103. Synthesis of Benzo[*a*]heptalene

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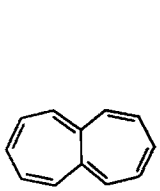
Dedicated to *Oscar Jeger* on the occasion of his 80th birthday

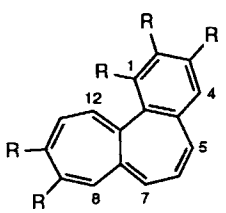
(7. V. 97)

Benzo[*a*]heptalene has been synthesized by two different approaches. The first one follows a pathway to hexahydrobenzo[*a*]heptalenone **19a** that has been already described by *Wenkert* and *Kim* (*Scheme 1*). Indeed, **19a** was obtained in a mixture with its double-bond-shifted isomer **19b**. Reduction of this mixture to the corresponding secondary alcohols **26a**/**26b** and elimination of H_2O lead to a mixture of the tetrahydrobenzo[*a*]heptalenes **23a**–**d** (*Scheme 7* and *8*). Reaction of **23a**–**d** with 2 equiv. of triphenylmethylium tetrafluoroborate in boiling $CHCl_3$, followed by treatment with Me_3N in CH_2Cl_2, generated directly **2**, unfortunately in a mixture with Ph_3CH that could not be separated from **2** (*Scheme 10* and *11*). The second approach *via* dimethyl benzo[*a*]heptalene-6,7-dicarboxylate (**30**) (*Scheme 12*) that was gradually transformed into the corresponding carbaldehydes **37** and **43** (*Scheme 14*) both of which, on treatment with the *Wilkinson* catalyst [$RhCl(PPh_3)_3$] at 130° in toluene, smoothly decarbonylated, finally gave pure **2** as an unstable orange, viscous oil. UV/VIS, NMR, and mass spectra of **2** are discussed in detail (*cf. Chapt. 3*).

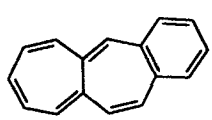
1. Introduction. – Whereas heptalene (**1**) has already been synthesized more than 35 years ago [1], followed by a number of further syntheses (*cf.* [2] and lit. cit. there), its two possible benzo-anellated forms **2** and **3** are still unknown, despite the fact that benzo[*a*]heptalene (**2**) represents the underlying parent structure of all naturally occurring colchicines (*cf.* **5**) and colchicinoid compounds (*cf.* [3]).



1



2 R = H
4 R = MeO



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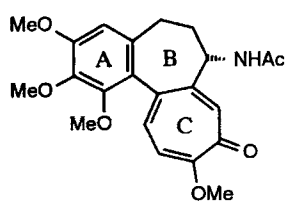

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In going from **1** to **2** or **3**, one can expect that some main features of the heptalene core will be changed. First of all, the rapid thermal double-bond shifts (DBS), characteristic for **1** ($E_a < 14.7$ kJ mol^{-1} [4]), should almost be suppressed in **2** and its [*b*]-anellat-

[1]) Part of the planned Ph. D. thesis of *J. G.*, University of Zurich.
[2]) Part of the diploma theses of *R. K.* and *M. L.*, University of Zurich.

ed analogue **3**, due to the energy difference between the anellated aromatic π-system and the corresponding *o*-quinodimethane substructure that has to be formed in the DBS step. Indeed, 1,2,3,9,10-pentamethoxybenzo[*a*]heptalenes (*cf.* **4**), derived from colchine (**5**) and its 4-alkyl derivatives [2], as well as all other derivatives of **2** that have become available over the past years by *Hafner*'s heptalene-1,2-dicarboxylate synthesis show localized double bonds at the heptalene core [5–8][3]). In addition, one can excpect that the electronic absorption spectrum of **1**, which is characterized by two absorption bands at 256 and 352 nm (ε = 21'400 and 4'100, resp.) [1] [4] [10], followed by an extremely long tailing up to above 650 nm, should also be altered markedly, especially in the long-wavelength region, for **2** and **3**. Therefore, we were interested to see to what extent the general absorption feature of substituted heptalenes, represented by three band regions above 250 nm (*cf.* [11]), is also reflected by **2** as the parent structure of all benzo[*a*]heptalenes. An X-ray crystal-structure analysis of 1,2,3,9,10-pentamethoxybenzo[*a*]heptalene (**4**) [2] had shown already that the torsion angles at the central σ-bond of the heptalene core are with 51–52° distinctly larger than that of dimethyl heptalene-3,8-dicarboxylate (37.9° [12]) which may be taken as a reference value for that of **1**. On the other hand, the torsion angles of **4** are comparable with those of other heptalenes, carrying one *peri*-substituent (*e.g.*, dimethyl heptalene-4,5-dicarboxylate: 51–54° [13]).

2. Syntheses of 2. – 2.1. *Following the Route of* Wenkert *and* Kim *to a Precursor of Colchicine* (**5**). The essential part of the formal colchicine synthesis of *Wenkert* and *Kim* is the construction of ring C of **5** by a thermal divinylcyclopropane → cycloheptadiene rearrangement [14] (see also [15]). The necessary precursor (*Z*)-**10** is thereby formed in three steps (*cf. Scheme 1*), starting with the $[Rh_2(OAc)_4]$-catalyzed decomposition of ethyl diazopyruvate (**6**) in the presence of excess buta-1,3-diene in CH_2Cl_2 [16] leading to the formation of the *trans*-configured α-keto ester **7**. The following *Wittig* reaction with the easily available phosphonium salt **8** gives then the crucial divinylcyclopropane intermediate (*Z*)-**10** which, on heating in xylene, is rearranged to the desired **12**. After base-catalyzed isomerization of **12** into **14**, the *Dieckmann* reaction under *Ruggli-Ziegler* conditions gives rise to the formation of ring B of **5**. Acid-catalyzed hydrolysis and decarboxylation of the formed β-keto ester yields finally the hexahydrobenzo[*a*]-heptalenone **18a**. The formal colchicine synthesis of *Wenkert* and *Kim* is then concluded by selective hydrogenation of the C(8)=C(9) bond, followed by reductive amination of the keto function *via* the corresponding oxime and acetylation. The so formed 7-acetamido-octahydro-1,2,3-trimethoxybenzo[*a*]heptalene is the decisive intermediate in *Nakamura*'s colchicine synthesis [17].

Since *Wenkert* and *Kim* performed *Steps 2–4* of their synthesis also in the demethoxy series as model reactions (*cf. Scheme 1*), we decided to choose this way for the formation of 5,6,7,10,11,12-hexahydrobenzo[*a*]heptalen-7-one (**19a**) as precursor for the synthesis of **2**.

In the following part, we comment briefly on *Steps 1–4* of the synthesis of **19a**.

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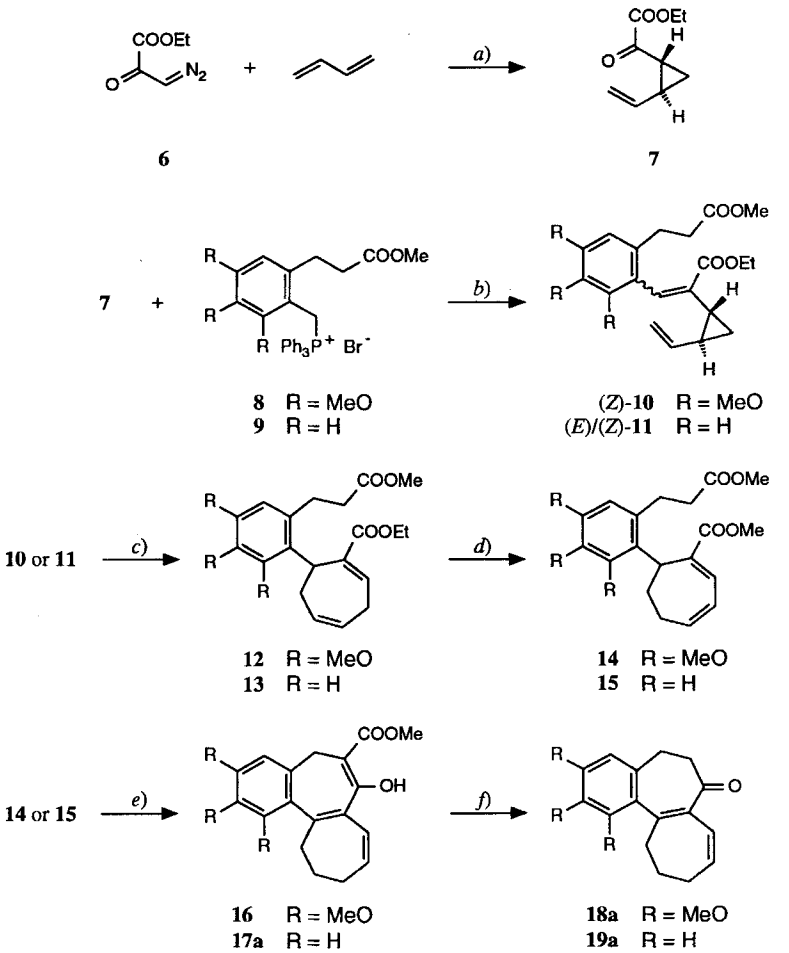
[3]) Some hydro derivatives of benzo[*b*]heptalene (**3**) are known [9a], and it seems that, up to now, only *Amiel* and *Ginsburg* have attempted a synthesis of **3** [9b] which, otherwise, has merely been a model compound for theoreticians [9c].

Scheme 1

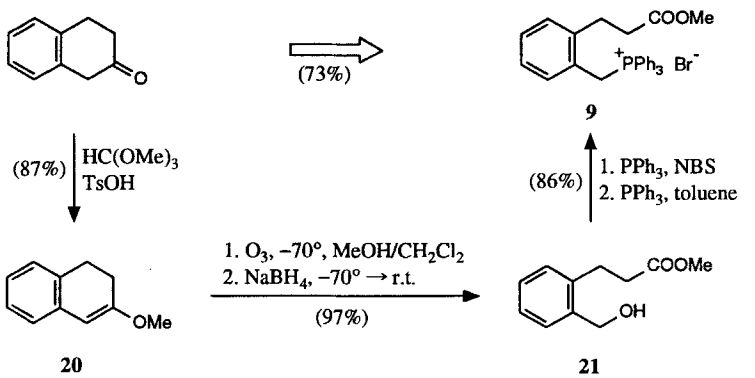


a) $[Rh_2(OAc)_4]$ (cat.), CH_2Cl_2, r.t. *b*) LDA, THF, $-20° \rightarrow$ r.t. *c*) Xylene, Δ. *d*) MeONa, MeOH, reflux. *e*) MeONa, xylene, reflux. *f*) 5% aq. HCl/dioxane/AcOH/H_2O (1:2:1:1), reflux.

Step 1: The $[Rh_2(OAc)_4]$-catalyzed addition of ethyl diazopyruvate (**6**) to buta-1,3-diene gave **7** and a dihydro-oxepine derivative, arising from the retro-*Claisen* rearrangement of the primarily formed *cis*-isomer of **7** [16], in almost the same yields as described by *Wenkert et al.* [16]. The compounds were separated by flash chromatography leading to pure **7** (38–40%) and the dihydro-oxepine (31%).

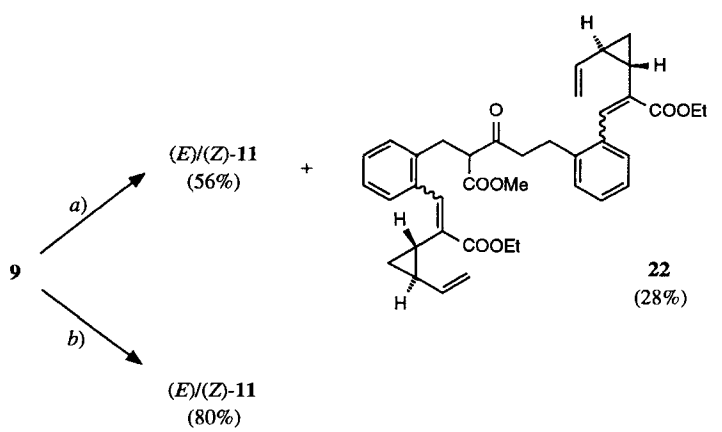
Step 2: The conditions for the synthesis of the phosphonium salt **9** were slightly altered allowing a remarkable improvement of the total yield of **9** (73%) as compared to the procedure of *Wenkert* and *Kim* (33%; *cf. Scheme 2*). We avoided to use Me_2S for the reductive workup of the ozonide of **20** to give the formyl derivative of **21** which is then reduced with $NaBH_4$ to the desired hydroxymethyl-ester **21** in a total yield of 58%, since treatment of the ozonide with $NaBH_4$ gave in one step **21** in a yield of 97%. The

Scheme 2



bromomethyl derivative of **21** was formed with NBS/PPh_3 in CH_2Cl_2 (89%) instead of Br_3P in Et_2O (81%). The formation of the phosphonium salt **9** from the latter compound was accomplished without problems. *Wenkert* and *Kim* performed the subsequent *Wittig* reaction of **7** and **9** with LDA in THF at $-10°$. We observed under these conditions, beside (*E*)/(*Z*)-**11** (56%), the formation of appreciable amounts (up to 28%) of the *Claisen*-condensation product **22** of (*E*)/(*Z*)-**11** (*Scheme 3*). However, when we used MeONa as base in THF/MeOH (1000:1) for the *Wittig* reaction of **7** and **9**, we obtained (*E*)/(*Z*)-**11** in a yield of 80%, free of **22**. But, transesterification had occurred under these conditions, so that (*E*)/(*Z*)-**11** contained up to 80% of the corresponding dimethyl esters (see *Exper. Part*).

Scheme 3

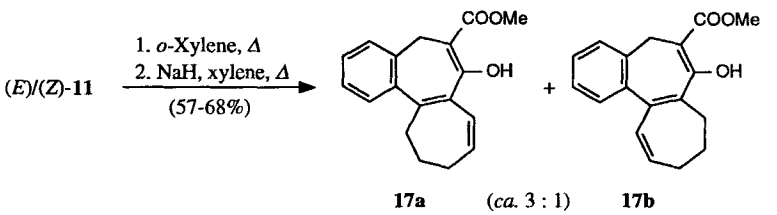


a) LDA, THF, $-20°$; 2. **7**, $-20°$ → r.t. *b*) 1. MeONa, THF/MeOH (1000:1), $-20°$ → r.t.; 2. **7**, $-20°$ → r.t.

Steps 3 and 4: The thermal rearrangement of (*E*)/(*Z*)-**11** in boiling *o*-xylene was performed as described in [14]; however, in contrast to the procedures of *Wenkert* and *Kim*, the formed **13** was not isolated, but its solution in *o*-xylene just subjected to the conditions of the *Dieckmann* condensation, using NaH instead of MeONa as a base. As a result, a 3:1 mixture of **17a** and its double-bond-shifted isomer **17b** was obtained in a

total yield of 57 to 68% (*Scheme 4*). Compound **17b** was not observed by *Wenkert* and *Kim*. An analytical sample of pure **17a** and **17b** was obtained by chromatography on silica gel. The structural assignment of both compounds is based on ^{1}H-NOE measurements ($CDCl_3$): Whereas **17a** showed, on iradiation of the signal of H–C(8) (*d*, ^3J(8, 9) = 11.4 Hz) at 6.94 ppm, only on enhancement effect on the signal of H–C(9), **17b** displayed, on irradiation of the signal of H–C(12) (*d*, ^3J(11, 12) = 11.0 Hz) at 6.28 ppm, an enhancement effect not only on the signal of H–C(11) but also on the signal of H–C(1) at the neighboring benzo moiety.

Scheme 4

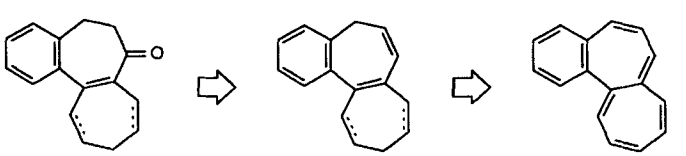


17a (*ca.* 3 : 1) **17b**

The last transformation step, acid-catalyzed hydrolysis and decarboxylation, was performed with mixture **17a**/**17b** 3:1 according to *Wenkert* and *Kim* and led to a *ca.* 2:1 mixture of the heptalenones **19a**/**19b** in a yield of 86%. The mixture could not be separated by chromatography. However, the hydrolysis and decarboxylation of a pure sample of **17a** gave **19a** which was accompanied only by small amounts of **19b** (17%) according to the ^{1}H-NMR analysis of the olefinic region for H–C(8) at 6.24 ppm (*d*, ^3J(8, 9) = 11.7 Hz) and H–C(9) at 6.14 ppm (*dt*, ^3J(8,9) = 11.7 and ^3J(9,10) = 5.0 Hz). The ^{1}H-NMR spectrum of the 2:1 mixture **19a**/**19b** showed the corresponding signals for **19b** at 6.40 ppm (*dt*, ^3J(11,12) = 11.1 and ^3J(11,10) = 5.9 Hz; H–C(11)) and at 6.12 ppm (H–C(12)), with the latter one partially covered by the lines of H–C(9) of **19a**.

Further efforts for the synthesis of **2**, starting with the mixture **19a**/**19b**, (*Scheme 5*), involved introduction of an additional double bond between C(6) and C(7), and dehydrogenation of the expected mixture of **23a** and **23b** to **2.**

Scheme 5

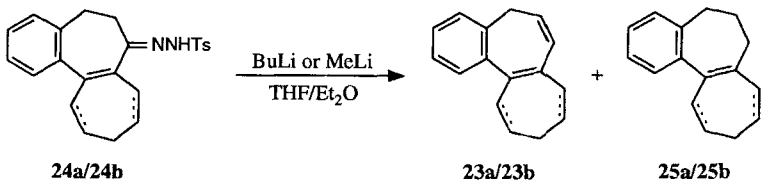


19a/19b **23a/23b** **2**

One of the most attractive methods for the formation of a C=C bond *ex* ketone is *Shapiro*'s variant of the *Bamford-Stevens* reaction [18]. However, when we deprotonated the corresponding mixture of *p*-tosylhydrazones **24a**/**24b** with 2.5 equiv. of BuLi or MeLi in THF and Et_2O, respectively, we obtained, after workup, not only the expected mixture of olefins **23a**/**23b** but also a mixture of the reduced forms **25a**/**25b** in appreciable

amounts (*Scheme 6*)[4]). The structure of the formed olefins was not further investigated. However, from GC/MS analyses, the presence of reduced olefines was obvious.

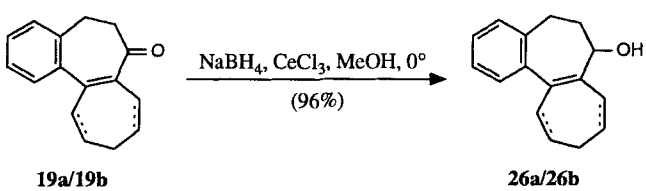
Scheme 6



24a/24b **23a/23b** **25a/25b**

To avoid the formation of hexahydrobenzo[*a*]heptalenes, the mixture of ketones **19a**/**19b** was first reduced to the corresponding secondary alcohols **26a**/**26b** (*Scheme 7*). Recrystallization from hexane led to a 2.3:1 mixture. A single crystal of this mixture was subjected to an X-ray crystal-structure analysis (*Fig. 1*). The diffraction pattern allowed a clear recognition of the C(7a)=C(12a) bond, whereas the location of the C=C bond in ring C was obscured by disorder effects (*cf. Exper. Part*). However, most probably it is C(8) and C(9) as shown in *Fig. 1*. A point of interest is the fact that the crystal subjected to X-ray analysis contained only one enantiomer of **26a**, *i.e.*, the mixture of crystals of **26a** and **26b** represented, at least with respect to **26a**, a conglomerate.

Scheme 7



19a/19b **26a/26b**

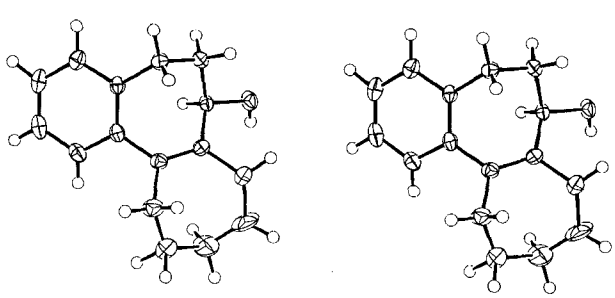
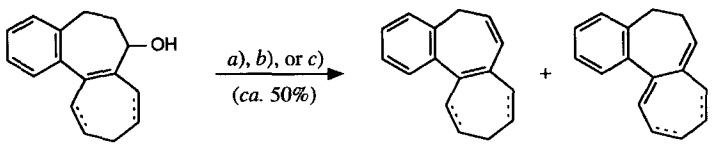


Fig. 1. *Stereoscopic view of the X-ray crystal structure of 5,6,7,10,11,12-hexahydrobenzo[a]heptalen-7-ol* (**26a**)

[4]) We found no precedent for this behavior in the literature (*cf.* [18]). Nevertheless, careful repetitions of the experiments did not change the product composition. It might be that the hydrazones are partially isomerized to corresponding azo structures which are then attacked by the alkyllithium reagent at the N=N bond, thus leading finally to the reduced forms.

For the dehydration of the mixture **26a**/**26b**, we tested three methods (*Scheme 8*). The conventional procedure with $POCl_3$ in pyridine at 60° led, in an isolated yield of 50%, to a mixture of olefins, mainly consisting of the tetrahydrobenzo[*a*]heptalenes **23a** and **23b**. However, a GC/MS analysis revealed that the mixture of olefins contained, beside **23a** and **23b**, also an HCl addition product of **23a**/**23b** as well as dimethylphenanthrenes. The latter compounds were identified by their fragmentation patterns in comparison to those loaded in a data base (> 95% correspondence)[5]).

Scheme 8



26a/26b **23a/23b** **23c/23d**

a) $POCl_3$, pyridine, 60°. *b*) 1 equiv. *Martin*'s reagent [19], $CHCl_3$, r.t. *c*) 1.1 equiv. *Burgess*' reagent [20], $CHCl_3$, 50°.

Best results were obtained with the sulfurane-dehydration reagent of *Martin* and *Ahart* [19] which gave in > 60% yield **23a**/**23b** 4.7:1, accompanied by small amounts of two further tetrahydrobenzo[*a*]heptalenes, presumably **23c**/**23d**. A similar mixture of olefins **23a**–**d** was formed when the betaine-dehydration reagent of *Burgess et al.* [20] was applied on **26a**/**26b**. However, the mixture of olefins, generated with the sulfurane reagent, contained Ph_2S which could not be separated from the mixture, neither by distillation nor by chromatography. In contrast to this finding, *Burgess*' reagent gave, in 50% yield, a mixture of olefins **23a**–**d** that could easily be purified by chromatography.

