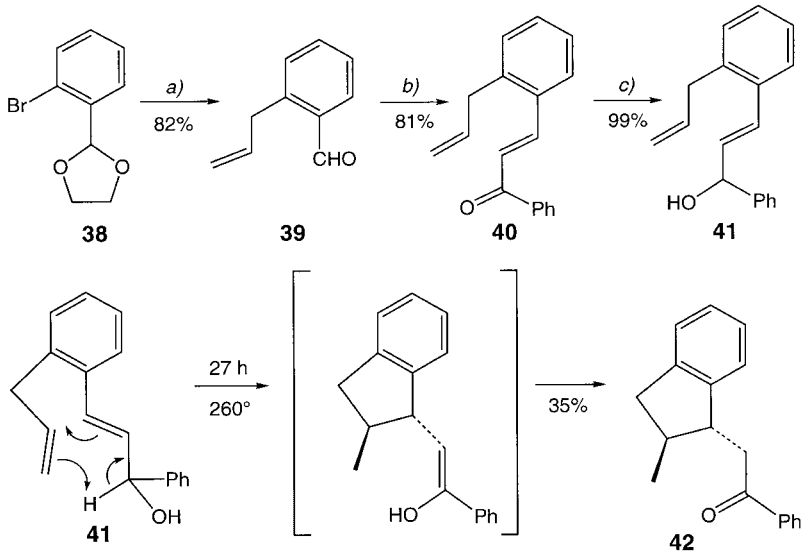


a) 1. Methyl acrylate, $NiCl_2 \cdot 6\,H_2O$, Zn, Et_3N, py, THF, 21 h reflux; 2. $LiAlH_4$, THF, 1 h, 0°. *b*) DMSO, $(COCl)_2$, Et_3N, CH_2Cl_2, −78°. *c*) $(MeO)_2P(O)CH_2COOMe$, tetramethylguanidine, THF, 18 h, 25°. *d*) DIBAH, 40 min, −78°. *e*) 5 Equiv. pyridinium chlorochromate (PCC), NaOAc, CH_2Cl_2, 15 min 0°. *f*) PhMgBr, THF, 5 min, 25°.

The last test substrate **41** was prepared as shown in *Scheme 5*. Coupling of the *Grignard* reagent derived from **38** with allyl bromide ([15]), followed by acidic workup furnished the aldehyde **39**, which was transformed into **41** according to our standard protocol. The ensuing oxy-ene reaction furnished the indane derivative **42** in only 35% yield. Seemingly, the increased strain of benzocyclopentanes compared to their six-membered 1,2,3,4-tetrahydronaphthalene analogues is already noticeable in the transition-state leading from **41** to **42**.

3. Discussion and Outlook. – The results of our investigation, summarized in *Table 1*, show that the purely thermal oxy-ene reaction is feasible under certain restrictions: it seems to work well in the case of primary allylic alcohols or in situations where no β-dehydration of the substrate can occur. An obvious improvement over the

Scheme 5



a) 1. Mg, THF, 2. allyl bromide, 1 h reflux. *b*) Acetophenone, 2M NaOH, EtOH 17 h 25°. *c*) $NaBH_4$, 17 h −30°.

latter limitation would be to pyrolyze the corresponding alkoxides instead of the free alcohols. Indeed, in the case of model compound **35** the yield of product **37** could be increased from 23 to 79% by heating the corresponding lithium alkoxide for 4 h at 200° [16][2]). Another line of future investigation will be the introduction of two different substituents at the terminus of the vinyl group; the concertedness of the oxy-ene reaction should then allow for the diastereoselective creation of three contiguous asymmetric centers. A further point of interest will be the stereochemical outcome of this reaction when (*Z*)-configured allylic alcohols are thermolyzed.

We thank the *Swiss National Science Foundation* for generous financial support.

Experimental Part

General. See [17]. All chiral compounds were obtained as racemic mixtures.

General Procedure for the Thermolyses. A 30 mM soln. of the model substrate in 10 ml of benzene under Ar was placed in a stainless-steel cylinder (100 mm long, outside diameter 25 mm, inside diameter 12 mm) with a Cu seal and closed with a screwed-on stainless-steel cap. After heating at the mentioned temp. for the indicated time, the apparatus was cooled to 25°, opened, and the solvent was evaporated. The residue was chromatographed (silica gel; pentane/Et_2O 9:1) to furnish the desired oxy-ene products in the specified yields.

2′-Ethenyl-1,1′-biphenyl-2-carbaldehyde (**19**). A soln. of 2.13 ml (18.4 mmol) of 2-bromobenzaldehyde (*Fluka*, *purum*) and 87 mg (0.56 mmol) of $[Pd(PPh_3)_4]$ (*Fluka*, *purum*) in 80 ml of DME under Ar was stirred at 25° for 10 min. After addition of a soln. of 3.00 g (20.3 mmol) of **18** in 18 ml of EtOH and a soln. of 3.90 g (36.8 mmol) of Na_2CO_3 in 18 ml of H_2O, the clear-yellow soln. was refluxed for 16 h. After cooling, the mixture was diluted with Et_2O and worked up with brine. The crude product was chromatographed (silica gel; pentane/Et_2O 9:1) to furnish 3.51 g (92%) of **19**. Colorless, viscous oil. IR ($CHCl_3$): 2855*w*, 2755*w*, 1694*s*, 1655*w*, 1629*w*, 1599*s*, 1472*w*, 1447*w*, 1418*w*, 1393*w*, 1280*w*, 1252*m*, 1194*m*, 1161*w*, 1112*w*, 1004*w*, 991*w*, 920*m*, 828*m*, 644*w*. ^{1}H-NMR (400 MHz, $CDCl_3$): 9.71 (*d*, *J* = 0.8, 1 H); 8.04–8.01 (*m*, 1 H); 7.68–7.61 (*m*, 2 H); 7.53–7.49 (*m*, 1 H); 7.44–7.40 (*m*, 1 H); 7.37–7.32 (*m*, 2 H); 7.25–7.23 (*m*, 1 H); 6.40 (*dd*, *J* = 17.4, 11.0, 1 H); 5.67 (*dd*, *J* = 17.4, 1.1,

1 H); 5.16 (*dd*, *J* = 11.0, 1.1, 1 H). ^{13}C-NMR (100 MHz, $CDCl_3$): 192.1 (*d*); 144.6 (*s*); 137.0 (*s*); 136.4 (*s*); 134.7 (*d*); 134.3 (*s*); 133.6 (*d*); 131.2 (*d*); 130.7 (*d*); 128.6 (*d*); 128.0 (*d*); 127.6 (*d*); 127.1 (*d*); 125.4 (*d*); 116.3 (*t*). EI-MS: 208 (3, M^+), 180 (40), 179 (100), 178 (68), 165 (25), 152 (23).

