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1-Phenyl-1,2-cyclohexadiene: Generation, Interception by Activated Olefins, Dimerisation and Trimerisation**

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Dedicated to Professor Waldemar Adam on the occasion of his 72nd birthday

Abstract: Four possible precursors of 1-phenyl-1,2-cyclohexadiene (**2**) were examined, namely, 6,6-dibromo-1-phenylbicyclo[3.1.0]hexane, (1α,5α,6α)-6-bromo-6-fluoro-1-phenylbicyclo-[3.1.0]hexane, 1-bromo-2-phenylcyclohexene and 1-bromo-6-phenylcyclohexene. All four compounds could be converted into **2**, as demonstrated by the products of the interception of **2** with activated olefins. Styrene, 1,1-diphenylethene, indene, furan and 2,5-dimethylfuran were employed as such. Whereas the first three gave [2+2] cycloadducts of **2**, the last two provided one [4+2] cycloadduct each. To create the [2+2] cycloadducts, the π bond of **2** that is more remote from the phenyl group reacted, whereas the π bond of **2** conjugated with the phenyl group exclusively produced the [4+2] cycloadducts. The generation of **2** in the absence of a trapping reagent brought about relatively good yields of a dimer or a trimer of **2** depending on the mode of the liberation of **2**. Being derivatives of triphenylene, the dimer as well as the trimer have unusual structures, thereby indicating that a phenyl group is participating in the formation of these compounds. The most surprising structure of the trimer was elucidated by X-ray crystal diffraction. As to the mechanisms, diradical intermediates are proposed both for the cycloadditions and for the dimerisation. The initial steps of the latter seem to proceed also in the trimerisation.

Keywords: cyclic allenes · cycloaddition · diradicals · polycycles · regioselectivity

Introduction

Six-membered cyclic allenes, in which the ring contains second-row elements exclusively or even a sulfur atom, are extremely short-lived intermediates, of which only very few could be observed directly.[1,2] Nevertheless, many of them have been efficiently intercepted by appropriate trapping reagents in [2+2] and [4+2] cycloadditions, thus indicating a significant synthetic potential.[1] This was impressively confirmed by the preparation of dozens of new cephalosporin derivatives by means of the dihydro-5δ²-1,3-thiazine intermediate **1**.[1,3]

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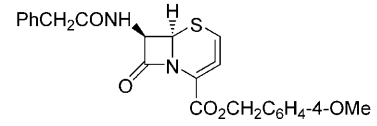

Compared with the unsubstituted 1,2-cyclohexadiene, which has been investigated extensively, there are ten simply substituted derivatives, the reactivity of which has been only fragmentarily studied.[1] One of them is 1-phenyl-1,2-cyclohexadiene (**2**), although it was the target of three research groups. In addition to the Würzburg team, some results of which were reported in a review,[1] Tolbert, Johnson et al.[4] as well as Ceylan and Budak[5] examined the inter-

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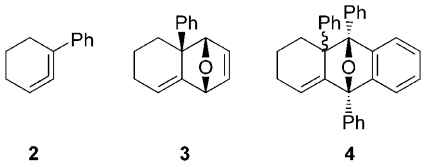
[**] Cycloallenes, Part 21. For Part 20, see reference [13].



2 3 4

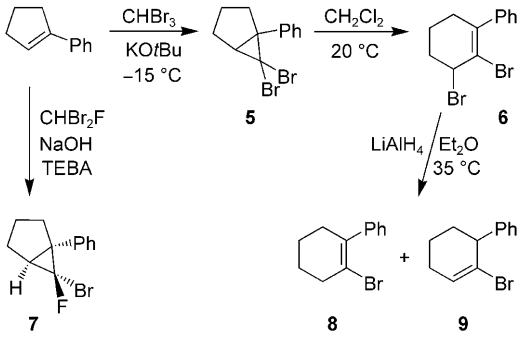
mediacy of **2**. The American group[4] proved the existence of **2** by trapping it with furan and 1,3-diphenylisobenzofuran, resulting in the formation of the [4+2] cycloadducts **3** and **4**. As the mode for the generation of **2**, the photolysis or the thermolysis of the potassium salt of 1-chloro-2-phenylcyclohexene was employed. Compound **4** also emerged from the Doering–Moore–Skattebøl reaction of 6,6-dibromo-1-phenylbicyclo[3.1.0]hexane (**5**) in the presence of 1,3-diphenylisobenzofuran.[4] The Turkish group[5] treated 1-bromo-2-phenylcyclohexene (**8**) with potassium *tert*-butoxide (KO*t*Bu), but obtained only rather indirect evidence in favour of the intermediate **2** (see below).

Including our previous results, which have been described only briefly to date,[1] we herein report on the generation of **2** from **5** and from the bromofluorophenylbicyclohexane **7** by the Doering–Moore–Skattebøl reaction as well as from **8** and its isomer **9** by β eliminations. For the trapping of **2**, activated olefins were utilised that are typical reaction partners of six-membered cyclic allenes.[1] In the absence of such a reagent, **2** underwent a dimerisation or trimerisation depending on the mode of the liberation, with the dimer and the trimer having unusual structures. The ultimate goal of our studies was the enantioselective generation of **2**, which permitted the examination of the stereochemical course of the cycloadditions onto **2**.[6]

Results and Discussion

Preparation of the precursors for 2: The straightforward precursors for the title allene **2** are the dibromcarbene adduct **5** of 1-phenylcyclopentene and 1-bromo-2-phenylcyclohexene (**8**), which should release **2** by an α and a β elimination, respectively. Thus, we treated bromoform with KO*t*Bu in the presence of 1-phenylcyclopentene and obtained the dibromophenylbicyclohexene **5** in 54% yield (Scheme 1). Tolbert, Johnson et al.[4] arrived at merely 20% yield and characterised **5**, which served as precursor of **2** en route to **4**, only as being "thermally unstable". Ceylan and Budak[5] described **5** as a colourless liquid, collected in 67% yield, whereas we isolated colourless crystals with m.p. 44.5–45 °C. In addition, our ^{13}C NMR spectroscopic data are severely at variance with the published ones.[5]

On the basis of the readily occurring rearrangement of the unsubstituted 6,6-dibromobicyclo[3.1.0]hexane[7] and its 1-methyl derivative,[8] it could not be expected that **5** is highly persistent at room temperature. In fact, it can be stored over extended periods only at −30 °C. Dissolved in dichloromethane or chloroform, it transformed virtually



Scheme 1. Preparation of the precursors **5** and **7**–**9** for **2**. TEBA = benzyltriethylammonium chloride.

