The First Examples of Successful Anionic Oxy-Ene Reactions

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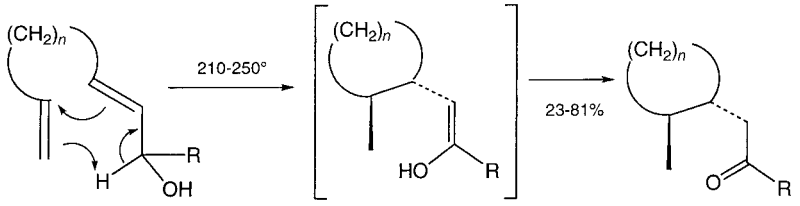
The first examples of successful anionic oxy-ene reactions are reported. The corresponding reactions **16** → **15** (Li^+ as counter ion) and **18** → **21** (K^+ as counter ion) proceeded with good yields and high diastereoselectivities. In the latter case, the reaction proceeds under very mild conditions (3 h reflux in toluene) in 65% yield with more than 96% d/s. However, when the phosphazene base P_4-(*t*-Bu) was allowed to interact with the same or similar substrates, entirely different products resulted at ambient temperature. In the case of **1**, the benzoyl-dibenzocyclooctene **4** was formed in 80% yield, while treatment of the closely related substrate **8** furnished the cyclobutanol derivative **11** with similar efficiency. In both cases, the unexpected product structures were established by means of X-ray crystallography.

1. Introduction. – We have recently demonstrated that certain allylic alcohols that contain a styrene unit within the same molecule undergo thermally induced oxy-ene reactions, which are remarkably diastereoselective [1]. As shown in *Scheme 1*, the required temperatures are in the range of 200 to 250°, and the yields of the products **C** vary, depending on the substitution pattern of the starting material. A favorable case at hand is the reaction **1** → **2** (*Scheme 2*) where no concurrent β-dehydration of the starting material is to be feared. A possible solution to avoid this side reaction that, in a more general situation, can become the dominant process would consist in reacting not the free alcohol, but the corresponding alkoxide. Therefore, the fate of our established model substrates under basic conditions was investigated.

Scheme 1

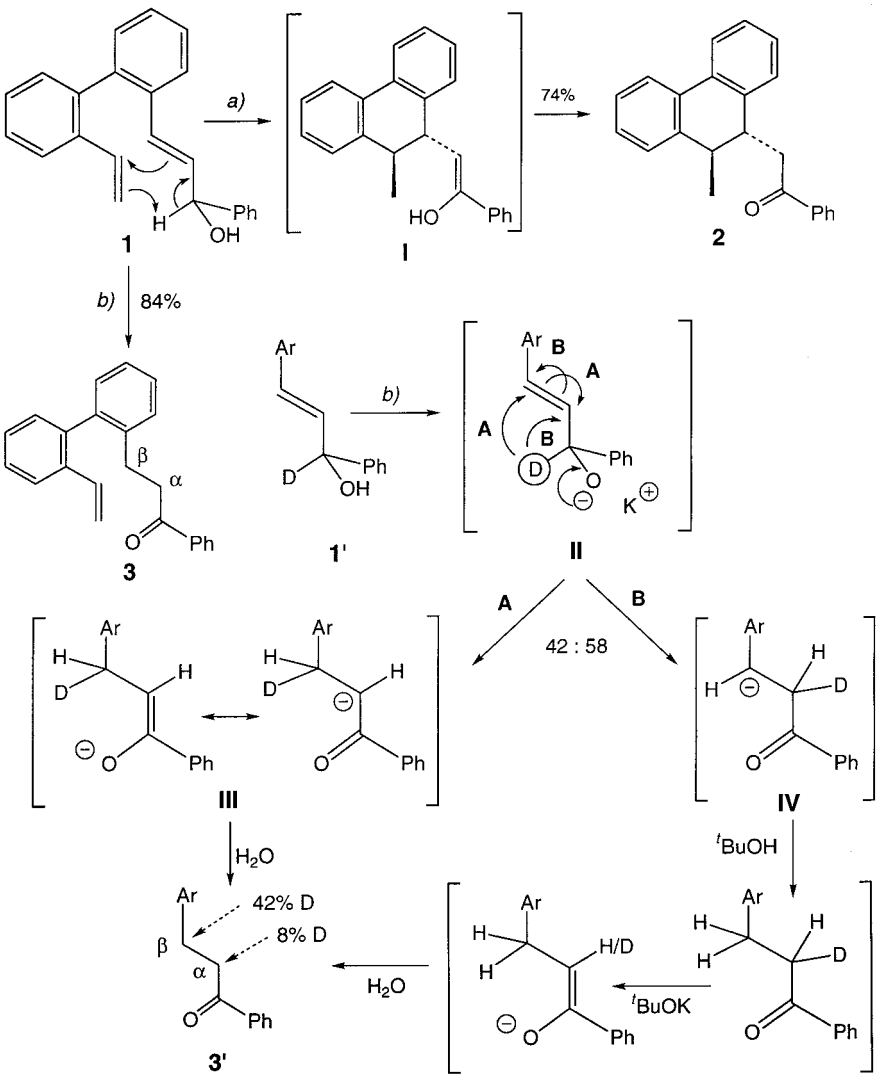


A R = H, Me, Ph **B** R = H, Me, Ph **C** R = H, Me, Ph

2. Results. – In keeping with the beneficial effect of employing potassium salts in the vaguely related oxy-*Cope* reaction [2], we first treated the readily available allylic alcohol **1** [1] with ^{t}BuOK in toluene. After 2 h at 25°, the starting material was

[1]) From the Ph.D. thesis of *G. S.*

Scheme 2



a) Benzene, 19 h, 210°. *b*) *t*BuOK, toluene, 2 h, 25°.

consumed completely; however, the product formed, isolated in 84% yield, was clearly not identical to the known oxy-ene product **2**. Spectroscopic evidence pointed to the constitutionally isomeric structure **3** for this product (*Scheme 2*). This type of isomerization process was discovered as early as 1906 by *Tiffeneau* [3], and analogous reactions were reported subsequently [4]. Some mechanistic studies of this base-promoted isomerization of allylic alcohols to saturated ketones are available, but these investigations involved quite different reaction conditions (fourfold excess of BuLi or other base combinations [5]). To obtain at least some information about this process

under our reaction conditions, the fate of the deuterated analogue **1′** [1] was investigated. An analysis of the deuterium content of the isolated **3′** showed that only 50% of the label was retained. According to the ^{1}H- and ^{13}C-NMR spectra, 84% of the remaining deuterium resided in the β-position and 16% in the position α to the C=O group of **3′**. The most simple, but not necessarily correct, interpretation of these findings could be that the alkoxide **II** undergoes two competing hydride shifts. Process *A* (1,3-shift occurring to the extent of 42%) leads to the enolate **III** with deuterium in the unexchangeable[2]) β-position. The concurring process *B* (1,2-D shift) furnishes homoenolate **IV** with the label in the α-position, from which it is removed to a large extent by subsequent acid-base exchange processes.

After this rather uneventful outcome, the effect of a strong, uncharged base on **1** was investigated next. While employment of 1,8-bis(dimethylamino)naphthalene ('proton sponge™') led to no reaction, the use of *Schwesinger*'s base P_4-(*t*-Bu) (*Scheme 3*) at ambient temperature rapidly led to a novel product in 80% yield. A control experiment showed that a similar treatment of **3** led to the same product in almost quantitative yield. The new compound is isomeric with the starting materials **1** and **3**, but has no olefinic C=C bonds. A strong IR band at 1680 cm^{-1} pointed to the presence of a benzoyl unit, which is also apparent in the mass spectrum (strong peaks at *m/z* 105 and at 207 ($[M-105]^+$) and in the NMR spectra (8.02 (*m*, 2 H): *ortho* to an aryl-bound C=O group, 203.7 (*s*) in the ^{13}C-NMR spectrum). According to the latter spectrum, the aliphatic section contains three CH_2 groups resonating between 35 and 31 ppm, and a methine unit (48.3 ppm), the H-atom of which can be exchanged with D by treatment with base in MeOD. The tentative benzoyl-dibenzocyclooctene structure **4** was confirmed by means of an X-ray single-crystal analysis of the corresponding 2,4-dinitrophenylhydrazone **5**[3]) (*Figs. 1* and *2*, and *Table 1*). An analogous treatment of the deuterated substrate **1′** furnished a 88:12 mixture of **4** and **4′**. That the label shows up exclusively at C(6) rules out any 1,3- or transannular hydride shift when P_4-(*t*-Bu) is used as base. We, therefore, tentatively propose the mechanism depicted in *Scheme 3* for the observed reaction.