*(*E*)-3-(2′-Ethenyl-1,1′-bipenyl-2-yl)-1-phenylprop-2-en-1-one* (**20**). To a soln. of 2.61 g (12.5 mmol) of **19** and of 1.50 g (12.5 mmol) of acetophenone (*Fluka, puriss.*) in 40 ml of EtOH were added 2 ml of a 2M aq. NaOH soln. After stirring for 18 h at 25°, the resulting clear yellow mixture was poured into an aq. buffer soln. (pH 7) and neutralized by addition of 2 ml of 2M aq. HCl. Workup with Et_2O and purification by chromatography (silica gel; pentane/Et_2O 9 : 1) furnished 3.52 g (96%) of a yellow oil, containing 5% of acetophenone, which was removed after the next step. IR ($CHCl_3$): 3090*w*, 3065*m*, 1665*s*, 1640*s*, 1608*s*, 1595*s*, 1580*s*, 1490*w*, 1471*m*, 1449*m*, 1418*w*, 1332*s*, 1318*s*, 1287*m*, 1269*m*, 1180*m*, 1161*w*, 1082*w*, 1072*w*, 1034*m*, 1018*s*, 1003*m*, 989*m*, 917*m*, 696*m*. ^{1}H-NMR (400 MHz, $CDCl_3$): 7.88 – 7.83 (*m*, 3 H); 7.73 – 7.68 (*m*, 1 H); 7.59 – 7.28 (*m*, 10 H); 7.23 – 7.18 (*m*, 1 H); 6.43 (*dd*, *J* = 17.4, 11.0, 1 H); 5.67 (*dd*, *J* = 17.4, 1.2, 1 H); 5.13 (*dd*, *J* = 11.0, 1.2, 1 H). ^{13}C-NMR (100 MHz, $CDCl_3$): 190.9 (*s*); 143.6 (*d*); 142.2 (*s*); 138.7 (*s*); 138.0 (*s*); 136.3 (*s*); 134.9 (*d*); 133.9 (*s*); 132.6 (*d*); 131.2 (*d*); 130.5 (*d*); 129.8 (*d*); 128.5 (*d*); 128.5 (*d*); 128.2 (*d*); 127.9 (*d*); 127.7 (*d*); 126.9 (*d*); 125.3 (*d*); 123.8 (*d*); 115.3 (*t*). EI-MS: 310 (6, M^+), 205 (55), 191 (31), 179 (19), 178 (44), 120 (16), 105 (100), 77 (65), 51 (16), 28 (82).

*(*E*)-3-(2′-Ethenyl-1,1′-biphenyl-2-yl)-1-phenylprop-2-en-1-ol* (**21**). To a soln. of 2.24 g (7.21 mmol) of **20** in 13 ml of THF and 6.5 ml of MeOH at −30° were added 0.82 g (22 mmol) of $NaBH_4$ in small portions. After stirring for 30 min at −30°, the mixture was warmed to 25°, quenched with brine, and worked up with Et_2O. The crude product was chromatographed (silica gel; hexane/AcOEt 4 : 1) to furnish 2.03 g (90%) of a colorless, viscous oil, consisting of a 1 : 1 mixture of two diastereoisomers. IR ($CHCl_3$): 3605*m*, 3440*w* (br.), 3090*m*, 3065*m*, 2880*w*, 1958*w*, 1928*w*, 1827*w* (br.), 1733*m*, 1629*w*, 1604*w*, 1494*m*, 1471*m*, 1455*m*, 1415*m*, 1375*m*, 1101*m*, 1069*m*, 1004*m*, 992*m*, 969*m*, 915*m*, 636*w*, 621*w*, 610*w*. ^{1}H-NMR (400 MHz, $CDCl_3$): 7.67 – 7.64 (*m*, 2 H); 7.60 – 7.56 (*m*, 2 H); 7.38 – 7.21 (*m*, 18 H); 7.17 – 7.11 (*m*, 4 H); 6.41 (*dd*, *J* = 17.5, 11.0, 1 H); 6.37 (*dd*, *J* = 17.5, 11.0, 1 H); 6.36 (*d*, *J* = 15.8, 1 H); 6.35 (*d*, *J* = 15.8, 1 H); 6.22 (*dd*, *J* = 15.8, 6.9, 1 H); 6.21 (*dd*, *J* = 15.8, 6.9, 1 H); 5.66 (*dd*, *J* = 17.5, 1.2, 1 H); 5.64 (*dd*, *J* = 17.5, 1.2, 1 H); 5.14 (*dd*, *J* = 6.8, 3.0, br. 2 H); 5.10 (*dd*, *J* = 11.0, 1.2, 1 H); 5.05 (*dd*, *J* = 11.0, 1.2, 1 H); 1.90 (br. *d*, *J* = 3.6, 1 H); 1.88 (br. *d*, *J* = 3.6, 1 H). ^{13}C-NMR (100 MHz, $CDCl_3$): 142.6 (*s*); 142.6 (*s*); 139.8 (*s*); 139.7 (*s*); 139.5 (2*s*); 136.2 (*s*); 136.1 (*s*); 135.4 (*d*); 135.2 (*d*); 135.3 (*s*); 135.2 (*s*); 132.7 (*d*); 132.5 (*d*); 130.5 (2*d*); 130.5 (*d*); 130.5 (*d*); 129.3 (*d*); 129.2 (*d*); 128.4 (*d*); 128.4 (*d*); 127.7 (2*d*); 127.6 (*d*); 127.6 (*d*); 127.6 (*d*); 127.5 (*d*); 127.4 (*d*); 127.4 (*d*); 127.4 (*d*); 127.4 (*d*); 126.2 (*d*); 126.1 (*d*); 125.5 (*d*); 125.4 (*d*); 124.8 (*d*); 124.8 (*d*); 114.6 (*t*); 114.4 (*t*); 75.2 (*d*); 75.1 (*d*). EI-MS: 294 (56, $[M-18]^+$), 279 (29), 215 (21), 205 (40), 203 (63), 192 (43), 191 (29), 189 (17), 179 (44), 178 (100), 165 (20), 105 (20), 91 (17), 77 (18).

*(*E*)-3-(2′-Ethenyl-1,1′-biphenyl-2-yl)-1-phenyl[$^2H_1$]prop-2-en-1-ol* (**21′**). Prepared as described for **21** above, with $NaBD_4$ as reducing agent and prolonging the reaction time by stirring an additional 30 min at 25°. Yield: 93%. The ^{1}H-NMR spectrum (400 MHz) showed alterations at: 6.22 (*d*, *J* = 15.8, 1 H); 6.21 (*d*, *J* = 15.8, 1 H); no signal at 5.14; 1.90 (br. *s*, 1 H); 1.88 (br. *s*, 1 H).