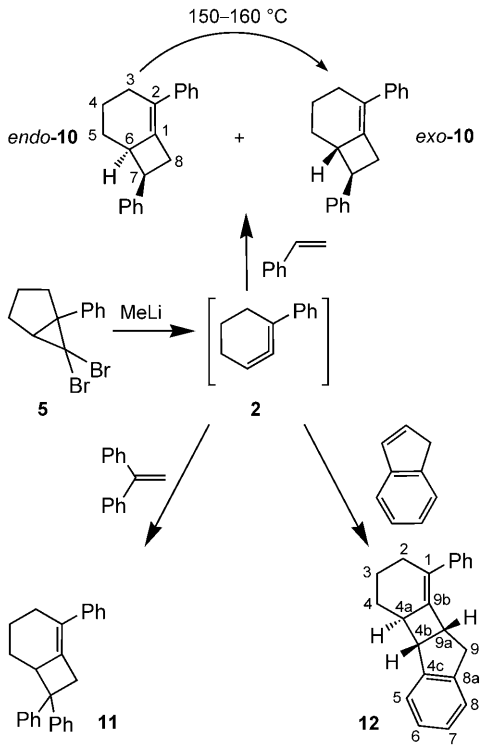
quantitatively to the allyl dibromide **6** at room temperature within 11 h and three days, respectively. Ceylan and Budak claimed to have achieved this rearrangement by heating at 150 °C, whereas heating at 180 °C gave rise to biphenyl.[5] In our hands, biphenyl was formed already at much lower temperatures from **5**,[9] and **6** could only be obtained by keeping a solution of **5** at room temperature. Previously, **6** was described as being a colourless liquid,[5,9] but we have now isolated colourless crystals with m.p. 55 °C. The published ^{13}C NMR spectroscopic data[5] deviate substantially from ours.

As a precursor of **2** in terms of a β elimination, **8** was prepared. It had formerly been obtained as the single product by the reduction of **6** with $LiAlH_4$ in tetrahydrofuran.[5,9] Performing this reaction in diethyl ether, we arrived at a 1.7:1.0 mixture of **8** and its isomer **9**, which we isolated in 32 and 8% yield, respectively. Ceylan and Budak[5] reported ^{1}H and ^{13}C NMR spectroscopic data of **8**. Whereas the former agree with ours, the latter differ from ours.

For the enantioselective generation of **2** by employing the Doering–Moore–Skattebøl reaction,[6] compound **5** is a candidate since it is chiral. However, we expected problems in the resolution of the racemate by chromatography on a chiral and enantiopure phase due to its thermolability. Therefore, we envisaged the synthesis of the bromofluorocarbene adduct **7** of 1-phenylcyclopentene. Our experience with *exo*-6-bromo-*endo*-6-fluorobicyclo[3.1.0]hexane derivatives[10] made us confident that **7** should rearrange much slower than **5**. The significantly higher energy of a C–F relative to a C–Br bond[11] is the basis for this anticipation.

Performed under the conditions of the phase-transfer catalysis, the addition of bromofluorocarbene onto 1-phenylcyclopentene afforded **7** in 16% yield (Scheme 1). We did not observe any indication of the thermal rearrangement of **7**, and it could be subjected to chromatography without decomposition. Because of the rather small yield of **7**, we assume that its diastereomer was also formed. Since this compound should be similarly reactive as **5**, it most probably underwent an S_N1 process with rearrangement in the polar reaction medium, the product of which could well have been lost during the workup.

Cycloadditions of 2 with activated olefins: The interception of a six-membered cyclic allene by an activated olefin with formation of a [2+2] or [4+2] cycloadduct is adequate proof for the existence of such an intermediate.[1] Because of its rather rapid trapping of the parent 1,2-cyclohexadiene,[1,12] at first styrene was chosen as reagent, and **2** was generated from **5** by methyllithium. The diastereomeric [2+2] cycloadducts *endo*- and *exo*-**10** were obtained as a 1:1 mixture in 51% yield (Scheme 2). Dissolved in light petroleum ether, such a mixture furnished crystals of pure *endo*-**10** on storage at −30°C.



Scheme 2. Generation of **2** from **5** by methyllithium and interception of **2** by styrene, 1,1-diphenylethene and indene.

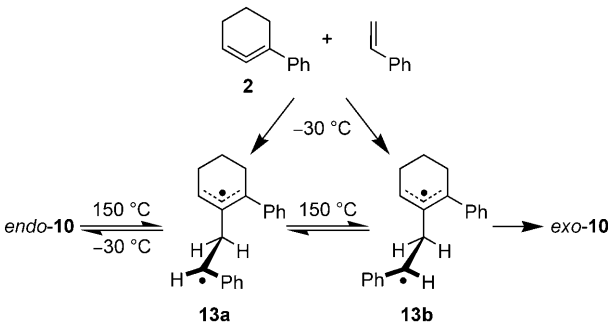
The same products **10** in the same ratio could be prepared in a one-pot procedure from 1-phenylcyclopentene without isolation of **5**, but the yield was only 24%. To that end, a solution of 1-phenylcyclopentene and tetrabromomethane in diethyl ether was treated with methyllithium at −60°C. The resulting solution of **5** was admixed with styrene, and then a second batch of methyllithium was added at −30°C, giving rise to **2**, which underwent the addition onto styrene.

Dissolved in pentane, the 1:1 mixture of *endo*- and *exo*-**10** turned out not to be persistent for long periods at room temperature. After two months, it had completely and cleanly converted into a product that could be a 1:1 mixture of isomers according to the NMR spectra, but the structure of which was not elucidated.

Styrene as trapping reagent of six-membered cyclic allenes leads to various ratios of *endo*- and *exo*-[2+2] cycloadducts. In some cases, only the *exo* isomer was observed; in others, the *endo* compound emerged as the minor component of the isomeric mixture,[1] and **1** and two of its derivatives[1,3] as well as 1-oxa-2,3-cyclohexadiene[1,10a] furnished both diastereomers in the same amount. The latter outcome is an unambiguous indication of the kinetic control of the product formation, since in the examples examined so far, namely, the styrene adducts of 1,2-cyclohexadiene, its 1-methyl derivative[8] and 1-oxa-2,3-cyclohexadiene,[10a] the *exo* diastereomer is the thermodynamically more stable one, as demonstrated by establishing the equilibrium by thermolysis. Accordingly, we now heated a solution of pure *endo*-**10** in C_6D_6 at 150–160°C and noticed the generation of *exo*-**10**. After six hours, the ratio of *endo*-/*exo*-**10** was determined to be about 1:1, after 26 h about 1:10. Because of the slow decomposition of the sample, occurring under these conditions, the equilibrium ratio could be smaller than 1:10.

The comparison of the temperature necessary for the above isomerisation with that required in the case of the styrene adducts of 1,2-cyclohexadiene, the equilibrium ratio *endo*/*exo* of which amounts to 1:13,[8] proves that the phenyl group at the six-membered ring of **10** does not accelerate the interconversion of the diastereomers.

We assume that the reaction between **2** and styrene proceeds in two steps via the diradicals **13a** and **13b** (Scheme 3) and its enantiomers. At −30°C, they probably



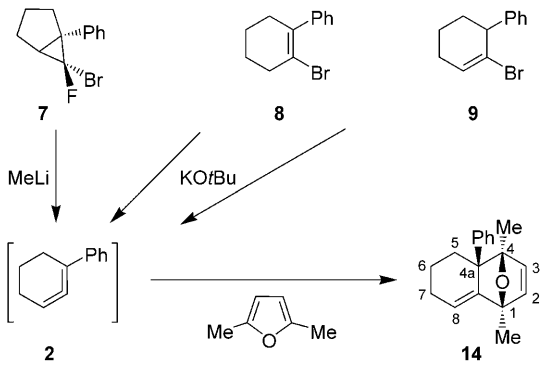
Scheme 3. Mechanisms proposed for the formation of *endo*- and *exo*-**10** from **2** and styrene and the conversion of *endo*- into *exo*-**10**.

emerge in the ratio of 1:1 and then collapse to give *endo*- and *exo*-**10**, respectively, without equilibration, that is, without rotations around the newly formed single bond and the one that results from the double bond of styrene. More details about the stereochemical course of this cycloaddition are provided by the utilisation of the enantioselectively generated **2**.[6] At about 150°C, the ring closure becomes reversible, thereby leading to the equilibration of **13a** and **13b** and eventually to the thermodynamically more stable compound *exo*-**10**. The instability of *endo*-**10** is caused by the steric crowding between the *endo*-oriented phenyl group and the cyclohexene moiety. However, no clear-cut reason can be given for the regioselectivity of the cycloaddition, which comes down to the regioselective collapse of the di-

radicals **13a** and **13b** at the less-substituted allyl-radical terminus.