Especially during experiments on a small scale, a persistent impurity in the ^{1}H-NMR spectra of crude **4** was noticed, the most characteristic feature being an isolated *AB* system centred at 3.58 and 3.32 ppm ($^2J = 11.2$ Hz). Eventually, this by-product could be isolated in pure state by chromatography of an enriched sample, pooled from several independent experiments. The spectroscopic properties clearly pointed to structure **6** (*Scheme 4*) for this product[4]), a known compound first prepared by *Cope* and *Smith* in 1956 [7]. It had obviously been formed through oxidation of the enolate **VII** by means of oxygen. A single-electron transfer from this enolate to $^3O_2$,

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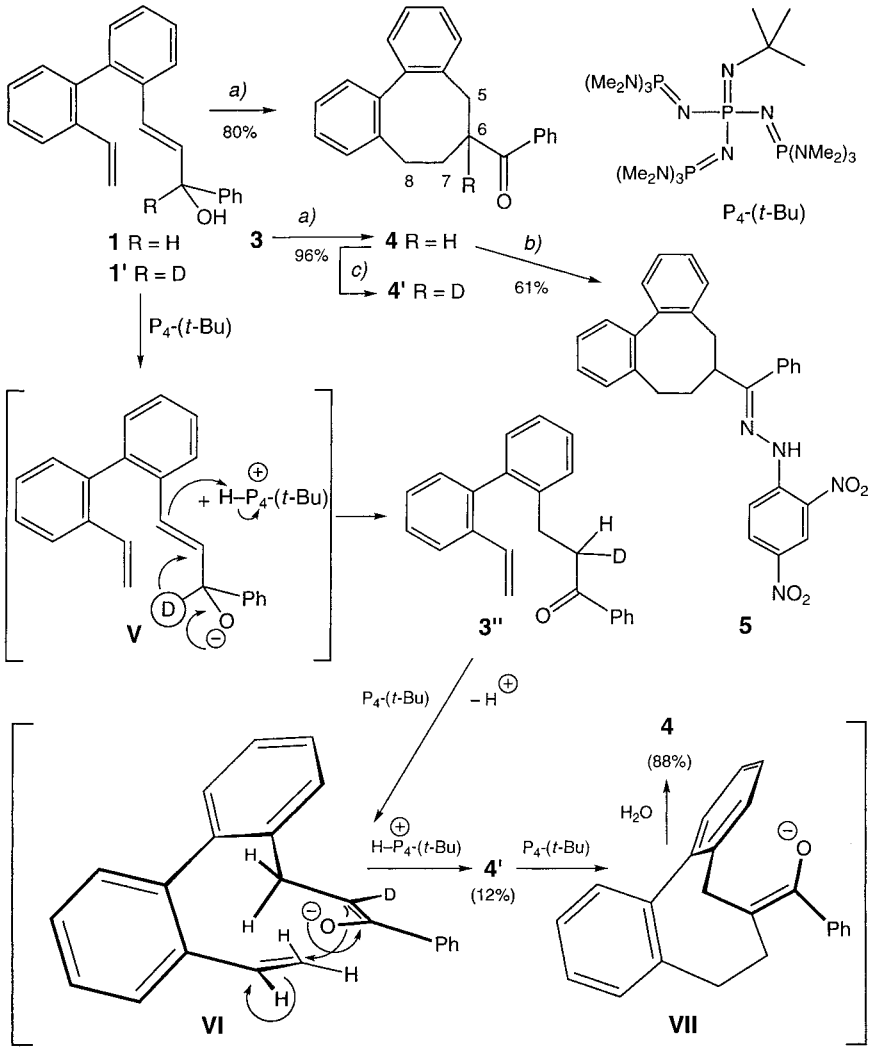
[2]) At least under the conditions employed (^{t}BuOK, toluene, 2 h, 25°). For the generation of homoenolates from saturated ketones, see [6].

[3]) We thank Dr. *B. Schweizer*, Laboratory for Organic Chemistry (ETH-Zürich), for the determination of the X-ray structures of compounds **5** and **13**.

[4]) Naively, one would expect the H-atoms of the isolated CH_2 group to be isochronous as they are enantiotopic in the planar conformation of **6**. Obviously, the ground state of **6** is represented by a chiral, non-planar conformation, which must be rather rigid since there is no sign of coalescence even at 80° in C_6D_6 (300 MHz). This finding points to a barrier of at least 17.5 kcal/mol between different conformers (and the two antipodal forms) of **6**.

Scheme 3



a) P_4-(*t*-Bu), toluene, 1 h, 25°. *b*) 2,4-Dinitrophenylhydrazine, EtOH, 2M HCl, 18 h, reflux. *c*) CH_3OD, ^{t}BuOK, 18 h, 25°.

followed by radical combination and ring-closure, would lead to the elusive spirocyclic 1,2-dioxetane **VIII**, which rapidly decays to **6** and benzoate (for a precedent, see [8]). Indeed, when **1** was treated with P_4-(*t*-Bu) in a flask deliberately exposed to air, ketone **6** became the virtually exclusive reaction product.

We next investigated the reactivity of **8** (*Scheme 5*), formally derived from **1** by an allylic rearrangement. This compound was readily available from the aldehyde **7** [1] and (*E*)-*β*-bromostyrene according to the methodology of *Neumann* and *Seebach* [9].

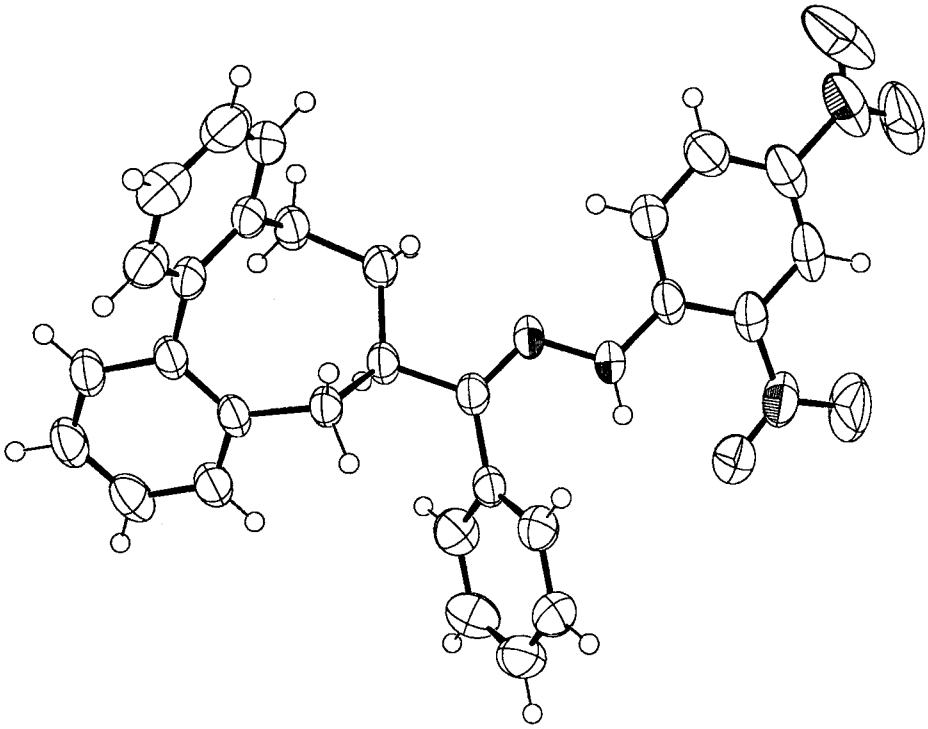


Fig. 1. *ORTEP View of* **5**. The thermal ellipsoids are scaled at the 30% level.

Whereas pyrolysis of **8** (20 h at 210°) furnished the rearranged oxy-ene product **2** in 33% yield [10], treatment with P_4-(*t*-Bu) gave a non-ketonic compound as a single diastereoisomer in 81% yield. Spectroscopic arguments based on HSQC-, H/H-COSY- and HMBC experiments pointed to the tertiary alcohols **11** or **12** as the only reasonable structural proposals for the new compound[5]). The size of the direct ^{1}H,^{13}C-coupling constants ($^1J = 136-141$ Hz for H–C(1) and CH_2(16)) rendered the cyclobuta-fused derivative **11** the more likely candidate, because the expected values for a cyclopenta-fused derivative would be expected to amount to less than 130 Hz. An unambiguous decision between the two possibilities in favor of the cyclobuta compound **11** could be reached by means of an X-ray single-crystal structure analysis of the derived *p*-nitrobenzoate **13**[3] (*Figs. 3* and *4*, and *Table 2*). The proposed mechanism for the formation of **11** is very similar to the one discussed above for the generation of **4** from **1** or **3**. The only major difference, besides the different constitution of the starting materials, is the conformation of the last intermediate on the way to **4** and **11**, respectively. In the former case, there is no significant interaction between the anionic benzylic site and the C=O group in the intermediate following **VII**, whereas, in the case of **XII**, these two reactive centers are perfectly aligned for an intramolecular collapse to give the observed cyclobuta-fused alcohol **11**.