*Methyl (*E*)-3-(2′-Ethenyl-1,1′-biphenyl-2-yl)prop-2-enoate* (**22**). A soln. of 931 mg (4.47 mmol) of **19** in 20 ml of THF was added at 25° to a soln. of 652 mg (5.81 mmol) of *t*-BuOK and 0.97 ml (6.71 mmol) of trimethyl phosphonoacetate (*Fluka*, *purum*) in 30 ml of THF. The resulting colorless mixture was stirred under Ar at 25° for 30 min. Then, the mixture was poured onto ice and worked up with Et_2O. Purification by chromatography (silica gel; pentane/Et_2O 9 : 1) furnished 1063 mg (90%) of **22**. Colorless oil. IR ($CHCl_3$): 3065*w*, 2955*w*, 1712*s*, 1706*s*, 1633*m*, 1600*w*, 1490*w*, 1470*m*, 1438*m*, 1319*s*, 1287*m*, 1175*s*, 1039*w*, 1004*w*, 987*m*, 917*m*, 863*w*. ^{1}H-NMR (400 MHz, $CDCl_3$): 7.72 – 7.69 (*m*, 1 H); 7.68 – 7.65 (*m*, 1 H); 7.44 – 7.36 (*m*, 3 H); 7.42 (*d*, *J* = 16.0, 1 H); 7.31 (*td*, *J* = 7.5, 1.4, 1 H); 7.24 – 7.22 (*m*, 1 H); 7.13 (*ddd*, *J* = 7.5, 1.5, 0.5, 1 H); 6.36 (*dd*, *J* = 17.5, 11.0, 1 H); 6.31 (*d*, *J* = 16.0, 1 H); 5.64 (*dd*, *J* = 17.5, 1.2, 1 H); 5.09 (*dd*, *J* = 11.0, 1.2, 1 H); 3.69 (*s*, 3 H). ^{13}C-NMR (100 MHz, $CDCl_3$): 167.2 (*s*); 143.2 (*d*); 141.8 (*s*); 138.5 (*s*); 136.4 (*s*); 134.9 (*d*); 133.3 (*s*); 131.2 (*d*); 130.5 (*d*); 129.6 (*d*); 128.1 (*d*); 127.8 (*d*); 127.5 (*d*); 126.3 (*d*); 125.3 (*d*); 118.7 (*d*); 115.2 (*t*); 51.6 (*q*). EI-MS: 264 (11, M^+), 232 (13), 231 (26), 205 (62), 204 (66), 203 (89), 202 (47), 189 (21), 178 (100), 165 (12).

*(*E*)-3-(2′-Ethenyl-1,1′-biphenyl-2-yl)prop-2-en-1-ol* (**23**). To a soln. of 399 mg (1.51 mmol) of **22** in 20 ml of THF under Ar at −70° were added 3.8 ml (2.5 equiv.) of a 1M soln. of DIBAH in hexane (*Fluka*, *purum*). After stirring for 60 min at −70°, the mixture was warmed up and quenched with 2M aq. NaOH soln. Workup with Et_2O and chromatography (silica gel; pentane/AcOEt 2 : 1) furnished 346 mg (97%) of **23**. Colorless oil. IR ($CHCl_3$): 3605*m*, 3435*w* (br.), 3090*w*, 3060*m*, 2930*w*, 2875*w*, 1958*w*, 1928*w*, 1826*w*, 1732*w*, 1629*w*, 1599*w*, 1490*w*, 1471*m*, 1445*m*, 1415*m*, 1380*m*, 1100*m*, 1081*m*, 1048*w*, 1004*s*, 993*s*, 968*s*, 948*m*, 912*s*, 651*w*, 621*w*, 613*w*. ^{1}H-NMR (400 MHz, $CDCl_3$): 7.67 – 7.61 (*m*, 2 H); 7.37 – 7.26 (*m*, 4 H); 7.16 – 7.13 (*m*, 2 H); 6.39 (*dd*, *J* = 17.5, 11.0, 1 H); 6.29 (*d*, *J* = 15.9, 1 H); 6.23 (*dd*, *J* = 15.9, 5.0, 1 H); 5.64 (*dd*, *J* = 17.5, 1.3, 1 H); 5.08 (*dd*, *J* = 11.0, 1.3, 1 H); 4.10 (*d*, *J* = 4.4, 2 H); 1.41 (br. *s*, 1 H). ^{13}C-NMR (100 MHz, $CDCl_3$): 139.7 (*s*); 139.6 (*s*); 136.1 (*s*); 135.3 (*d*); 135.2

(*s*); 130.6 (*d*); 130.5 (*d*); 129.7 (*d*); 129.5 (*d*); 127.7 (*d*); 127.7 (*d*); 127.4 (*d*); 127.3 (*d*); 125.3 (*d*); 124.8 (*d*); 114.5 (*t*); 63.8 (*t*). EI-MS: 236 (3, M^+), 218 (57), 217 (45), 205 (37), 203 (67), 202 (51), 192 (28), 191 (35), 189 (28), 179 (60), 178 (100), 165 (29), 101 (15).

*(*E*)-3-(2′-Ethenyl-1,1′-biphenyl-2-yl)prop-2-enal* (**24**). A soln. of 783 mg (3.31 mmol) of **23** in 17 ml of CH_2Cl_2 was added slowly to a suspension of 3.5 g (5 equiv.) of PCC (*Fluka*, *purum*) and of 1.7 g (6 equiv.) of NaOAc in 17 ml of CH_2Cl_2. After stirring for 1 h at 0°, 340 ml of Et_2O/pentane 1:1 were added, and the resulting mixture was filtered through *Celite*. Chromatography (silica gel; pentane/Et_2O 9:1) furnished 543 mg (70%) of **24**. Colorless oil. ^{1}H-NMR (400 MHz, $CDCl_3$): 9.42 (*d*, *J* = 7.7, 1 H); 7.77–7.74 (*m*, 1 H); 7.71–7.68 (*m*, 1 H); 7.50–7.40 (*m*, 3 H); 7.34 (*td*, *J* = 7.5, 1.4, 1 H); 7.30–7.27 (*m*, 1 H); 7.20 (*d*, *J* = 16.0, 1 H); 7.16 (*ddd*, *J* = 7.6, 1.5, 0.5, 1 H); 6.61 (*dd*, *J* = 16.0, 7.7, 1 H); 6.36 (*dd*, *J* = 17.5, 11.0, 1 H); 5.66 (*dd*, *J* = 17.5, 1.1, 1 H); 5.13 (*dd*, *J* = 11.0, 1.1, 1 H). ^{13}C-NMR (100MHz, $CDCl_3$): 194.0 (*d*); 151.0 (*d*); 142.1 (*s*); 138.1 (*s*); 136.4 (*s*); 134.6 (*d*); 132.7 (*s*); 131.2 (*d*); 130.6 (*d*); 130.5 (*d*); 129.2 (*d*); 128.3 (*d*); 128.1 (*d*); 127.6 (*d*); 126.4 (*d*); 125.2 (*d*); 115.5 (*t*).