1,1-Diphenylethene and indene as trapping reagents for **2** also gave rise to [2+2] cycloadducts, and with the same regioselectivity as with styrene (Scheme 2). Whereas the adduct **11** of 1,1-diphenylethene was obtained by a one-pot procedure from 1-phenylcyclopentene through **5** in 25% yield, the indene adduct **12** was prepared from pure **5**, but could be isolated in only 7% yield. The configuration indicated by formula **12** was not proven but assumed in analogy to the indene adducts of **1**[3] and $3\delta^2$-1*H*-naphthalene.[13] The desired products of both experiments were accompanied by significant amounts of the trimer **17** of **2**, described below. This finding characterises these activated olefins as sluggishly reacting allenophiles. Although benzofuran gave an adduct with **1** in 63% yield,[3] no reaction of **2** with benzofuran occurred and only **17** was observed.

Furan and substituted furans were frequently employed to intercept six-membered cyclic allenes and, as a rule, gave rise to [4+2] cycloadducts of these.[1,13] As demonstrated by the products **3** and **4**,[4] this rule is valid also for **2**. We now trapped **2** by 2,5-dimethylfuran and arrived at the [4+2] cycloadduct **14** (Scheme 4). The intermediate **2** was liberated



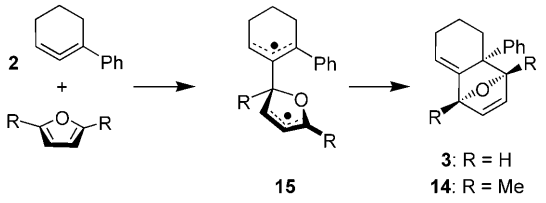
Scheme 4. Generation of **2** from **7**, **8** and **9** by methyllithium and potassium *tert*-butoxide, respectively, and its interception by 2,5-dimethylfuran.

from three precursors, namely, from **7** by methyllithium in a Doering–Moore–Skattebøl reaction, with the yield of **14** amounting to 22%, and from **8** as well as **9** by KO*t*Bu in β eliminations.

Tolbert, Johnson et al.[4] had prepared the furan adduct **3** of **2** in 50% yield, having generated **2** by photolysis or thermolysis of the potassium salt of 1-chloro-2-phenylcyclohexene, and noticed that the liberation of **2** from **5** in a Doering–Moore–Skattebøl reaction failed due to furan lithiation. On treatment of a mixture of **8** and **9** with KO*t*Bu in the presence of furan, we now obtained **3** as well. Different from these findings, Ceylan and Budak[5] reported the formation of 1-phenylnaphthalene on reaction of **8** with KO*t*Bu in the presence of furan. Their explanation of this result cannot be correct, since they did not assume **3** as product of the trapping of **2** but its regioisomer with the phenyl group located at the ethene subunit. This regioisomer was observed neither by the American group[4] nor by us.

The constitution of the products **3** and **14** can easily be derived from their ^{1}H NMR spectra, which contain three signals of olefinic protons and thus determine the position selectivity of the furan cycloaddition onto **2**. Moreover, Tolbert, Johnson et al.[4] proved the structure of **3** by X-ray diffraction. Given these facts, the trapping reactions of **2** proceed with different regiospecifities, as the allene double bond remote from the phenyl group is active in the [2+2] cycloadditions, whereas the double bond carrying the phenyl group reacts in the [4+2] cycloadditions. This phenomenon is not unusual with six-membered cyclic allenes.[1] However, the concerted process proposed for the [4+2] cycloadditions of 1-oxa-2,3-cyclohexadiene[10a] will most probably not meet the reality, since quantum chemical calculations[14] and the experimental result of the addition of (*Z*,*Z*)-1,4-dideuterio-1,3-butadiene onto 1,2-cyclohexadiene[1] clearly favour two-step reactions via diradicals.

In consequence, we assume that diradicals of type **15** emerge as intermediates en route to **3** and **14** (Scheme 5). But why the 1→4 ring closure of the diradicals **13**

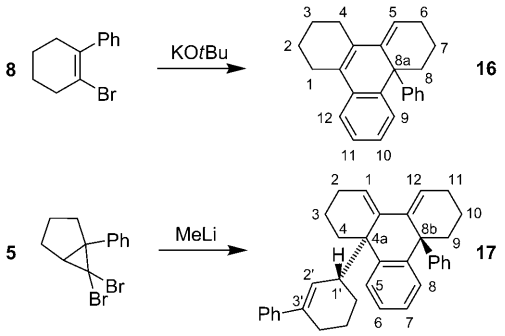


Scheme 5. Mechanism proposed for the formation of the [4+2] cycloadducts **3** and **14** of **2**.

(Scheme 3) takes place at the less substituted terminus of the phenylallyl-radical moiety and the 1→6 collapse of the diradicals **15** at the phenyl-substituted one, cannot be explained satisfactorily up to now. A theoretical study of these reactions would be highly desirable.

Dimerisation and trimerisation of 2: Short-lived six-membered cyclic allenes oligomerise if they are generated in the absence of a trapping reagent. Presumably, some do so unspecifically, because a homogeneous product could not be identified. Others, particularly 1,2-cyclohexadiene and its simply substituted derivatives, furnish dimers, which contain a 1,2-bismethylenecyclobutane subunit[1] and are thus analogous to the dimers of non-cyclic allenes.[15–17] The information given by Tolbert, Johnson et al.[4] as well as by Ceylan and Budak[5] as to the liberation of **2** in the absence of a trapping reagent appears to indicate a behaviour of **2** that deviates from the above rules, since only biphenyl was observed, which should emerge from **2** by base-catalysed rearrangement and subsequent dehydrogenation.

Different from these findings, we now observed that, dependent on the mode of the generation of **2**, the triphenylene derivatives **16** or **17** (Scheme 6) are formed in significant



Scheme 6. Formation of the dimer **16** and the trimer **17** of **2**.

amounts. These products are a dimer and a trimer of **2**, respectively. Interestingly, the dimer **16** only emerged on the β elimination route to **2**, that is, on treatment of **8** with KO*t*Bu, whereas the trimer **17** exclusively resulted as product of the Doering–Moore–Skattebøl reaction of **5**. We did not observe biphenyl as a consecutive product of **2**, but we did not search for this compound in detail, either.

The identity of **17** was established by single-crystal X-ray diffraction and was a great surprise, which is why our previous proposal for the structure of the trimer, being based on NMR spectroscopic data only,[1,9] had to be revised. Figure 1 illustrates the structure of **17** in the solid state, in which the methylene group of position 17 (position 3 in Scheme 6) is disordered. The most abundant fragment of the MS spectrum (*m*/*z* 311) also supports this structure, since it indicates the loss of the phenylcyclohexenyl group from the molecular ion.