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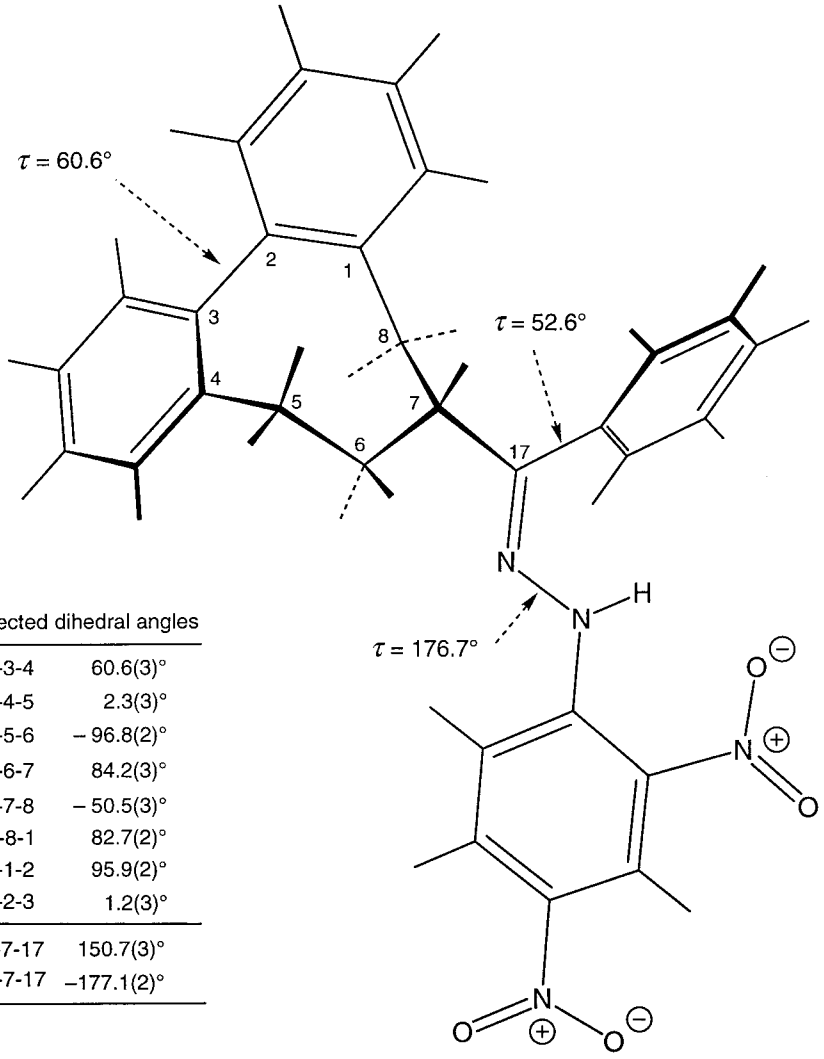
[5]) The authors would like to thank Prof. *B. Jaun*, Laboratory for Organic Chemistry, ETH-Zürich, for helpful discussions and suggestions concerning this and related structural problems.



Selected dihedral angles

1-2-3-4	60.6(3)°
2-3-4-5	2.3(3)°
3-4-5-6	– 96.8(2)°
4-5-6-7	84.2(3)°
5-6-7-8	– 50.5(3)°
6-7-8-1	82.7(2)°
7-8-1-2	95.9(2)°
8-1-2-3	1.2(3)°
1-8-7-17	150.7(3)°
5-6-7-17	–177.1(2)°

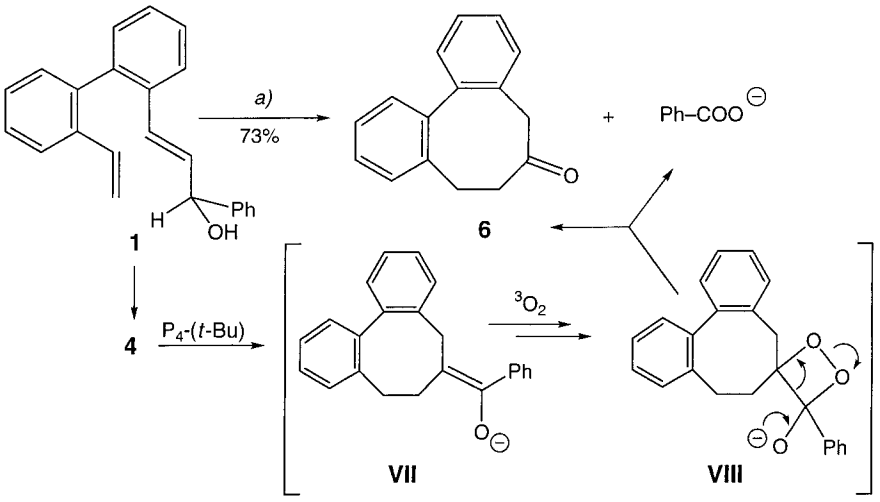
Fig. 2. *View of* **5** *based on its crystal structure.* Unlabelled substituents represent H-atoms; arbitrary numbering.

We then turned our attention towards the conformationally more flexible model system **14** (*Scheme 6*), which gave a rather poor result in the purely thermal oxy-ene reaction (23% yield of **15**) [1]. While treatment of **14** with either ^{t}BuOK or P_4-(*t*-Bu) led to an isomerization yielding only **17**, heating the corresponding Li^+ salt for 6 h at 200° gave **15** in 79% yield. To the best of our knowledge, this outcome represents the first case of a successful anionic oxy-ene process. Application of similar conditions to substrate **1** furnished the known cyclization compound **2** in 65% yield. Not surprisingly, the corresponding Na^+ salt behaved like its K^+ analogue in yielding the H-shift product **3** at 150°.

Table 1. *Crystallographic Data of* rac-**5**

Empirical formula	$C_{29}H_{24}N_4O_4$	
Formula weight	492.52	
Temp.	293(2) K	
Wavelength	1.54184 Å	
Crystal system	Triclinic	
Space group	*P*-1	
Unit cell dimensions	$a = 7.8760(1)$ Å	$\alpha = 80.06(2)^\circ$
	$b = 10.810(3)$ Å	$\beta = 74.92(2)^\circ$
	$c = 14.931(4)$ Å	$\gamma = 87.31(2)^\circ$
V	1209.0(5) Å^3	
Z	2	
Density (calc.)	1.353 Mg/m^3	
Absorption coefficient	0.750 mm^{-1}	
$F(000)$	516	
Crystal size	$0.30 \times 0.30 \times 0.05$ mm	
θ Range	3.11 to 65.94°	
Index ranges	$0 \le h \le 9, -12 \le k \le 12, -16 \le l \le 17$	
Reflections collected	4208	
Independent reflections 4208 [R(int) = 0.0000]		
Max/min. transmission	0.9635 and 0.8064	
Refinement method	Full-matrix least-squares on F^2	
Data/restraints/parameters	3055/0/338	
Goodness-of-fit on F^2	1.479	
Final R indices [$I > 3\sigma(I)$]	$R1 = 0.0643$, $wR2 = 0.1778$	
R Indices (all data)	$R1 = 0.0868$, $wR2 = 0.11898$	
$\Delta\varrho$ (max; min)	0.283 and -0.472 e · A^{-3}	

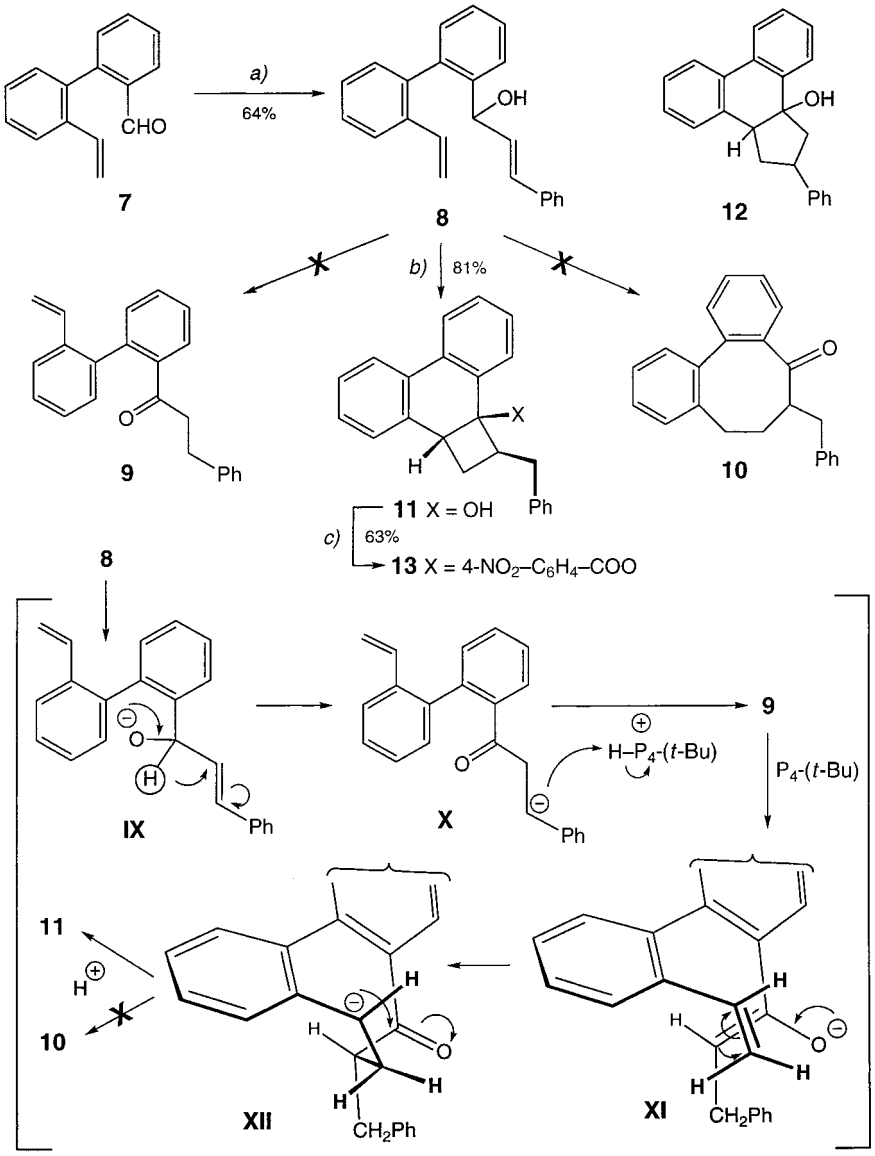
Scheme 4



a) P_4-(*t*-Bu), toluene, $^3O_2$, 10 min, 25°.