*(*E*)-3-(2′-Ethenyl-1,1′-biphenyl-2-yl)but-3-en-2-ol* (**25**). To a soln. of 470 mg (2.01 mmol) of **24** in 10 ml of THF were added 1.5 ml of a 1.6M soln. of MeLi in Et_2O at 0° under Ar. After stirring for 5 min at 0°, the mixture was quenched with brine and worked up with Et_2O. Chromatography (silica gel; pentane/AcOEt 4:1) furnished 447 mg (89%) of **25** as a 1:1 mixture of two diastereoisomers. Colorless oil. IR ($CHCl_3$): 3605*w*, 3445*w* (br.), 3090*w*, 3060*w*, 2980*m*, 2925*w*, 2875*w*, 1628*w*, 1489*w*, 1471*m*, 1445*m*, 1413*w*, 1380*w*, 1365*w*, 1252*w*, 1247*w*, 1243*w*, 1238*w*, 1144*w*, 1077*w*, 1042*m*, 1023*w*, 1007*w*, 993*w*, 970*m*, 940*w*, 916*m*. ^{1}H-NMR (400 MHz): 7.67–7.59 (*m*, 4 H); 7.38–7.26 (*m*, 8 H); 7.17–7.13 (*m*, 4 H); 6.39 (*dd*, *J* = 17.5, 11.0, 1 H); 6.38 (*dd*, *J* = 17.5, 11.0, 1 H); 6.23 (br. *d*, *J* = 16.0, 1 H); 6.22 (br. *d*, *J* = 16.0, 1 H); 6.12 (*dd*, *J* = 15.9, 6.5, 1 H); 6.11 (*dd*, *J* = 15.9, 6.5, 1 H); 5.65 (*dd*, *J* = 17.5, 1.2, 1 H); 5.64 (*dd*, *J* = 17.5, 1.2, 1 H); 5.09 (*dd*, *J* = 11.0, 1.2, 1 H); 5.08 (*dd*, *J* = 11.0, 1.2, 1 H); 4.26 (br. *dq*, *J* = 6.3, 6.3, 2 H); 1.42 (br. *s*, 2 H); 1.23 (*d*, *J* = 6.3, 1 H); 1.22 (*d*, *J* = 6.3, 1 H). ^{13}C-NMR (100 MHz): 139.7 (*s*); 139.7 (*s*); 139.6 (2*s*); 136.2 (2*s*); 135.4 (*d*); 135.3 (*d*); 135.4 (*s*); 135.3 (*s*); 134.7 (*d*); 134.6 (*d*); 130.6 (2*d*); 130.5 (*d*); 130.5 (*d*); 128.0 (*d*); 127.9 (*d*); 127.7 (2*d*); 127.6 (*d*); 127.6 (*d*); 127.4 (2*d*); 127.2 (2*d*); 125.3 (*d*); 125.2 (*d*); 124.8 (*d*); 124.8 (*d*); 114.4 (*t*); 114.4 (*t*); 69.1 (*d*); 69.0 (*d*); 23.2 (*q*); 23.1 (*q*). EI-MS: 250 (0.07, M^+), 248 (0.9), 232 (25), 217 (33), 215 (30), 203 (34), 202 (39), 191 (100), 178 (58), 165 (22).

*2-[(9*RS*,10*RS*)-9,10-Dihydro-10-methylphenanthren-9-yl)-1-phenylethanone* (**26**). *General Procedure:* 117 mg (375 μmol) of **21** in 10 ml of benzene, 19 h at *ca.* 210°. Chromatography (silica gel; pentane/Et_2O 9:1) furnished 86 mg (74%) of **26** (92% de). Colorless crystals. M.p. 108–110° (cyclohexane). IR ($CHCl_3$): 3075*m*, 2970*m*, 2930*w*, 2900*w*, 2875*w*, 1688*s*, 1682*s*, 1600*m*, 1582*w*, 1486*m*, 1451*s*, 1444*m*, 1407*w*, 1375*w*, 1362*m*, 1320*w*, 1283*w*, 1264*m*, 1182*w*, 1160*w*, 1081*w*, 1048*w*, 1003*w*, 978*w*, 909*s*, 692*m*, 621*w*. ^{1}H-NMR (400 MHz): 7.82–7.73 (*m*, 4 H); 7.50–7.45 (*m*, 1 H); 7.36–7.28 (*m*, 5 H); 7.26–7.20 (*m*, 2 H); 7.15–7.13 (*m*, 1 H); 3.55 (*ddd*, *J* = 8.3, 5.7, 1.6, 1 H); 3.07 (*dd*, *J* = 16.9, 8.3, 1 H); 3.01 (*qd*, *J* = 7.1, 1.6, 1 H); 2.95 (*dd*, *J* = 16.9, 5.7, 1 H); 1.11 (*d*, *J* = 7.1, 3 H). ^{13}C-NMR (100 MHz): 199.3 (*s*); 140.1 (*s*); 138.0 (*s*); 137.2 (*s*); 133.0 (*d*); 132.7 (*s*); 132.3 (*s*); 129.8 (*d*); 129.3 (*d*); 128.4 (*d*); 128.1 (*d*); 128.0 (*d*); 128.0 (*d*); 127.4 (*d*); 127.2 (*d*); 123.8 (*d*); 123.7 (*d*); 43.5 (*t*); 41.4 (*d*); 38.7 (*d*); 21.5 (*q*). EI-MS: 312 (0.03, M^+), 310 (0.05), 192 (100), 178 (10).

*2-[(9*RS*,10*RS*)-9,10-Dihydro-10-([*$^2H_1$*]methyl)phenanthren-9-yl]-1-phenylethanone* (**26′**). As described above, with **21′** as starting material, 21 h at 240°. Yield: 31% (89% de). ^{1}H-NMR (400 MHz): aliphatic region: 3.55 (*ddd*, *J* = 8.3, 5.7, 1.6, 1 H); 3.06 (*dd*, *J* = 16.9, 8.3, 1 H); 3.00 (br. *t*, *J* = 7.1, 1 H); 2.94 (*dd*, *J* = 16.9, 5.7, 1 H); 1.09 (*dm*, *J* = 6.9, 3 H). ^{13}C-NMR (100 MHz): aliphatic region: 43.5 (*t*); 41.4 (*d*); 21.4 (*t*, $^2J(^2H,^{13}C) = 19.4$). EI-MS: 193 (100, $[M-120]^+$), 178 (16), 105 (11), 86 (11), 84 (18).