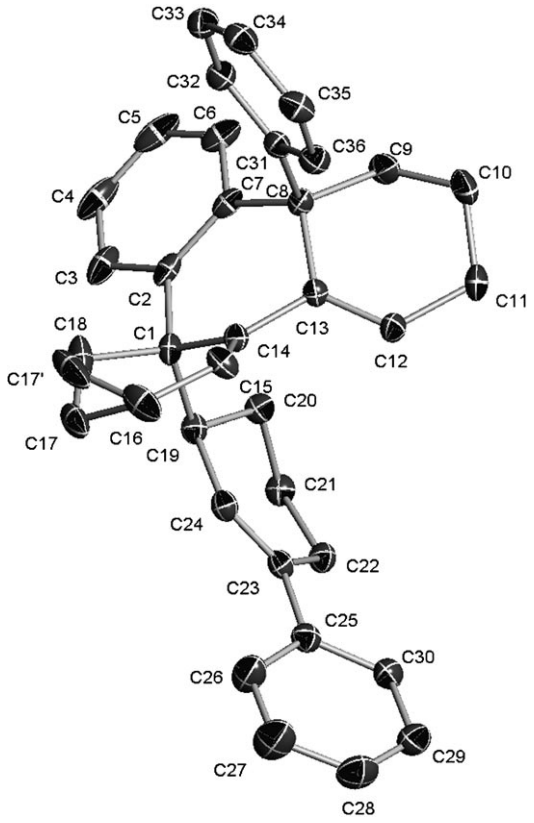
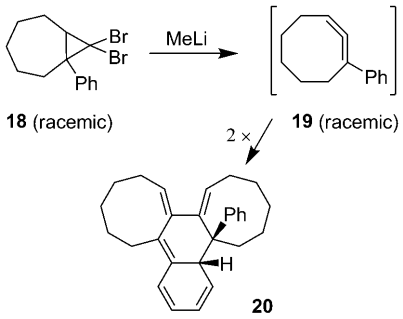


Figure 1. Molecular structure of **17** as determined by single-crystal X-ray diffraction. The anisotropic displacement parameters are depicted at the 50% probability level. The methylene group of position 17 (position 3 in Scheme 6) is disordered.

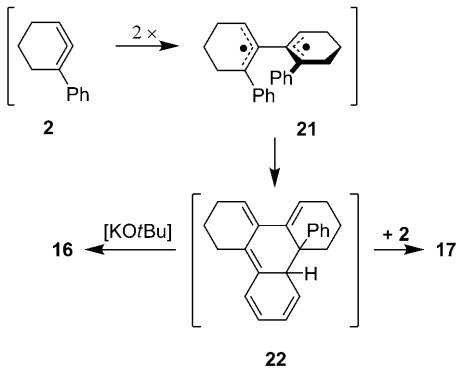
As is manifest by the triphenylene skeleton of **16** and **17**, a phenyl group of **2** actively participated in the product formation. In the synthesis of rubrene from chlorotriphenylallene, such a step has been employed since 1926,[18] even though the mechanism was only recognised in 1979.[19] Other examples are provided by the thermolysis of the 1,2-bismethylenecyclobutane derivatives produced at low temperatures upon dimerisation of triphenylallene[20] and 1-(2,2′-biphenylylen)-3-phenylallene.[17] Heretofore, only one case has been documented that describes the isolation of a primary product resulting from the attack of a radical centre of a phenyl-substituted tetramethyleneethane diradical at the phenyl group of the second molecule half, that is, the dimer **20** of racemic 1-phenyl-1,2-cyclooctadiene (**19**), which was generated from racemic 8,8-dibromo-1-phenylbicyclo-[5.1.0]octane (**18**; Scheme 7).[16,21]



Scheme 7. Dimerisation of racemic 1-phenyl-1,2-cyclooctadiene (**19**).[16,21]

The first two steps from **2** en route to **16** and **17** should be analogous to the pathway proposed for the conversion of **19** into **20**.[16,21] Thus, two molecules of **2** should combine to give the tetramethyleneethane diradical **21**, which then does not undergo the standard reaction of such species with formation of a 1,2-bismethylenecyclobutane derivative,[1] but collapses by bond formation of a phenyl-bearing allyl-radical terminus with the phenyl group of the second molecule half furnishing the 1-methylene-2,4-cyclohexadiene derivative **22** (Scheme 8). Corresponding exactly to **20**, derivative **22** is not isolable, since it is transformed to **16** or **17** under the reaction conditions.

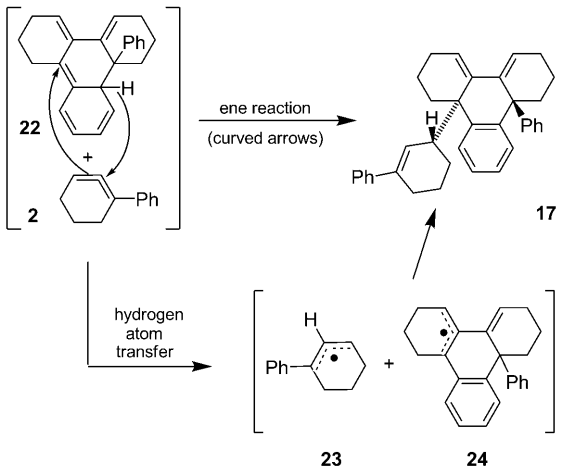
The presence of the strong base KO*t*Bu should lead to the deprotonation of the methylenecyclohexadiene subunit of **22** with aromatisation, that is, the generation of a 1-phenyl-allyl anion moiety, which is then reprotonated in position 3 with the formation of **16**. This pathway has a precise parallel in the dimerisation of 1-phenyl-1,2-cycloheptadiene liberated from appropriate precursors by β elimination with KO*t*Bu.[1,9]



Scheme 8. Mechanism proposed for the dimerisation of **2** with formation of **22**, which should be converted into **16** or **17** depending on the reaction conditions.

When **2** is generated from **5**, the intermediate **22** is exposed to methyllithium, which is also a rather strong base, and yet a deprotonation does not occur. Instead, **22** seems to react with another molecule of **2** and thus produces the trimer **17** (Scheme 8). Apparently, methyllithium is subject to a fast bromine–lithium exchange with **5**, and the resulting carbenoid rapidly eliminates lithium bromide to give **2**. Hence, **22** never faces a large concentration of the base, when methyllithium is slowly added to a solution of **5**. There may be a second reason for the failure of methyllithium and the carbenoid generated by it to deprotonate **22**, namely, the well-known phenomenon that, at a given p*K* value, carbon atom bases abstract protons considerably more slowly than hetero atom bases such as KO*t*Bu.[22]

Scheme 9 illustrates two possible mechanisms for the conversion of **22** into **17**. One is a one-step process, that is, an ene reaction. As the shape of the molecule **17** (Figure 1) demonstrates, the transition state could suffer from steric overcrowding, thereby reducing the likelihood for this concerted reaction. The alternative pathway would proceed in two steps, with the first being a hydrogen-atom transfer from **22** to **2**, which would give rise to the phenylallyl-radical derivatives **23** and **24**. This radical pair could collapse to **17**, but there would be several other possibilities for product formation, with the routes to the three diastereomers of **17** being the most prominent ones. Indeed, **17** was the major component of the product mixture and the only compound identified, yet one side product showed signals of three olefinic protons in the ^{1}H NMR spectrum that are very similar to those of **17** and thus could originate from a diastereomer of **17**.