It turned out that replacement of the Ph group by a H-atom had a beneficial effect in that the modified substrate **18** underwent an analogous reaction under significantly milder conditions. The crude reaction product consisted of the expected aldehyde **19**,

Scheme 5



a) 1. β-Bromostyrene, ^{t}BuLi, THF, $-78°$, 2. **7** in THF, 5 min at $-78°$. *b*) P_4-(*t*-Bu), toluene, 1 h, 25°. *c*) 1. BuLi, THF, 10 min 25°; 2. 4-nitrobenzoyl chloride, 15 h, 25°.

accompanied by the consecutive *Cannizzaro* products **20** and **21**. To obtain unbiased information on the success of this reaction, the crude mixture was reduced with $LiAlH_4$ to give **21** as the sole product, obtained in 72% yield over both steps. Actually, the reaction could even be run at 110° (3 h in refluxing toluene), when K^+ was employed as

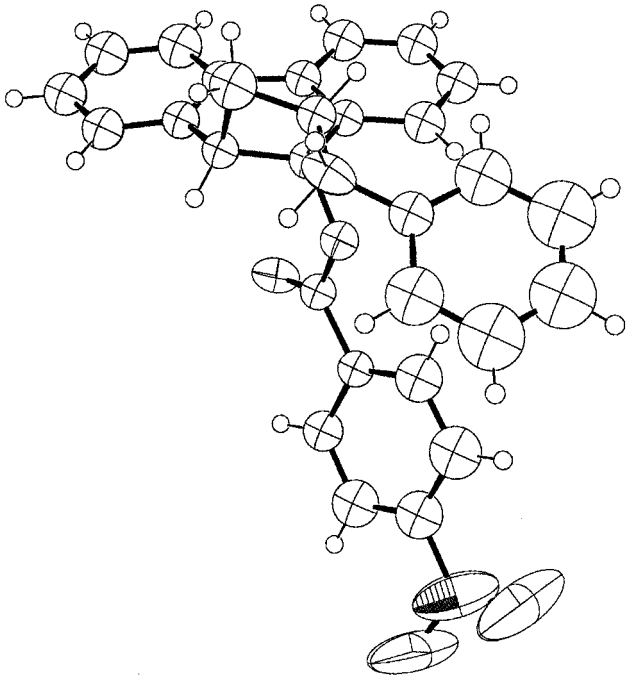
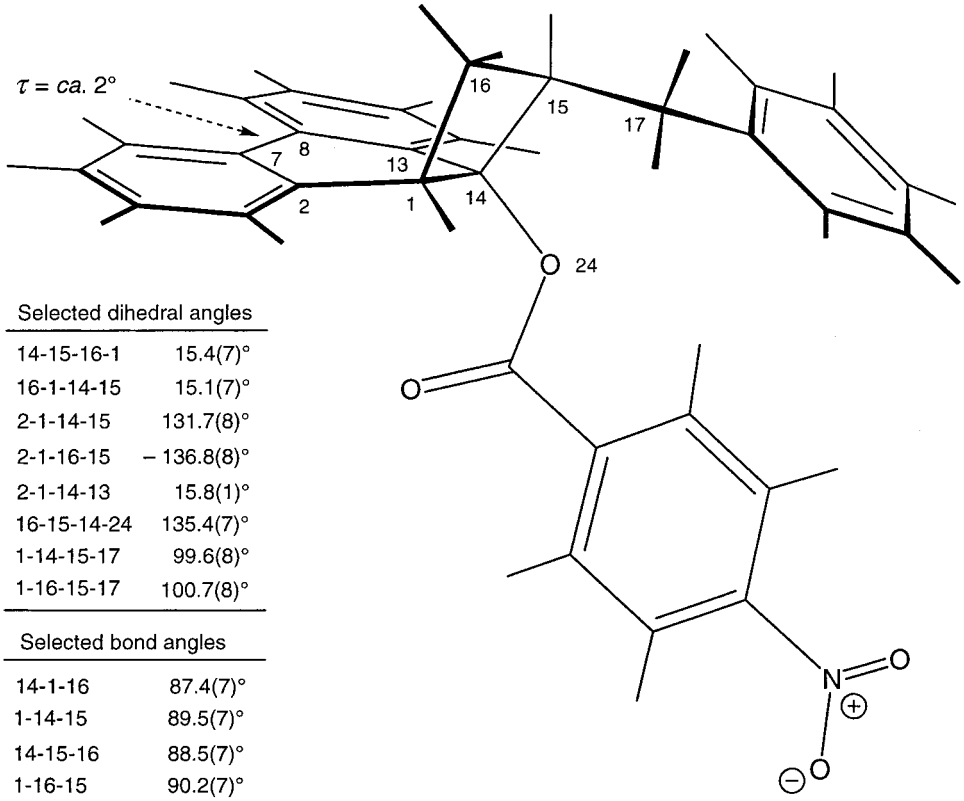


Fig. 3. *ORTEP View of* **13**. The thermal ellipsoids are scaled at the 30% level.

counter ion, and if 1 equiv. of H_2O was added deliberately to push the *Cannizzaro* reaction to completion. It seems that, in the case of *primary* allylic alcohols, heating the K^+ salts does not lead to simple isomerization of the starting material as in the case of the secondary alcohols **1** and **14**, presumably because the K^+ counter ion exerts a significant accelerating effect in favor of the concurrent ene reaction. Although this effect is not quite as spectacular as in the case of the related oxy-*Cope* rearrangement [2], it nevertheless constitutes a major breakthrough in the field of ene reactions due to its roughly million-fold rate enhancement when compared to the purely thermal cases [1]. Once again, treatment of the same starting material with *Schwesinger*'s base furnished none of the anionic oxy-ene product **19**, but instead a compound, which, according to extensive 2D-NMR studies, must be the tetrahydrofuran derivative **22**. Presently, we have no really satisfactory mechanistic explanation for the (reproducible!) formation of this unexpected isomerization product.

3. Conclusion. – While the formation of the P_4-(*t*-Bu) products **4**, **11**, and **22** may remain as curiosities in the chemical literature, the successful anionic oxy-ene reactions described in *Scheme 6* hopefully will pave the way to a new and valuable methodology in organic synthesis. At present, it appears that pyrolysis of the K^+ salts works best in the case of primary allylic alcohols, as the conditions are very mild and the diastereoselectivities accordingly high. Thermolysis of the Li^+ salts, so far, represents the best method in the case of secondary alcohols that can undergo concurrent β-elimination.



Selected dihedral angles	
14-15-16-1	15.4(7)°
16-1-14-15	15.1(7)°
2-1-14-15	131.7(8)°
2-1-16-15	– 136.8(8)°
2-1-14-13	15.8(1)°
16-15-14-24	135.4(7)°
1-14-15-17	99.6(8)°
1-16-15-17	100.7(8)°

Selected bond angles	
14-1-16	87.4(7)°
1-14-15	89.5(7)°
14-15-16	88.5(7)°
1-16-15	90.2(7)°
2-1-14	119.0(8)°
2-1-16	114.3(8)°
14-15-17	114.3(7)°
13-14-15	113.4(7)°
13-14-24	109.6(7)°

Fig. 4. *View of* **13** *based on its crystal structure.* Unlabelled substituents represent H-atoms; arbitrary numbering.

Otherwise, purely thermal treatment of the free allylic alcohols seems to constitute the method of choice to obtain the anticipated oxy-ene products [1]. The range of application of these procedures is presently being explored further in our laboratory.

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

Experimental Part

General. See [11]. All new chiral compounds were obtained as racemic mixtures.