*(9*RS*,10*RS*)-(10-Methyl-9,10-dihydrophenanthren-9-yl)acetaldehyde* (**27**). According to *General Procedure*, starting material **23**, 30 h, *ca.* 250°. Yield: 71%, 84% de. Colorless oil. IR ($CHCl_3$): 3065*m*, 2965*m*, 2925*m*, 2895*m*, 2870*m*, 2825*w*, 2725*w*, 1721*s*, 1485*m*, 1452*m*, 1441*m*, 1402*w*, 1388*w*, 1374*w*, 1360*w*, 1348*w*, 1080*w*, 1048*w*, 1009*w*, 945*w*, 913*w*, 619*w*. ^{1}H-NMR (400 MHz): 9.67 (*t*, *J* = 1.6, 1 H); 7.78–7.75 (*m*, 2 H); 7.34–7.23 (*m*, 5 H); 7.19–7.16 (*m*, 1 H); 3.36 (*td*, *J* = 7.1, 1.6, 1 H); 2.92 (*qd*, *J* = 7.1, 1.6, 1 H); 2.54 (*ddd*, *J* = 17.3, 7.5, 1.8, 1 H); 2.46 (*ddd*, *J* = 17.3, 6.8, 1.5, 1 H); 1.09 (*d*, *J* = 7.1, 3 H). ^{13}C-NMR (100 MHz): 201.5 (*d*); 139.6 (*s*); 137.0 (*s*); 132.7 (*s*); 132.2 (*s*); 129.7 (*d*); 129.1 (*d*); 128.2 (*d*); 128.0 (*d*); 127.6 (*d*); 127.3 (*d*); 124.0 (*d*); 123.9 (*d*); 49.0 (*t*); 40.0 (*d*); 39.0 (*d*); 21.2 (*q*). EI-MS: 236 (5, M^+), 193 (32), 192 (100), 178 (35), 28 (91).

*[(9*RS*,10*RS*)-9,10-Dihydro-10-methylphenanthren-9-yl]propan-2-one* (**28**). According to *General Procedure*, starting material **25**, 27 h, *ca.* 250°. Yield: 62%, 92% de. Colorless oil. IR ($CHCl_3$): 3070*m*, 2965*m*, 2925*m*, 2875*m*, 1714*s*, 1485*m*, 1451*m*, 1441*m*, 1403*w*, 1373*m*, 1361*m*, 1315*w*, 1255*w*, 1160*m*, 1080*w*, 1048*w*, 1009*w*, 909*m*, 620*w*. ^{1}H-NMR (400 MHz): 7.78–7.74 (*m*, 2 H); 7.33–7.15 (*m*, 6 H); 3.34 (*ddd*, *J* = 7.7, 6.5, 1.6, 1 H); 2.89 (*qd*, *J* = 7.1, 1.6, 1 H); 2.51 (*dd*, *J* = 17.0, 7.7, 1 H); 2.43 (*ddm*, *J* = 17.0, 6.5, 1 H); 1.93 (*s*, 3 H); 1.06 (*d*, *J* = 7.1, 3 H). ^{13}C-NMR (100 MHz): 207.8 (*s*); 140.1 (*s*); 137.7 (*s*); 132.5 (*s*); 132.3 (*s*); 129.7 (*d*); 129.0 (*d*); 128.0 (*d*);

127.9 (*d*); 127.3 (*d*); 127.1 (*d*); 123.8 (*d*); 123.8 (*d*); 48.6 (*t*); 40.9 (*d*); 38.8 (*d*); 30.9 (*q*); 21.3 (*q*). EI-MS: 250 (0.4, M^+), 193 (29), 192 (100), 191 (22), 178 (27), 165 (12).

3-(2-Ethenylphenyl)propan-1-ol (**30**). A suspension of 6.34 g (34.7 mmol) of 2-bromostyrene [15], 5.9 ml (65.8 mmol) of methyl acrylate (*Fluka*, *purum*), 3.3 g (13.9 mmol) of $NiCl_2 \cdot 6H_2O$, 20.8 g (318 mmol) of Zn powder, and 7.8 ml (97.0 mmol) of pyridine in 100 ml of THF under Ar was refluxed for 21 h. The mixture was cooled to 25°, filtered through *Celite* and worked up with Et_2O/2M HCl. To the dried Et_2O phase ($MgSO_4$) were added 2.9 g (76.3 mmol) of $LiAlH_4$ at 0°. After stirring for 1 h, the mixture was poured onto ice and worked up with Et_2O. Chromatography (silica gel; pentane/AcOEt 2:1) furnished 3.43 g (61%) of **30**. Colorless oil. IR ($CHCl_3$): 3625*w*, 3460*w*, 2940*m*, 2875*w*, 1627*w*, 1485*w*, 1450*w*, 1057*w*, 1053*w*, 1021*w*, 990*w*, 917*m*. ^{1}H-NMR (400 MHz): 7.50–7.48 (*m*, 1 H); 7.21–7.15 (*m*, 3 H); 7.01 (*dd*, *J* = 17.4, 11.0, 1 H); 5.65 (*dd*, *J* = 17.4, 1.4, 1 H); 5.30 (*dd*, *J* = 11.0, 1.4, 1 H); 3.68 (*t*, *J* = 6.3, 2 H); 2.80–2.76 (*m*, 2 H); 1.88–1.81 (*m*, 2 H); 1.41 (br. *s*, 1 H). ^{13}C-NMR (100 MHz): 139.2 (*s*); 136.5 (*s*); 134.6 (*d*); 129.5 (*d*); 127.8 (*d*); 126.4 (*d*); 125.9 (*d*); 115.6 (*t*); 62.3 (*t*); 33.8 (*t*); 29.4 (*t*). EI-MS: 162 (11, M^+), 144 (40), 131 (32), 129 (100), 128 (30), 118 (47), 117 (63), 116 (29), 115 (63), 105 (12), 91 (32).