Scheme 9. Mechanisms proposed for the conversion of the assumed dimer **22** of **2** into the trimer **17** by **2**.

Why does the reaction stop at the dimer **20** in the case of racemic 1-phenyl-1,2-cyclooctadiene (**19**), whereas the analogous dimer **22** of **2** binds an additional monomer to give **17** under very similar conditions? This variation is certainly caused by different strain energies of **2** and **19**, which are estimated to be 32 and 5 kcal mol^{-1}, respectively, if the calculated values of the parent hydrocarbons 1,2-cyclohexadiene and 1,2-cyclooctadiene[23] are applied. Clearly, the strain-energy difference of 27 kcal mol^{-1} brings about a much higher reactivity of **2** relative to that of **19**, which is why **2** readily attacks **22** to afford **17** as proposed in Scheme 9, whereas **19** does not interact with **20**. Definitely supported by the weakness of the respective C–H bond of the methylenecyclohexadiene subunit of **22**, the ability of **2** to abstract a hydrogen atom or to perform an ene reaction is unprecedented for six-membered cyclic allenes.

Conclusion

Both the Doering–Moore–Skattebøl reaction and the β-elimination route were shown to be suitable for the generation of 1-phenyl-1,2-cyclohexadiene (**2**). This intermediate behaves towards activated olefins in the same way as 1,2-cyclohexadiene and a number of its derivatives studied previously.[1] Accordingly, it is intercepted with the formation of [2+2] or [4+2] cycloadducts. Up to now, a satisfactory explanation has not been advanced for the astounding phenomenon that the π bond of **2** that is more remote of the phenyl group is employed in the [2+2] cycloadditions, whereas the π bond conjugated with the phenyl group is exclusively active in the [4+2] cycloadditions. The liberation of **2** in the absence of a trapping reagent leads to the formation of the dimer **16** or the trimer **17** of **2**, depending on the mode of the generation of **2**. Both products exhibit unusual structures, since the phenyl group of one molecule of **2** actively participates in the assembly of the skeletons. In addition, the association of the third molecule of **2** en route to **17** is unprecedented in the reactivity of six-membered cyclic allenes.

The preparation of a precursor of **2** that would allow the enantioselective generation of **2** was the most important goal of this investigation, which was fully reached by the synthesis of the racemic bromofluorocarbene adduct **7** of 1-phenylcyclopentene and the demonstration of the trapping of **2**, generated from **7**, by 2,5-dimethylfuran, which gave

rise to the [4+2] cycloadduct **14**. In the following paper in this issue, we report the results obtained on liberation of **2** from enantiopure **7** in the presence of activated olefins.

Experimental Section

General: NMR: Bruker AC 200, AC 250, Avance 400, and DMX 600 spectrometers; chemical shifts (δ) in ppm relative to Me_4Si ($\delta=0.00$ ppm) by using solvent signals as internal reference [$CDCl_3$: $\delta=7.26$ ppm (^{1}H NMR of $CHCl_3$) and 77.0 ppm (^{13}C NMR); C_6D_6: $\delta=7.16$ ppm (^{1}H NMR of C_6D_5H) and 128.0 ppm (^{13}C NMR)]. IR: Perkin–Elmer 1420 ratio recording infrared spectrophotometer. UV: Perkin–Elmer UV/Vis spectrophotometer 330, JASCO V-570 UV/Vis/NIR spectrophotometer. MS: Varian MAT CH 7, Finnigan MAT 8200 and MAT 90. Elemental analysis: LECO CHNS 932. Frequently used solvents: DEE = diethyl ether, EA = ethyl acetate, PE = light petroleum ether (b.p. 30–50 or 40–65 °C), THF = tetrahydrofuran.

6,6-Dibromo-1-phenylbicyclo[3.1.0]hexane (5): KO*t*Bu (13.1 g, 117 mmol) was suspended in a solution of 1-phenylcyclopentene[24] (12.1 g, 83.9 mmol) in PE (120 mL). The mixture was vigorously stirred and treated dropwise with a solution of bromoform (23.3 g, 92.2 mmol) in PE (30 mL) at −15 °C. After the cooling bath had been removed, the reaction mixture was allowed to warm to 20 °C and was cautiously hydrolysed (50 mL). Some solid material was filtered off, and the layers were separated. The organic layer was dried with $MgSO_4$, and the solvent was evaporated in vacuo without warming. The remaining orange-red oil (21.8 g) was dissolved in methanol (150 mL) at 20 °C, and the solution was kept at −30 °C overnight, which gave rise to colourless crystals of **5** (14.3 g, 54 %). M.p. 43–45 °C; m.p. 44.5–45 °C after one recrystallisation from methanol; ^{1}H NMR (250 MHz, $CDCl_3$): $\delta=1.76$–1.96 (m, 2H), 2.12 (m, 1H), 2.18–2.41 (m, 2H), 2.43–2.58 (m, 2H), 7.14–7.40 ppm (m, 5H); ^{13}C NMR (63 Hz, $CDCl_3$): $\delta=26.0$ (C3), 30.3 (C4), 37.9 (C2), 42.8 (C5), 46.3 (C1), 49.8 (C6), 127.1 (*p*-C), 128.1, 128.2 (*m*-C, *o*-C), 140.8 ppm (*i*-C); the assignment is based on the comparison of the values with those of the unsubstituted 6,6-dibromobicyclo[3.1.0]hexane and its 1-methyl derivative;[8] MS (70 eV, EI): *m*/*z* (%): 318, 316, 314 (0.6, 1.2, 0.6) $[M]^+$; 237, 235 (26, 27) $[M-Br]^+$; 156 (45) $[M-Br_2]^+$, 155 (100), 153 (12), 141 (14), 129 (15), 128 (41), 127 (15), 117 (14), 115 (37), 102 (13), 91 (57), 78 (19), 77 (38), 76 (21), 64 (12), 63 (15), 51 (27), 39 (17); elemental analysis calcd (%) for $C_{12}H_{12}Br_2$: C 45.61, H 3.83; found: C 45.73, H 3.68.

1,6-Dibromo-2-phenylcyclohex-1-ene (6): A solution of **5** (15.0 g, 47.5 mmol) in CH_2Cl_2 (150 mL) was kept at room temperature for about 11 h. Then the solvent was evaporated in vacuo at 20 °C. The remaining crystals (14.6 g, 97 %) were identified to be virtually pure **6**.

In a previous experiment, a solution of **5** (1.00 g, 3.16 mmol) in chloroform (10 mL) was stirred at room temperature. As shown by monitoring the progress of the rearrangement by NMR spectroscopy, the reaction was almost complete after 3 d. The evaporation of the solvent in vacuo at 20 °C gave rise to an orange-yellow oil, which was dissolved in PE (5 mL). Storage of this solution at −30 °C overnight afforded colourless crystals of **6** (900 mg, 90 %). M.p. 55 °C; ^{1}H NMR (400 MHz, $CDCl_3$): $\delta=1.91$ (m, 1H), 2.25 (m, 2H), 2.39 (m, 1H), 2.56 (m, 2H), 5.05 (m, 1H), 7.22 (m, *o*-H), 7.27–7.40 ppm (m, *m*-H, *p*-H); ^{13}C NMR (63 MHz, $CDCl_3$): $\delta=18.0$ (C4), 33.8, 34.0 (C3, C5), 56.6 (C6), 120.3 (C1), 127.3 (*o*-C), 127.6 (*p*-C), 128.1 (*m*-C), 142.0, 142.5 ppm (C2, *i*-C); as far as specified, the assignment is based on a C,H COSY spectrum; MS (70 eV, EI): *m*/*z* (%): 318, 316, 314 (3, 5, 3) $[M]^+$; 237 (83), 236 (22), 235 (84), 234 (32), 232 (22), 156 (54), 155 (100), 154 (21), 153 (32), 152 (34), 151 (36), 149 (35), 137 (40), 135 (40), 128 (27), 115 (24), 91 (56), 77 (42), 76 (40), 55 (24), 41 (57); elemental analysis calcd (%) for $C_{12}H_{12}Br_2$: C 45.61, H 3.83; found: C 45.52, H 3.83.