*2-[(9*RS*,10*RS*)-9,10-Dihydro-10-methylphenanthren-9-yl]-1-phenylethanone* (**2**). *Method A* and characterization, see [1]. *Method B:* To a soln. of 112 mg (0.359 mmol) of **1** [1] in 10 ml of benzene were added 0.39 ml (1.1 equiv.) of a 1M soln. of lithum hexamethyldisilazide (LiHMDS) in hexane (*Fluka, pract.*). The mixture was transferred into the stainless-steel autoclave described in [1] and heated to 200° for 5 h. The cold mixture was

Table 2. *Crystallographic Data of* **13**

Empirical formula	$C_{30}H_{23}NO_4$	
Formula weight	461.49	
Temp.	293(2) K	
Wavelength	0.71069 Å	
Crystal system	Orthorhombic	
Space group	*P*212121	
Unit-cell dimensions	$a = 7.357(2)$ Å	$\alpha = 90°$
	$b = 11.071(3)$ Å	$\beta = 90°$
	$c = 28.674(9)$ Å	$\gamma = 90°$
V	2335.5(12) Å^3	
Z	4	
Density (calc.)	1.313 Mg/m^3	
Absorption coefficient	0.087 mm^{-1}	
$F(000)$	968	
Crystal size	0.30 × 0.30 × 0.05 mm	
θ Range	1.42 to 24.95 deg.	
Index ranges	$0 \leq h \leq 8, 0 \leq k \leq 13, 0 \leq l \leq 34$	
Reflections collected	2049	
Independent reflections	2049 [R(int) = 0.0000]	
Max/min. transmission	0.9957 and 0.9743	
Refinement method	Full-matrix least-squares on F^2	
Data/restraints/parameters	2049/0/166	
Goodness-of-fit on F^2	1.162	
Final R indices [$I > 3\sigma(I)$]	$R1 = 0.0767$, $wR2 = 0.1903$	
R Indices (all data)	$R1 = 0.2514$, $wR2 = 0.2441$	
$\Delta\varrho$ (max; min)	0.446 and −0.286 e · A^{-3}	

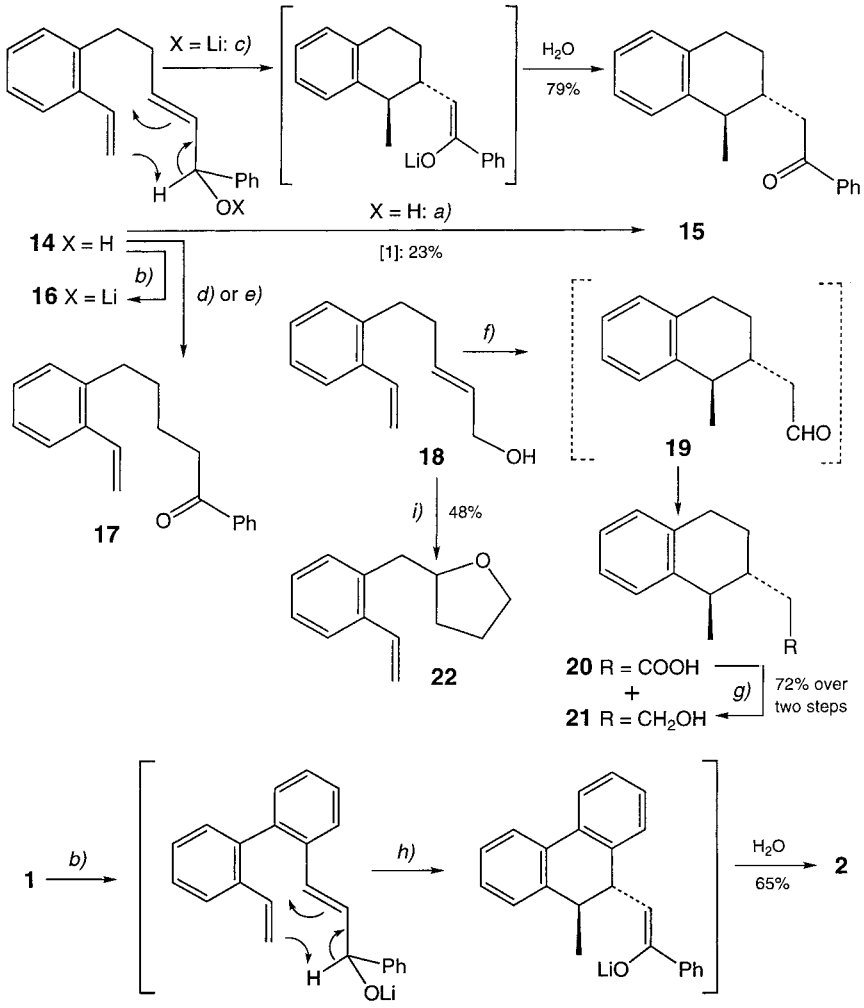
diluted with Et_2O and neutralized with 2N aq. HCl soln. The org. phase was evaporated and chromatographed (silica gel; pentane/Et_2O 9:1) to yield 73 mg (65%) of **2** [1] (96% ds).

3-(2′-Ethenyl-1,1′-biphenyl-2-yl)-1-phenylpropan-1-one (**3**). To a soln. of 141 mg (451 μmol) of **1** [1] in 10 ml of toluene under Ar were added 101 mg (902 μmol) of ^{t}BuOK at 25°. After stirring for 2 h at 25°, the reaction was quenched by addition of 1M phosphate buffer (pH 7) and extracted with Et_2O. Chromatography (silica gel; pentane/Et_2O 9:1) furnished 118 mg (84%) of **3**. Colorless, viscous oil. IR ($CHCl_3$): 3060*m*, 1689*s*, 1683*s*, 1629*w*, 1600*m*, 1583*w*, 1496*w*, 1474*m*, 1450*s*, 1412*w*, 1364*m*, 1320*m*, 1288*m*, 1270*m*, 1183*m*, 1116*w*, 1023*w*, 1006*m*, 1002*m*, 994*m*, 978*m*, 917*m*, 691*s*. ^{1}H-NMR (400 MHz, $CDCl_3$): 7.70–7.64 (*m*, 3 H); 7.51–7.46 (*m*, 1 H); 7.40–7.20 (*m*, 8 H); 7.15–7.13 (*m*, 1 H); 6.45 (*dd, J* = 17.6, 11.0, 1 H); 5.66 (*dd, J* = 17.6, 1.2, 1 H); 5.11 (*dd, J* = 11.0, 1.2, 1 H); 2.98–2.94 (*m*, CH_2(2)); 2.94–2.75 (*m*, CH_2(3)). ^{1}H-NMR (500 MHz, C_6D_6): aliphatic region: 3.01–2.91 (*m*, CH_2(2)); 2.83–2.76 (*m*, CH_2(3)). ^{13}C-NMR (100 MHz, $CDCl_3$): 199.3 (*s*); 140.3 (*s*); 140.1 (*s*); 139.3 (*s*); 136.5 (*s*); 135.9 (*s*); 135.0 (*d*); 132.9 (*d*); 130.3 (*d*); 130.1 (*d*); 129.3 (*d*); 128.5 (*d*); 128.0 (*d*); 127.8 (*d*); 127.7 (*d*); 127.6 (*d*); 126.1 (*d*); 125.0 (*d*); 114.8 (*t*); 39.9 (*t*, (C(2)); 28.7 (*t*, (C(3)). EI-MS: 312 (3, M^+), 310 (3), 205 (12), 192 (100), 191 (27), 179 (85), 178 (56), 165 (18), 134 (22), 105 (44), 77 (29).

Partially Deuterated 3-(2′-Ethenyl-1,1′-biphenyl-2-yl)-1-phenylpropan-1-one (**3′**). As described above, with **1′** [1] as the starting material and stirring for 6 h at 25° (combined yield of **3** and **3′**: 61%). ^{1}H-NMR (500 MHz, C_6D_6): aliphatic region: 3.01–2.91 (*m*, 1.58 H, H/D–C(2)); 2.83–2.76 (*m*, 1.92 H, H/D–C(3)). ^{13}C-NMR (125 MHz, C_6D_6): aliphatic region, ^{1}H-decoupled: 39.9 (*s*, C(2)); 28.79 (*s*, H–C(3)); 28.48 (*t*, $^1J(^2H,^{13}C) = 19.9$, D–C(3)).

*Phenyl(5,6,7,8-Tetrahydrodibenzo[*a,c*]cyclooct-1-yl)methanone* (**4**). *Method A:* To a soln. of 123 mg (394 μmol) of **1** in 10 ml of toluene under Ar were added 0.40 ml of a 1M soln. of the phosphazene-base P_4-(*t*-Bu) in hexane (*Fluka*, *purum*) at −78°. After stirring at 25° for 1 h, the reaction was quenched with 2M HCl and extracted with Et_2O. The crude product was chromatographed (silica gel; pentane/Et_2O 9:1) to furnish 98 mg (80%, 96% ds) of **4**. Colorless, viscous oil. IR ($CHCl_3$): 3065*m*, 2940*m*, 2865*w*, 1680*s*, 1600*m*, 1583*m*, 1500*w*, 1485*m*, 1450*s*, 1372*m*, 1328*w*, 1298*m*, 1279*m*, 1181*m*, 1009*w*, 1003*w*, 987*w*, 976*m*, 949*w*, 930*w*, 913*w*, 699*m*, 695*m*, 662*w*, 623*w*. ^{1}H-NMR (550 MHz, $CDCl_3$): 8.03–8.00 (*m*, 2 H); 7.61–7.58 (*m*, 1 H); 7.53–7.49 (*m*, 2 H); 7.38–

Scheme 6



a) Benzene, 6 h, 230°. *b*) LiN(Me_3Si)$_2$, benzene. *c*) Benzene, 4 h, 200°. *d*) ^{t}BuOK, toluene, 6 h, 25°. *e*) P_4-(*t*-Bu), toluene, 4 h, 25°. *f*) ^{t}BuOK (3 equiv.), H_2O (1 equiv.), benzene, 3 h, 150°. *g*) THF, $LiAlH_4$. *h*) Benzene, 5 h, 200°. *i*) P_4-(*t*-Bu), toluene, 45 min. reflux.