The structure of the tetrahydrobenzo[*a*]heptalenes was deduced from the ^{1}H-NMR spectrum (C_6D_6) of the mixture **23a**–**d** in comparison to the ^{1}H-NMR spectra of the precursor alcohols **26a**/**26b** as well as from their UV spectra after HPLC separation on an analytical column (see *Exper. Part* and *Table 1*). The formation of **23a** and **23b** can be interpreted as the result of a 1,2 elimination of H_2O from **26a** and **26b**, respectively. The main isomer, **23a**, shows a d(^3J = 11.1 Hz) at 6.11 ppm for H–C(8). In the second isomer, **23b**, the corresponding signal for H–C(12) (d, ^3J = 11.0 ppm) appears at lower field, *i.e.*, at 6.46 ppm, due to the neighborhood of the deshielding plane of the benzo ring. On the other hand, one finds for both isomers a deshielding effect also for H–C(1) of the benzo ring which is – as expected – larger for **23b** (7.48 ppm; d, ^3J = 7.8 Hz) than for **23a** (7.39 ppm; d, ^3J = 7.6 Hz). The third olefin, **23c**, which was present in the mixture to an extent of *ca.* 9%, showed three recognizable signals for olefinic H-atoms. A *t*-like signal ($^3J \approx 4$ Hz) occurred at comparably high field (5.18 ppm) and had to be assigned to H–C(7). The two other signals at 5.75 ppm (dt, ^3J = 11 and 5 Hz) and at 5.83 ppm (d, ^3J = 8 Hz) could only stem from H–C(10) and H–C(12), respectively. The remaining signal for H–C(11) (dd) must be buried under a group of lines of olefinic H-atoms of **23a**

[5]) The standard fragmentation patterns did not allow to distinguish between dimethylanthracenes and -phenanthrenes. However, the given benzo[*a*]heptalene skeleton suggests that dimethylphenanthrenes had been formed.

and **23b** in the range of 5.7 ppm. The structure of **23c** is in agreement with a 1,6 elimination of H_2O from **26b** under the influence of *Burgess'* reagent. The structure of **23d**, which was present in the mixture to an extent of < 3%, is tentatively assigned, taking into account a 1,4 elimination of H_2O from **26a**. Moreover, its UV spectrum (80% MeCN/20% H_2O) is, in comparison to the spectra of the other isomers, **23a–c**, in accordance with the proposed structures (see *Table 1*).

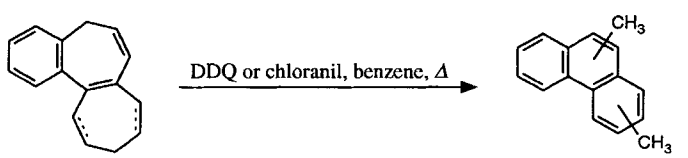
Table 1. *UV Spectra of the Tetrahydrobenzo[a]heptalenes* **23a–d**[a])

Heptalene	λ_{max}[nm][b])		λ_{min}[nm]	
	I	II	I	II
23a	296 (0.09)	227 (0.14)	254	214
23b	290 (0.07)	236 (0.15)	260	221
23c	278 (0.07)	223 (sh, 0.14)	247	–
23d	278 (0.05)	219 (sh, 0.15	245	–

[a]) Measured with a photodiode-array detector in MeCN/H_2O 4:1 during HPLC separation.
[b]) In parentheses are given the relative intensities.

The discussed mixture of tetrahydrobenzo[*a*]heptalenes **23a–d** was not further separated, since the mixture turned out to be sensitive to chromatographic procedures. Therefore, all dehydrogenation reactions, in order to build **2**, were performed with the mixture. First attempts to dehydrogenate the mixture with DDQ or chloranil in boiling benzene resulted in the formation of a mixture of dimethylphenanthrenes (*Scheme 9*) which were only characterized by their fragmentation pattern in the GC/MS analyses (see above and *Footnote 5*).

Scheme 9



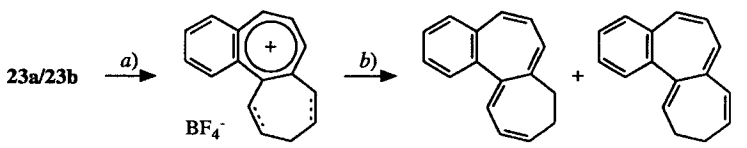
23a/23b

Also not very successful were attempts of allylic brominations of the mixture with NBS in CCl_4, followed by base-induced dehydrobromination with DBN or DBU in boiling THF. Similarly, no better results brought the addition of 1 equiv. of Br_2 to the mixture of olefins, followed by treatment with DBN or DBU in boiling THF as well as treatment with potassium triphenylmethanide in diglyme at 0° [21].

On the basis of the structure of **23a** and **23b**, one can assume that these two olefins should easily lead to corresponding benzotropylium ions of type **27a** and **27b** on treatment with hydride-ion acceptors such as $Ph_3C^+BF_4^-$. Deprotonation of **27a**/**27b** with a tertiary base such as Me_3N (*cf.* [1] [2]) should then result in the formation of the dihydrobenzo[*a*]heptalenes **28a**/**28b** (*Scheme 10*). Experiments with the mixture of **23a–d** showed that no reaction occurred with a twofold amount of $Ph_3C^+BF_4^-$ in $CHCl_3$ at 20° (see *Table 2*). However, at 50°, we observed, after treatment with Me_3N, in the GC/MS

analysis a peak (80%) with $M^{+\cdot}$ at *m/z* 206, most probably due to the presence of expected **28a/28b**, but also, on the flank of the first peak, a slightly slower-moving peak (*ca.* 20%) with $M^{+\cdot}$ at *m/z* 204, and a fragmentation pattern (see *Chapt. 3*) which could only be interpreted as that of the searched benzo[*a*]heptalene (**2**). A third peak, the most prominent one (*ca.* 70% with respect to those of **28a/28b** and **2**), could be unequivocally assigned to that of Ph_3CH ($M^{+\cdot}$ at *m/z* 244). When the hydride-transfer reaction with $Ph_3C^+BF_4^-$ was carried out in boiling $CHCl_3$, **28a/28b** could no longer be observed, *i.e.*, **2** and Ph_3CH were the only detectable compounds by GC/MS analysis (*cf. Fig. 2*). When only 1 equiv. of $Ph_3C^+BF_4^-$ with respect to the mixture of **23a–d** was applied, **28a/28b** (70%) were, beside Ph_3CH, again the main components in the reaction mixture after treatment with Me_3N.

Scheme 10



27a/27b **28a** **28b**

a) $Ph_3C^+BF_4^-$, $CHCl_3$. *b*) Me_3N, CH_2Cl_2, r.t.

Table 2. *Product Distribution after Treatment of the Mixture of Tetrahydrobenzo[a]heptalenes* **23a–d** *with* $Ph_3C^+BF_4^-$ *and then* Me_3N

Entry	Mol-equiv. $Ph_3C^+BF_4^-$	Reaction temp. [°C][a])	Ratio [%] (**28a/28b**)/**2**[b])
1	2	20	[c])
2	2	50	80:20
3	2	61	<1:100
4	1	61	70:30

[a]) Reaction time 1 h.
[b]) Determined by GC/MS analysis.
[c]) Starting material recovered unchanged.

A preparative run including the isolation of the intermediate benzotropylium BF_4^- salts by precipitation with Et_2O/hexane 3:1, followed by washing with Et_2O, suspension in CH_2Cl_2, and deprotonation with Me_3N at 20°, confirmed the results. We isolated a 2.3:1 mixture of Ph_3CH/**2**. Unfortunately, we were not able to remove Ph_3CH by chromatography on silica gel or aluminum oxide with different solvent systems, since **2** turned out to be not very stable under the applied conditions, and both compounds showed nearly identical R_f values causing long times for chromatography. Nevertheless, benzo[*a*]heptalene (**2**) could be unambiguously characterized by its 600-MHz ^{1}H-NMR spectrum in the presence of Ph_3CH as well as by its UV spectrum after separation of Ph_3CH on an analytical HPLC column, and its MS fragmentation pattern from GC/MS analysis (see *Exper. Part* and later).

We assume that the formation of **2** from the mixture of tetrahydrobenzo[*a*]heptalenes is due to the formation of **28a/28b** under the forcing conditions ($Ph_3C^+BF_4^-$ in boiling

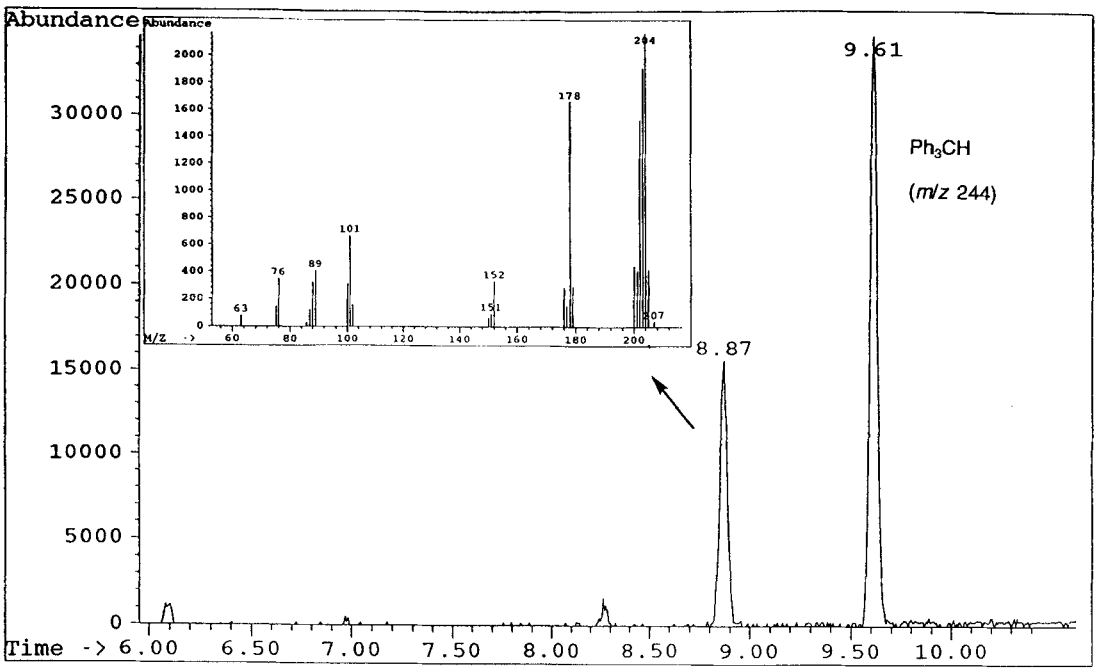
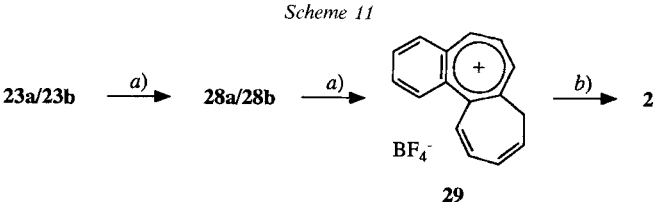


Fig. 2. GC/MS of **2** *from the mixture of* **2** *and* Ph_3CH

$CHCl_3$), which lose a second hydride ion in the presence of excess $Ph_3C^+BF_4^-$ to form benzotropylium ions of type **29** (*Scheme 11*). Deprotonation of the latter with Me_3N then results in the formation of **2**. However, it might be that **29** is protonated by the formed HBF_4, and it, indeed, represents a dication. The whole process seems not to be very efficient, since the calculated yield of **2** from the mixture of **23a–d** lies in the range of 5%, whereby some of **2** might have been destroyed in the purification steps. The fact that **2** is contaminated with Ph_3CH shows that not all of the triphenylmethylium salt is consumed by hydride-ion transfer so that the residual salt is precipitated with the benzotropylium salts, and, later on, in the deprotonation reaction with Me_3N, reduced by the base to the observed Ph_3CH.

Scheme 11



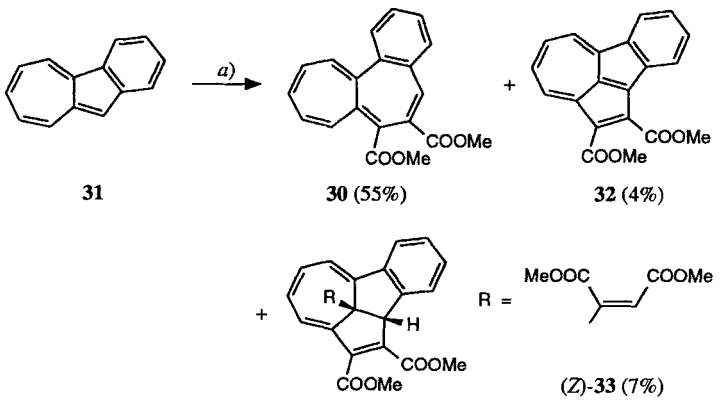
29

a) $Ph_3C^+BF_4^-$, $CHCl_3$, reflux. *b*) Me_3N, CH_2Cl_2, r.t.

2.2. *Following a Stepwise Degradation of Dimethyl Benzo[*a*]heptalene-6,7-dicarboxylate* (**30**). About three years ago, we showed that *Hafner*'s heptalene synthesis can also be applied to the formation of benzo[*a*]heptalene-6,7-dicarboxylates, when benz[*a*]-

azulenes are reacted with acetylenedicarboxylates [5]. The reaction is also applicable to benz[*a*]azulene (**31**) itself and dimethyl acetylenedicarboxylate (ADM) [7] (see also [6]) and opens an easy access to **30** particularly, in view of a new synthesis of **31** that has been developed by us [22] (see also [23]). A detailed study of the formation of benzo[*a*]heptalene-6,7-dicarboxylates from benz[*a*]azulenes and acetylenedicarboxylates showed that the thermal reaction in aromatic hydrocarbons such as toluene gave the best yields of the benzo[*a*]heptalenedicarboxylates with a minimum number of by-products (see also [8] [24]). *Scheme 12* displays the best results we attained in the thermal reaction of **28** and ADM in mesitylene.

Scheme 12



31 **30** (55%) **32** (4%) (*Z*)-**33** (7%)

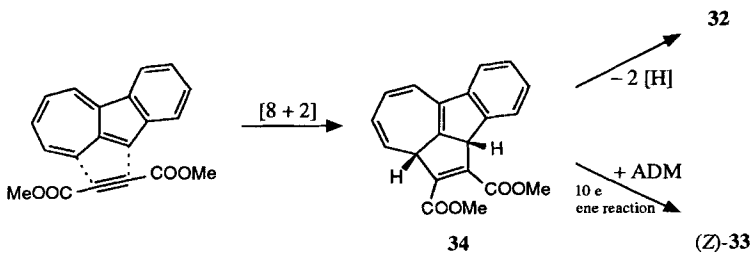
a) In a sealed tube, a 0.3M solution of **31** in mesitylene was heated in the presence of 1.5 equiv. of ADM at 160° for 24 h.

As a new product, accompanying **30** and the benzo[*a*]cyclopent[*cd*]azulenedicarboxylate **32** (*cf.* [5] [7]), we found the (1 + 2) adduct (*Z*)-**33** in an amount of 7%. The latter two products seem to arise from a common precursor **34** which represents a thermally allowed [8 + 2] cycloadduct of **31** and ADM. It reflects the accentuated heptafulvene substructure of **31** (*cf.* [23]), since heptafulvene shows exactly this type of periselectivity in cycloaddition reactions (*cf.* [25]). On the other hand, in contrast to **31**, azulenes give, when heated in the presence of ADM in apolar solvents, insignificant amounts of products that arise from corresponding [8 + 2] cycloaddition reactions (*cf.* [26]), in agreement with the small orbital coefficients at C(4) and C(8) in the HOMO of the azulenes (*cf.* [27]). The formation of **32** from **34** represents a thermal dehydrogenation reaction. The (*Z*)-configuration of the (1 + 2) adduct **33** indicates that its generation must be the result of a concerted thermal process of **34** and ADM which can be understood as a thermally allowed, bisvinylogous ene reaction *via* a 10-e transition state (*Scheme 13*)[6]).

The structure of the benzo[*a*]heptalenedicarboxylate **30** was secured by an X-ray crystal-structure analysis (see *Exper. Part* and later). The structure of (*Z*)-**33** was de-

[6]) We observed this type of reaction also in Et_2AlCl-catalyzed reactions of azulenes with ADM [27]. However, in these cases, the addition of the second molecule of ADM occurs stepwise, and, as a result, (*Z*)- as well as (*E*)-forms of the (1 + 2) adducts are found in the reaction mixtures.

Scheme 13



duced from its ^{1}H- and ^{13}C-NMR spectra in combination with ^{1}H-NOE measurements (see *Exper. Part*). Important for the assignment of the (*Z*)-configuration of the 1,2-bis-(methoxycarbonyl)ethenyl substituent at C(10c) was the observation that irradiation of the signal of the H-atom at C(2′) (sharp *s* at 4.24 ppm) caused strong ^{1}H-NOE effects on the signals of H–C(10b) at 3.96 ppm (*s*), H–C(3) at 6.68 ppm (*d*, ^3J = 6.8 Hz), and H–C(6) at 7.13 ppm (*d*, ^2J = 6.8 Hz). In addition, we found a long-range ^{1}H,^{13}C-coupling constant in the order of 11 Hz between H–C(2′) and the carbonyl C-atom at C(1′) which is only compatible with a *trans*-arrangement of the coupling partners, in agreement with the (*Z*)-configuration of the ethenyl bond.

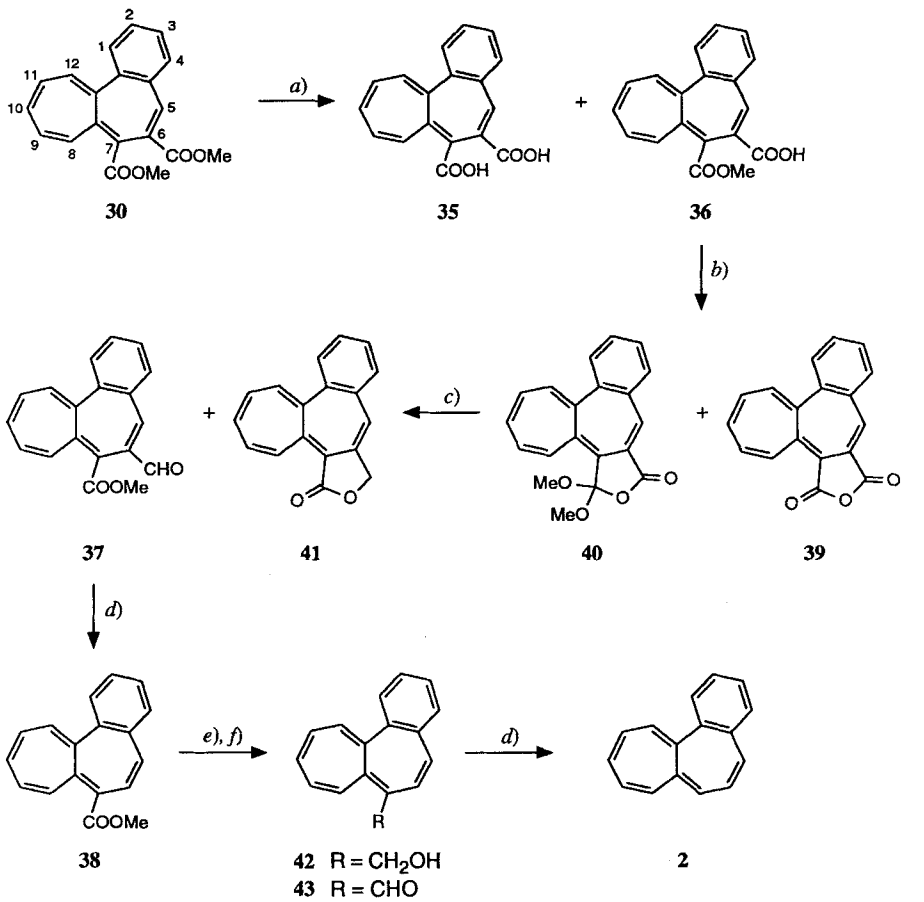
First attempts to prepare **2** directly from the diester **30** or its corresponding dicarboxylic acid **35**, which is easily obtained by saponification of **30**, by established decarboxylation methods of esters (H_3PO_4: [28]; LiBr in HMPTA: [29]; pyridine in DMF: [30]) and carboxylic acids (CF_3SO_3H in 1,2-dichloroethane: [31]; $Pb(OAc)_4$ in pyridine/MeCN: [32]) failed, since mainly decomposition and polymerization occurred. Therefore, we decided to choose a stepwise degradation of both ester groups. The idea was to transform **30** *via* the mono-acid **36** into the formyl-ester **37** (*cf. Scheme 14*). That heptalenecarbaldehydes can be decarbonylated with the *Wilkinson* catalyst has already been shown by *Hafner et al.* [33] (see also [34]). A repetition of this degradation sequence with the mono-ester **38** should finally lead to the target molecule **2**.

We have already reported earlier [35] that heptalene-4,5-dicarboxylates can regioselectively be saponified at the sterically less hindered ester function at C(4) with KOH in $EtOH/H_2O$ at room temperature. When we applied this procedure to **27**, a *ca.* 1:3 mixture of the required mono-carboxylic acid **36** and the dicarboxylic acid **35** was obtained. It seems that, under the applied conditions, the steric hindrance of the ester function at C(7) is not sufficient to differentiate it chemically from the ester function at C(6). However, when **30** was treated with an excess of LiOH in boiling $MeOH/H_2O$ for only 10 min, a more favorable (10 – 5):1 mixture **36**/**35** was formed (*Scheme 14*). Both acids can be separated by repeated recrystallization from AcOEt/hexane, giving isolated yields of 66 to 88% of **36** and 6 to 15% of **35**[7]). Both acids, when heated above the melting point, lose MeOH and H_2O, respectively, and give the corresponding dark-red-colored anhydride **39**. The structure of **36** was additionally established by an X-ray crystal-structure analysis (see *Exper. Part* and later).

Since model reactions with 9-isopropyl-5-(methoxycarbonyl)-1,6-dimethylheptalene-4-carboxylic acid [35] had shown that the reduction of the acid function with diborane

[7]) The dicarboxylic acid **35** can principally be recycled by esterification with CH_2N_2 in Et_2O.