1-Bromo-2-phenyl- (8) and 1-bromo-6-phenylcyclohex-1-ene (9): A solution of **6** (11.1 g, 35.1 mmol) in DEE (20 mL) was added dropwise to a stirred suspension of $LiAlH_4$ (2.52 g, 66.4 mmol) in DEE (100 mL) at 20 °C. The mixture was then heated at reflux for 18 h and thereafter hydrolysed with a saturated solution of Na_2SO_4 (50 mL). The precipitate formed was filtered off and washed with DEE (2×10 mL). The filtrate and the washings were combined, extracted with water (20 mL) and dried with $MgSO_4$. After the evaporation of the solvent in vacuo, a yellow oil (6.47 g, 78 %) remained, which essentially consisted of **8** and **9** in the ratio of 1.7:1.0 according to the ^{1}H NMR spectrum. A 2.35 g portion of this material was subjected to flash chromatography (silica gel, PE), which furnished **8** (970 mg, 32 %) and **9** (228 mg, 8 %) as colourless oils.

Compound ***8***: ^{1}H NMR (400 MHz, $CDCl_3$): $\delta=1.76$–1.85 (m, 4H), 2.39 (m, 2H), 2.64 (m, 2H), 7.22 (*o*-H), 7.27 (*p*-H), 7.34 ppm (*m*-H); ^{13}C NMR (50 MHz, $CDCl_3$): $\delta=22.7$, 24.6 (C4,C5), 33.8, 36.7 (C3, C6), 120.0 (C1), 126.9 (*p*-C), 127.9 (*o*-C), 128.0 (*m*-C), 137.6, 143.3 ppm (C2, *i*-C); as far as specified, the assignment is supported by a C,H COSY spectrum; MS (70 eV, EI): *m*/*z* (%): 238, 236 (32, 32) $[M]^+$; 157 (50), 142 (12), 129 (62), 128 (29), 127 (11), 115 (31), 91 (100), 79 (20), 77 (25), 76 (13), 64 (13), 63 (12), 51 (18); elemental analysis calcd (%) for $C_{12}H_{13}Br$: C 60.78, H 5.53; found: C 61.10, H 5.29.

Compound ***9***: characterised by NMR spectroscopy only. ^{1}H NMR (400 MHz, $CDCl_3$): $\delta=1.51$–1.67 (m, 2H), 1.80 (m, 1H), 2.10–2.22 (m, 3H), 3.70 (m, 1H), 6.35 (td, $J=4.0$, 1.2 Hz, 1H), 7.21–7.28 (*o*-H, *p*-H), 7.33 ppm (*m*-H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta=17.8$ (C4), 27.7 (C5), 33.8 (C3), 49.7 (C6), 124.3 (C1), 126.6 (*p*-C), 128.2, 128.3 (*m*-C, *o*-C), 131.9 (C2), 143.3 ppm (*i*-C); the assignment is supported by a DEPT spectrum.

(1α,5α,6α)-6-Bromo-6-fluoro-1-phenylbicyclo[3.1.0]hexane (7): A solution of 1-phenylcyclopentene[24] (10.0 g, 69.3 mmol), benzyltriethylammonium chloride (250 mg, 1.10 mmol) and dibromofluoromethane[25] (21.4 g, 111.6 mmol) in CH_2Cl_2 (20 mL) was cooled in an ice bath. After addition of aqueous sodium hydroxide (15 g, 375 mmol in 15 mL of water), which was pre-cooled to 5 °C, the mixture was vigorously stirred for 3 d. During that period, the ice of the cooling bath was not replaced as it melted. Thus, the mixture reached room temperature after several hours. After 3 d, water (50 mL) was admixed and the layers were separated. The aqueous phase was extracted with CH_2Cl_2 (3×30 mL), the combined organic layers were dried with $MgSO_4$ and the solvent was evaporated in vacuo. The remaining brown oil was purified by flash chromatography (silica gel; PE/EA, 50:1) to give pure **7** (2.84 g, 16 %) as a colourless liquid. ^{1}H NMR (600 MHz, $CDCl_3$): $\delta=1.72$ (d quint d, $J_{3\alpha,3\beta}=13.0$ Hz, (average of $J_{2\alpha,3\beta}$, $J_{2\beta,3\beta}$, $J_{3\beta,4\alpha}$ and $J_{3\beta,4\beta}$) = 9.3 Hz, $J_{3\beta,F}=6.0$ Hz, 1H; H3$^\beta$), 1.92 (qm, (average of $J_{2\alpha,3\alpha}$, $J_{3\alpha,3\beta}$ and $J_{3\alpha,4\alpha}$) ≈ 10 Hz, 1H; H3$^\alpha$), 2.23 (dt, $J_{2\alpha,2\beta}=13.5$ Hz, $J_{2\alpha,3\alpha}=J_{2\alpha,3\beta}=9.7$ Hz, 1H; H2$^\alpha$), 2.25–2.33 (m, 3H; H4$^\alpha$, H4$^\beta$, H5), 2.59 (dddt, $J_{2\alpha,2\beta}=13.5$ Hz, $J_{2\beta,3\beta}=9.0$ Hz, $J=1.1$, 0.8 Hz, 1H; H2$^\beta$), 7.25 (m, 2H; *o*-H), 7.29 (tt, 1H; *p*-H), 7.35 ppm (m, 2H; *m*-H); the assignment is based on an HSQC spectrum; ^{13}C NMR (151 Hz, $CDCl_3$): $\delta=24.9$ (d, $J_{C,F}=10.3$ Hz; C3), 28.0 (d, $J_{C,F}=1.2$ Hz; C4), 35.1 (d, $J_{C,F}=2.6$ Hz; C2), 39.0 (d, $J_{C,F}=11.2$ Hz; C5), 46.7 (d, $J_{C,F}=10.9$ Hz; C1), 90.8 (d, $J_{C,F}=321.8$ Hz; C6), 127.1 (*p*-C), 128.186 (*m*-C), 128.195 (d, $J_{C,F}=2.9$ Hz; *o*-C), 140.0 ppm (d, $J_{C,F}=1.7$ Hz; *i*-C); the assignment is based on an HMBC spectrum; UV (hexane): λ_{max} (log ε) = 260 (2.29), 254 (2.43), 248 (2.40), 2.33 (sh, 3.71), 218 (4.11), 208 nm (4.13); MS (70 eV, EI): *m*/*z* (%): 236 (25), 234 (36) $[M-HF]^+$, 175 (77), 155 (100), 154 (27), 153 (40), 152 (32), 129 (24), 115 (32), 109 (25), 91 (59), 77 (37), 76 (46), 51 (21); HRMS (70 eV, EI): *m*/*z*: calcd for $C_{12}H_{12}F$ $[M-Br]^+$: 175.0918; found 175.0917.