7.24 (*m*, 8 H); 3.61 (*dddd*, *J* = 13.4, 10.2, 4.6, 0.5, 1 H); 2.87 (*dd*, *J* = 13.8, 0.5, 1 H); 2.84 (*ddd*, *J* = 13.7, 8.2, 1.1, 1 H); 2.47 (*dd*, *J* = 13.8, 10.2, 1 H); 2.36 (*ddd*, *J* = 13.7, 12.0, 0.9, 1 H); 2.29 (*dddd*, *J* = 14.0, 8.2, 4.6, 0.9, 1 H); 1.82 (*dddd*, *J* = 14.0, 13.4, 12.0, 1.1, 1 H). ^{13}C-NMR (125 MHz, $CDCl_3$): 203.7 (*s*); 141.5 (*s*); 141.2 (*s*); 140.3 (*s*); 140.1 (*s*); 136.1 (*s*); 133.1 (*d*); 129.5 (*d*); 129.3 (*d*); 129.2 (*d*); 129.1 (*d*); 128.8 (*d*); 128.4 (*d*); 128.1 (*d*); 128.0 (*d*); 126.3 (*d*); 126.2 (*d*); 48.33 (*d*); 34.4 (*t*); 32.7 (*t*); 31.3 (*t*). EI-MS: 312 (30, M^+), 207 (21), 192 (100), 179 (43), 178 (33), 165 (34), 105 (68), 77 (31).

Method B: As *Method A*, but starting with **3**. Yield: 96% of **4**.

*Phenyl(5,6,7,8-Tetrahydro[6-$^2H_1$]dibenzo[*a,c*]cyclooct-6-yl)methanone* (**4′**). *Method A:* A soln. of 20 mg of **4** and 5 mg of ^{t}BuOK in 2 ml of MeOD was stirred under Ar for 18 h at 25°. After addition of 2 ml of pentane, the mixture was filtered through *Celite* and evaporated. The following spectroscopic parameters of **4′** obtained

were different from the undeuterated material **4**: IR ($CHCl_3$): 2260*w*. ^{1}H-NMR (500 MHz, $CDCl_3$): 2.86 (*d*, *J* = 14.4, 1 H); 2.84 (br. *dd*, *J* = 13.6, 8.0, 1 H); 2.47 (*d*, *J* = 13.8, 1 H); 2.35 (*ddd*, *J* = 13.6, 12.0, 0.9, 1 H); 2.28 (br. *dd*, *J* = 14.0, 8.4, 1 H); 1.82 (br. *t*, *J* = 12.8, 1 H). ^{13}C-NMR (125 MHz, $CDCl_3$): 47.8 (*s*, ^1J (^{2}H,^{13}C) = 19.5); 34.3 (*t*); 32.6 (*t*); 31.3 (*t*). EI-MS: 313 (31, M^+), 208 (21), 192 (100), 180 (30), 179 (50), 178 (31), 166 (24), 165 (34), 105 (65), 77 (19).

Method B: As described for the preparation of **4** from **1**, with **1′**, as starting material [1] and stirring for 2 h at 25°. The crude product was chromatographed (silica gel; pentane/Et_2O 9 :1) to give a mixture of **4**/**4′** (61% combined yield). The ^{1}H-NMR signal at 3.61 ppm (H–C(6)) displayed an integral amounting to only 0.88 H as compared to all other signals (1.00 H or multiples thereof).

(Z)-*Phenyl(5,6,7,8-tetrahydrodibenzo[*a,c*]cycloocten-6-yl)methanone (2,4-Dinitrophenyl)hydrazone* (**5**). To a soln. of 67 mg (215 μmol) of **4** in 5 ml of EtOH were added 85 mg (430 μmol) 2,4-dinitrophenylhydrazine (*Fluka*, *puriss.*) and 3 drops of 2M HCl. After 18 h reflux, the solvent was evaporated, and the crude product was chromatographed (silica gel; pentane/Et_2O 9 :1) and recrystallized from THF/cyclohexane to yield 65 mg (61%) of **5**. M.p. 224–225° (THF/cyclohexane). ^{1}H-NMR (400 MHz, $CDCl_3$): 11.08 (br. *s*, 1 H); 9.04 (*d*, *J* = 2.4, 1 H); 8.27 (*ddd*, *J* = 9.6, 2.6, 0.8, 1 H); 7.98 (*d*, *J* = 9.6, 1 H); 7.64–7.55 (*m*, 3 H); 7.39–7.26 (*m*, 9 H); 7.15–7.13 (*m*, 1 H); 3.15 (br. *d*, *J* = 13.5, 1 H); 2.99 (*dddd*, *J* = 13.4, 10.0, 4.4, 0.5, 1 H); 2.84 (br. *dd*, *J* = 13.2, 8.2, 1 H); 2.44 (*dd*, *J* = 13.4, 10.0, 1 H); 2.33 (*dddd*, *J* = 14.1, 8.2, 4.4, 0.3, 1 H); 2.28 (*ddd*, *J* = 13.3, 12.2, 0.3, 1 H); 1.80 (*dddd*, *J* = 14.1, 13.4, 12.2, 1.2, 1 H). ^{13}C-NMR (100 MHz, $CDCl_3$): 162.9 (*s*); 145.0 (*s*); 141.7 (*s*); 140.8 (*s*); 140.4 (*s*); 140.3 (*s*); 137.7 (*s*); 133.4 (*s*); 130.3 (*d*); 130.0 (*d*); 129.9 (*d*); 129.4 (*d*); 129.3 (*d*); 129.2 (*d*); 129.0 (*d*); 128.1 (*d*); 128.0 (*d*); 127.0 (*d*); 126.4 (*d*); 126.2 (*d*); 123.4 (*d*); 116.5 (*d*); 49.6 (*d*); 35.9 (*t*); 33.7 (*t*); 31.5 (*t*).

From a crystal of size 0.30 × 0.30 × 0.05 mm, 4208 reflections were measured on an *Enraf Nonius CAD-4* diffractometer with CuK_α radiation (graphite monochromator, $\lambda = 1.54184$ Å). Part of the structure was solved by direct methods with SIR97 [12]. The non-H-atoms were refined anisotropically with *SHELXL-97* [13]. The H-atoms were calculated at idealized positions and either included in the structure-factor calculation or refined (H(O)) with isotropic displacement parameter. Drawings of the molecule were performed with *PLUTO*, *ORTEP* [14]. For final *R* values and experimental data, see *Table 1*. Crystallographic data have been deposited with the *Cambridge Crystallographic Data Centre* as supplementary publication No. CCDC 151720. Copies of the data can be obtained, free of charge, on application to CCDC, 12 Union Road, Cambridge CB2 1EZ UK, (fax: +44(1223)336033; e-mail: deposit@ccdc.cam.ac.uk).

*5,6,7,8-Tetrahydrodibenzo[*a,c*]cycloocten-6-one* (**6**). A soln. of 27 mg (86 μmol) of **1** and 0.10 ml of a 1M soln. of phosphazene-base (P_4-(*t*-Bu)) in hexane (*Fluka, purum*) in 10 ml of toluene was stirred in an open flask for 10 min at 25°. Quenching with 2M HCl, followed by extraction with Et_2O and chromatography (silica gel; pentane/Et_2O 9 :1) gave 14 mg (73%) of **6**. Colorless crystals. M.p. 108–109° ([7]: 110.9–111.6°). IR ($CHCl_3$): 3065*w*, 2960*w*, 2940*w*, 2870*w*, 1703*s*, 1498*w*, 1483*m*, 1453*m*, 1442*m*, 1418*w*, 1346*w*, 1288*w*, 1273*w*, 1254*w*, 1130*w*, 1085*w*, 1010*w*. ^{1}H-NMR (500 MHz, $CDCl_3$): 7.42–7.28 (*m*, 8 H); 3.58 (*d*, *J* = 11.2, 1 H); 3.32 (*d*, *J* = 11.2, 1 H); 2.80 (*ddd*, *J* = 13.0, 6.0, 2.5, 1 H); 2.69–2.59 (*m*, 2 H); 2.54 (*ddd*, *J* = 13.0, 12.3, 3.0, 1 H). ^{1}H-NMR (400 MHz, C_6D_6): 7.34–7.32 (*m*, 1 H); 7.18–7.01 (*m*, 6 H); 6.89–6.86 (*m*, 1 H); 3.27 (*dm*, *J* = 11.0, 1 H); 3.14 (*d*, *J* = 11.0, 1 H); 2.36 (*ddm*, *J* = 14.5, 5.9, 1 H); 2.25 (*ddd*, *J* = 13.5, 12.8, 1.8, 1 H); 2.18 (*ddd*, *J* = 13.5, 5.9, 3.3, 1 H); 2.10 (*ddd*, *J* = 14.5, 12.8, 3.3, 1 H). ^{13}C-NMR (125 MHz, $CDCl_3$): 207.8 (*s*); 141.4 (*s*); 140.6 (*s*); 139.9 (*s*); 132.6 (*s*); 129.5 (*d*); 129.4 (*d*); 129.2 (*d*); 129.0 (*d*); 128.4 (*d*); 128.1 (*d*); 127.5 (*d*); 127.2 (*d*); 48.7 (*t*); 44.4 (*t*); 29.7 (*t*). EI-MS: 222 (59, M^+), 194 (25), 193 (12), 180 (21), 179 (100), 178 (44), 165 (32), 89 (11), 28 (26).