Scheme 14



a) LiOH, MeOH/H_2O, 70°. *b*) 1. $(COCl)_2$, DMF, MeCN, 0°; 2. MeOH, 0° → r.t. *c*) 1M DIBAH, hexane/toluene, −76°. *d*) $[RhCl(Ph_3P)_3]$, toluene, sealed flask, 130°. *e*) 1M DIBAH, hexane/THF, 0°. *f*) MnO_2, CH_2Cl_2, r.t.

in THF [36] always led to the corresponding heptaleno[1,2-*c*]furan-1-one (*cf.* [37]), we chose another reduction procedure that had already been successfully applied in other cases (*cf.* [38]). Reaction of **36** with $(COCl)_2$/DMF in MeCN, followed by addition of MeOH, provided the pseudo-ester **40** as major product (61–79%) together with minor amounts of the anhydride **39** (6–7%) (*cf.* [39]). The anhydride resulted from small amounts **35**, present in crude **36**. Reduction of the pseudo-ester **40** with 2 equiv. of diisobutylaluminum hydride (DIBAH) in toluene at −78° led to the formation of the expected formyl-ester **37** in 72% yield. The heptaleno[1,2-*c*]furan-1-one **41** was formed under these conditions only in minor amounts. However, substantial amounts of **41** were formed, when the reduction with DIBAH was performed in THF as solvent. The elimination of the CHO function of **37** was straightforward: Heating **37** in the presence of 1.1 equiv. of $[RhCl(Ph_3P)_3]$ in toluene at 130° in a sealed tube gave the mono-carboxylate **38** in 92% yield as an orange, unstable, viscous oil, after removal of Ph_3P by

chromatography. It was reduced with DIBAH in THF at 0° to benzo[*a*]heptalene-7-methanol (**42**) which crystallized from hexane/Et_2O in 81% yield in yellow needles. Dehydrogenation of **42** with basic MnO_2 [40] in CH_2Cl_2 at room temperature furnished readily the crystalline 7-carbaldehyde **43** in 72% yield after purification by chromatography on silica gel[8]). The decarbonylation of the orange-colored **43** was performed as described for **37** and led to the desired benzo[*a*]heptalene (**2**). However, the ^{1}H-NMR spectrum ($CDCl_3$) of the product mixture still indicated the presence of Ph_3P, since **2** and PPh_3 hat similar R_f values on silica gel or aluminum oxide with hexane as eluant. Eventually, the contaminating Ph_3P could be removed as phosphonium salt, by reaction of the mixture with excess of MeI. The thus purified **2** was obtained in 44% yield (overall yield, starting with **30**: 7–12%) as a yellow, unstable, viscous oil that withstood so far all attempts of crystallizing it. In general, **2** decomposes on standing, even in a refrigerator, under formation of a yellow amorphous powder. It can be better stored in diluted and degassed hexane solutions in the cold.

3. Spectroscopic Properties of 2. – 3.1. *Electronic Absorption Spectrum.* As expected, the UV/VIS spectrum of **2** (*Fig. 3*) resembles in its total habitus very much that of 1,2,3,9,10-pentamethoxybenzo[*a*]heptalene (**4**; *cf. Table 3*) [2]. However, whereas band III and II (*cf.* [11]) of **2** exhibit a distinct hypsochromic shift in comparison to **4**, this shift is much less pronounced for the longest-wavelength band I at 350 nm. That this band is quite typical for heptalenes shows a comparison with the UV/VIS spectrum of dimethyl heptalene-4,5-dicarboxylate (**44**; *Fig. 4*)[9]) which can be regarded as a good model compound, since it carries the two ester groups at the place of the benzo junction in **2**. Therefore, we can expect for **2** and **44** a similar degree of twisting of the heptalene core (*cf.* also *Chapt. 1*). The MeO substituent at C(1) of **4** will, therefore, not add a relevant increment to the twisting of the heptalene core in **4** as compared to **2** as has been argued already in *Introduction*. Clear displacement of band III and II to longer wavelengths as well as the hyperchromic effect of band II in **4** in comparison to **2** can, therefore, be attributed to the π-donor property of the MeO groups in **4**. Band II appears in **2** only as a weak shoulder which is much more pronounced in **4** and clearly visible as a separate band in the CD spectra of the antipodes of **4** (see [2]).

In conclusion, we can state that the electronic absorption spectrum of **2** and its simply substituted derivatives are characterized by three bands (I–III). The second one (band II) appears merely as a shoulder on the long-wavelength flank of band III. The broad, longest-wavelength band I can be regarded as typical heptalene band which responds as such much stronger to the steric influence of substituents that they exert on the twisting of the heptalene core than to the π-donor or π-acceptor qualities that these substituents

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[8]) Attempts to reduce the ester **38** directly to the carbaldehyde **43** with DIBAH or lithium tris(diethylamino)aluminum hydride in THF at low temperatures failed, since only **42** was formed.

[9]) The ^{1}H-NMR spectrum (600 MHz; $CDCl_3$) of **44** shows at 300 K, due to the rapid DBS process, a line broadening of all signals, except for that of H–C(10) at 5.18 ppm (*d*, $^3J(9,10) = 6.1$ Hz) and the two signals (*s*) of the MeOCO groups at 3.70 and 3.80 ppm. At 260 K, one observes sharp signals for all H-atoms of **44**. Additional signals that could be attributed to the DBS isomer of **44**, *i.e.*, dimethyl heptalene-1,2-dicarboxylate, are not visible. This means that the amount of the DBS isomer of **44** in thermal equilibrium at 260 K must be $< 0.2\%$. Therefore, *Fig. 4* shows, indeed, the UV/VIS spectrum of pure **44**.

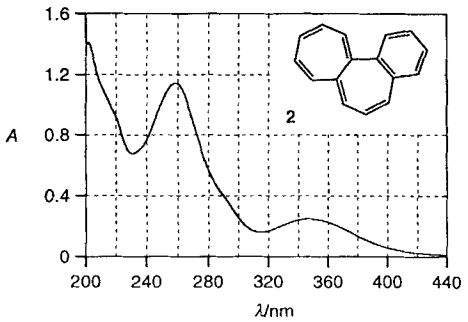


Fig. 3. *UV/VIS Spectrum* (hexane) *of* **2**

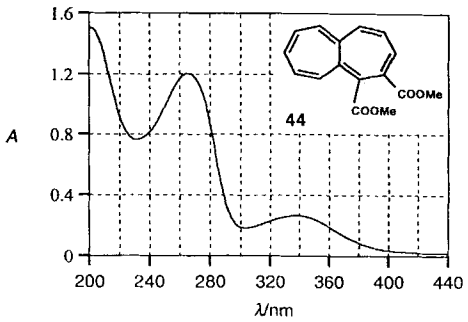


Fig. 4. *UV/VIS Spectrum* (hexane) *of* **44**

Table 3. *Comparison of the UV/VIS Spectra of Benzo[*a*]heptalene* (**2**) *and Its 1,2,3,9,10-Pentamethoxy Derivative* **4**

Heptalene	λ_{max}[nm]			λ_{min}[nm]	
	I	II	III	I	II
2[a])	347 (0.24)	295 (sh, 0.31)	259 (1.14)	314 (0.15)	231 (0.67)
4[b])	351 (3.66)	302 (sh)	271 (4.37)	332 (3.75)	244 (4.28)

[a]) In hexane. In parentheses *A*.
[b]) In cyclohexane. In parentheses log ε.

wield over the twisted π-system of the benzo[*a*]heptalenes, provided that the substituents do not represent extended π-systems in itself (*cf.* [38]).

3.2. *NMR Spectra.* The data of the fully assigned ^{1}H- and ^{13}C-NMR spectra are summarized in *Table 4*. In addition, the ^{1}H-NMR spectrum (600 MHz; $CDCl_3$) is displayed in *Fig. 5*. The chemical shifts of the olefinic H-atoms span a range of 1.15 ppm with the signal of H–C(5) at lowest field, since H–C(5) reaches into the deshielding area of the adjacent benzo ring, and the signal of H–C(7) at highest field due to the position of H–C(7) at the 'methylene end' of the heptafulvene structure that is inscribed in the benzo[*a*]heptalene skeleton of **2**. Moreover, the signal of C(7) appears also at highest field in the ^{13}C-NMR spectrum. Both observations are in full agreement with the corresponding chemical shifts of heptalene itself [41] (see also [23]).

The vicinal coupling constants at the s-*cis*-buta-1,3-diene substructures of **2** are of special interest, since their size is a measure for the degree of twisting of the benzo[*a*]heptalene skeleton, as expressed by the corresponding torsion angles. The averaged coupling constant amounts to 6.6 Hz (*cf. Table 4*). We find just an averaged vicinal coupling constant of the same order for **44**, if we neglect $^3J(2,3) = 6.2$ Hz in **44** which may be influenced by the MeOCO substituent at C(4) as strong electron-acceptor group. Therefore, we can conclude that **2** and **44** must, indeed, have a very similar degree of twisting of the heptalene core. The vicinal coupling constants across formal single bonds that we have found at ring C for **30**, **35**, and **36** are slightly smaller. Their averaged value is in the range of 6.4 Hz, in agreement with the stronger twisted heptalene core of these compounds due to the steric interactions of the additional substituents at C(6) and C(7). This tendency is also found in the corresponding torsion angles of the X-ray crystal-structure analyses of **39**, **36**, and **44** (*cf. Table 5*).

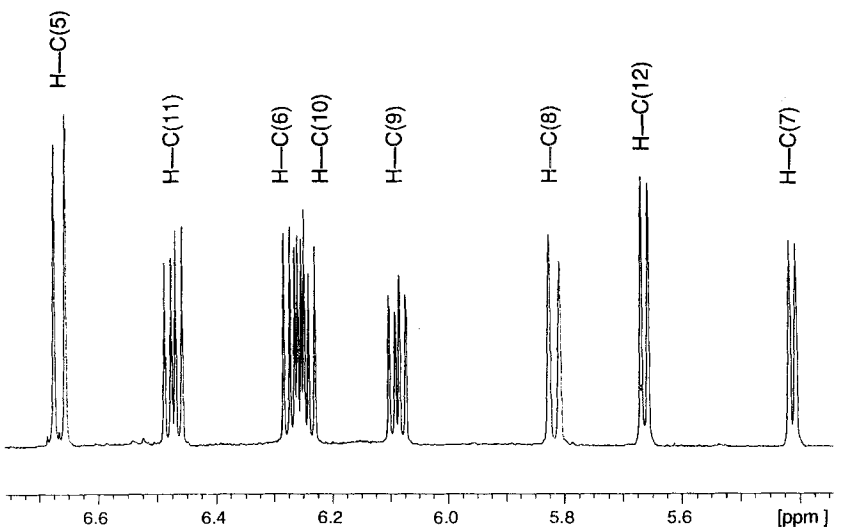


Fig. 5. *^{1}H-NMR Spectrum* (600 MHz) *of* **2** *in* $CDCl_3$. Region of the olefinic H-atoms.

Table 4. *^{13}C- and ^{1}H-NMR Data of Benzo[a]heptalene* (**2**)[a])

Atom	$\delta(^{13}C)$ [ppm]	$\delta(^1H)$ [ppm]	$^1H,^1H$ Couplings [Hz]
H–C(1)	129.10	7.10	$^3J(1,2) = 7.6$
H–C(2)	130.45	7.39	$^3J(2,3) = {}^3J(2,1) = 7.6$, $^4J(2,4) = 1.3$
H–C(3)	127.89	7.28	$^3J(3,2) \approx {}^3J(3,4) \approx 7.6$, $^4J(3,1) = 1.3$
H–C(4)	128.87	7.11	$^3J(4,3) = 7.6$
C(4a)	138.80	–	–
H–C(5)	132.89	6.66	$^3J(5,6) = 11.6$
H–C(6)	128.95	6.27	$^3J(6,5) = 11.6$, $^3J(6,7) = 6.5$
H–C(7)	125.98	5.41	$^3J(7,6) = 6.5$
C(7a)	139.61	–	–
H–C(8)	130.06	5.82	$^3J(8,9) = 10.9$, $^4J(8,10) = 0.6$
H–C(9)	130.65	6.09	$^3J(9,8) = 10.9$, $^3J(9,10) = 6.5$, $^4J(9,11) = 0.4$
H–C(10)	130.45	6.25	$^3J(10,11) = 11.3$, $^3J(10,9) = 6.5$, $^4J(10,8) = {}^4J(10,12) = 0.7$
H–C(11)	133.29	6.47	$^3J(11,10) = 11.2$, $^3J(11,12) = 6.8$, $^4J(11,9) = {}^5J(11,8) = 0.9$
H–C(12)	130.28	5.66	$^3J(12,11) = 6.8$, $^4J(12,10) = 0.4$
C(12a)	140.51	–	–
C(12b)	139.27	–	–

[a]) At 150 and 600 MHz, resp., in $CDCl_3$.

3.3. *Mass Spectrum.* The MS of **2** (*Fig. 6*) is very characteristic and useful for the detection of **2** in mixtures with its hydro forms *via* GC/MS analyses (see before). Noteworthy, beside the prominent $M^{+\cdot}$ peak at *m/z* 204 (100 rel. %), are the peaks at *m/z* 203 (89 rel. %) and 202 (72 rel. %), followed by peaks at *m/z* 178 (81 rel. %) and 152 (13 rel. %). Further intense peaks are observed at *m/z* 101 (31 rel. %) and 76 (14 rel. %). Since **2** possesses only H–C(sp^2) bonds, which should not be cleaved so easily, the appearance of strong $[M-1]^{+\cdot}$ and $[M-2]^{+\cdot}$ peaks indicates ring-closure reactions of

Table 5. *Torsion Angles from the X-Ray Crystal-Structure Analyses of Dimethyl Benzo[a]heptalene-6,7-dicarboxylate* (**30**), *Its 7-Carboxylic Acid* **36**, *and Dimethyl Heptalene-4,5-dicarboxylate* (**44**)

Torsion Angles Θ[a]) [°]	**30**	**36**	**44**[b])
C(5)–C(6)–C(7)–C(7a)	39.9	29.9	35.7
C(6')–C(6)–C(7)–C(7')	44.0	33.6	39.8
C(7)–C(7a)–C(12a)–C(12)	128.3	128.3	134.3
C(7)–C(7a)–C(12a)–C(12b)	−57.1	−54.9	−51.1
C(8)–C(7a)–C(12a)–C(12)	−58.7	−57.7	−53.8
C(8)–C(7a)–C(12a)–C(12b)	115.9	119.5	120.8
C(8)–C(9)–C(10)–C(11)	−30.0	−30.0	−28.5
C(10)–C(11)–C(12)–C(12a)	31.0	31.4	28.8
C(12)–C(12a)–C(12b)–C(1)	57.0	48.4	–

[a]) With respect to the (*M*)-configuration at the central heptalene bond (C(7a)–C(12a)); C(6'),C(7')=CO at C(6) and C(7), respectively.

[b]) Data from [13]. Numbering as in **30** and **36** with C(1) and C(2) of **44** (new numbering; *cf.* Footnote 2 in [42]) in place of C(12b) and C(4a) of **30** and **36**.

2 that may occur purely thermally or after ionization in the radical cation of **2**. The strong peak at *m/z* 178 marks the easy loss of an ethyne molecule $[M - HC{\equiv}CH]^{+\cdot}$, in agreement with the formation of cyclobutene substructures in the ring-closure processes (*cf. Scheme 15*). Thus, ring closure at ring B would lead to **A** which, on loss of ethyne, forms the radical cation of benz[*a*]azulene (**31**). An analogous reaction at ring C would generate

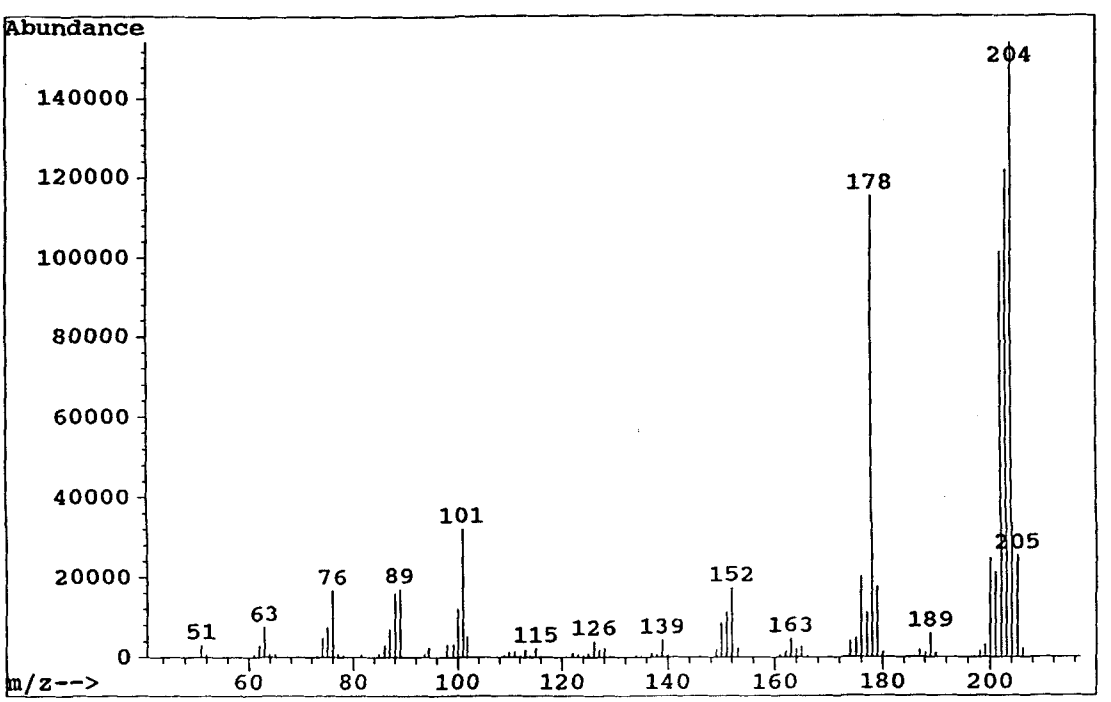


Fig. 6. *GC/MS of* **2** *from an artificial* ca. *1:1 mixture* **2**/**31**

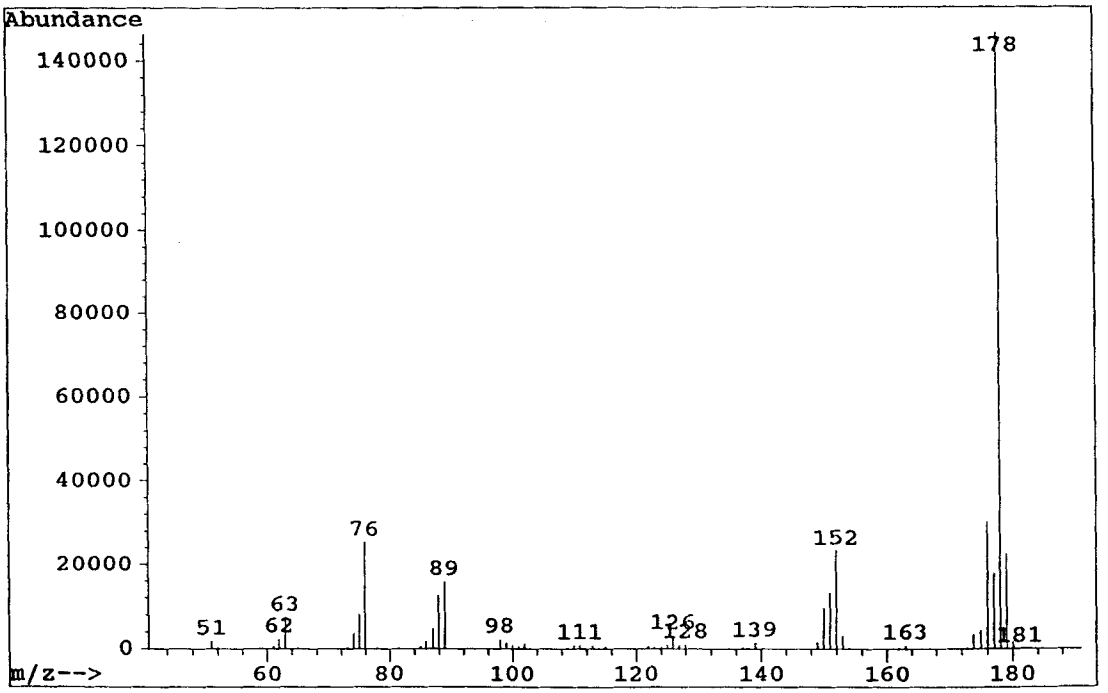
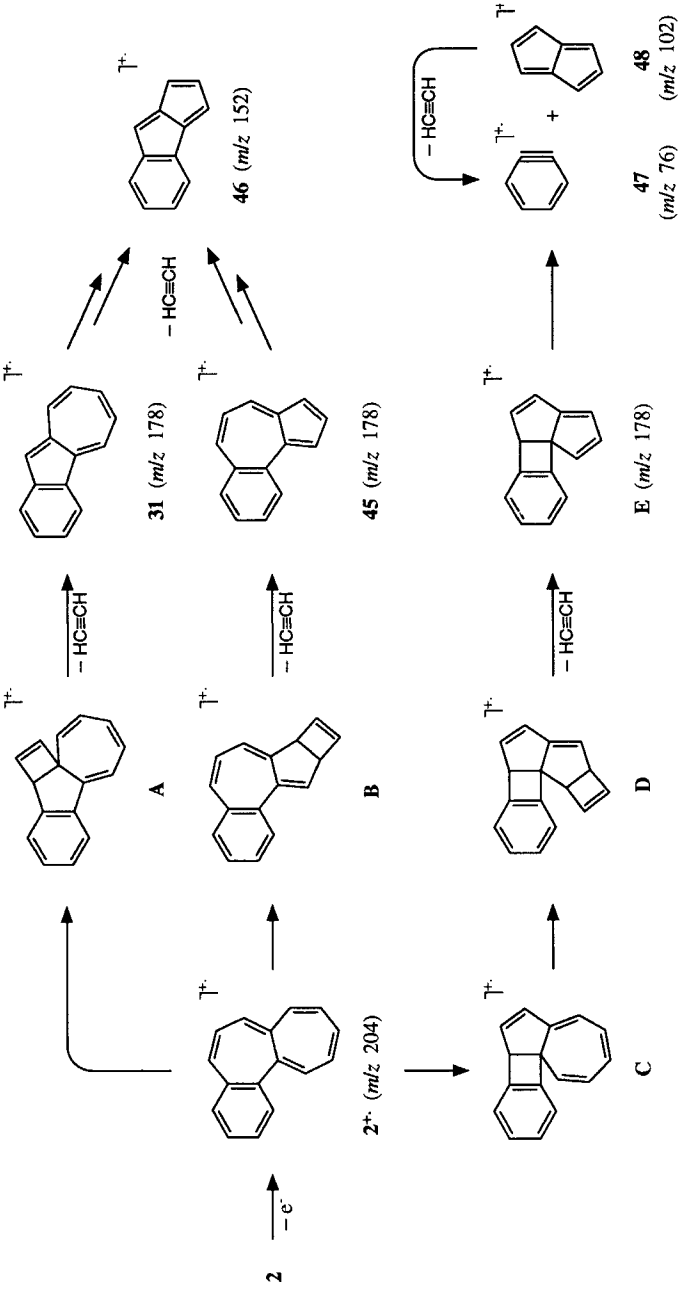


Fig. 7. *GC/MS of* **31** *from an artificial* ca. *1:1 mixture* **2**/**31**

B, which, on loss of ethyne, is transformed into the radical cation of benz[*e*]azulene (**45**). Moreover, aromatic radical cations are formed on both fragmentation paths, indicating the ease of loss of one HC≡CH molecule. That, indeed, **31** might be the crucial intermediate is supported by the MS of **31** (*Fig. 7*) which resembles in its fragmentation behavior, including the $[M-1]^{+\cdot}$ and $[M-2]^{+\cdot}$ peaks, very much the lower-mass region of **2** (*cf. Figs. 6* and *7*). This is also true for the intensity of the $[M-HC{\equiv}CH]^{+\cdot}$ peak at *m/z* 152 which must result from the formation of the radical cation of benzo[*a*]pentalene (**46**). As an antiaromatic structure, its formation should be much less favorable than that of the aromatic structures of **31** or **45** by a similar process. Therefore, we can state that the fragmentation pattern of **2** flows, after loss of HC≡CH, into that of benz[*a*]azulene (**31**) and, possibly, to a certain extent into that of benz[*e*]azulene (**45**).