3-(2-Ethenylphenyl)propionaldehyde (**31**). To a soln. of 1.71 ml (19.9 mmol) of oxalyl chloride (*Fluka*, *purum*) in 34 ml of CH_2Cl_2 under Ar at −78° was added a soln. of 3.10 ml (43.2 mmol) of DMSO in 7.5 ml of CH_2Cl_2, and stirring was continued for 30 min. After adding a soln. of 2.70 g (16.6 mmol) of **30** in 7.5 ml of CH_2Cl_2 at −78°, stirring was continued for 30 min. Then, 11.6 ml (83.0 mmol) of Et_3N, and the turbid mixture was warmed to 25°. Workup with H_2O/CH_2Cl_2 and chromatography (silica gel; pentane/Et_2O 4:1) furnished 2.66 g (99%) of **31**. Colorless oil. IR ($CHCl_3$): 3090*w*, 3065*w*, 2950*w*, 2890*w*, 2825*m*, 2725*w*, 1723*s*, 1627*w*, 1486*m*, 1451*w*, 1410*m*, 1388*w*, 1356*w*, 1102*w*, 1062*w*, 1022*w*, 988*m*, 919*m*. ^{1}H-NMR (400 MHz): 9.81 (*t*, *J* = 1.3, 1 H); 7.50–7.46 (*m*, 1 H); 7.23–7.14 (*m*, 3 H); 6.94 (*dd*, *J* = 17.3, 11.2, 1 H); 5.65 (*dd*, *J* = 17.3, 1.4, 1 H); 5.33 (*dd*, *J* = 11.2, 1.4, 1 H); 3.03–2.99 (*m*, 2 H); 2.74–2.72 (*m*, 2 H). ^{13}C-NMR (100 MHz): 201.3 (*d*); 137.6 (*s*); 136.6 (*s*); 134.2 (*d*); 129.3 (*d*); 128.0 (*d*); 126.8 (*d*); 126.2 (*d*); 116.3 (*t*); 44.8 (*t*); 25.6 (*t*). EI-MS: 160 (23, M^+), 145 (13), 142 (44), 141 (45), 131 (30), 129 (44), 128 (37), 127 (26), 118 (89), 117 (88), 116 (39), 115 (100), 104 (19), 91 (52), 77 (18).

*Methyl (*E*)-5-(2-Ethenylphenyl)pent-2-enoate* (**32**). To a soln. of 2.96 g (18.5 mmol) of **31** in 50 ml of THF under Ar at −78° were added 2.60 ml (20.3 mmol) of tetramethylguanidine (*Fluka*, *puriss.*) and 2.85 ml (19.7 mmol) of trimethyl phosphonoacetate (*Fluka*, *purum*), then the mixture was allowed to reach 25° and stirring was continued for 18 h. Workup with brine followed by chromatography (silica gel; pentane/Et_2O 9:1) furnished 3.68 g (92%) of **32** as a colorless oil. IR ($CHCl_3$): 2955*w*, 1719*s*, 1660*m*, 1628*w*, 1485*w*, 1451*w*, 1439*m*, 1342*w*, 1321*m*, 1282*m*, 1154*w*, 1042*w*, 1016*w*, 989*w*, 919*w*. ^{1}H-NMR (400 MHz): 7.50–7.46 (*m*, 1 H); 7.22–7.18 (*m*, 2 H); 7.14–7.10 (*m*, 1 H); 7.01 (*dt*, *J* = 15.6, 6.9, 1 H); 6.94 (*dd*, *J* = 17.3, 11.0, 1 H); 5.85 (*dt*, *J* = 15.6, 1.6, 1 H); 5.65 (*dd*, *J* = 17.3, 1.4, 1 H); 5.31 (*dd*, *J* = 11.0, 1.4, 1 H); 3.72 (*s*, 3 H); 2.85–2.81 (*m*, 2 H); 2.49–2.43 (*m*, 2 H). ^{13}C-NMR (100 MHz): 167.0 (*s*); 148.3 (*d*); 138.1 (*s*); 136.5 (*s*); 134.3 (*d*); 129.3 (*d*); 127.9 (*d*); 126.7 (*d*); 126.0 (*d*); 121.4 (*d*); 116.0 (*t*); 51.4 (*q*); 33.4 (*t*); 31.8 (*t*). EI-MS: 216 (3, M^+), 157 (41), 130 (14), 129 (14), 117 (100), 115 (55), 91 (20).

*(*E*)-5-(2-Ethenylphenyl)pent-2-en-1-ol* (**33**). To a soln. of 3.46 g (16 mmol) of **32** in 150 ml of THF under Ar at −78° were added 40 ml (2.5 equiv.) of a 1M soln. of DIBAH in hexane (*Fluka*, *purum*). After stirring for 40 min at −78°, the mixture was allowed to reach 25° and was worked up with Et_2O. Chromatography (silica gel; pentane/AcOEt 2:1) furnished 2.97 g (99%) of **33**. Colorless oil. IR ($CHCl_3$): 3615*m*, 3450*w*, 3095*w*, 3060*m*, 2940*w*, 2875*m*, 1670*w*, 1628*w*, 1603*w*, 1485*m*, 1462*w*, 1451*w*, 1416*w*, 1385*w*, 1085*m*, 988*s*, 970*s*, 917*m*. ^{1}H-NMR (400 MHz): 7.50–7.46 (*m*, 1 H); 7.22–7.17 (*m*, 2 H); 7.15–7.11 (*m*, 1 H); 6.97 (*dd*, *J* = 17.4, 11.0, 1 H); 5.78–5.62 (*m*, 2 H); 5.64 (*dd*, *J* = 17.4, 1.4, 1 H); 5.29 (*dd*, *J* = 11.0, 1.4, 1 H); 4.09–4.07 (*m*, 2 H); 2.78–2.74 (*m*, 2 H); 2.34–2.28 (*m*, 2 H); 1.43 (*s*, 1 H). ^{13}C-NMR (100 MHz): 139.0 (*s*); 136.4 (*s*); 134.6 (*d*); 132.2 (*d*); 129.6 (*d*); 129.5 (*d*); 127.8 (*d*); 126.4 (*d*); 125.8 (*d*); 115.5 (*t*); 63.6 (*t*); 33.5 (*t*); 32.9 (*t*). EI-MS: 188 (0.3, M^+), 170 (12), 157 (19), 155 (17), 141 (17), 129 (66), 128 (29), 117 (100), 115 (15), 91 (19), 28 (27).

*(*E*)-5-(2-Ethenylphenyl)pent-2-enal* (**34**). A soln. of 927 mg (4.92 mmol) of **33** in 25 ml of CH_2Cl_2 was added to a suspension of 5.7 g (5 equiv.) of PCC (*Fluka*, *purum*) and of 2.6 g (6 equiv.) of AcONa in 25 ml of CH_2Cl_2 at 0°, and the resulting mixture was stirred for 15 min at 0°. After addition of 500 ml of Et_2O/pentane 1:1, the mixture was filtered through *Celite*, the solvent was evaporated, and the resulting residue was chromatographed (silica gel; pentane/AcOEt 4:1) to give 706 mg (77%) of **34**. Colorless oil. ^{1}H-NMR (400 MHz): 9.50 (*d*, *J* = 7.9, 1 H); 7.51–7.49 (*m*, 1 H); 7.25–7.20 (*m*, 2 H); 7.16–7.11 (*m*, 1 H); 6.95 (*dd*, *J* = 17.3, 11.0, 1 H); 6.86 (*dt*, *J* = 15.6, 6.7, 1 H); 6.14 (*ddt*, *J* = 15.6, 7.9, 1.5, 1 H); 5.66 (*dd*, *J* = 17.3, 1.4, 1 H); 5.33 (*dd*, *J* = 11.0, 1.4, 1 H); 2.91–2.87 (*m*, 2 H); 2.64–2.58 (*m*, 2 H). ^{13}C-NMR (100 MHz): 193.9 (*d*); 157.2 (*d*); 137.6 (*s*); 136.6 (*s*); 134.2 (*d*); 133.3 (*d*); 129.4 (*d*); 128.0 (*d*); 126.9 (*d*); 126.2 (*d*); 116.3 (*t*); 33.8 (*t*); 31.5 (*t*).