*(*E*)-1-(2′-Ethenyl-1,1′-biphenyl-2-yl)-3-phenylprop-2-en-1-ol* (**8**). A soln. of 675 mg (3.69 mmol) of purified (*E*)-*β*-bromostyrene [9] in 50 ml of THF was cooled to −78° under Ar. Then, slowly, 2.1 ml (3.1 mmol) of a 1.5M soln. of *t*BuLi in pentane were added. To the resulting light-green soln. was added a cold soln. (−78°) of 512 mg (2.46 mmol) of **7** [1] in 10 ml of THF *via* canula. After stirring for 5 min and subsequent quenching with brine, the mixture was worked up with Et_2O. Chromatography (silica gel; pentane/Et_2O 9 :1) furnished 492 mg (64%) of **8**. Colorless oil. IR ($CHCl_3$): 3605*m*, 3440*w*, (br.), 3090*w*, 3065*m*, 2960*w*, 2935*w*, 2880*w*, 1830*w*, 1652*w*, 1629*w*, 1601*w*, 1580*w*, 1497*m*, 1472*m*, 1450*m*, 1415*w*, 1374*w*, 1302*w*, 1282*w*, 1180*w*, 1161*w*, 1117*w*, 1083*m*, 1018*m*, 1005*s*, 995*s*, 966*s*, 910*s*, 868*w*, 844*w*, 695*m*, 652*w*, 634*w*, 622*w*. ^{1}H-NMR (400 MHz, $CDCl_3$): 7.69–7.63 (*m*, 4 H); 7.46–7.08 (*m*, 22 H); 6.52 (*dd*, *J* = 17.5, 11.0, 1 H); 6.31 (*dd*, *J* = 17.5, 11.0, 1 H); 6.32–6.13 (*m*, 4 H); 5.69 (*dd*, *J* = 17.5, 1.2, 1 H); 5.55 (*dd*, *J* = 17.5, 1.2, 1 H); 5.21 (br. *dd*, *J* = 5.7, 1.5, 1 H); 5.17 (*dd*, *J* = 11.0, 1.2, 1 H); 5.14 (br. *dd*, *J* = 4.7, 2.0, 1 H); 5.01 (*dd*, *J* = 11.0, 1.2, 1 H); 1.97 (br. *d*, *J* = 2.9, 1 H); 1.85 (br. *d*, *J* = 3.1, 1 H). ^{13}C-NMR (100 MHz, $CDCl_3$): 141.1 (*s*); 140.8 (*s*); 139.4 (*s*); 139.3 (*s*); 139.2 (*s*); 139.1 (*s*); 136.8 (*s*); 136.7 (*s*); 136.4 (*s*); 135.8 (*s*); 135.2 (*d*); 135.1 (*d*); 131.1 (*d*); 130.8 (*d*); 130.6 (*d*); 130.3 (*d*); 129.9 (2 × *d*); 128.4 (*d*); 128.4 (*d*); 128.2 (*d*); 128.2 (*d*); 127.9 (2 × *d*); 127.6 (*d*); 127.5 (*d*); 127.5 (2 × *d*); 127.4 (*d*); 127.3 (*d*); 126.5 (2 × *d*); 126.4 (*d*);

126.4 (*d*); 125.0 (*d*); 125.0 (*d*); 115.3 (*t*); 114.7 (*t*); 71.8 (*d*); 71.5 (*d*). EI-MS: 310 (2, $[M-2]^+$), 294 (89), 279 (40), 215 (33), 205 (74), 203 (97), 192 (35), 179 (59), 178 (100), 165 (24), 84 (30).

*2-Benzyl-2,2a-dihydro-1*H*-cyclobuta[l]phenanthren-2a-ol* (**11**). To a soln. of 282 mg (903 μmol) of **8** in 40 ml of toluene under Ar at −78° were added 0.91 ml of a 1M soln. of phosphazene-base (P_4-(*t*-Bu)) in hexane (*Fluka*, *purum*). After stirring for 1 h at 25°, the reaction was quenched with 2M HCl and worked up with Et_2O. Chromatography (silica gel; pentane/Et_2O 9:1) furnished 228 mg (81%) of **11** as a single diastereoisomer. Colorless oil. IR ($CHCl_3$): 3595*m*, 3420*w* (br.), 3070*m*, 2980*w*, 2945*m*, 2860*w*, 1603*w*, 1498*m*, 1488*m*, 1452*m*, 1443*m*, 1178*w*, 1160*w*, 1138*m*, 1093*m*, 1068*w*, 1054*w*, 1031*w*, 949*w*, 942*w*, 909*m*, 701*m*, 618*w*. ^{1}H-NMR (400 MHz, $CDCl_3$): 7.93–7.90 (*m*, 2 H); 7.51–7.49 (*m*, 1 H); 7.39–7.15 (*m*, 10 H); 3.79 (*dd*, *J* = 9.9, 8.6, 1 H); 3.38 (*dd*, *J* = 13.7, 5.4, 1 H); 2.97 (*dd*, *J* = 13.7, 10.3, 1 H); 2.92–2.85 (*m*, 1 H); 2.08 (br. *s*, 1 H); 2.04 (*ddd*, *J* = 11.3, 9.9, 3.2, 1 H); 1.56 (*ddd*, *J* = 11.3, 8.6, 7.7, 1 H). ^{13}C-NMR (100 MHz, $CDCl_3$): 140.6 (*s*); 139.6 (*s*); 136.1 (*s*); 131.8 (*s*); 130.9 (*s*); 129.0 (*d*); 128.7 (*d*); 128.6 (*d*); 128.3 (*d*); 128.3 (*d*); 128.0 (*d*); 127.9 (*d*); 127.2 (*d*); 125.9 (*d*); 123.4 (*d*); 122.6 (*d*); 71.4 (*s*); 49.2 (*d*); 44.5 (*d*); 35.9 (*t*); 28.2 (*t*). HSQC: 123.4/7.91; 122.6/7.92; 49.2/2.88; 44.5/3.79; 35.9/3.38; 2.97; 28.2/2.04, 1.56. EI-MS: 294 (11, $[M-18]^+$), 194 (100), 165 (60), 118 (44), 117 (57), 91 (22), 82 (17).

*2-Benzyl-2,2a-dihydro-1*H*-cyclobuta[l]phenanthren-2a-yl 4-Nitrobenzoate* (**13**). To a soln. of 208 mg (666 μmol) of **11** in 5 ml of THF under Ar were added 0.42 ml of BuLi (1.6M in hexane) at 0°. The resulting dark-yellow soln. was stirred at 25° for 10 min. Then, a soln. of 136 mg (733 μmol) *p*-nitrobenzoyl chloride in 5 ml of THF was added. The resulting pale yellow soln. was kept at 25° for 15 h and worked up with Et_2O and sat. aq. $NaHCO_3$ soln. The crude product was chromatographed (silica gel; $CHCl_3$/pentane 9:1) to furnish 193 mg (63%) of **13**, a yellow solid, which crystallized from CH_2Cl_2/cyclohexane as thin plates. M.p. 160–161° or 173–174°, depending on the chosen crystal (CH_2Cl_2/cyclohexane). ^{1}H-NMR (500 MHz, $CDCl_3$): 8.16–8.13 (*m*, 2 H); 8.04 (*d*, *J* = 8.0, 2 H); 7.88–7.85 (*m*, 2 H); 7.52 (*dd*, *J* = 7.7, 1.3, 1 H); 7.42–7.27 (*m*, 9 H); 7.18–7.16 (*m*, 1 H); 4.19 (*dd*, *J* = 10.3, 9.2, 1 H); 3.60 (*dd*, *J* = 13.0, 6.0, 1 H); 3.21 (*ddddm*, *J* = 9.3, 8.1, 6.0, 2.6, 1 H); 3.17 (*dd*, *J* = 13.0, 9.3, 1 H); 2.18 (*ddd*, *J* = 11.5, 10.3, 2.6, 1 H); 1.77 (*ddd*, *J* = 11.5, 9.2, 8.1, 1 H). ^{13}C-NMR (125 MHz, $CDCl_3$): 163.1 (*s*); 150.4 (*s*); 139.9 (*s*); 136.9 (*s*); 135.9 (*s*); 135.5 (*s*); 133.3 (*s*); 130.8 (*d*); 130.5 (*s*); 128.7 (*d*); 128.6 (*d*); 128.5 (*d*); 128.3 (*d*); 127.7 (*d*); 127.1 (*d*); 127.0 (*d*); 126.5 (*d*); 126.3 (*d*); 123.6 (*d*); 123.3 (*d*); 122.7 (*d*); 77.7 (*s*); 48.6 (*d*); 43.2 (*d*); 37.2 (*t*); 29.0 (*t*).

From a crystal of size 0.30 × 0.30 × 0.05 mm 2049 reflections were measured on a *Enraf Nonius CAD-4* diffractometer with MoK_α radiation (graphite monochromator, $\lambda = 0.71069$ Å). Part of the structure was solved by direct methods with SIR97 [12], the remaining non-H-atoms were found from a difference *Fourier* map. Because of the poor crystal quality, only a selected number of the non-H atoms were refined anisotropically with *SHELXS-97* [13]. The H-atoms were calculated at idealized positions and included in the structure-factor calculation with fixed isotropic displacement parameters. Drawings of the molecule were performed with *PLUTO*, *ORTEP* [14]. For final *R* values and experimental data see *Table 2*. Cristallographic data have been deposited with the *Cambridge Crystallographic Data Centre* as supplementary publication No. CCDC 151721. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44(1223)336033; e-mail: deposit@ccdc.cam.ac.uk).