There is only one exception. The MS of **2** displays a comparably intense mass peak at *m/z* 101 with satellite peaks at *m/z* 102 and 100 which are not present to this extent in the MS of at least **31** (*Fig. 7*). This observation allows the conclusion that $\mathbf{2}^{+\cdot}$ can enter a fragmentation path at the very beginning in competition to those leading to **A** and perhaps **B**. A possibility would be that **C** and then **D** are formed by cylization reactions. The latter structure could lose HC≡CH to form **E** and then, by fragmentation, the radical cations of 1,2-didehydrobenzene (**47**) and pentalene (**48**). The loss of HC≡CH from the latter could also result in the formation of the radical cation of **47** or an equivalent structure. Intramolecular cyclization of **48** are responsible for the loss of H-atoms to give the radical cations at *m/z* 101 and 100. However, more MS experiments

Scheme 15


2
– e⁻
2+· (m/z 204)
C
D
E (m/z 178)
– HC≡CH
47 (m/z 76)
48 (m/z 102)
A
B
31 (m/z 178)
45 (m/z 178)
46 (m/z 152)

would be necessary for a sound analysis and understanding of the fragmentation behavior of **2**.

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Experimental Part

General. Solvents and reagents of the grade '*puriss.*' were used without further purification. Solvents of the grade "*purum*" were distilled and, where necessary, dried (Et_2O and hexane over NaH; CH_2Cl_2 over CaH_2) before distillation. THF, toluene and *o*-xylene were freshly distilled from K or Na. TLC: Aluminum sheets pre-coated with silica gel *60* F_{254} from *Merck*; visualization by UV light. Column chromatography (CC) and flash chromatography (FC): on silica gel *60* (40–63 mm), *Chemie Uetikon AG* or aluminum oxide, *Fluka*, type *5016 A* basic, *Brockmann* grade IV. HPLC: *Bischoff* HPLC pump; *Waters 991*, photodiode-array detector; stationary phase: *Spherisorb* nitrile, 12.5 cm, 4.0 mm, 3 µm, or *Spherisorb ODS2*, C_{18}, 25 cm, 4 mm, 5 µm; mobile phase hexane or MeCN/H_2O. M.p. (not corrected): *Mettler-FP5/52* apparatus. UV/VIS Spectra: *Perkin-Elmer* spectrophotometer, model *Lambda 9*, λ in nm (log ε). IR Spectra: *Perkin-Elmer* spectrophotometer, model *FT-IR 1600*; $\tilde{\nu}_{max}$ in cm^{-1}. ^{1}H-NMR Spectra: *Bruker ARX 300* and *Bruker AMX 600* spectrometer; δ in ppm rel. to internal Me_4Si (= 0 ppm), *J* in Hz. ^{13}C-NMR Spectra: *Bruker ARX 300* and *Bruker AMX 600* spectrometer; δ in ppm rel. to $CDCl_3$ (δ(C) = 77.0 ppm, *t*, ^1J(C, D) = 31.5 Hz), Assignments were confirmed by ^{1}H, ^{1}H-correlation data (DQF-COSY, NOESY), one-bond ^{1}H, ^{13}C correlation data (HSQC), and long-range ^{1}H, ^{13}C-correlation data (HMBC). MS: *Finnigan MAT 90* (CI and *SSQ 700* (EI, 70 eV); *m/z* (rel. %). GC-MS: *Hewlett-Packard HP-5971 Series* (mass-selective detector (EI, 70 eV)) and *HP-5890 Series II* (GC); carrier gas: He. GC Conditions for *Sect. 1*: WCOT capillary column *HP-5*, 30 min; injector temp. 320°, starting temp. 200° for 4 min, rate 10°/min, end temp. 295° for 5 min; GC conditions for *Sect. 2*: *WCOT* capillary column *HP-5*, 15 min; injector temp. 280°, starting temp. 150° for 2 min, rate 10°/min for 7 min and 20°/min for 3 min, end temp. 280° for 4 min. Elemental analyses were performed by the Mikroanalytisches Laboratorium des Organisch-chemischen Institutes der Universität Zürich.

1. Benzo[*a*]heptalene (2) *via* 5,6,7,10,11,12- and 5,6,7,8,9,10-Hexahydro-7-oxobenzo[*a*]heptalene (19a and 19b, resp.). – 1.1. *{2-[2-(Methoxycarbonyl)ethyl]phenylmethyl}triphenylphosphonium Bromide* (**9**). 1.1.1. *1,2-Dihydro-3-methoxynaphthalene* (**20**). β-Tetralone (39.7 g, 0.27 mol) and trimethyl orthoformiate (32.1 g, 0.30 mol) were mixed and cooled to −6°. At this temp., vacuum-dried (92°/2 mbar, 2 h) TsOH (0.26 g, 1.37 mmol) was added within 5 min under vigorous stirring. The temp. was raised to 20° within 30 min and stirring continued at r.t. for 8 h. Formed MeOH and HCOOMe were removed under reduced pressure at 40–60° and the residue distilled at 97°/0.08 mbar: **20** (38 g, 87%). Colorless liquid (GC purity: *ca.* 98%).

Data of **20**: R_f (hexane/AcOEt 3:1) 0.59. IR (film): 3061*m*, 3012*s*, 2939*s*, 2890*s*, 2834*s*, 1903*vw*, 1646*vs*, 1601*m*, 1571*vs*, 1486*vs*, 1463*s*, 1452*s*, 1438*s*, 1384*vs*, 1321*s*, 1296*m*, 1260*vs*, 1194*vs*, 1174*vs*, 1155*vs*, 1108*s*, 1038*s*, 1022*s*, 974*m*, 934*w*, 888*s*, 866*w*, 812*vs*, 783*m*, 754*vs*, 727*s*, 652*vs*, 588*w*, 546*w*, 507*vw*, 458*w*. ^{1}H-NMR (300 MHz, $CDCl_3$): 7.13–6.94 (*m*, 4 arom. H); 5.54 (*s*, H–C(4)); 3.70 (*s*, MeO); 2.88 (m_c (*t*-like), *AA'BB'*, CH_2(2)); 2.40 (m_c (*t*-like), *AA'BB'*, CH_2(1)). ^{13}C-NMR (75.5 MHz, $CDCl_3$); 160.32 (*s*, C(3)); 135.51, 132.03 (2*s*, 2 arom. C), 127.00, 126.51, 124.75, 124.40 (4*d*, 4 arom. C); 96.23 (*d*, C(4)); 54.76 (*q*, MeO); 28.61, 27.37 (2*t*, 2 CH_2). CI-MS: 162 (12), 161 (100, $[M + H]^+$), 160 (21, M^+). Anal. calc. for $C_{11}H_{12}O$ (160.22): C 82.46, H 7.55; found: C 82.40, H 7.68.

1.1.2. *Methyl 3-[2-(Hydroxymethyl)phenyl]propanoate* (**21**). Compound **20** (17.96 g, 0.112 mol) was dissolved in a dry 3:1 mixture MeOH/CH_2Cl_2 (360 ml) and cooled to −78°. At this temp., an O_2/O_3 mixture (*ca.* 5% O_3) was introduced through a glass fritte at a rate of 85 l/h until O_3 was not longer absorbed (after *ca.* 1 h). The O_2/O_3 stream was substituted by an N_2 stream, and, after 1 h, $NaBH_4$ (8.48 g, 0.224 mmol) was added portionwise during 30 min at −78°. The temp. was slowly raised to 0° and stirring was continued during 3.5 h. Glacial AcOH (15 ml) was added at −30° and the mixture worked up in the usual way to give **21** (20.85 g, 96%). Colorless oil after drying in high vacuum.

Data of **21**: R_f (hexane/AcOEt 1:1) 0.37. IR (film): 3412*s* (br.), 2951*s*, 1736*vs*, 1604*w*, 1491*m*, 1438*vs*, 1367*s*, 1294*s*, 1264*s*, 1204*vs*, 1104*m*, 1012*s*, 904*w*, 840*w*, 758*s*, 611*w*. ^{1}H-NMR (300 MHz, $CDCl_3$): 7.38–7.18 (*m*, 4 arom. H); 4.73 (*d*, ^3J = 5.2, CH_2OH); 3.66 (*s*, MeO); 3.04 (*t*, ^3J = 7.6, CH_2(2)); 2.70 (*t*, ^3J = 7.6, CH_2(3));

2.22 (br. *t*, OH). ^{13}C-NMR (75.5 MHz, $CDCl_3$): 173.65 (*s*, C=O); 138.68, 138.50 (2*s*, 2 arom. C); 128.95, 128.91, 128.12, 126.63, (4*d*, 4 arom. C); 63.07 (*t*, CH_2OH); 51.66 (*q*, MeO); 35.14 (*t*, C(2)); 26.92 (*t*, C(3)). EI-MS: 194 (36, $M^{+\cdot}$), 192 (11), 191 (11), 190 (14), 177 (9), 176 (53, $[M - H_2O]^+$), 163 (29, $[M - OMe]^+$), 162 (59), 161 (27), 160 (11), 159 (9), 148 (11), 145 (38), 144 (17), 134 (28), 133 (50), 132 (18), 131 (29), 130 (21), 129 (12), 121 (12), 120 (39), 119 (62), 118 (21), 117 (100, $[M - (H_2O + COOMe)]^+$), 116 (74), 115 (57), 107 (79), 105 (39), 104 (33), 103 (31), 102 (10), 93 (12), 92 (16), 91 (93), 89 (14), 88 (14), 79 (30), 78 (24), 77 (57), 65 (19), 63 (16), 59 (11), 51 (23), 50 (10), 39 (17). Anal. calc. for $C_{11}H_{14}O_3$ (194.23): C 68.02, H 7.27; found: C 67.74, H 7.51.

1.1.3. *Methyl 3-[2(Bromomethyl)phenyl]propanoate* (**46**). Alcohol **21** (20.0 g, 0.103 mol) and Ph_3P (28.4 g, 0.108 mol) were dissolved in precooled CH_2Cl_2 (250 ml). At −30°, *N*-bromosuccinimide (19.1 g, 0.104 mol) was added portionwise under stirring. After additional stirring at −30° for 20 min, the cooling bath was removed. The temp. raised within 15 min to 0°. Stirring was continued for 75 min at r.t. The mixture was then added under vigorous stirring to hexane (1000 ml) which contained a suspension of *Celite* (*ca.* 10 g). The solid (*Celite*, Ph_3PO, and succinimide) was removed by filtration and the filtrate evaporated. The residue, which contained a colorless solid, was further purified by filtration over silica gel (200 g, hexane/Et_2O 2:1): title compound (23.6 g, 89%) as a colorless oil which was not further purified. R_f (hexane/Et_2O 1:1) 0.50. IR (film): 3022*w*, 2951*m*, 1737*vs*, 1604*vw*, 1493*m*, 1436*s*, 1366*m*, 1290*m*, 1212*s*, 1170*s*, 1083*w*, 1023*w*, 985*w*, 874*w*, 838*w*, 762*s*, 607*s*, 745*w*. ^{1}H-NMR (300 MHz, $CDCl_3$): 7.36–7.18 (*m*, 4 arom. H); 4.57 (*s*, CH_2Br); 3.69 (*s*, MeO); 3.08 (m_c (*t*-like), *AA'BB'*, CH_2(3)). ^{13}C-NMR (75.5 MHz, $CDCl_3$): 173.08 (*s*, C=O); 129.40, 135.60 (2*s*, 2 arom. C); 130.68, 129.42, 129.16, 126.96 (4*d*, 4 arom. C); 51.67 (*q*, MeO); 34.76 (*t*, C(2)); 31.39 (*t*, CH_2Br); 27.08 (*t*, C(3)). CI-MS: 277 (10), 276 (100), 274 (100, $[M + NH_4]^+$), 177 (16, $[M - Br]^+$). Anal. calc. for $C_{11}H_{13}BrO_2$ (257.13): C 51.38, H 5.10; found: C 51.46, H 5.15.

1.1.4. *Formation of* **9**. Compound described in *1.1.3* (18.64 g, 0.073 mol) was dissolved in dry toluene (600 ml), Ph_3P (19.67 g, 0.075 mol) was added, and the mixture heated at reflux under N_2 for 45 h. The formed precipitate was isolated by filtration at 0°, washed with ice-cooled Et_2O, and dried at 55°/high vacuum: **9** (36.5 g, 97%). Colorless crystals.

Data of **9**: M.p. 218.1–218.8°. IR (KBr): 3482*w*, 3052*m*, 2985*m*, 2960*m*, 2840*m*, 2877*s*, 1721*vs*, 1602*w*, 1586*w*, 1495*w*, 1486*m*, 1435*vs*, 1417*m*, 1344*m*, 1266*s*, 1177*m*, 1110*vs*, 1050*w*, 1019*m*, 996*m*, 950*w*, 905*vw*, 881*vw*, 851*w*, 789*s*, 749*vs*, 726*m*, 715*m*, 692*vs*, 614*vw*, 601*vw*, 537*m*, 508*vs*, 456*w*. ^{1}H-NMR (300 MHz, $CDCl_3$): 7.85–7.79 (*m*, 3 arom. H); 7.67–7.61 (*m*, 12 arom. H); 7.26–7.22, 7.06–7.00 (2*m*, each 2 arom. H); 5.32 (*d*, ^2J(H, P) = 14.1, CH_2P); 3.63 (*s*, MeO); 2.37, 2.11 (2*t*, ^3J = 8.4, CH_2CH_2). ^{13}C-NMR (75.5 MHz, $CDCl_3$): 172.66 (*s*, C=O); 140.60, 140.52 (2*s*); 134.94, 134.90, 133.85, 133.72, 131.56, 131,49, 140.04, 129.87, 129.23, 129.19, 128.88, 128.83, 126.98, 126.94. (14*d*, partially multiple intensity), 124.92 (*s*); 124.81 (*s*); 117.54 (*s*); 116.40 (*s*); 51.49 (*q*, MeO); 34.14 (*t*, CH_2); 27.59, 26.97 (*dt*, CH_2P); 26.29 (*t*, CH_2). CI-MS: 279 (13), 276 (5), 274 (6), 264 (9), 263 (94, $[Ph_3P + H]^+$), 181 (10), 180 (100), 177 (6), 163 (10), 161 (13). Anal. calc. for $C_{29}H_{28}BrO_2P$ (519.43): C 67.06, H 5.43; found: C 66.75, H 5.66.

1.2. *Ethyl 2-(*trans*-2-Ethenylcyclopropyl)-2-oxoethanoate* (**7**). 1.2.1. *Ethyl 3-Diazo-2-oxopropanoate* (**6**). The procedures described by *Ernest* [43], and by *Ratusky* and *Šorm* [44] were slightly modified. CH_2N_2 was generated in the usual manner from *p*-toluenesulfonyl-*N*-methyl-*N*-nitrosamide (50.0 g, 0.233 mol) and co-distilled with Et_2O into a cooled flask (−10 to 20°) that contained already a small amount of Et_2O (25 ml). To the etheral solution of CH_2N_2 was dropped, within 20 min under vigorous stirring and cooling to −5 to −15°, a soln. of ClCOOEt (8.54 g, 0.063 mol) in Et_2O (60 ml). The mixture was warmed up to r.t. within 45 min and stirring continued for 1 h at this temp. The excess of CH_2N_2 was distilled off with Et_2O at 35° and destroyed with PhCOOH. When the volume of the mixture had been reduced to 60 ml, the mixture was cooled to −40°, leading to the precipitation of most of **6** (6.51 g, 73%) as yellow crystals in a purity of *ca.* 95% (GC evidence). The mother liquor gave on further removal of Et_2O a brownish oil which consisted mainly of ethyl 2-(chloromethyl)oxirane-2-carboxylate (84%) and only to an extent of 5% of **6** (GC analysis). The synthesis of **6** was repeated 3 times under the same conditions and gave crystalline **6** in an average yield of 72%.

Data of **6**: R_f (hexane/AcOEt 1:1) 0.46. M.p. 72.3–74.5° (dec.) ([48]: 72.5–74°; [49]: 74–75°). IR (KBr): 3457*w*, 3239*w*, 3080*vs*, 2996*m*, 2942*w*, 2908*w*, 2431*vw*, 2158*vs*, 2104*vs*, 1740*vs*, 1698*m*, 1622*vs*, 1598*vs*, 1476*m*, 1458*w*, 1442*w*, 1377*vs*, 1354*vs*, 1260*vs*, 1152*s*, 1112*vs*, 1074*s*, 1021*vs*, 929*m*, 868*m*, 803*vs*, 638*s*, 568*s*, 484*w*. ^{1}H-NMR (300 MHz, $CDCl_3$): 6.18 (*s*, $CH{=}N_2$); 4.35 (*q*, ^3J = 7.1, CH_2O); 1.38 (*t*, ^3J = 7.1, $MeCH_2$). ^{13}C-NMR (75.5 MHz, $CDCl_3$): 176.85 (*s*, C(2)); 160.23 (*s*, C(1)); 62.81 (*t*,CH_2O); 56.86 (*d*, $CH{=}N_2$); 13.85 (*q*, $MeCH_2$). CI-MS: 225 (4), 177 (3), 161 (5), 160 (100, $[M + NH_4]^+$), 143 (13, $[M + H]^+$). Anal. calc. for $C_5H_6N_2O_3$ (142.12): C 42.26, H 4.26, N 19.71; found: C 42.47, H 4.38, N 19.50.

1.2.2. *Formation of* **7**. $[Rh_2(OAc)_4]$ (0.026 g) was suspended in CH_2Cl_2 (130 ml), stirred for 30 min, and cooled to −40°. At this temp., buta-1,3-diene (*ca.* 2.5 g, 46.2 mmol) was condensed into the soln., followed by the

dropwise addition of a soln. of **6** (6.56 g, 46.2 mmol) in CH_2Cl_2 (525 ml) within 9.7 h. During this period, additional amounts of buta-1,3-diene (in total 15 g, 0.277 mol) were also condensed into the mixture. Stirring was continued for 19.5 h at r.t. A last amount of buta-1,3-diene (2.5 g, 46.2 mmol) was added, and CH_2Cl_2 was distilled off at 30° to yield a yellow oil (7.78 g). A part of this oil (1.022 g) was chromatographed on silica gel (40 g) with hexane/CH_2Cl_2 1:1 to give three fractions. The first one contained **7** (0.353 g, 35%), the second one (0.071 g) a mixture of **7** (7%) and an unidentified side product, and the third one (0.298 g, 29%) ethyl 4,7-dihydrooxepine-2-carboxylate. A residual amount of the oil (6.76 g) was chromatographed on silica gel (275 g) with hexane/Et_2O 10:1 whereby the chromatography was stopped after **7** (2.53 g, 37%) had been eluted.

Data of **7**: R_f (hexane/AcOEt 4:1) 0.40; R_f (CH_2Cl_2) 0.47. IR (film): 3087*vw*, 2985*m*, 1751*vs* (sh), 1731*vs*, 1712*vs*, 1638*m*, 1445*m*, 1386*m*, 1367*m*, 1294*m*, 1264*vs*, 1202*w*, 1090*vs*, 1051*s*, 1015*m*, 990*m*, 913*m*, 837*m*, 765*w*, 726*w*, 661*vw*. ^{1}H-NMR (300 MHz, $CDCl_3$): 5.47 (*ddd*, *M* of *ABMX*, $^3J_{AM}$ = 18.4, $^3J_{BM}$ = 10.1, $^3J_{MX}$ = 8.4, CH–C*H*=CH$_2$); 5.21, 5.06 (2 br. *d*, *AB* of *ABMX*, $^3J_{AM}$ = 16.6, $^3J_{BM}$ = 10.1, CH–CH=C*H*$_2$); 4.35 (*q*, ^3J = 7.1, CH$_2$O); 2.81, 2.22, 1.65 (3m_c, 3 CH of cyclopropyl); 1.39 (*t*, ^3J = 7.1, *Me*CH$_2$); 1.29 (m_c, 1 CH of cyclopropyl). ^{13}C-NMR (75.5 MHz, $CDCl_3$): 192.27 (*s*, C=O); 160.89 (*s*, *C*OOEt); 137.32 (*d*, CH=CH$_2$); 115.89 (*t*, CH=*C*H$_2$); 62.52 (*t*,CH$_2$O); 32.01 (*d*, C(1) of cyclopropyl); 27.00 (*d*, C(2) of cyclopropyl); 20.28 (*t*, CH$_2$ of cyclopropyl); 13.98 (*q*, *Me*CH$_2$). CI-MS: 203 (10), 187 (9), 186 (100, $[M + NH_4]^+$), 172 (4), 169 (5, $[M + H]^+$). Anal. calc. for $C_9H_{12}O_3$ (168.19): C 64.27, H 7.19; found: C 63.99, H 7.45.