*(*E*)-5-(2-Ethenylphenyl)-1-phenylpent-2-en-1-ol* (**35**). The *Grignard* reagent, prepared from 0.50 ml (4.7 mmol) of PhBr and 0.14 g (5.6 mmol) of Mg turnings in 3 ml of THF, was transferred *via* canula to a soln. of 695 mg (3.73 mmol) of **34** in 10 ml of THF. After 5 min, the mixture was worked up with brine and Et_2O, and chromatographed (silica gel; pentane/Et_2O 4 : 1) to 819 mg (83%) of **35**. Colorless oil. IR ($CHCl_3$): 3605*m*, 3430*w* (br.), 3085*w*, 3065*m*, 3005*m*, 2940*w*, 2870*w*, 1667*w*, 1628*w*, 1603*w*, 1494*m*, 1486*m*, 1451*m*, 1373*w*, 1070*w*, 991*m*, 972*m*, 918*m*. ^{1}H-NMR (400 MHz): 7.50–7.46 (*m*, 1 H); 7.36–7.25 (*m*, 5 H); 7.21–7.15 (*m*, 2 H); 7.13–7.09 (*m*, 1 H); 6.96 (*dd*, *J* = 17.4, 11.0, 1 H); 5.79 (*dtd*, *J* = 15.3, 6.5, 0.8, 1 H); 5.67 (*ddt*, *J* = 15.3, 6.6, 1.2, 1 H); 5.63 (*dd*, *J* = 17.4, 1.4, 1 H); 5.28 (*dd*, *J* = 11.0, 1.4, 1 H); 5.15 (br. *d*, *J* = 6.3, 1 H); 2.79–2.75 (*m*, 2 H); 2.34–2.30 (*m*, 2 H); 1.85 (br. *d*, *J* = 2.7, 1 H). ^{13}C-NMR (100 MHz): 143.2 (*s*); 139.0 (*s*); 136.5 (*s*); 134.6 (*d*); 133.0 (*d*); 131.5 (*d*); 129.6 (*d*); 128.5 (*d*); 127.8 (*d*); 127.5 (*d*); 126.4 (*d*); 126.2 (*d*); 125.8 (*d*); 115.5 (*t*); 75.1 (*d*); 33.5 (*t*); 32.8 (*t*). MS: 264 (0.4, M^+), 246 (22), 168 (21), 155 (45), 142 (47), 129 (100), 128 (48), 117 (31), 116 (34), 115 (50), 105 (15), 91 (23), 77 (14).

*2-[(1*RS*,2*RS*)-1-Methyl-1,2,3,4-tetrahydronaphthalen-2-yl]acetaldehyde* (**36**). According to the *General Procedure*, starting material, **33**. 28 h, *ca.* 250°. Yield: 81%, 78% de. Colorless oil. IR ($CHCl_3$): 2965*m*, 2935*m*, 2875*m*, 2840*w*, 2725*w*, 1723*s*, 1491*m*, 1467*w*, 1448*w*, 1377*w*, 1039*w*. ^{1}H-NMR (400 MHz): 9.84 (*t*, *J* = 2.0, 1 H); 7.15–7.06 (*m*, 4 H); 2.98–2.92 (*m*, 1 H); 2.88–2.84 (*m*, 2 H); 2.56–2.38 (*m*, 3 H); 1.75–1.69 (*m*, 2 H); 1.15 (*d*, *J* = 7.2, 3 H). ^{13}C-NMR (100 MHz): 202.3 (*d*); 142.1 (*s*); 135.4 (*s*); 129.0 (*d*); 129.0 (*d*); 125.9 (*d*); 125.7 (*d*); 47.4 (*t*); 36.3 (*d*); 32.4 (*d*); 28.7 (*t*); 23.8 (*t*); 17.9 (*q*). EI-MS: 188 (11, M^+), 155 (12), 144 (100), 129 (65), 118 (26), 117 (28), 91 (10).

*1-Phenyl-2-[(1*RS*,2*SR*)-1,2,3,4-tetrahydro-1-methylnaphthalen-2-yl]ethanone* (**37**). According to the *General Procedure*, starting material, **35**, 6 h, *ca.* 230°. Yield: 23%, 84% de. Colorless oil. IR ($CHCl_3$): 2965*m*, 2930*m*, 2875*w*, 1681*s*, 1600*m*, 1582*w*, 1490*m*, 1467*w*, 1449*s*, 1376*w*, 1279*m*, 1181*w*, 1038*w*, 1003*w*, 988*w*, 697*m*, 690*m*. ^{1}H-NMR (400 MHz): 8.00–7.96 (*m*, 2 H); 7.58–7.53 (*m*, 1 H); 7.48–7.44 (*m*, 2 H); 7.11–7.05 (*m*, 4 H); 3.07 (*dd*, *J* = 16.0, 6.1, 1 H); 3.06–2.99 (*m*, 1 H); 2.93 (*dd*, *J* = 16.0, 8.0, 1 H); 2.87–2.83 (*m*, 2 H); 2.63–2.55 (*m*, 1 H); 1.78–1.71 (*m*, 2 H); 1.19 (*d*, *J* = 7.2, 3 H). ^{13}C-NMR (100 MHz): 199.9 (*s*); 142.5 (*s*); 137.3 (*s*); 135.6 (*s*); 133.0 (*d*); 129.0 (*d*); 128.9 (*d*); 128.6 (*d*); 128.1 (*d*); 125.7 (*d*); 125.6 (*d*); 41.9 (*t*); 36.3 (*d*); 34.1 (*d*); 28.9 (*t*); 23.8 (*t*); 18.1 (*q*). EI-MS: 144 (100, $[M-120]^+$ (PhC(=O)Me)), 129 (36), 105 (23), 77 (18).