Preparation of (6α,7β)- (*endo*-10) and (6α,7α)-2,7-diphenylbicyclo[4.2.0]oct-1-ene (*exo*-10) from 5: Under nitrogen, a stirred solution of **5** (3.07 g, 9.71 mmol) in styrene (10 mL) was cooled to −25 °C and was treated dropwise with methyllithium (12.0 mmol, 15 mL of 0.8 M in DEE) in a manner so that the temperature remained at −25 °C. After removal of the cooling bath, the temperature was allowed to rise to 20 °C, and the mixture was then cautiously hydrolysed (10 mL). The layers were separated, the aqueous layer was extracted with DEE (2×10 mL) and the combined organic phases were dried with $MgSO_4$ and concentrated in vacuo (15 mbar). From the remaining oil, the excess of styrene was distilled off in a kugelrohr (30 °C/0.04 mbar). The residue, a light yellow oil, was purified by flash chromatography (silica gel, pentane) to give a 1:1 mixture of *endo*- and *exo*-**10** (1.29 g, 51 %) as a colourless oil. Attempts to separate the diastereomers by chromatography on silica gel were un-

successful. However, dissolution of the mixture in a small amount of PE and storage of the solution at −30 °C led to the crystallisation of pure *endo*-**10**.

*Compound endo-**10***: M.p. 75 °C; ^{1}H NMR (600 MHz, $CDCl_3$; values in square brackets refer to C_6D_6 as solvent): $\delta = 0.73$ [0.92] (dddd, $J_{5\beta,6} = 13.4$ Hz, $J_{5\alpha,5\beta} = 12.2$ Hz, $J_{4\alpha,5\beta} = 11.0$ Hz, $J_{4\beta,5\beta} = 3.0$ Hz, 1H; H5$^{\beta}$), 1.38 [1.37] (≈ddt, $J_{5\alpha,5\beta} = 12.2$ Hz, $J_{4\beta,5\alpha} = 6.4$ Hz, $J_{5\alpha,6} = 3.7$ Hz, $J_{4\alpha,5\alpha} = 3.1$ Hz, 1H; H5$^{\alpha}$), 1.63 [1.58] (≈tddd, $J_{3\beta,4\alpha} = 13.9$ Hz, $J_{4\alpha,4\beta} = 13.1$ Hz, $J_{4\alpha,5\beta} = 11.0$ Hz, $J_{3\alpha,4\alpha} = 5.8$ Hz, $J_{4\alpha,5\alpha} = 3.1$ Hz, 1H; H4$^{\alpha}$), 1.88 [1.77] (≈ddtd, $J_{4\alpha,4\beta} = 13.1$ Hz, $J_{4\beta,5\alpha} = 6.4$ Hz, $J_{3\beta,4\beta} = 4.2$ Hz, $J_{4\beta,5\beta} = 3.0$ Hz, $J_{3\alpha,4\beta} = 1.7$ Hz, 1H; H4$^{\beta}$), 2.26 [2.24] (≈ddtt, $J_{3\alpha,3\beta} = 16.8$ Hz, $J_{3\alpha,4\alpha} = 5.8$ Hz, $J_{3\alpha,8\alpha} = 3.1$ Hz, $J_{3\alpha,8\beta} = 2.4$ Hz, $J_{3\alpha,4\beta} = 1.7$ Hz, $J_{3\alpha,6} = 1.2$ Hz, 1H; H3$^{\alpha}$), 2.55 [2.48] (≈ddqd, $J_{3\alpha,3\beta} = 16.8$ Hz, $J_{3\beta,4\alpha} = 13.9$ Hz, $J_{3\beta,4\beta} = 4.2$ Hz, $J_{3\beta,6} = 3.2$ Hz, $J_{3\beta,8\alpha} = 3.1$ Hz, $J_{3\beta,8\beta} = 1.5$ Hz, 1H; H3$^{\beta}$), 2.96 [3.08] (dtt, $J_{8\alpha,8\beta} = 14.3$ Hz, $J_{3\alpha,8\beta} = J_{7,8\beta} = 2.4$ Hz, $J_{3\beta,8\beta} = J_{6,8\beta} = 1.5$ Hz, 1H; H8$^{\beta}$), 3.52 [3.38] (≈ddtq, $J_{5\beta,6} = 13.4$ Hz, $J_{6,7} = 9.1$ Hz, $J_{5\alpha,6} = 3.7$ Hz, $J_{3\beta,6} = 3.2$ Hz, $J_{6,8\alpha} = 1.6$ Hz, $J_{6,8\beta} = 1.5$ Hz, $J_{3\alpha,6} = 1.2$ Hz, 1H; H6), 3.65 [3.49] (ddtd, $J_{8\alpha,8\beta} = 14.3$ Hz, $J_{7,8\alpha} = 9.1$ Hz, $J_{3\alpha,8\alpha} = J_{3\beta,8\alpha} = 3.1$ Hz, $J_{6,8\alpha} = 1.6$ Hz Hz, 1H; H8$^{\alpha}$), 3.77 [3.62] (td, $J_{6,7} = J_{7,8\alpha} = 9.1$ Hz, $J_{7,8\beta} = 2.4$ Hz, 1H; H7), 7.08 [7.36] (m, 2H; *o*-H of 7-Ph), 7.16 [7.12] (tt, 1H; *p*-H of 7-Ph), 7.23 [7.26] (m, 2H; *m*-H of 7-Ph), 7.32–7.42 [6.98–7.10] ppm (m, 5H; 2-Ph); the assignment is based on H,H COSY and NOESY spectra; ^{13}C NMR (151 MHz, $CDCl_3$): $\delta = 22.2$ (C4), 23.1 (C5), 26.8 (C3), 38.8 (C8), 42.5 (C7), 47.5 (C6), 125.3 (C2), 125.8 (*p*-C of 7-Ph), 125.9 (*o*-C of 2-Ph), 126.1 (*p*-C of 2-Ph), 127.7 (*o*-C of 7-Ph), 128.05 (*m*-C of 7-Ph), 128.15 (*m*-C of 2-Ph), 138.9 (C1), 139.5 (*i*-C of 2-Ph), 141.8 ppm (*i*-C of 7-Ph); the assignment is based on HSQC and HMBC spectra; elemental analysis calcd (%) for $C_{20}H_{20}$: C 92.26, H 7.74; found: C 91.57, H 8.13.

*Compound exo-**10***: ^{1}H NMR (600 MHz, $CDCl_3$): $\delta = 1.40$ (m, 1H; H5$^{\beta}$), 1.66 (m, 1H; H4$^{\alpha}$), 2.03–2.14 (m, 2H; H4$^{\beta}$, H5$^{\alpha}$), 2.33 (m, 1H; H3$^{\alpha}$), 2.70 (m, 1H; H3$^{\beta}$), 3.15–3.26 (m, 3H; H6, H7, H8$^{\alpha}$), 3.31 (m, 1H; H8$^{\beta}$), 7.20–7.40 ppm (m, 10H; 2-Ph, 7-Ph); the assignment is based on H,H COSY and NOESY spectra; ^{13}C NMR (151 MHz, $CDCl_3$): $\delta = 22.8$ (C4), 27.0 (C3), 28.3 (C5), 40.8 (C8), 46.4 (C7), 51.0 (C6), 124.6 (C2), 125.9 (*o*-C of 2-Ph), 126.0 and 126.1 (*p*-C of 2-Ph and 7-Ph), 126.5 (*o*-C of 7-Ph), 128.1 and 128.3 (*m*-C of 2-Ph and 7-Ph), 136.3 (C1), 139.7 (*i*-C of 2-Ph), 144.5 ppm (*i*-C of 7-Ph); the assignment is based on HSQC and HMBC spectra.