Data of Ethyl 4,7-Dihydrooxepine-2-carboxylate (**47**): R_f (hexane/AcOEt 4:1) 0.32; R_f (CH_2Cl_2) 0.26. IR (film): 3630*vw*, 3419*vw*, 2982*s*, 2906*m*, 2868*m*, 1726*vs*, 1656*vs*, 1448*s*, 1396*s*, 1368*s*, 1322*s*, 1256*vs*, 1223*s*, 1172*s*, 1126*vs*, 1077*s*, 1049*vs*, 1002*m*, 937*m*, 905*m*, 867*w*, 810*w*, 763*m*, 738*m*, 690*w*, 651*m*, 549*vw*. ^{1}H-NMR (300 MHz, $CDCl_3$): 6.21 (*t*, ^3J = 5.4, H–C(3)); 5.92–5.81 (*m*, H–C(5), H–C(6)); 4.55 (m_c, CH$_2$(7)); 4.24 (*q*, ^3J = 7.1, MeC*H*$_2$); 3.09 (m_c, CH$_2$(4)); 1.31 (*t*, ^3J = 7.1, *Me*CH$_2$). ^{13}C-NMR (75.5 MHz, $CDCl_3$): 164.05 (*s*, C(1)); 148.26 (*s*, C(2)); 130.11 (*d*); 127.86 (*d*); 117.69 (*d*); 67.94 (*t*, CH$_2$O); 61.16 (*t*, CH$_2$O); 27.06 (*t*, C(4)); 14.21 (*q*, *Me*CH$_2$). EI-MS: 169 (17), 168 (25, $M^{+\cdot}$), 96 (5), 95 (88, $[M - COOEt]^+$, 94 (29), 68 (6), 67 (100), 66 (8), 65 (11), 55 (6). Anal. calc. for $C_9H_{12}O_3$ (168.19): C 64.27, H 7.19; found: C 64.57, H 6.90.

1.3. Wittig *Reaction of* **7** *and* **9**. 1.3.1. *In the Presence of Lithium Diisopropylamide (LDA)*. LDA was generated from (i-Pr)$_2$NH (0.338 g, 3.33 mmol) and BuLi (1.35 ml of a 2.47M soln. in hexane, 3.33 mmol) in THF (25 ml) at −70 to −50°. To this soln. was added at −50° a suspension of phosphonium salt **9** (1.88 g, 3.62 mmol) in THF. The orange-colored mixture was warmed up within 1 h to r.t. and stirring continued for additional 80 min. The now red ylide soln. was again cooled to −24° and **7** (0.513 g, 3.05 mmol) added dropwise within 10 min. The mixture turned yellow, and Ph_3PO precipitated. The reaction was completed by stirring at r.t. for 40 min. The mixture was neutralized with 10% aq. HCl soln. and added to 200 ml hexane and *Celite* (5 g) to complete precipitation of Ph_3PO. Filtration and evaporation gave a yellow oil (0.905 g, 92%). The oil was chromatographed on silica gel (36 g) with hexane/AcOEt 15:1 resulting in the isolation of two fraction the first one consisted of a *ca.* 55:45 mixture of *ethyl* (E)- and (Z)-*2-(*trans-*2-ethenylcyclopropyl)-3-{2[2-(methoxycarbonyl)ethyl]phenyl}-prop-2-enoate* ((*E*)- and (*Z*)-**11**, resp.) (0.561 g, 56%), contaminated with small amounts (*ca.* 8%) of the corresponding dimethyl ester of (*Z*)-**11** (^{1}H-NMR evidence). The second fraction contained a mixture of stereoisomers of **22** (0.267 g, 28%) (see *Scheme 3*).

Data of (Z)-**11**: R_f (hexane/Et_2O 3:1) 0.30. IR (film): 3069*w*, 2981*m*, 2952*m*, 1737*vs*, 1716*vs* (sh), 1636*m*, 1484*w*, 1437*m*, 1367*m*, 1297*m*, 1226*vs*, 1193*vs*, 1094*m*, 1021*m*, 987*m*, 950*w*, 901*m*, 863*w*, 755*m*, 674*vw*. ^{1}H-NMR (300 MHz, $CDCl_3$): 7.23–7.03 (*m*, 4 arom. H); 6.73 (*s*, PhC*H*=); 5.52 (*ddd*, *M* of *ABMX*, $^3J_{AM}$ = 17.1, $^3J_{BM}$ = 10.2, $^3J_{MX}$ = 8.3, CH–C*H*=CH$_2$); 5.15, 4.96, (2*dd*, *AB* of *ABMX*, $^3J_{AM}$ = 17.1, $^3J_{BM}$ = 10.2, $^4J_{AX}$ = 1.3, $^4J_{BX}$ = 1.5, CH–CH=C*H*$_2$); 3.96 (*q*, ^3J = 7.1, CH$_2$O); 3.68 (*s*, MeO); 2.91 (m_c, C*H*$_2$COOMe); 2.56 (m_c, PhC*H*$_2$); 1.81, 1.72, 1.16, 0.97 (4m_c, 4 CH of cyclopropyl); 0.90 (*t*, ^3J = 7.1, *Me*CH$_2$). ^{13}C-NMR (75.5 MHz, $CDCl_3$): 173.36 (*s*, *C*OOMe); 168.33 (*s*, *C*OOEt); 140.05 (*d*, *C*H=CH$_2$); 138.03 (*s*, 1 arom. C); 136.66 (*s*, C(2)); 136.04 (*s*, 1 arom. C); 130.51, 128.63, 128.55 (3*d*, 3 arom. C); 127.82 (*d*, C(3)); 126.14 (*d*, 1 arom. C); 113.09 (*t*, CH=*C*H$_2$); 60.42 (*t*, CH$_2$O); 51.58 (*q*, MeO); 34.63 (*t*, *C*H$_2$COOMe); 28.82 (*t*, PhCH$_2$); 24.60, 24.18 (2*d*, 2 CH of cyclopropyl); 14.22 (*t*, CH$_2$ of cyclopropyl); 13.56 (*q*, *Me*CH$_2$). CI-MS: 347 (24), 346 (100, $[M + NH_4]^+$), 329 (17, $[M + H]^+$), 317 (5), 301 (5), 300 (33), 283 (6).

Data of (E)-**11**: R_f (hexane/Et_2O 3:1) 0.25. ^{1}H-NMR (300 MHz, $CDCl_3$): 7.77 (*s*, PhC*H*=); 7.37–7.17 (*m*, 4 arom. H); 5.38 (*ddd*, *M* of *ABMX*, $^3J_{AM}$ = 17.1, $^3J_{BM}$ = 10.2, $^3J_{MX}$ = 8.5, CH–C*H*=CH$_2$); 4.93–4.84 (*m*, *AB* of *ABMX*, CH=C*H*$_2$); 4.26 (m_c (*ABq*), CH$_2$O); 3.65 (*s*, MeO); 2.96 (m_c, C*H*$_2$COOMe); 2.54 (m_c, PhC*H*$_2$); 1.68, 1.48 (2m_c, 2 CH of cyclopropyl); 1.35 (*t*, ^3J = 7.1, MeCH$_2$); 0.92–0.79 (*m*, 2 CH of cyclopropyl). ^{13}C-NMR (75.5 MHz, $CDCl_3$): 173.04 (*s*, *C*OOMe); 167.63 (*s*, *C*OOEt); 140.41 (*d*, *C*H=CH$_2$); 138.99 (*s*, 1 arom. C); 137.90 (*d*, C(3)); 134.21 (*s*, C(2)); 133.26 (*s*, 1 arom. C); 130.21, 128.83, 128.50, 126.13 (4*d*, 4 arom. C); 112.84 (*t*, CH=*C*H$_2$); 60.74 (*t*, CH$_2$O); 51.61 (*q*, MeO); 34.73 (*t*, *C*H$_2$COOMe); 28.69 (*t*, PhCH$_2$); 25.35, 20.04 (2*d*, 2 CH of cyclopropyl); 15.89 (*t*, CH$_2$ of cyclopropyl); 14.30 (*q*, *Me*CH$_2$).

Data of the Mixture of Stereoisomers of **22**: R_f (hexane/Et_2O 3:1) 0.14. IR (film): 3409vw, 3068*m*, 2981*s*, 1748vs (sh), 1714vs, 1636*s*, 1483*m*, 1448*s*, 1398*m*, 1366*s*, 1337*s*, 1248vs, 1158vs, 1078vs, 1022*s*, 988*m*, 950*m*, 899*s*, 755*s*, 660vw, 490vw. ^{1}H-NMR (300 MHz, $CDCl_3$): 7.72, 7.71, 7.70 (3*s*, PhC*H*=, (*E*)-config. double bond); 7.33-7.02 (*m*, 8 arom. H); 6.68, 6.67, 6.65 (3*s*, PhC*H*=, (*Z*)-config. double bond); 5.57–5.30 (*m*, *M* of *ABMX*, CH–C*H*=CH_2, 2 H); 5.16–5.10, 4.97–4.83 (each *m*, *AB* of *ABMX*, CH–C*H*=CH_2, 4 H); 4.24 (m_c, $COOCH_2$Me at (*E*)-config. double bond); 3.95 (m_c, 1 $COOCH_2CH_3$ at (*Z*)-config. double bond); 3.82–3.59 (*m*, O=C–C*H*COOMe), superimposed by 3.65, 3.63, 3.61, 3.60 (4*s*, MeO); 3.19–3.11 (*m*, CH_2); 2.86–2.72 (*m*, 3 H, CH_2); 2.63–2.47 (*m*, 1 H, CH_2); 1.79–1.41 (*m*, each 2 CH of cyclopropyl at (*E*)- and (*Z*)-config. double bond); 1.36–1.29 (*m*, $COOCH_2$*Me* at (*E*)-config. double bond); 1.26–1.09 (*m*, 1 CH of cyclopropyl at (*Z*)-config. double bond); 0.98–0.78 (*m*, 2 CH of cyclopropyl at (*E*)-config. double bond, $COOCH_2$*Me*, 1 CH of cyclopropyl at (*Z*)-config. double bond). ^{13}C-NMR (75.5 MHz, $CDCl_3$): 203.57, 203.33 (2*s*, CH_2*C*=O); 169.44, 168.22, 167.44 (3*s*, *C*OOMe, *C*OOEt); 140.36, 140.25, 140.00, 139.92 (4*d*); 139.12, 138.18 (2*s*); 137.88, 137.44, 137.38 (3*d*); 137.11, 136.65, 136.16, 135.93, 135.85, 134.36, 134.19, 133.58, 133.27 (9*s*); 130.45 (*d*); 130.36 (*s*); 130.34, 130.11, 129.65, 129.49, 128.85, 128.74, 128.60, 128.47, 128.41, 127.82, 126.62, 126.04, 125.99, 125.95 (14*d*); 113.19, 113.14, 112.95, 112.86 (4*t*, CH=*C*H_2); 60.73, 60.51, 60.43 (3*t*, CH_2O); 59.20, 59.11, 58.83, 58.71 (4*d*, O=C–*C*HCOOMe); 52.38 (*q*, MeO); 43.53, 43.38, 43.10 (3*t*, *C*H_2C=O); 31.91, 31.76 (2*t*, PhCH_2CH–COOMe); 27.09, 26.99, 26.89, 26.81 (4*t*, PhCH_2CH_2); 25.44, 25.27, 24.69, 24.59, 24.22, 24.14, 20.07 (7*d*, CH of cyclopropyl); 15.84 (*t*, CH_2 of cyclopropyl at (*E*)-config. double bond); 14.29 (*q*, $COOCH_2$*Me* at (*E*)-config. double bond); 14.24, 14.20, 14.17 (3*t*, CH_2 of cyclopropyl at (*Z*)-config. double bond); 13.65 (*q*, $COOCH_2$*Me* at (*Z*)-config. double bond). CI-MS: 644 (11), 643 (45), 642 (100, $[M + NH_4]^+$), 625 (2, $[M + H]^+$), 579 (4), 533 (3).

1.3.2. *In the Presence of MeONa.* MeONa (1.59 g, 29.5 mmol) was suspended in dry THF (550 ml). The mixture was cooled to −30° and the **9** (16.39 g, 31.6 mmol) added portionwise under stirring. Ylide formation was started by addition of MeOH (0.5 ml). The deprotonation was completed by stirring at r.t. for 3.5 h (−30° to r.t., 1.5 h). The orange-red ylide soln. was cooled again to −15 to −20° and **7** (3.50 g, 20.8 mmol) added within 5 min. A decoloration to light-orange was observed and Ph_3PO precipitated. The temp. was raised to 0° (30 min) and stirring was continued until the temp. reached r.t. (1.5 h). TLC showed that all keto-ester had been consumed. The mixture was neutralized with 10% aq. HCl soln. at −10°. The precipitate was removed by filtration after addition of $MgSO_4$. The filtrate was partially evaporated and residual amounts of Ph_3PO precipitated by addition of hexane. It was removed by filtration and the residual yellow oil of the filtrate (6.61 g, *ca.* 100%) chromatographed on silica gel (92 g) with hexane/Et_2O 3:1. A composite (5.32 g, 81%), consisting of a mixture of 20% of **11** and 80% of the dimethyl ester of **11**, both with an (*E*)/(*Z*) ratio of *ca.* 3:1, was obtained as a colorless oil.

*Data of the (*E*)/(*Z*)-Mixture of* **11** (20%) *and its Dimethyl Ester* (DME, 80%): R_f ((*Z*)-**11**) (hexane/Et_2O 3:1) 0.30; R_f((*E*)-**11** and (*Z*)-DME) 0.25; R_f((*E*)-DME) 0.20. IR (film): 3068*w*, 3000*m*, 2951*s*, 2844*w*, 1738vs, 1725vs, 1635*s*, 1484*m*, 1436vs, 1365*m*, 1250vs, 1197vs, 1152vs, 1069*w*, 987*m*, 900*m*, 836*w*, 770*s*, 659vw, 604vw, 489vw. ^{1}H-NMR (300 MHz, $CDCl_3$): 7.77 (*s*, 0.74 H, PhC*H*=, (*E*)-isomers); 7.37–7.03 (*m*, 4 arom. H); 6.72 (*s*, PhC*H*=, (*Z*)-isomers, 0.26 H); 5.58–5.31 (*m*, *M* of *ABMX*, CH–C*H*=CH_2); 5.18–4.83 (*m*, *AB* of *ABMX*, CH=CH_2); 4.26 (m_c (*AB q*), 0.30 H, CH_2O, (*E*)-**11**); 3.96 (*q*, ^3J = 7.1, 0.10 H, CH_2O, (*Z*)-**11**); 3.81 (*s*, 1.77 H, MeO, (*E*)-DME); 3.68 (*s*, 0.78 H MeO, (*Z*)-isomers); 3.65 (*s*, 2.22 H, MeO, (*E*)-isomers); 3.51 (*s*, 0.63 H, MeO, (*Z*)-DME); 2.99–2.89 (*m*, CH_2COOMe); 2.59–2.51 (*m*, PhCH_2); 1.81, 1.72 (2m_c, 0.52 H, 2 CH of cyclopropyl); 1.68, 1.48 (2m_c, 1.48 H, 2 CH of cyclopropyl, (*E*)-isomers); 1.35 (*t*, ^3J = 7.1, 0.45 H, *Me*CH_2, (*E*)-**11**); 1.16, 0.97 (2m_c, 0.52 H, 2 CH of cyclopropyl, (*Z*)-isomers); 0.93–0.78 (*m*, 1.68 H, 2 CH of cyclopropyl of (*E*)-isomers, *Me*CH_2 of (*Z*)-**11**). ^{13}C-NMR (75.5 MHz, $CDCl_3$): (*E*)- and (*Z*)-DME: 172.97 (*s*, *C*OOMe, (*Z*)); 172.67 (*s*, *C*OOMe, (*E*)); 168.53 (*s*, conj. *C*OOMe, (*Z*)); 167.64 (*s*, conj. *C*OOMe, (*E*)); 140.06 (*d*, *C*H=CH_2, (*E*)); 139.73 (*d*, *C*H=CH_2, (*Z*)); 138.76 (*s*, 1 arom. C, (*E*)); 137.95 (*d*, C(3), (*E*)); 137.84 (*s*, (*Z*)); 137.65 (*d*, (*Z*)); 135.99 (*s*, (*Z*)); 135.50 (*s*, (*Z*)); 133.92 (*s*, C(2), (*E*)); 132.70 (*s*, 1 arom. C. (*E*)); 130.32 (*d*, (*Z*)); 129.95, 128.61 (2*d*, 2 arom. C, (*E*)); 128.40 (*d*, (*Z*)); 128.32 (*d*, 1 arom. C, (*E*)); 128.17 (*d*, (*Z*)); 127.68 (*d*, (*Z*)); 125.91 (*d*, 1 arom. C, (*E*)); 112.91 (*t*, CH=*C*H_2, (*Z*)); 112.66 (*t*, CH=*C*H_2, (*E*)); 51.59 (*q*, MeO, (*E*)); 51.29 (*q*, MeO, (*E*), and (*Z*)); 51.21 (*q*, MeO, (*Z*)); 34.44 (*t*, *C*H_2COOMe, (*E*)); 34.36 (*t*, *C*H_2COOMe, (*Z*)); 28.53 (*t*, PhCH_2, (*Z*)); 28.42 (*t*, PhCH_2, (*E*)); 24.97 (*d*, 1 CH of cyclopropyl, (*E*)); 24.38, 24.01 (2*d*, 2 CH of cyclopropyl, (*Z*)); 19.83 (*d*, 1 CH of cyclopropyl (*E*)); 15.63 (*t*, CH_2 of cyclopropyl, (*E*)); 13.98 (*t*, CH_2 of cyclopropyl, (*Z*)). CI-MS: 346 (18, $[M$(**11**) + $NH_4]^+$), 333 (18), 332 (100, $[M$(DME) + $NH_4]^+$), 329 (7, $[M$(**11**) + $H]^+$), 316 (6), 315 (27, $[M$(DME) + $H]^+$), 300 (16), 283 (24), 282 (7).

1.4. Cope *Rearrangement of the (*E*)/(*Z*)-Mixture of* **11** (20%) *and its Dimetyhl Ester* (80%). The mixture (2.17 g, 6.83 mmol) was dissolved in *o*-xylene (60 ml) and a portion of *o*-xylene (12 ml) was distilled off to remove residual traces of H_2O. The residual soln. was heated under reflux during 54 h. This mixture was stored at −18°

to avoid decomposition. A part of the soln. was evaporated and the residue chromatographed on silica gel with hexane/Et_2O mixture. In this way, pure ethyl *7-{[2-(methoxycarbonyl)ethyl]phenyl}cyclohepta-1,4-diene-1-carboxylate* (**13**) and mixture of **13** and its dimethyl ester were obtained. Both compounds decomposed readily, even under storage at −18°. However, they were stable in *o*-xylene soln. at −18°.

Data of **13**: R_f (hexane/Et_2O 3:1) 0.22. ^{1}H-NMR (300 MHz, $CDCl_3$): 7.19 (m_c, H−C(2)); 7.17–7.07 (*m*, 4 arom. H); 5.87, 5.59 (2m_c, H–C(4), H–C(5)); 4.37 (m_c, H−C(7)); 3.99 (m_c, CH_2O); 3.71 (*s*, MeO); 3.16–2.40 (*m*, 4 CH_2); 1.05 (*t*, ^3J = 7.1, *Me*CH_2). GC-MS: 328 (1, $M^{+\cdot}$), 283 (9), 282 (35), 254 (10), 251 (8), 250 (18), 242 (6), 233 (5), 223 (11), 222 (22), 221 (9), 209 (11), 208 (13), 207 (12), 205 (6), 196 (17), 195 (100), 194 (16), 193 (12), 191 (6), 185 (5), 181 (24), 180 (24), 179 (34), 178 (20), 167 (26), 166 (20), 165 (42), 155 (8), 154 (5), 153 (13), 152 (13), 141 (21), 135 (5), 133 (9), 129 (13), 128 (21), 127 (8), 121 (6), 119 (5), 117 (8), 116 (7), 115 (25), 105 (5), 91 (21), 89 (5), 77 (7).

Data of the Dimethyl Ester of **13** (taken from the mixture with **13**): R_f (hexane/Et_2O 3:1) 0.18. IR (film) of **13** and of its dimethyl ester: 3028*m*, 2950*s*, 2847*w*, 1737v*s*, 1712v*s*, 1641*m*, 1488*m*, 1436*s*, 1366*m*, 1241v*s*, 1172*s*, 1106*m*, 1092*m*, 1034*s*, 986*w*, 892v*w*, 795*w*, 758*s*, 689*w*, 572v*w*. ^{1}H-NMR (300 MHz, $CDCl_3$): 7.21 (m_c, H−C(2)); 7.18–7.06 (*m*, 4 arom. H); 5.85, 5.56 (2m_c, H–C(4), H–C(5)); 4.50 (m_c, H–C(7)); 3.71 (*s*, MeO); 3.55 (*s*, α,β-unsat. COO*Me*); 3.18–2.41 (*m*, 4 CH_2). ^{13}C-NMR (75.5 MHz, $CDCl_3$): 173.67 (*s*, *C*OOMe); 168.38 (*s*, α,β-unsat. *C*OOMe); 141.40 (*s*, C(1)); 139.79 (*d*, C(2)); 137.47, 135.47 (2*s*, 2 arom. C); 129.83, 129.41, 129.10, 128.38, 126.38, 125.92 (6*d*, 4 arom. C, C(4), C(5)); 51.66, 51.58 (2*q*, 2 MeO); 38.04 (*d*, C(7)); 35.13 (*t*, *C*H_2COOMe); 32.25 (*t*, C(3)); 28.22, 27.73 (2*t*, Ph*C*H_2, C(6)). GC-MS: 314 (1, $M^{+\cdot}$), 283 (12), 282 (44), 254 (8), 251 (7), 250 (18), 241 (6), 233 (5), 228 (8), 223 (10), 222 (20), 221 (8), 209 (11), 208 (14), 207 (11), 205 (6), 199 (8), 196 (18), 195 (100), 194 (15), 193 (12), 191 (7), 182 (5), 181 (24), 180 (24), 179 (33), 178 (19), 168 (7), 167 (26), 166 (21), 165 (43), 155 (11), 153 (15), 152 (16), 142 (6), 141 (20), 133 (12), 129 (11), 128 (23), 127 (9), 221 (8), 118 (6), 117 (8), 116 (8), 115 (26), 105 (6), 91 (22), 89 (7), 77 (7), 65 (5), 59 (9).