*(*E*)-1-Phenyl-3-[2-(prop-2-enyl)phenylprop-2-en-1-one* (**40**). To a soln. of 1.50 g (10.3 mmol) of **39** [15] and of 1.23 g (10.3 mmol) of acetophenone in 15 ml of EtOH was added 1 ml of 2M aq. NaOH soln. at 25°. After stirring for 17 h, the mixture was neutralized by addition of buffer soln. of pH 7 and 2M HCl. Workup with Et_2O and chromatography (silica gel; pentane/Et_2O 20 : 1) furnished 2.06 g (81%) of **40**. Clear-yellow oil. IR ($CHCl_3$): 3065*w*, 2930*w*, 2860*w*, 1663*s*, 1640*m*, 1608*s*, 1597*s*, 1580*m*, 1572*m*, 1482*m*, 1449*m*, 1332*s*, 1321*m*, 1309*m*, 1287*m*, 1181*m*, 1034*w*, 1018*s*, 994*w*, 978*m*, 920*m*, 697*m*, 662*w*. ^{1}H-NMR (400 MHz): 8.11 (*d*, *J* = 15.5, 1 H); 8.03–8.02 (*m*, 1 H); 8.01–8.00 (*m*, 1 H); 7.73 (*dd*, *J* = 7.7, 1.4, 1 H); 7.61–7.56 (*m*, 1 H); 7.53–7.48 (*m*, 2 H); 7.44 (*d*, *J* = 15.5, 1 H); 7.36 (*td*, *J* = 7.4, 1.4, 1 H); 7.31–7.24 (*m*, 2 H); 5.97 (*ddt*, *J* = 17.1, 10.1, 6.2, 1 H); 5.08 (*dq*, *J* = 10.1, 1.5, 1 H); 4.99 (*dq*, *J* = 17.1, 1.7, 1 H); 3.56 (*dt*, *J* = 6.2, 1.6, 1 H). ^{13}C-NMR (100 MHz): 190.6 (*s*); 142.4 (*d*); 140.0 (*s*); 138.2 (*s*); 136.6 (*d*); 133.9 (*s*); 132.8 (*d*); 130.5 (*d*); 130.4 (*d*); 128.6 (*d*); 128.6 (*d*); 126.9 (*d*); 126.7 (*d*); 123.6 (*d*); 116.5 (*t*); 37.5 (*t*). EI-MS: 248 (10, M^+), 207 (74), 143 (26), 128 (71), 115 (17), 105 (100), 77 (40).

*(*E*)-1-Phenyl-3-[2-(prop-2-enyl)phenyl]prop-2-en-1-ol* (**41**). To a soln. of 1.32 g (5.30 mmol) of **40** in 10 ml of THF and 5 ml of MeOH were added 0.40 g (10.6 mmol) of $NaBH_4$ in small portions at −30°. The resulting mixture was kept at −30° for 17 h and was then allowed to reach 25° within 3 h. Workup with brine and Et_2O, followed by chromatography (silica gel; pentane/Et_2O 4 : 1) furnished 1.31 g (99%) of **41**, which solidified in the refrigerator. IR ($CHCl_3$): 3605*m*, 3430*w* (br.), 3065*m*, 2980*w*, 1638*w*, 1602*w*, 1494*m*, 1485*m*, 1454*m*, 1372*w*, 1068*m*, 1030*m*, 998*m*, 969*s*, 919*s*. ^{1}H-NMR (400 MHz): 7.46–7.27 (*m*, 6 H); 7.20–7.13 (*m*, 3 H); 6.91 (*dm*, *J* = 15.7, 1 H); 6.27 (*dd*, *J* = 15.7, 6.4, 1 H); 5.94 (*ddt*, *J* = 17.1, 10.1, 6.2, 1 H); 5.39 (br. *dd*, *J* = 6.3, 2.8, 1 H); 5.05 (*dq*, *J* = 10.1, 1.7, 1 H); 4.95 (*dq*, *J* = 17.1, 1.7, 1 H); 3.45 (*dt*, *J* = 6.2, 1.6, 2 H); 2.04 (br. *d*, *J* = 3.7, 1 H). ^{13}C-NMR (100 MHz): 142.8 (*s*); 137.3 (*s*); 136.8 (*d*); 135.6 (*s*); 133.2 (*d*); 129.8 (*d*); 128.6 (*d*); 128.2 (*d*); 127.9 (*d*); 127.8 (*d*); 126.6 (*d*); 126.4 (*d*); 126.2 (*d*); 115.9 (*t*); 75.2 (*d*); 37.6 (*t*). EI-MS: 250 (2, M^+), 232 (28), 141 (38), 130 (60), 129 (57), 128 (100), 115 (47), 105 (57), 91 (29), 77 (29).

*2-[(1*RS*,2*RS*)-2,3-Dihydro-2-methyl-1*H*-inden-1-yl]-1-phenylethanone* (**42**). According to the *General Procedure*, starting material, **41**, 27 h, *ca.* 250°. Yield: 35%, 92% de. Colorless oil. IR ($CHCl_3$): 3070*w*, 2960*m*, 2935*m*, 2875*w*, 2845*w*, 1720*w*, 1688*s*, 1600*m*, 1582*w*, 1532*w*, 1478*m*, 1450*s*, 1409*w*, 1377*w*, 1367*m*, 1341*w*, 1318*w*, 1284*m*, 1264*m*, 1181*w*, 1160*w*, 1118*w*, 1108*w*, 1018*w*, 1002*w*, 990*w*, 910*w*, 690*m*, 656*w*. ^{1}H-NMR (400 MHz): 7.99–7.96 (*m*, 2 H); 7.58–7.53 (*m*, 1 H); 7.48–7.43 (*m*, 2 H); 7.22–7.11 (*m*, 4 H); 3.87 (*q*, *J* = 7.1, 1 H); 3.27 (*dd*, *J* = 17.3, 7.8, 1 H); 3.19 (*dd*, *J* = 17.3, 6.6, 1 H); 3.06 (*dd*, *J* = 15.4, 7.2, 1 H); 2.86–2.76 (*m*, 1 H); 2.59 (*dd*, *J* = 15.4, 5.4, 1 H); 0.92 (*d*, *J* = 7.0, 3 H). ^{13}C-NMR (100 MHz): 199.6 (*s*); 146.0 (*s*); 143.1 (*s*); 137.3 (*s*); 133.0 (*d*); 128.6

(*d*); 128.1 (*d*); 126.6 (*d*); 126.2 (*d*); 124.7 (*d*); 124.0 (*d*); 43.4 (*d*); 39.7 (*t*); 38.6 (*t*); 37.1 (*d*); 15.7 (*q*). EI-MS: 250 (1, M^+), 130 (100), 129 (13), 115 (12), 105 (22), 77 (16).

X-Ray Crystal-Structure Determination of **26**. From a crystal of size $0.4 \times 0.4 \times 0.25$ mm, 2948 reflections were measured on an *Enraf Nonius CAD-4* Diffractometer with MoK_α radiation (graphite monochromator, $\lambda =$ 0.71069 Å). The structure was solved by the direct method SIR97 [19]. The non-H-atoms were refined anisotropically with SHELXL-97 [20]. The H-atoms were calculated at idealized positions and included in the structure-factor calculation with fixed isotropic displacement parameters. Crystallographic data have been deposited with the *Cambridge Crystallographic Data Centre* as supplementary publication No. CCDC 150153. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44-(0)1223-336033 or e-mail: deposit@ccdc.cam.ac.uk).

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Received September 29, 2000