*2-[(1*RS,*2*SR*)-1,2,3,4-Tetrahydro-1-methylnaphthalen-2-yl]-1-phenylethanone* (**15**). *Method A* and characterization: see [1].

Method B: To a frozen soln. of 135 mg (0.511 mmol) of **14** in 10 ml of benzene at −78° were added 0.61 ml of an 1M soln. of LiHMDS in hexane (*Fluka*, *purum*). The mixture was allowed to reach 25°, and the resulting colorless soln. was transferred into a stainless-steel autoclave and heated to 200° for 6 h. Workup and purification as described above gave 107 mg (79%) of **15** (96% ds).

5-(2-Ethenylphenyl)-1-phenylpentan-1-one (**17**). To a soln. of 95 mg (359 μmol) of **14** in 10 ml of toluene were added 0.36 ml of a 1M soln. of phosphazene-base (P_4-(*t*-Bu)) in hexane (*Fluka*, *purum*) at −78°. After stirring at 25° for 4 h, the reaction was quenched with 2M HCl and worked up with Et_2O. Chromatography (silica gel; pentane/Et_2O 9:1) furnished 29 mg (30%) of **17**.

*2-[(1*RS,*2*RS*)-1,2,3,4-Tetrahydro-1-methylnaphthalen-2-yl]ethanol* (**21**). *Method A:* To a soln. of 99 mg (527 μmol) of **18** in 10 ml of benzene were added 10 mg (1 equiv.) of H_2O, and the resulting emulsion was added to 129 mg (1.71 mmol) of *t*BuOK in a stainless-steel autoclave. After heating to 150° for 3 h, the mixture was cooled to 25° and added to a stirred suspension of 99 mg (2.65 mmol) of $LiAlH_4$ in 50 ml of THF at 0°. After stirring for 15 min at 25°, the mixture was refluxed for another 15 min. Workup with 2N HCl and Et_2O, followed by chromatography (silica gel; pentane/AcOEt 3:1), furnished 71 mg (72%) of **21** (95% ds). Colorless oil. IR ($CHCl_3$): 3625*m*, 3460*m* (br.), 3065*w*, 3020*w*, 2970*m*, 2935*s*, 2885*m*, 1491*m*, 1468*w*, 1449*w*, 1436*w*, 1376*w*, 1077*w*, 1060*w*, 1045*m*, 1018*m*, 991*w*. ^{1}H-NMR (400 MHz, $CDCl_3$): 7.10–7.05 (*m*, 4 H); 3.77 (*t*, *J* = 6.9, 2 H); 2.88 (*qd*, *J* = 7.2, 4.7, 1 H); 2.85–2.79 (*m*, 2 H); 2.00–1.92 (*m*, 1 H); 1.72–1.52 (*m*, 4 H); 1.40 (br. *s*, 1 H); 1.12 (*q*, *J* = 7.2,

3 H). ^{13}C-NMR (100 MHz, $CDCl_3$): 143.0 (*s*); 135.9 (*s*); 129.1 (*d*); 128.9 (*d*); 125.6 (*d*); 125.5 (*d*); 61.2 (*t*); 36.5 (*d*); 36.2 (*t*); 34.0 (*d*); 29.2 (*t*); 23.5 (*t*); 17.6 (*q*). EI-MS: 190 (35, M^+), 172 (41), 157 (66), 155 (23), 144 (78), 143 (99), 129 (100), 128 (53), 118 (70), 117 (65), 115 (45), 91 (29).

Method B: To a soln. of 120 mg (637 μmol) of **18** in 10 ml of toluene were added 12 mg (1 equiv.) of H_2O and 214 mg (3 equiv.) of ^{t}BuOK under Ar. After refluxing for 3 h, the mixture was cooled to 25° and added to a stirred suspension of 120 mg (5 equiv.) of $LiAlH_4$ in 30 ml of THF at 0°. After stirring for 15 min at 25°, the mixture was refluxed for another 15 min. Workup with 2N HCl and Et_2O, followed by chromatography (silica gel; pentane/AcOEt 3 : 1), furnished 78 mg (65%) of **21**.

2-(2-Ethenylbenzyl)-2,3,4,5-tetrahydrofuran (**22**). To a soln. of 95 mg (504 μmol) of **18** in 10 ml of toluene were added 0.50 ml of a 1M soln. of phosphazene-base (P_4-(*t*-Bu)) in hexane (*Fluka*, *purum*) at 0°. After stirring at reflux temp. for 45 min, the reaction was quenched with aq. buffer soln. (pH 7) and worked up with Et_2O. Chromatography (silica gel; pentane/Et_2O 20 : 1) furnished 46 mg (48%) of **22** as the only identified reaction product. Colorless oil. IR ($CHCl_3$): 3065*w*, 2970*m*, 2870*m*, 1688*m*, 1628*w*, 1486*m*, 1452*m*, 1417*w*, 1375*w*, 1084*m*, 1060*s*, 990*m*, 918*m*. ^{1}H-NMR (500 MHz, $CDCl_3$): 7.50 – 7.47 (*m*, 1 H); 7.22 – 7.19 (*m*, 3 H); 7.04 (*dd*, *J* = 17.4, 11.0, 1 H); 5.63 (*dd*, *J* = 17.4, 1.4, 1 H); 5.29 (*dd*, *J* = 11.0, 1.4, 1 H), 4.05 (*tt*, *J* = 7.0, 6.2, 1 H); 3.92 – 3.88 (*m*, 1 H); 3.75 – 3.70 (*m*, 1 H); 3.04 (*dd*, *J* = 13.8, 6.3, 1 H); 2.79 (*dd*, *J* = 13.8, 6.8, 1 H); 1.93 – 1.79 (*m*, 3 H); 1.61 – 1.54 (*m*, 1 H). ^{13}C-NMR (125 MHz, $CDCl_3$): 137.0 (*s*); 136.3 (*s*); 134.9 (*d*); 130.4 (*d*); 127.7 (*d*); 126.6 (*d*); 125.8 (*d*); 115.6 (*t*); 79.4 (*d*); 67.9 (*t*); 39.0 (*t*); 31.0 (*t*); 25.6 (*t*). HETCOR: 134.9/7.04; 130.4/7.20; 127.7/7.20; 126.6/7.20; 125.8/7.49; 115.6/5.63 and 5.29; 79.4/4.05; 67.9/3.90 and 3.73; 39.0/3.04 and 2.79; 31.0/1.86 and 1.58; 25.6/1.90 and 1.82. EI-MS: 188 (3, M^+), 71 (100), 43 (27).

REFERENCES

[1] G. A. Schmid, H.-J. Borschberg, *Helv. Chim. Acta* **2001**, *84*, 388.
[2] a) D. A. Evans, A. M. Golob, *J. Am. Chem. Soc.* **1975**, *97*, 4765; b) D. A. Evans, J. V. Nelson, *J. Am. Chem. Soc.* **1980**, *102*, 774.
[3] M. Tiffeneau, *Bull. Soc. Chim. Fr.* **1907**, *4. Série 1*, 1205; footnote on p. 1209.
[4] a) T. Cuvigny, M. Julia, L. Jullien, C. Rolando, *Tetrahedron Lett.* **1987**, *28*, 2687; b) H. M. R. Hoffmann, A. Köver, D. Pauluth, *J. Chem. Soc., Chem. Commun*. **1985**, 812.
[5] D. R. Dimmel, W. Y. Fu, S. B. Gharpure, *J. Org. Chem.* **1976**, *41*, 3092.
[6] a) D. Hoppe, *Angew. Chem., Int. Ed.* **1984**, *23*, 932; b) J. F. Biellmann, J. B. Ducep, 'Organic Reactions', J. Wiley & Sons Inc., New York, 1982; Vol. 27, 1.
[7] A. C. Cope, R. D. Smith, *J. Am. Chem. Soc.* **1956**, *78*, 1012.
[8] T. Hiramatsu, T. Harada. T. Yamaji, *Bull. Chem. Soc. Jpn.* **1981**, *54*, 985.
[9] H. Neumann, D. Seebach, *Chem. Ber.* **1978**, *111*, 2785.
[10] G. A. Schmid, H.-J. Borschberg, unpublished result.
[11] R. Stahl, R. Galli, R. Güller, H.-J. Borschberg, *Helv. Chim. Acta* **1994**, *77*, 2125.
[12] A. Altomare, B. Carrozzini, G. L. Cascarano, C. Giacovazzo, A. Guagliardi, A. G. Moliterni, R. Rizzi, Istituto di Ricerca per lo Sviluppo di Metodologie Cristallografiche, CNR, Campus Universitario, Via Orabona 4, I-70125 Bari, Italy.
[13] G. M. Sheldrick, 'SHELXL-97, Program for the Refinement of Crystal Structures', University of Göttingen, Germany.
[14] C. K. Johnson, 'ORTEP II, Report ORNL-5138 (1976)', Oak Ridge National Laboratory, Tennessee, USA.

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