1.4.1. *Base-Catalyzed Isomerization of the Mixture of* **13** *and Its Dimethyl Ester to Methyl 7-{2-[2-(Methoxycarbonyl)ethyl]phenyl}cyclohepta-1,3-diene-1-carboxylate.* The mixture of **13** and its dimethyl ester (0.435 g, 1.37 mmol) was dissolved in MeOH (10 ml) and MeONa (0.278 g, 5.15 mmol) added. The mixture was heated under reflux during 12 h and afterwards stirred for 3 h at r.t. The usual workup, after neutralization and chromatography on silica gel with hexane/Et_2O 3:1 gave, pure product (0.225 g, 52%). R_f (hexane/Et_2O 3:1) 0.25. IR (film): 3020*m*, 2950*s*, 2845*w*, 1737v*s*, 1706v*s*, 1639*w*, 1602*m*, 1487*m*, 1435v*s*, 1366*m*, 1268v*s*, 1228v*s*, 1172*s*, 1113*w*, 1099*m*, 1085*w*, 1042*m*, 1006*w*, 984*w*, 922*w*, 835v*w*, 813v*w*, 759*s*, 720*m*, 672*w*, 612v*w*, 574v*w*. ^{1}H-NMR (300 MHz, $CDCl_3$): 7.37 (*d*, ^3J = 8.0, H−C(2)); 7.20–7.04 (*m*, 3 arom. H); 6.80 (*dd*, ^3J = 7.5, ^4J = 1.4, 1 arom. H); 6.25 (m_c, H−C(4)); 6.08 (m_c, H−C(3)); 4.73 (m_c, H−C(7)); 3.71, 3.65 (2*s*, 2 MeO); 3.23–3.12 (*m*, 1 H, CH_2); 3.05–2.90 (*m*, CH_2); 2.72–2.60 (*m*, 1 H, CH_2); 2.33–2.25 (*m*, 1 H, CH_2); 2.03–1.81 (*m*, 3 H, CH_2). ^{13}C-NMR (75.5 MHz, $CDCl_3$): 173.65 (*s*, *C*OOMe); 168.37 (*s*, α,β-unsat. *C*OOMe); 142.55 (*d*, C(2)); 141.30 (*s*, C(1)); 137.37, 136.01 (2*s*, 2 arom. C); 135.35 (*d*, C(4)); 129.60, 128.78, 126.70, 126.02, 123.37 (5*d*, 4 arom. C, C(3)); 51.90, 51.59 (2*q*, 2 MeO); 41.18 (*d*, C(7)); 35.31 (*t*, *C*H_2COOMe); 28.18, 27.86, 27.75 (3*t*, Ph*C*H_2, C(5), C(6)). EI-MS: 315 (9), 314 (47, $M^{+\cdot}$), 283 (35), 282 (100), 254 (10), 251 (10), 250 (45), 222 (16), 208 (8), 196 (16), 195 (99), 194 (13), 181 (24), 180 (18), 179 (25), 178 (16), 167 (28), 166 (21), 165 (39), 153 (13), 152 (16), 141 (17), 129 (12), 128 (21), 116 (8), 115 (26), 91 (22), 77 (9), 59 (15), 39 (9). Anal. calc. for $C_{19}H_{22}O_4$ (314.38): C 72.59, H 7.05; found: C 72.53, H 7.05.

1.5. Dieckmann *Reaction of the Product Described in* 1.4.1. Diester (0.190 g, 0.60 mmol) was dissolved in *o*-xylene (5 ml) and slowly added over a period of 11 h to a boiling and stirred suspension of MeONa (0.111 g, 2.06 mmol) in *o*-xylene (10 ml). After additional heating at reflux for 1.5 h, the dark-violet-colored mixture was cooled to 0° and poured on ice in 1% aq. HCl soln. The org. layer was separated, washed, and dried (Na_2SO_4). Removal of *o*-xylene by evaporation in vacuum left a crude oil (0.130 g, 76%) which represented a 3:1 mixture of *methyl 5,10,11,12-tetrahydro-* and *methyl 5,8,9,10-tetrahydro-7-hydroxybenzo[a]heptalene-6-carboxylate* (**17a** and **17b**, resp.) and was further purified by chromatography on silica gel (25 g) with hexane/AcOEt 70:1. A first fraction (0.007 g) contained pure **17b**. A second one (0.059 g) represented a mixture **17a**/**17b**, followed by a third one (0.054 g), consisting of pure **17a**.

Data of **17a**: R_f (hexane/AcOEt 20:1) 0.32. IR (film): 3022*s*, 2949*s*, 2855*s*, 1740*w*, 1707*w*, 1643v*s*, 1601v*s*, 1551*s*, 1486*s*, 1441v*s*, 1362v*s*, 1316v*s*, 1268v*s*, 1233v*s*, 1117v*s*, 1050*m*, 1036*m*, 992*m*, 948*w*, 919*m*, 828*s*, 784*s*, 757*s*, 720*m*, 688*m*, 604v*w*, 500v*w*, 479*w*. ^{1}H-NMR (300 MHz, $CDCl_3$): 12.11 (*s*, OH); 7.46–7.42 (*m*, 1 arom. H); 7.35–7.15 (*m*, 3 arom. H); 6.49 (*d*, ^3J = 11.4, H−C(8)); 6.30–6.21 (*dt*, ^3J = 11.4, 5.7, H−C(9)); 3.82 (*s*, MeO); 3.68 (*d*, $^2J_{AB}$ = 13.7, H_{eq}−C(5)); 2.80–2.70 (*m*, CH_2(12)) superimposed by 2.72 (*d*, $^2J_{AB}$ = 13.7, H_{ax}−C(5)); 2.45–2.20 (*m*, CH_2(10), CH_2(11)). ^{1}H-NOE (400 MHz, $CDCl_3$): 12.11 (*s*, OH) → 3.82 (*s*, MeO); 6.49 (*d*, ^3J = 11.3, H−C(8)) → 6.29–6.21 (*dt*, H−C(9)). ^{13}C-NMR (75.5 MHz, $CDCl_3$): 171.51 (*s*, C(7)); 167.01 (*s*, C=O);

149.15 (*s*, C(7a)); 140.92 (*s*, C(12a)); 139.09 (*s*, C(4a)); 134.87 (*d*, C(9)); 131.37 (*s*, C(12b)); 128.07 (*d*, C(4)); 127.63 (*d*, C(3)); 127.33 (*d*, C(1)); 126.00 (*d*, C(2)); 125.84 (*d*, C(8)); 101.02 (*s*, C(6)); 51.89 (*q*, MeO); 35.87 (*t*, C(11)); 34.56 (*t*, C(12)); 29.77 (*t*, C(5)); 29.15 (*t*, C(10)). EI-MS: 283 (8, $[M + H]^+$), 282 (44, M^+), 250 (7), 224 (18), 223 (100, $[M - COOMe]^+$), 222 (14), 205 (4), 196 (4), 195 (15), 194 (11), 193 (6), 189 (4), 181 (6), 180 (9), 179 (17), 178 (17), 167 (9), 166 (12), 165 (29), 153 (7), 152 (12), 141 (7), 139 (4), 128 (8), 115 (9), 91 (4), 89 (5), 77 (4), 74 (9), 59 (14), 55 (4), 45 (9), 43 (4), 41 (5), 31 (23).

Data of **17b**: R_f (hexane/AcOEt 20:1) 0.37. IR (film): 3019*m*, 2948*s*, 1736*w*, 1708*w*, 1643v*s*, 1598v*s*, 1553*s*, 1485*m*, 1441v*s*, 1361v*s*, 1318v*s*, 1290v*s*, 1236v*s*, 1209v*s*, 1196v*s*, 1117v*s*, 1066*w*, 1048*m*, 1031*s*, 979*w*, 948v*w*, 919*w*, 828*s*, 788*m*, 762*s*, 734*m*, 706*w*, 688*w*, 672*m*, 645v*w*, 587v*w*, 516v*w*, 475*w*, 453v*w*. ^{1}H-NMR (300 MHz, $CDCl_3$): 12.06 (*s*, OH); 7.33–7.18 (*m*, 4 arom. H); 6.46–6.38 (*dt*, ^3J = 11.0, 5.0, H–C(11)); 6.28 (*d*, ^3J = 11.0, H–C(12)); 3.82 (*s*, MeO); 3.70 (*d*, $^2J_{AB}$ = 13.7, H_{eq}–C(5)); 2.77–2.66 (*m*, 1 CH of cycloheptadiene) superimposed by 2.74 (*d*, $^2J_{AB}$ = 13.7, H_{ax}–C(5)); 2.44–2.19 (*m*, 5 CH of cycloheptadiene). ^{1}H-NOE (400 MHz, $CDCl_3$): 12.06 (*s*, OH) → 3.82 (*s*, MeO); 6.28 (*d*, ^3J = 11.0, H–C(12)) → 7.33–7.18 (*m*, 4 arom. H), 6.46–6.38 (*dt*, H–C(11)). ^{13}C-NMR (75.5 MHz, $CDCl_3$): 171.50 (*s*, C(7)); 168.64 (*s*, C=O); 142.98 (*s*); 141.28 (*s*); 137.09 (*s*); 136.47 (*d*); 136.31 (*s*); 131.53, 128.48, 128.33, 126.27, 125.73 (5*d*); 99.79 (*s*, C(6)); 51.85 (*q*, MeO); 36.96, 29.80, 29.43, 27.57 (4*t*, 4 CH_2). EI-MS: 283 (7), 282 (42, $M^{+\cdot}$), 254 (6), 250 (7), 240 (4), 224 (19), 223 (100, $[M - COOMe]^+$), 222 (10), 210 (6), 205 (4), 196 (7), 195 (27), 194 (11), 193 (6), 189 (4), 181 (7), 180 (12), 179 (18), 178 (18), 167 (10), 166 (13), 165 (32), 153 (7), 152 (12), 141 (6), 139 (4), 128 (5), 115 (8), 104 (4), 91 (4), 89 (6), 77 (4), (4 (14), 59 (19), 45 (13), 43 (5), 41 (4), 31 (31).

1.5.1. Dieckmann *Reaction of the Mixture of* **13** (20%) *and Its Dimethyl Ester* (80%). The mixture (0.216 g, 0.68 mmol) was dissolved in *o*-xylene (5 ml) and added within 21 h to a boiling and stirred suspension of MeONa (0.124 g, 2.3 mmol) in *o*-xylene (10 ml). The described workup gave a *ca.* 3:1 mixture **17a**/**17b** (0.122 g, 63%), which contained small amounts of the corresponding ethyl carboxylates.

1.5.2. *With NaH as Base.* In further experiments MeONa was substituted by NaH as a base. Runs with the mixture of **13** and its dimethyl ester (0.4 to 0.6 g) led to yields of 57 to 68% of *ca.* 3:1 mixtures **17a**/**17b**.

1.6. *Formation of 5,6,7,10,11,12- and 5,6,7,8,9,10-Hexahydrobenzo[*a*]heptalen-7-one* (**19a** and **19b**, resp.). The mixture **17a**/**17b** (0.070 g, 0.25 mmol) was dissolved in a mixture of dioxane (2 ml), AcOH (1 ml), and 25% aq. HCl soln. (2 ml), and heated at reflux for 23.5 h. The mixture was extracted with AcOEt and the extract washed with H_2O, sat. aq. $NaHCO_3$ soln., and again H_2O, and dried (Na_2SO_4). The residue of the AcOEt extracts (0.066 g) was chromatographed on silica gel (10 g) with hexane/AcOEt 20:1 to give a pure *ca.* 2:1 mixture (^{1}H-NMR evidence) **19a**/**19b**.

Data of 2:1 Mixture **19a**/**19b**: IR (film): 3059*m*, 3019*s*, 2929v*s*, 2857*s*, 1675v*s*, 1582*m*, 1488*s*, 1448v*s*, 1401*m*, 1350*m*, 1323*m*, 1291*s*, 1263*s*, 1239*s*, 1212*m*, 1113*s*, 955*m*, 941*m*, 916*m*, 879*m*, 758v*s*, 646*w*. ^{1}H-NMR (300 MHz, $CDCl_3$): 7.45–7.42 (*m*, 0.2 arom. H); 7.33–7.10 (*m*, 3.8 arom. H); 6.40 (*dt*, ^3J = 11.1, ^3J = 5.9, 0.2 H, H–C(11) of **19b**); 6.24 (*d*, ^3J = 11.7, 0.8 H, H–C(8) of **19a**); 6.15–6.08 (*m*, 1 H); 2.99–2.64 (*m*, 5 H); 2.48–2.12 (*m*, 5 H). ^{13}C-NMR (75 MHz, $CDCl_3$): **19a**: 205.72 (*s*, C=O); 146.43, 139.85, 138.37 (3*s*); 136.98 (*d*, CH); 135.98 (*s*); 134.52, 127.13, 126.87, 126.80, 126.14 (5*d*, CH); 47.63, 35.60, 31.21, 29.63, 28.91 (5*t*, CH_2). **19b**: 206.38 (*s*, C=O); 141.47, 140.88, 139.63, 138.59 (4*s*); 133.26, 131.26, 130.73, 128.95, 127.51, 127.33, 126.95, 125.87, 125.57, 124.00 (10*d*, CH); 47.54, 46.67, 35.49, 33.32, 29.39, 28.73, 28.62, 27.33, 26.41, 26.13 (10*t*, CH_2). GC-MS: 225 (18), 224 (100, $M^{+\cdot}$), 223 (7), 206 (5), 205 (4), 197 (10), 196 (58, $[M - CO]^+$), 195 (22), 193 (4), 191 (5), 183 (6), 182 (9), 181 (43), 180 (9), 179 (10), 178 (17), 169 (6), 168 (34), 167 (61), 166 (25), 165 (54), 164 (5), 155 (11), 154 (15), 153 (37), 152 (32), 151 (7), 143 (9), 142 (12), 141 (27), 139 (10), 130 (5), 129 (13), 128 (27), 127 (9), 126 (4), 117 (8), 116 (10), 115 (30), 102 (5), 97 (4), 89 (17), 88 (4), 83 (10), 82 (8), 81 (10), 77 (10), 76 (10), 75 (4), 65 (5), 63 (8), 51 (7).

1.6.1. *Hydrolysis of Pure* **17a**. A repetition of the hydrolysis experiment with pure **17a** (0.043 g, 0.153 mmol) gave an oil (0.021 g, 60%) which mainly consisted of **17a** (83%). The rest represented **17b**.

1.7. *5,6,7,10,11,12- and 5,6,7,8,9,10-Hexahydrobenzo[*a*]heptalen-7-ol* (**26a** and **26b**, resp.). To an ice-cooled soln. of a *ca.* 2:1 mixture **17a**/**17b** (0.045 g, 0.200 mmol) and dried $CeCl_3$ (0.049 g, 0.200 mmol) in MeOH (2 ml) was added $NaBH_4$ (0.0076 g, 0.200 mmol) portionwise under stirring. After additional stirring for 15 min, the mixture was worked up by evaporating of MeOH. The yellowish residue was dissolved in 2.5% aq. HCl soln. and Et_2O added. The Et_2O extracts were washed, dried, and evaporated. The solid residue was recrystallized from Et_2O/hexane to yield colorless cubes of a mixture **26a**/**26b** (0.044 g, 97%); m.p. 102°. The second and the third run with **17a**/**17b** (0.111 g and 0.535 g, resp.) led again to the crystalline mixture **26a**/**26b** in 98 and 96% yield; m.p. 128°.

Data of **26a**/**26b**: M.p. 128°. UV/VIS (EtOH): λ_{max} 231 (3.78), 280 (3.84); λ_{min} 221 (3.74), 248 (3.47). IR (KBr): 3431v*s*, 3019*s*, 2941v*s*, 2849*s*, 1482*s*, 1433*s*, 1406*m*, 1340v*s*, 1291*s*, 1163*w*, 1089*s*, 1060v*s*, 946*w*, 832*w*, 760v*s*,

683*m*, 556*s*, 606*m*, 464*m*. ^{1}H-NMR (300 MHz, $CDCl_3$; *ca.* 70:30 mixture **26a**/**26b**): 7.31–7.14 (*m*, 4 arom. H); 6.37 (*d*, ^3J = 11.8, 0.7 H); 6.15 (m_c, 1 H); 6.05 (*d*, ^3J = 11.4, 0.3 H); 4.26 (*dd*, ^3J = 10.4, 6.5, 0.3 H, C*H*(OH)); 4.14 (*dd*, ^3J = 10.0, 6.6, 0.7 H, C*H*(OH)); 2.73–2.03 (*m*, 5 CH_2). ^{13}C-NMR (75 MHz, $CDCl_3$): **26a**: 140.51, 137.91, 135.58, 134.17 (4*s*); 132.67, 125.91, 124.76, 124.54, 124.14, 123.66 (6*d*, CH); 69.04 (*d*, CHOH); 40.28, 32.71, 30.15, 28.67, 28.46 (5*t*, CH_2). **26b**: 142.79, 138.75, 138.14, 129.38 (4*s*); 131.86, 128.40, 125.50, 124.06 (4*d*, CH); 69.57 (*d*, CHOH); 40.12, 31.86, 28.28, 27.32, 25.11 (5*t*, CH_2). CI-MS: 226 (22, M^+), 210 (14), 209 (100). Anal. calc. for $C_{16}H_{18}O$ (226.32): C 84.91, H 8.02; found: C 85.15, H 8.16.

A crystal of the mixture **26a**/**26b** was subjected to an X-ray crystal-structure analysis (see *Sect. 3* as well as *Fig. 1*).

1.8. *5,6,7,10,11,12- and 5,6,7,8,9,10-Hexahydrobenzo[a]heptalene* (**23a**/**23b** and **23c**/**23d**, resp.). Triethylammoniosulfonyl-*N*-methoxycarbonyl azanide (*Burgess*' reagent; 0.047 g, 0.2 mmol) was dissolved in $CHCl_3$ (1 ml) and placed in an ampoule. A mixture **26a**/**26b** (0.044 g, 0.2 mmol), dissolved in $CHCl_3$ (0.5 ml), was added dropwise. The ampoule was sealed and heated at 50°/3 h. TLC showed that all **26a**/**26b** had been consumed. H_2O was added and the aq. layer extracted with CH_2Cl_2. The residue of the dried CH_2Cl_2 extracts was chromatographed on silica gel (8 g) with hexane to yield a mixture of **23a** (*ca.* 80%) and **23b** (*ca.* 18%), accompanied by small amounts of **23c** (*ca.* 0.5%) and **23d** (*ca.* 1.5%).

Data of **23a**/**23b** *and* **23c**/**23d**: For the UV data of the individual components, see *Table 1*. IR (film): 3053*s*, 3017v*s*, 2924v*s*, 2881v*s*, 2854v*s*, 1639*w*, 1483v*s*, 1443v*s*, 1318*m*, 1300*m*, 1263*m*, 1158*m*, 1099*m*, 1042*m*, 832*s*, 795*s*, 747v*s*, 706*s*, 684*m*, 639*m*, 597*w*, 508*w*. ^{1}H-NMR (600 MHz, C_6D_6; *ca.* 85:15 mixture **23a**/**23b**): 7.48 (*d*, ^3J = 7.7, 0.15 arom. H); 7.39 (*d*, ^3J = 7.6, 0.85 arom. H); 7.16–6.34 (*m*, 3 arom. H); 6.46 (*d*, ^3J = 9.0, 0.15 H); 6.11 (*d*, ^3J = 11.1, 0.85 H); 6.03 (*dt*, ^3J = 10.0, 5.6, 0.3 H); 5.93 (*d*, ^3J = 10.0, 0.15 H); 5.90–5.83 (*m*, 1.55 H); 5.76–5.64 (*m*, 1 H); 3.10–2.73 (*m*, 6.0 H); 2.44 (*t*, ^3J = 6.0, 0.5 H); 2.35–2.30 (*m*, 1 H); 2.24–2.17 (*m*, 1 H); 2.10 (*q*, ^3J = 6.0, 2 H); 2.04 (*q*, ^3J = 6.6, 0.5 H); 1.96–1.90 (*m*, 3 H). ^{13}C-NMR (75 MHz, $CDCl_3$): Main isomer: 143.60, 140.18, 139.19, 134.27 (4*s*); 133.25, 131.53, 129.53, 127.65, 127.35, 127.09, 126.37, 125.62 (8*d*, CH); 35.59, 40.12, 34.63, 33.26, 30.49 (4*t*, CH_2). Other three isomers: 146.12, 144.30, 141.17, 140.07, 139.23, 138.68, 138.01, 137.48 (8*s*); 134.10, 133.12, 132.36, 130.79, 130.42, 127.87, 127.84, 127.54, 127.42, 127.03, 126.79, 126.57, 126.5, 125.76, 125.55, 124.80 (16*d*, CH); 36.35, 34.69, 34.43, 34.36, 32.74, 32.03, 30.93, 28.57 (8*t*, CH_2). GC/MS (main isomer): 210 (3), 209 (17), 208 (100, $M^{+\cdot}$), 207 (13), 202 (5), 170 (1), 194 (13), 193 (81), 192 (18), 191 (18), 190 (7), 189 (12), 181 (12), 180 (68), 179 (99), 178 (100), 177 (89), 176 (10), 167 (23), 166 (24), 165 (94), 165 (7), 164 (7), 163 (5), 154 (10), 153 (16), 152 (33), 151 (10), 142 (6), 141 (18), 139 (9), 129 (8), 128 (21), 127 (7), 115 (22), 102 (6), 101 (5), 95 (8), 94 (9), 91 (6), 89 (24), 88 (7), 82 (11), 77 (7), 76 (11), 63 (6).

Formation of **2**. $Ph_3C^+BF_4^-$ (0.223 g, 0.68 mmol) was dissolved in $CHCl_3$ (1 ml) in a glove-box and transferred into an ampoule. A soln. of the mixture of **19a**–**19d** (0.056 g, 0.27 mmol) in $CHCl_3$ (0.5 ml) was added, and the mixture heated at reflux in the sealed ampoule. Et_2O (1 ml) and then hexane (3 ml) were added whereby the dark green soln. became turbid. The again sealed ampoule was stored at 4° for 1 h. The dark green precipitate was filtered off under N_2, washed with hexane, dissolved in CH_2Cl_2 (1 ml), and saturated with Me_3N. The deep-yellow soln. was stirred for 30 min and then evaporated. The yellow-green residue was dissolved in CH_2Cl_2 and two times chromatographed on silica gel (1.8 g) with hexane to yield a deeply yellow material which consisted of **2** (*ca.* 30%) and Ph_3CH (*ca.* 70%) according to ^{1}H-NMR.

Data of **2** *from the Mixture with* Ph_3CH: UV/VIS (HPLC, MeCN/H_2O 80:20): λ_{max}, 222, 258, 348; λ_{min} 214, 254. ^{1}H-NMR (600 MHz, $CDCl_3$; signal of Ph_3CH at 5.56 ppm); olefinic region of **2**: 6.67 (*d*, ^3J = 11.8, H–C(5)); 6.48 (*dd*, ^3J = 11.4, 7.0, H–C(6)); 6.27 (*dd*, ^3J = 12.0, 6.1, H–C(11)); 6.25 (*dd*, ^3J = 10.9, 6.3, H–C(10)), 6.09 (*dd*, ^3J = 10.9, 6.4, H–C(9)); 5.82 (*d*, ^3J = 11.0, H–C(8)); 5.67 (*d*, ^3J = 6.7, H–C(7)); 5.42 (*d*, ^3J = 6.4, H–C(12)). GC/MS: 205 (20), 204 (100, $M^{+\cdot}$), 203 (89), 202 (72), 201 (18), 200 (19), 179 (13), 178 (81, $[M - C_2H_2]^+$), 177 (6), 190 (7), 176 (13), 152 (13, $[M - 2\,C_2H_2]^+$), 151 (4), 150 (3), 102 (6), 101 (31), 100 (13), 89 (20), 88 (13), 87 (5), 86 (1), 76 (14), 75 (6), 63 (3).

1.10. *Formation of the* p-*Tosylhydrazones* **24a** *and* **24b** *from the Mixture* **19a**/**19b**. A 2:1 mixture **19a**/**19b** (0.048 g, 0.21 mmol) was dissolved in MeOH (5 ml). *p*-Tosylhydrazine (0.039 g, 0.21 mmol) and 1 drop of H_2SO_4 were added, and the mixture was heated at reflux. MeOH was evaporated and the residue chromatographed on silica gel (4 g) with Et_2O/hexane 3:2. The *p*-tosylhydrazones of **24a** and **24b** (0.059 g, 70%) were obtained as a mixture of (*E*)- and (*Z*)-isomers with respect of the C=N bond.

Data of the (E)/(Z)-Mixture **24a**/**24b**: M.p. 155–157°. R_f (Et_2O/hexane 1:1): 0.21 and 0.18. IR (KBr): 3219*s*, 3020*w*, 2924*m*, 2852*w*, 1598*w*, 1489*w*, 1445*m*, 1396*s*, 1333v*s*, 1308*m*, 1294*m*, 1167v*s*, 1092*w*, 1044*m*, 910*m*, 815*m*, 754*s*, 706*m*, 688*s*, 546*s*. ^{1}H-NMR (300 MHz, $CDCl_3$): 7.83–7.79 (*m*, 2 arom. H); 7.28–7.00 (*m*, 6 arom. H); 6.35–7.32 (*m*, 0.5 H); 6.07–6.01 (*m*, 1.5 H); 2.82 (*t*, ^3J = 5.9, 2 H); 2.59–2.54 (*m*, 3 H); 2.28 (*t*, ^3J = 6.2, 1 H); 2.41 (*s*, Me); 2.28–2.14 (*m*, 4 H). ^{13}C-NMR (75 MHz, $CDCl_3$): 159.38 (*s*, C=N), 145.07, 244.32, 143.41, 141.95,

141.77, 139.70, 138.96, 138.81, 138.66, (9*s*); 138.22, 136.61 (2*d*, =CH–); 135.49, 133.96 (2*s*), 133.78 (*d*, =CH–); 133.41 (*s*); 132.64, 131.19, 129.57, 129.49, 128.80, 128.55, 128.48, 128.45, 128.34, 127.82, 127.72, 127.47, 127.29, 127.20, 127.11, 126.97, 126.91, 123.25 (18*d*, =CH–); 43.35, 37.22, 37.12, 36.82, 36.25, 35.78, 34.96, 34.51, 33.55, 32.70, 32.54, 32.22, 31.34, 31.02, 30.60, 29.06, 28.16, 27.83, 26.95, 26.70 (4×5*t*, CH_2); 21.84, 21.79 (2*q*, Me). CI-MS: 396 (6, $[M+4]^+$), 395 (24, $[M+3]^+$), 394 (29, $[M+2]^+$), 393 (100 $[M+1]^+$).

2. Benzo[*a*]heptalene (2) by Stepwise Degradation of Dimethyl Benzo[*a*]heptalene-6,7-dicarboxylate (30). – 2.1. *Thermal Reaction of the Benz[*a*]azulene* (**31**) *with Dimethyl Acetylene-dicarboxylate (ADM).* Azulene **31** (100 mg, 0.56 mmol) and ADM (0.1 ml, 0.84 mmol) were heated in mesitylene (2 ml) in a sealed flask for 24 h at 160°. The mixture was subjected to CC (silica gel; CH_2Cl_2/hexane 1:1) yielding in a first fraction the expected diester **30** (97.8 mg, 55%), in a second one *dimethyl benzo[*a*]cyclopent[*cd*]azulene-1,2-dicarboxylate* **32**; 6.4 mg, 4%), and in a third one *dimethyl 10c-[(Z)-1,2-bis(methoxycarbonyl)ethenyl]-10b,10c-dihydrobenzo[*a*]cyclopent-[*cd*]azulene-1,2-dicarboxylate* ((*Z*)-**33**; 18.4 mg, 7%).

Data of **30**: See [7]. For the X-ray crystal-structure analysis of **30**, see *Table 6*, and *Sect. 3*.

Data of **32**: See [7].

Data of **33**: Yellow foam. ^{1}H-NMR (600 MHz, $CDCl_3$): 7.74 (*dd*, ^3J(10.9) = 7.7, ^4J(10.8) = 0.7, H–C(10)); 7.64 (br. *d*, ^3J(7,8) = 7.8, H–C(7)); 7.39 (*td*, ^3J(9,8) ≈ ^3J(9,10) ≈ 7.6, ^4J(9,7) = 1.0, H–C(9)); 7.32 (br. *t*, ^3J(8,7) = ^3J(8,9) = 7.8, H–C(8)); 7.13 (*d*, ^3J(6,5) = 6.8, H–C(6)); 6.86 (*dd*, ^3J(5,4) = 10.9, ^3J(5,6) = 6.8, H–C(5)); 6.73 (*d*, ^3J(4,5) = 10.9, ^3J(4,3) = 6.8, H–C(4)); 6.68 (*d*, ^3J(3,4) = 6.8, H–C(3)); 5.57 (*s*, H–C(C(2')), 4.97 (*s*, H–C(10b)); 3.88 (*s*, MeOCO–C(1)); 3.87 (*s*, MeOCO–C(2)); 3.62 (*s*, MeOCO–C(1')); 3.61 (*s*, MeOCO–C(2')). ^{13}C-NMR (150 MHz, $CDCl_3$): 166.73 (O=*C*–C(1')); 165.07 (O=*C*–C(2)); 164.96 (O=*C*–C(2')); 163.63 (O=*C*–C(1)); 146.50 (C(1')); 142.46 (C(2)); 139.16 (C(6b)); 138.94 (C(10a)); 134.21 (C(1)); 134.07 (C(6a)); 131.51 (C(2a)); 131.38 (C(5)); 130.20 (C(9)); 128.41 (C(4)); 128.24 (C(8)); 126.61 (C(10)); 122.84 (C(3)); 121.28 (C(7)); 119.38 (C(2')); 116.47 (C(6)); 61.32 (C(10b)); 61.24 (C(10c)); 54.54 (*Me*OCO–C(2)); 52.22 (*Me*OCO–C(1)); 52.10 (*Me*OCO–C(1')); 51.83 (*Me*OCO–C(2')). ^{1}H-NOESY (300 MHz, $CDCl_3$): 5.58 (H–C(2')) → 7.12 (H–C(6)); 6.68 (H–C(3)); 3.61 (*Me*OCO–C(2')); 4.97 (H–C(10b)) → 7.74 (H–C(10)), 3.87 (MeOCO–C(1)), 3.62 (MeOCO–C(1')). CI-MS: 481 (27, $[M+1+NH_3]^+$), 480 (100, $[M+NH_3]^+$), 463 (28, $[M+1]^+$), 448 (6, $[M-Me]^+$), 431 (2, $[M-MeO]^+$), 273 (25).

2.2. *Selective Saponification of* **30**. To a soln. of **30** (1.17 g, 3.65 mmol) in boiling MeOH (60 ml) was added a warm soln. of $LiOH \cdot H_2O$ (4.6 g, 0.11 mmol) in H_2O (23 ml). The mixture was stirred for 10 min at 70° (prolonged heating yields the diacid as the main product.), then cooled to 0°, and neutralized with 2M aq. HCl solution. The yellow precipitate was filtered, washed with H_2O, and dried *in vacuo*. 1.0 g (90%) of product as a mixture **36**/**35** in the ratio of 8:1. The pure mono-acid was obtained by repeated crystallization from AcOEt/hexane.

*7-(Methoxycarbonyl)benzo[*a*]heptalene-6-carboxylic Acid* (**36**): Orange plates from AcOEt/hexane. M.p. ~155.7–157.0° (dec. to anhydride **39**). R_f (CH_2Cl_2/MeOH 9:1) 0.49. UV/VIS (MeOH): λ_{max} 223 (4.42), 269 (4.39), 339 (3.67). λ_{min} 213 (4.39), 243 (4.28), 316 (3.60). IR (KBr): 3025*w*, 3000*w*, 2994*w*, 2946*m*, 2822*m*, 2660*w*, 2548*w*, 1708*s*, 1688*s*, 1680*s*, 1610*m*, 1579*m*, 1434*m*, 1424*w*, 1298*s*, 1247*m*, 1210*m*, 1188*m*, 1162*m*, 1106*m*, 763*s*. ^{1}H-NMR (600 MHz, $CDCl_3$): 8.01 (*s*, H–C(5)); 7.47 (*td*, ^3J(2, 1) = ^3J(2,3) = 7.5, ^4J(2,4) = 1.4, H–C(2)); 7.42 (*td*, ^3J(3,2) = ^3J(3,4) = 7.6, ^4J(3,1) = 1.3, H–C(3)); 7.37 (*dd*, ^3J(4,3) = 7.6, ^4J(4,2) = 1.4, H–C(4)); 6.99 (*dd*, ^3J(1,2) = 7.6, ^4J(1,3) = 1.2, H–C(1)); 6.70 (*dd*, ^3J(11,10) = 11.1, ^3J(11,12) = 6.5, H–C(11)); 6.61 (*dd*, ^3J(10, 11) = 11.2, ^3J(10,9) = 6.5, H–C(10)); 6.39 (*dd*, ^3J(9,8) = 11.3, ^3J(9,10) = 6.5, H–C(9)); 6.14 (*d*, ^3J(8,9) = 10.9, H–C(8)); 6.09 (*d*, ^3J(12,11) = 6.4, H–C(12)); 3.64 (*s*, COOMe). ^{13}C-NMR (150 MHz, CD_3OD): 170.47 (O=*C*–C(6)); 169.12 (O=*C*–C(7a)); 143.63 (C(5)); 142.56 (C(12b)); 136.65 (C(4a)); 134.89 (C(12a)); 132.88 (C(2)); 132.84 (C(11)); 132.73 (C(6)); 132.70 (C(10)); 131.53 (C(4)); 131.17 (C(12)); 130.82 (C(1)); 130.40 (C(9)); 129.79 (C(3)); 126.13 (C(8)); 123.52 (C(7)); 52.18 (Me). CI-MS: 307 (31, $[M+1]^+$), 275 (100, $[M-MeO]^+$). For the X-ray crystal-strcture analysis of **36**, see *Table 6* and *Sect. 3*.

*Benzo[*a*]heptalene-6,7-dicarboxylic Acid* (**35**): Orange crystals from AcOEt/hexane. M.p. ~100° (dec. to anhydride **39**). UV/VIS (MeOH): λ_{max} 224 (4.38), 265 (4.42), 296 (sh, 3.97), 340 (3.57); λ_{min} 216 (4.37), 241 (4.27), 322 (3.53). IR (KBr): 3435*w*, 2959*m*, 2603*m*, 1686*s*, 1627*s*, 1577*m*, 1445*m*, 1408*m*, 1362*w*, 1284*s*, 1253*s*, 1219*m*, 1178*m*, 1130*w*, 953*w*, 932*m*, 893*w*, 798*m*, 783*m*, 760*m*, 730*m*, 626*w*, 512*w*. ^{1}H-NMR (600 MHz, CD_3OD): 7.88 (*s*, H–C(5)); 7.51–7.43 (*m*, H–C(2), H–C(3), H–C(4)); 6.97 (*d*, ^3J(1,2) = 7.4, H–C(1)); 6.69 (*dd*, ^3J(11,10) = 11.1, ^3J(11,12) = 6.4, H–C(11)); 6.61 (*dd*, ^3J(10,11) = 11.1, ^3J(10,9) = 6.4, H–C(10)); 6.37 (*dd*, ^3J(9,8) = 10.9, ^3J(9,10) = 6.4, H–C(9)); 6.18 (*d*, ^3J(8,9) = 10.8, H–C(8)); 6.06 (*d*, ^3J(12,11) = 6.4, H–C(12)). ^{13}C-NMR (150 MHz, CD_3OD): 168.11 (O=*C*–C(6)); 167.30 (O=*C*–C(7)); 143.33 (C(7a)); 140.72 (C(5)); 140.54 (C(12b)); 134.92 (C(4a)); 133.01 (C(12a)); 132.49 (C(6)); 131.50 (C(10)); 131.46 (C(11)); 131.42 (C(2)); 130.23

Table 6. *Crystallographic Data of* **30** *and* **36**

Substance	**30**	**36**
Crystallized from	Et_2O/hexane	EtOAc/hexane
Empirical formula	$C_{20}H_{16}O_4$	$C_{19}H_{14}O_4$
Formula weight	320.34	306.32
Crystal color, habit	yellow, prism	orange, plate
Crystal dimensions [mm]	0.18 · 0.22 · 0.50	0.45 · 0.40 · 0.08
Temperature [K]	173 (1)	173 (1)
Crystal system	triclinic	triclinic
Space group	$P\bar{1}$ (# 2)	$P\bar{1}$ (# 2)
Z	2	2
Reflections for cell determination	25	25
2θ Range for cell determination [°]	39–40	38–40
Unit cell parameters a [Å]	9.000 (2)	9.115 (3)
b [Å]	11.215 (4)	11.606 (7)
c [Å]	8.885 (1)	8.448 (3)
α [Å]	96.93 (2)	96.92 (4)
β [Å]	115.13 (1)	115.88 (2)
γ [Å]	95.04 (3)	96.92 (4)
V [Å^3]	796.3 (4)	763.1 (7)
$F(000)$	336	320
D_x[g cm^{-3}]	1.336	1.333
$\mu(MoK_\alpha)$ [mm^{-1}]	0.0928	0.0935
Scan type	$\omega/2\theta$	$\omega/2\theta$
$2\theta_{(max)}$ [°]	55	55
Total reflections measured	3909	3703
Symmetry independent reflections	3675	3487
R_{int}	0.017	0.026
Reflections used [$I > 2\sigma(I)$]	2910	2430
Parameters refined	282	255
Reflection/parameter ratio	10.3	9.53
Final R	0.0530	0.0484
wR	0.0605	0.0466
Weights: p in $w = [\sigma^2(F_o) + (pF_o)^2]^{-1}$	0.005	0.005
Goodness of fit	2.887	2.120
Secondary extinction coefficient	2.75×10^{-6}	–
Final Δ_{max}/σ	0.0001	0.001
$\Delta\rho$ (max; min) [e Å^{-3}]	0.31; −0.23	0.55; −0.30
Range of $\sigma(d(C-C))$[Å]	0.003–0.004	0.003–0.004

(C(4)); 129.42 (C(1)); 129.39 (C(12)); 128.56 (C(3)); 128.19 (C(9)); 125.37 (C(8)); 123.49 (C(7)). CI-MS: 293 (19, $[M + 1]^+$), 292 (100, $M^{+\cdot}$), 275 (9, $[M - OH]^+$).

2.3. *Formation of Pseudoster* **40**. DMF (2.10 ml, 26.78 mmol) in MeCN (12 ml) was reacted with a soln. of $(COCl)_2$ (0.68 ml, 7.88 mmol) in MeCN (6 ml) at 0° under N_2. CO_2 evolved after a short time, and the iminium salt precipitated as a thick paste which was kept stirring by dilution with MeCN. After 5 min at 0°, a mixture **36**/**35** 7:1 (0.96 g, *ca.* 3.15 mmol) was added and the mixture stirred until a clear soln. had been formed. To this soln., MeOH (1.28 ml, 31.50 mmol) was added. After stirring for 10 min at 0° and then for 10 min at r.t., H_2O was added and the mixture extracted with CH_2Cl_2. The CH_2Cl_2 extracts were dried (Na_2SO_4) and the solvent removed. Crystallization from Et_2O/hexane yielded first as by-product the anhydride **39** (50.0 mg, 7%). The mother liquor was subjected to CC (silica gel; hexane/Et_2O 3:1) yielding **40** (609.5 mg, 69%). Filtration of the crude mixture over Alox (act. IV) gave **40** as the sole product.

1,3-Dihydro-1,1-dimethoxybenzo[1,2]heptaleno[4,5-c]furan-3-one (**40**): Red rhombes from hexane/Et_2O. M.p. 144.2–144.4°. R_f (hexane/Et_2O 2:1) 0.41. UV/VIS (hexane): λ_{max} 224 (4.35), 271 (4.39), 283 (sh, 4.35), 308

(sh, 3.39), 375 (3.63); λ_{min} 219 (4.34), 241 (4.17), 338 (3.47). IR (KBr): 3021*w*, 2979*w*, 2942*m*, 1768*s*, 1625*m*, 1584*m*, 1559*w*, 1444*m*, 1301*s*, 1275*m*, 1252*s*, 1187*s*, 1158*m*, 1134*s*, 1068*m*, 1005*m*, 923*s*, 879*m*, 856*m*, 834*m*, 765*s*, 732*s*. ^{1}H-NMR (300 MHz, $CDCl_3$): 7.59 (*td*, $^3J(7,6) = {}^3J(7,8) = 7.5$, $^4J(7.5) = 1.3$, H–C(7)); 7.51 (*s*, H–C(4)); 7.36 (*td*, $^3J(6,5) = {}^3J(6,7) = 7.5$, $^4J(6,8) = 1.3$, H–C(6)); 7.26 (*d*, $^3J(5,6) = 7.5$, H–C(5)); 7.10 (*d*, $^3J(8,7) = 7.7$, H–C(8)); 6.58 (*dd*, $^3J(10,11) = 11.0$, $^3J(10,9) = 7.7$, H–C(10)); 6.41–6.31 (partially superimposed, *m*, H–C(11), and *m*, H–C(12)); 6.20 (*d*, $^3J(13,12) = 11.6$, H–C(13)); 5.73 (*d*, $^3J(9,10) = 7.2$, H–C(9)); 3.46, 3.25 (2*s*, 2 MeO). ^{13}C-NMR (75 MHz, $CDCl_3$): 167.51 (C(3)); 138.06 (C(8a)); 137.22 (C(8b)); 136.92 (C(4)); 136.85 (C(4a)); 136.55 (C(13a)); 134.66 (C(9)); 134.63 (C(7)); 134.12 (C(10)); 132.60 (C(12)); 131.24 (C(5)); 131.12 (C(11)); 130.08 (C(8)); 128.69 (C(6)); 127.42 (C(13)); 126.86 (C(3a)); 125.32 (C(13b)); 119.01 (C(1)); 51.76, 50.95 (2 MeO). EI-MS: 321 (10, $[M + 1]^+$), 320 (54, $M^{+\cdot}$), 289 (69, $[M - MeO]^+$), 261 (37, $[M - (MeO + CO)]^+$), 217 (23), 202 (100, $[M - (MeO)_2C{-}O{-}CO]^+$), 189 (40), 179 (61), 151 (20), 101 (21), 91 (46), 73 (26), 61 (77). Anal. calc. for $C_{20}H_{16}O_4$ (320.34): C 74.99, H 5.03; found: C 74.78, H 4.75.

1,3-Dihydrobenzo[1,2]heptaleno[4,5-c]furan-1,3-dione (**39**): Red crystals from hexane/Et_2O. M.p. 261.9–262.6°. R_f (hexane/Et_2O 2:1) 0.29. UV/VIS (CH_2Cl_2): λ_{max} 258 (4.21), 280 (sh, 4.22), 308 (4.34), 370 (3.80); λ_{min} 251 (4.20), 263 (4.21), 350 (3.77). IR (KBr): 3059*w*, 3023*w*, 1801*s*, 1749*s*, 1543*m*, 1621*m*, 1560*s*, 1520*m*, 1402*w*, 1272*s*, 1250*s*, 1215*s*, 1189*m*, 1137*w*, 1104*m*, 1015*w*, 930*s*, 921*s*, 912*m*, 886*m*, 870*m*, 806*m*, 773*s*, 758*m*, 746*m*, 736*m*, 684*m*, 660*m*, 483*w*. ^{1}H-NMR (600 MHz, $CDCl_3$): 7.73 (*td*, $^3J(7,6) = {}^3J(7,8) = 7.6$, $^4J(7.5) = 1.4$, H–C(7)); 7.62 (*s*, H–C(4)); 7.55 (*dd*, $^3J(5,6) = 7.7$, $^4J(5.7) = 1.0$, H–C(5)); 7.49 (*td*, $^3J(6,5) = {}^3J(6,7) = 7.6$, $^4J(6,8) = 1.0$, H–C(6)); 7.05 (*d*, $^3J(8,7) = 7.7$, H–C(8)); 6.92 (*dd*, $^3J(10,9) = 6.6$, $^3J(10,11) = 11.0$, H–C(10)); 6.91 (*d*, $^3J(13,12) = 11.0$, H–C(13)); 6.82 (*ddd*, $^3J(12,13) = 11.5$, $^3J(12,11) = 1.0$, $^4J(12,10) = 0.9$, H–C(12)); 6.68 (*dd*, $^3J(11,10) = 11.0$, $^3J(11,12) = 7.1$, H–C(11)); 6.13 (*d*, $^3J(9,10) = 7.6$, H–C(9)). ^{13}C-NMR (150 MHz, $CDCl_3$): 164.43 (C(3)); 160.40 (C(1)); 147.92 (C(13a)); 144.83 (C(3a)); 138.49 (C(9)); 137.48 (C(8a)); 136.94 (C(4)); 136.30 (C(12)); 136.21 (C(10)); 136.09 (C(4a)); 136.00 (C(7)); 133.28 (C(11)); 132.33 (C(5)); 131.05 (C(8)); 129.61 (C(6)); 127.39 (C(13)); 125.68 (C(13b)); 115.53 (C(8b)). EI-MS: 274 (100, $M^{+\cdot}$), 248 (15), 202 (86, $[M - OC{-}O{-}CO]^+$), 200 (29), 201 (17), 189 (29), 176 (10), 100 (16), 84 (13). Anal. calc. for $C_{18}H_{10}O_3$ (274.28): C 78.82, H 3.67; found: C 78.95, H 3.72.

2.4. *Reduction of* **40**. To a soln. of **40** (0.427 g, 1.33 mmol) in toluene (40 ml) was added dropwise during 40 min 1M DIBAH soln. in hexane (1.33 ml) at −78°. After stirring for 1 h, a second portion of DIBAH (1.3 ml) was added. The starting material had been consumed after stirring for an additional h. The mixture was quenched at −78° by addition of MeOH (30 ml) and, after reaching −40°, poured into 1M aq. HCl soln. (40 ml). After warming up to r.t., the mixture was extracted with Et_2O. The Et_2O extracts were washed with brine, dried (Na_2SO_4), and the solvent was removed. CC (silica gel; hexane/Et_2O 2:1) gave in a first fraction lactone **41** (0.041 g, 12%), and in a second fraction aldehyde **37** (0.279 g, 72%).

Methyl 6-Formylbenzo[a]heptalene-7-carboxylate (**37**): Yellow crystals from hexane/Et_2O. M.p. 145.2–145.8°. R_f (hexane/Et_2O 1:1) 0.30. UV/VIS (hexane): λ_{max} 226 (4.36), 271 (4.40), 283 (sh, 4.37), 301 (sh, 4.02), 358 (sh, 3.54); λ_{min} 217 (4.33), 243 (4.24). IR (KBr): 3021*w*, 3000*w*, 2945*w*, 2819*w*, 1703*s*, 1686*s*, 1615*m*, 1581*m*, 1560*w*, 1430*m*, 1295*s*, 1249*m*, 1223*m*, 1172*m*, 1160*w*, 1073*m*, 810*m*, 768*m*, 756*m*, 735*w*, 543*w*. ^{1}H-NMR (600 MHz, $CDCl_3$): 9.52 (*s*, CHO); 7.68 (*s*, H–C(5)); 7.51 (*td*, $^3J(2,1) = {}^3J(2,3) = 7.4$, $^4J(2,4) = 1.0$, H–C(2)); 7.43 (*td*, $^3J(3,2) = {}^3J(3,4) = 7.5$, $^4J(3,1) = 1.0$, H–C(3)); 7.39 (*d*, $^3J(4,3) = 7.4$, H–C(4)); 7.05 (*d*, $^3J(1,2) = 7.6$, H–C(1)); 6.66 (*dd*, $^3J(11,10) = 11.1$, $^3J(11,12) = 6.6$, H–C(11)); 6.59 (*dd*, $^3J(10,11) = 11.1$, $^3J(10,9) = 6.6$, H–C(10)); 6.41 (*dd*, $^3J(9,8) = 11.0$, $^3J(9,10) = 6.6$, H–C(9)); 6.18 (*d*, $^3J(8,9) = 11.0$, H–C(8)); 6.06 (*d*, $^3J(12,11) = 6.5$, H–C(12)); 3.68 (*s*, COOMe). ^{13}C-NMR (150 MHz, $CDCl_3$): 192.42 (CHO); 166.88 (*C*OOMe); 151.04 (C(5)); 146.05 (C(7a)); 141.35 (C(12b)); 139.16 (C(6)); 134.96 (C(4a)); 133.31 (C(12a)); 132.62 (C(2)); 131.83 (C(10)); 131.71 (C(11)); 130.99 (C(12)); 130.32 (C(4)); 130.01 (C(1)); 129.51 (C(9)); 128.58 (C(3)); 125.33 (C(8)); 120.40 (C(7)); 51.71 (MeO). CI-MS: 291 (100, $[M + 1]^+$), 259 (47, $[M - MeO]^+$). Anal. calc. for $C_{19}H_{14}O_3$ (290.32): C 78.61, H 4.86; found: C 78.45, H 4.99.

1,3-Dihydrobenzo[1,2]heptaleno[4,5-c]furan-1-one (**41**): Unstable red oil. ^{1}H-NMR (600 MHz, $CDCl_3$): 7.46 (*td*, $^3J(7,6) = {}^3J(7,8) = 7.6$, $^4J(7,5) = 1.3$, H–C(7)); 7.31 (*td*, $^3J(6,5) = {}^3J(6,7) = 7.6$, $^4J(6,8) = 1.3$, H–C(6)); 7.04 (*dd*, $^3J(5,6) = 7.8$, $^4J(5,7) = 1.1$, H–C(5)); 6.97 (*d*, $^3J(12,13) = 11.0$, H–C(13); 6.96 (*dd*, $^3J(8,7) = 7.8$, $^4J(8,6) = 1.3$, H–C(8)); 6.71 (*ddt*, $^3J(10,11) = 11.0$, $^3J(10,9) = 7.4$, $^4J(10,12) = {}^5J(10,13) = 1.0$, H–C(10)); 6.54 (*ddd*, $^3J(12,13) = 11.3$, $^3J(12,11) = 7.0$, $^4J(12,10) = 1.2$, H–C(12)); 6.51 (br. *s*, H–C(4)); 6.48 (*ddt*, $^3J(11,10) = 11.0$, $^3J(11,12) = 6.9$, $^4J(11,9) \approx {}^4J(11,13) = 1.0$, H–C(11)); 5.87 (*d*, $^3J(9,10) = 7.3$, H–C(9)); 4.93, 4.74 (2*d*, $^2J = 13.1$, CH_2(3)). ^{13}C-NMR (150 MHz, $CDCl_3$): 168.49 (C=O); 146.61 (C(13a)); 137.93 (C(4a)); 137.34 (C(8b)); 136.59 (C(3a)); 136.43 (C(8a)); 135.40 (C(9)); 134.87 (C(10)); 134.02 (C(12)); 132.42 (C(11)); 132.23 (C(7)); 130.51 (C(8)); 128.88 (C(6)); 128.83 (C(5)); 127.27 (C(13)); 125.71 (C(4)); 117.48 (C(13b)); 69.38 (CH_2).

2.5. *Decarbonylation of* **37**. Compound **37** (0.029 g, 0.10 mmol) was reacted with $[RhCl(Ph_3P)_3]$ (0.102 g, 0.11 mmol) in toluene (2 ml) in a sealed flask for 9 h at 130°. The mixture was subjected to CC (silica gel, toluene) yielding the expected ester **38** (0.024 g, 92%).

*Methyl Benzo[*a*]heptalene-7-carboxylate* (**38**): Unstable orange oil. R_f (hexane/Et_2O 2:1) 0.57. UV/VIS (hexane): λ_{max} 202 (4.45), 225 (sh, 4.37), 262 (4.28), 352 (3.68); λ_{min} 199 (4.45), 243 (4.23), 312 (3.35). IR ($CHCl_3$): 3080*w*, 3008*w*, 2952*w*, 1708*s*, 1631*w*, 1565*w*, 1434*m*, 1293*m*, 1253*s*, 1169*m*, 1100*w*, 1044*w*. ^{1}H-NMR (600 MHz, $CDCl_3$): 7.39 (*td*, $^3J(2,1) = {}^3J(2,3) = 7.5$, $^4J(2,4) = 1.2$, H–C(2)); 7.34 (*td*, $^3J(3,2) = {}^3J(3,4) = 7.5$, $^4J(3,1) = 1.2$, H–C(3)); 7.20 (*d*, $^3J(4,3) = 7.6$, H–C(4)); 6.96 (*d*, $^3J(1,2) = 7.5$, H–C(1)); 6.92 (*d*, $^3J(5,6) = 12.1$, H–C(5)); 6.74 (*d*, $^3J(6,5) = 12.1$, H–C(6)); 6.71 (*dd*, $^3J(11,10) = 12.2$, $^3J(11,12) = 6.7$, H–C(11)); 6.59 (*m*, H–C(8), H–C(10)); 6.46 (*dd*, $^3J(9,8) = 10.8$, $^3J(9,10) = 6.5$, H–C(9)); 5.99 (*d*, $^3J(12,11) = 6.6$, H–C(12)); 3.74 (*s*, COOMe). ^{13}C-NMR (150 MHz, $CDCl_3$): 165.92 (C=O); 145.21 (C(7a)); 139.52 (C(12b)); 137.19 (C(4a)); 134.74 (C(12a)); 134.00 (C(5)); 131.93 (C(11)); 131.15 (C(10)); 130.08 (C(2)); 129.85 (C(12)); 129.29 (C(1)); 128.69 (C(9)); 128.32 (C(4)); 128.19 (C(3)); 127.46 (C(6)); 125.58 (C(8)); 122.45 (C(7)); 51.60 (MeO). CI-MS: 263 (100, $[M + 1]^+$). Anal. calc. for $C_{18}H_{14}O_2$ (262.31): C 82.42, H 5.38; found: C 82.47, H 5.68.

2.6. *Reduction of* **38** *with DIBAH*. The ester **38** (0.303 g, 1.15 mmol) was dissolved in THF (30 ml). After cooling at 0°, 1M DIBAH soln. in hexane (4.6 ml) was added. The mixture was stirred for 10 min, then H_2O (1 ml) and Et_2O (15 ml) were added, and the org. phase was washed with 2N aq. H_2SO_4 soln. (3 × 30 ml), brine (3 × 30 ml), and dried (Na_2SO_4). The solvent was evaporated and the residue subjected to CC (Alox basic, act. IV; CH_2Cl_2) yielding methanol **42** (0.217 g, 81%).

*Benzo[*a*]heptalene-7-methanol* (**42**): Yellow needles from hexane/Et_2O. M.p. 122.4–123.7°. R_f (hexane/Et_2O 1:1) 0.27. UV/VIS (hexane): λ_{max} 222 (sh, 4.34), 259 (4.39), 290 (sh, 3.97), 337 (3.68); λ_{min} 235 (4.17), 311 (3.54). IR (KBr): 3230*s*, 3012*s*, 2945*m*, 1637*w*, 1577*m*, 1480*m*, 1465*m*, 1419*m*, 1134*m*, 1019*m*, 992*s*, 804*s*, 788*s*, 758*s*, 737*s*, 690*s*, 640*m*, 475*m*. ^{1}H-NMR (600 MHz, $CDCl_3$): 7.39 (*td*, $^3J(2,1) = {}^3J(2,3) = 7.5$, $^4J(2,4) = 1.2$, H–C(2)); 7.32 (*td*, $^3J(3,2) = {}^3J(3,4) = 7.6$, $^4J(3,1) = 1.2$, H–C(3)); 7.19 (*d*, $^3J(4,3) = 7.6$, H–C(4)); 7.07 (*d*, $^3J(1,2) = 7.7$, H–C(1)); 6.90 (*d*, $^3J(5,6) = 11.8$, H–C(5)); 6.60 (*dd*, $^3J(11,10) = 11.2$, $^3J(11,12) = 6.6$, H–C(11)); 6.43 (*dd*, $^3J(10,11) = 11.2$, $^3J(10,9) = 6.3$, H–C(10)); 6.39 (*d*, $^3J(6,5) = 11.8$, $^3J(6)$); 6.32 (*dd*, $^3J(9,8) = 10.7$, $^3J(9,10) = 6.2$, H–C(9)); 5.94 (*d*, $^3J(8,9) = 10.7$, H–C(8)); 5.82 (*d*, $^3J(12,11) = 6.6$, H–C(12)); 4.27, 4.20 (*AB*, $J_{AB} = 12.0$, CH_2(7)). ^{13}C-NMR (150 MHz, $CDCl_3$): 139.41 (C(12b)); 138.56 (C(12a)); 137.64 (C(4a)); 135.08 (C(7a)); 134.70 (C(5)); 132.58 (C(11)); 132.14 (C(7)); 130.86 (C(9)); 130.54 (C(6)); 130.20 (C(10)); 130.03 (C(2)); 128.92 (C(12)); 128.89 (C(1)); 128.67 (C(4)); 127.89 (C(3)); 124.60 (C(8)); 61.7 (CH_2). CI-MS: 235 (6, $[M + 1]^+$), 234 (4, $M^{+\cdot}$), 218 (17, $[(M + 1) - OH]^+$), 217 (100, $[M - OH]^+$). Anal. calc. for $C_{17}H_{14}O$ (234.30): C 87.15, H 6.02; found: C 87.08, H 6.01.

2.7. *Formation of Aldehyde* **43**. Methanol **42** (0.21 g, 0.89 mmol) was dissolved in CH_2Cl_2 (20 ml). MnO_2 [40] (2.10 g) was added and the mixture stirred vigorously during 2 h at r.t. MnO_2 was removed by filtration over *Celite* and washed with CH_2Cl_2. CC (silica gel, CH_2Cl_2) gave the pure aldehyde **43** (0.15 g, 72%).

*Benzo[*a*]heptalene-7-carbaldehyde* (**43**): Orange crystals from hexane/Et_2O. M.p. 118.4–119.3°. R_f (hexane/Et_2O 2:1) 0.53. UV/VIS (hexane): λ_{max} 223 (4.39), 271 (4.34), 369 (3.66); λ_{min} 211 (4.35), 252 (4.26), 319 (3.36). IR (KBr): 3060*w*, 3020*w*, 2862*w*, 1667*s*, 1627*m*, 1566*m*, 1480*w*, 1450*w*, 1413*m*, 1396*w*, 1269*m*, 1206*m*, 1137*m*, 806*s*, 790*m*, 767*s*, 730*s*, 452*w*. ^{1}H-NMR (600 MHz, $CDCl_3$): 10.07 (*s*, CHO); 7.42 (*td*, $^3J(2,1) = {}^3J(2,3) = 7.5$, $^4J(2,4) = 1.3$, H–C(2)); 7.36 (*td*, $^3J(3,2) \approx {}^3J(3,4) = 7.6$, $^4J(3,1) = 1,3$, H–C(3)); 7.22 (*dd*, $^3J(4,3) = 7.6$, $^4J(4,2) = 1.0$, H–C(4)); 7.01 (*dd*, $^3J(1,2) = 7.6$, $^4J(1,3) = 1.1$, H–C(1)); 6.94 (*d*, $^3J(5,6) = 12.0$, H–C(5)); 6.78 (*m*, H–C(11)); 6.70 (*d*, $^3J(6,5) = 12.0$, H–C(6)); 6.66–6.61 (partially superimposed, *m*, H–C(10), and *m*, H–C(9)); 6.50 (*d*, $^3J(8,9) = 11.5$, H–C(8)); 6.05 (*d*, $^3J(12,11) = 6.9$, H–C(12)). ^{13}C-NMR (150 MHz, $CDCl_3$): 190.43, 190.33 (^2J(C,H) = 15.1, CHO); 148.81 (C(7a)); 138.25 (C(12b)); 137.35 (C(4a)); 135.47 (C(12a)); 135.01 (C(5)); 133.59 (C(11)); 133.28 (C(9)); 131.18 (C(10)); 130.57 (C(12)); 130.48 (C(2)); 129.56 (C(1)); 129.08 (C(4)); 128.59 (C(3)); 126.84 (C(7)); 124.21 (C(6)); 121.56 (C(8)). EI-MS: 233 (12, $[M + 1]^+$), 232 (68, $M^{+\cdot}$), 206 (100, $[M - C_2H_2]^+$), 203 (80, $[M - CHO]^+$), 202 (70, $[M - CH_2O]^+$), 190 (11), 178 (23), 176 (10), 101 (18). Anal. calc. for $C_{17}H_{12}O$ (320.34): C 87.91, H 5.21; found: C 87.70, H 5.24.

2.8. *Formation of* **2**. Aldehyde **43** (0.096 g, 0.41 mmol) was reacted with $[RhCl(Ph_3P)_3]$ (0.187 g, 0.45 mmol) in degassed toluene (8 ml) in a sealed flask for 6 h at 130°. The following purification procedures were performed in a glove-box under N_2 atmosphere. Degassed hexane and silica gel were used. The cooled mixture was subjected to FC (silica gel; hexane) yielding a mixture of **2** and Ph_3P, which was treated with MeI (1 ml) for 1 h at r.t. to remove Ph_3P as the phosphonium salt. After a second flash CC (silica gel; hexane) **2** was obtained as an unstable yellow oil (*ca.* 0.037 g, 44%).

*Benzo[*a*]heptalene* (**2**): R_f (hexane) 0.48. UV/VIS (HPLC, hexane): *Fig. 3* and *Table 3*). IR (film): 3019*m*, 1651*w*, 1644*m*, 1634*m*, 1556*w*, 1480*m*, 1454*m*, 1434*m*, 1416*w*, 1260*m*, 1110*m*, 891*m*, 841*m*, 569*w*. ^{1}H-NMR

(600 MHz, $CDCl_3$): See *Fig. 5* and *Table 4*. ^{13}C-NMR (150 MHz, $CDCl_3$): See *Table 4*. EI-MS (GC/MS; see also *Fig. 6* and *Scheme 15*): 205 (17), 204 (100, $M^{+\cdot}$), 203 (79), 202 (66), 201 (14), 200 (16), 189 (2), 179 (11), 178 (75, $[M - C_2H_2]^+$), 177(7), 176 (13), 152 (11, $[M - 2\,C_2H_2]^+$), 151 (7), 150 (6), 102 (4), 101 (22), 100 (8), 92 (31), 91 (51), 89 (10), 63 (10), 57 (13). CI-MS: 205 (100, $[M + 1]^+$).

Dimethyl Heptalene-4,5-dicarboxylate (**44**)[10]: UV/VIS (hexane): See *Fig. 4*. ^{1}H-NMR (600 MHz, $CDCl_3$, 260 K): 7.40 (*d*, ^3J(3,2) = 6.1, H–C(3)); 6.56 (*dd*, ^3J(9,8) = 11.1, ^3J(9,10) = 6.6, H–C(9)); 6.43 (*dd*, ^3J(8,9) = 11.1, ^3J(8,7) = 6.5, H–C(8)); 6.27 (*dd*, ^3J(7,6) = 11.0, ^3J(7,8) = 6.5, H–C(7)); 6.20 (*dd*, ^3J(2,1) = 10.4, ^3J(2,3) = 6.2, H–C(2)); 5.94 (*d*, ^3J(6,7) = 11.1, H–C(6)); 5.92 (*d*, ^3J(1,2) = 10.5, H–C(1)); 5.75 (*d*, ^3J(10,9) = 6.5, H–C(10)). ^{13}C-NMR (150 MHz, $CDCl_3$, 260 K): 167.49 (O=C–C(4)); 167.19 (O=C–C(5)); 145.96 (C(5a)); 141.05 (C(3)); 137.42 (C(1)); 135.24 (C(4)); 132.71 (C(9)); 132.15 (C(8)); 131.34 (C(10)); 131.07 (C(2)); 130.71 (C(7)); 130.61 (C(10a)); 124.23 (C(6)); 122.75 (C(5)); 52.41 (*Me*OOC–C(4)); 51.92 (*Me*OOC–C(5)).

3. Crystal-Structure Determinations of 26a/26b, 30, and 36[11]. – All measurements were conducted at low temp. on a *Rigaku AFC5R* diffractometer using graphite-monochromated MoK_α radiation (λ = 0.71069 Å) and a 12-kW rotating anode generator. The intensities were collected using $\omega/2\theta$ scans, except for **26a/26b**, where ω scans were employed. Three standard reflections, which were measured after every 150 reflections, remained stable throughout each data collection. The intensities were corrected for *Lorentz* and polarization effects, and, in the case of **36**, an absorption correction based on ψ-scans [45] was applied. Each structure was solved by direct methods using SHELXS86 [46] which revealed the positions of all non-H-atoms. The non-H-atoms were refined anisotropically. The H-atoms were located in difference electron-density maps, and their positions were refined together with individual isotropic displacement parameters; except that for **36**, the positions of the H-atoms of the Me group were geometrically idealized and held fixed. A correction for secondary extinction was applied for **30**. All refinements were carried out on F using full-matrix least-squares procedures which minimized the function $\sum w(|F_o| - |F_c|)^2$, where $w = [\sigma^2(F_o) + (0.005F_o)^2]^{-1}$. The data collection and refinement parameters for compounds **30** and **36** are listed in *Table 6*. Neutral atom scattering factors for non-H-atoms were taken from [47a] and the scattering factors for H-atoms from [48]. Anomalous dispersion effects were included in F_c [49]; the values for f' and f'' were taken from [47b]. All calculations were performed using the TEXAN [50] crystallographic software package and the figures were produced with ORTEPPII [51].

In **36**, intermolecular H-bonds involving the carboxylic-acid function link the molecules into dimeric units. The bond lengths within the heptalene ring systems of **30** and **36** show characteristic distances for relatively localized single and double bonds. The crystals of **26a/26b** are enantiomerically pure, but the enantiomer used in the refinement was chosen arbitrarily. The molecules are linked by intermolecular H-bonds into infinite one-dimensional zig-zag chains which run parallel to the z-axis. It has not been possible to definitively deduce the bonding in the outer seven-membered ring [atoms C(7a)–C(12a)] of **26a/26b**. The fusion bond, C(7a)–C(12a), is clearly a double bond. The atoms C(9) and C(11) show very slight evidence of possible disorder and for the refinement, C(9) and C(11) were each defined as being disordered over two sites with occupation factors of 54:46. After refinement of the disordered model, an analysis of bond lengths gives the impression of a pattern of alternating double and single bonds between C(8) and C(12) which is disordered in the direction. The disordered sites are, therefore, alternately –CH= and $-CH_2-$, however, the reliability of the bond lengths in the disordered refinement is not high and these results should be treated cautiously.

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[11]) Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the *Cambridge Crystallographic Data Centre* as supplementary publication No. CCDC-10/50. Copies of the data can be obtained, free of charge, on application to the Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44-(0)1223-336033 or email: teched@chemcrys.cam.ac.uk).

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