*Mixture of endo- and exo-**10** in the ratio of 1:1*: UV (hexane): λ_{max} ($\log\varepsilon$) = 275 (sh, 3.97), 258 (4.24), 222 (sh, 4.11), 216 (sh, 4.24), 208 (sh, 4.30), 202 nm (sh, 4.34); the UV spectra of the isolated diastereomers, measured with the pure enantiomers,[6] are virtually the same; MS (70 eV, EI): *m*/*z* (%): 260 (16) [*M*]$^+$, 183 (28), 182 (100), 167 (26), 154 (19), 142 (16), 141 (39), 129 (17), 128 (18), 115 (35), 105 (36), 104 (32), 91 (55), 77 (24).

Thermolysis of *endo*-10: A solution of *endo*-**10** (74 mg) in C_6D_6 (1.2 mL) was sealed in an NMR spectroscopy tube and heated at 150–160 °C. After 6 h, about one half of the amount of *endo*-**10** had rearranged to *exo*-**10**. After 26 h, the ratio of *endo*-/*exo*-**10** was about 1:10. Prolonged heating led to the decomposition of the sample.

Transformation of *endo*- and *exo*-10 at room temperature: After standing at room temperature for 2 months, *endo*- and *exo*-**10** (1 g of the 1:1 mixture), dissolved in pentane (10 mL), had completely and cleanly converted into a product that could be a 1:1 mixture of two isomers. The structure was not elucidated. ^{13}C NMR (63 MHz, $CDCl_3$): $\delta = 18.2$, 18.7, 21.8, 27.9, 28.5, 30.0, 31.8, 34.4 (8CH_2), 36.3, 40.9, 43.8, 47.3 (4CH), 62.1 (double intensity), 65.5, 67.8 (4$C_{quart.}$), 126.0, 126.20, 127.2, 127.3 (4*p*-C), 126.23, 126.25, 126.5, 127.9, 128.16 (double intensity), 128.21, 128.4 (4*o*-C, 4*m*-C), 139.1, 139.5, 141.3, 143.9 (4*i*-C).

One-pot preparation of *endo*- and *exo*-10 from 1-phenylcyclopentene: Under nitrogen, a stirred solution of 1-phenylcyclopentene (5.00 g, 34.7 mmol) and tetrabromomethane (12.6 g, 38.0 mmol) in anhydrous DEE (50 mL) was cooled to −60 °C and was treated dropwise with methyllithium (38.0 mmol, 29.2 mL of 1.3 M in DEE) in a manner so that the temperature remained at −60 °C. Thereafter, the mixture was stirred for 1 h at −60 °C and was then allowed to warm to −30 °C. After styrene (20.8 g, 200 mmol) had been admixed at once, methyllithium (38.0 mmol, 29.2 mL of 1.3 M in DEE) was added dropwise, while the temperature of the mixture was kept at −30 °C. Stirring was continued for 1.5 h at −25 °C, and the mixture was then cautiously hydrolysed (20 mL) at 0 °C. The workup as in the preceding preparation afforded a brown oil (5.5 g), which gave rise to a 1:1 mixture of *endo*- and *exo*-**10** (2.20 g, 24 %) after flash chromatography.

2,7,7-Triphenylbicyclo[4.2.0]oct-1-ene (11): Under nitrogen, a stirred solution of 1-phenylcyclopentene (2.00 g, 13.9 mmol) and tetrabromomethane (5.00 g, 15.1 mmol) in anhydrous DEE (15 mL) was cooled to −60 °C and was treated dropwise with methyllithium (13.9 mmol, 10.7 mL 1.3 M in DEE) in a manner so that the temperature remained at −60 °C (30 min). Thereafter, the mixture was stirred for 1 h at −60 °C and was then allowed to warm to −30 °C. After 1,1-diphenylethene (7.00 g, 38.8 mmol) had been admixed at once, methyllithium (13.9 mmol, 10.7 mL 1.3 M in DEE) was added dropwise, while the temperature was kept at −30 °C. Stirring was continued for 2 h at −30 °C, and the mixture was then cautiously hydrolysed (30 mL) at 0 °C. The layers were separated, and the aqueous layer was extracted with DEE (2 × 20 mL). The combined organic layers were washed with a saturated aqueous solution of NaCl (20 mL), dried with $MgSO_4$ and concentrated in vacuo. Purification of the residue by flash chromatography (silica gel; at first PE and then PE/CH_2Cl_2, 2:1) furnished, in the order of elution, 1-phenylcyclopentene, 1,1-diphenylethene, a fraction (1.61 g) consisting mainly of **11** (about 1.2 g, 25 %), and the almost pure trimer **17** (542 mg, 25 %). The fraction with **11** afforded crystals after standing for several months at −20 °C, which were recrystallised from PE to give almost pure **11**. M.p. 81–83 °C; ^{1}H NMR (600 MHz, $CDCl_3$): $\delta = 0.72$ (tdd, $J_{5\beta,6} = J_{5\alpha,5\beta} = 13.0$ Hz, $J_{4\alpha,5\beta} = 10.5$ Hz, $J_{4\beta,5\beta} = 3.0$ Hz, 1H; H5$^{\beta}$), 1.66–1.75 (m, 2H), 1.90 (m, 1H), 2.26 (br d, $J_{3\alpha,3\beta} = 16.2$ Hz, 1H; H3$^{\alpha}$), 2.51 (m, 1H; H3$^{\beta}$), 3.63 (dtd, $J_{8\alpha,8\beta} = 14.7$ Hz, $J = 3.1$, 1.7 Hz, 1H), 3.72 (dm, $J_{8\alpha,8\beta} = 14.7$ Hz, 1H; H8$^{\alpha}$, H8$^{\beta}$), 3.86 (m, 1H; H6), 6.95 (m, 2H; *o*-H of 7$^{\beta}$-Ph), 7.10 (tt, 1H; *p*-H of 7$^{\beta}$-Ph), 7.14 (m, 2H; *m*-H of 7$^{\beta}$-Ph), 7.21–7.27 (m, 4H), 7.32–7.40 ppm (m, 6H); the assignment is based on the comparison with the spectra of *endo*- and *exo*-**10**; ^{13}C NMR (151 MHz, $CDCl_3$): $\delta = 22.3$ (t, $J_{C,H} = 127.8$ Hz; C4), 24.5 (t, $J_{C,H} = 128.9$ Hz; C5), 27.0 (t, $J_{C,H} = 125.8$ Hz; C3), 46.3 (t, $J_{C,H} = 137.2$ Hz; C8), 52.9 (d, $J_{C,H} = 135.9$ Hz; C6), 54.5 (s; C7), 125.62 (s; C2), 125.66, 125.8, 126.2 (3dt; 3*p*-C), 125.9, 127.0, 127.5 (3dt; 3*o*-C), 127.8, 128.17, 128.20 (3dd; 3*m*-C), 135.1, 139.5, 143.7, 150.4 ppm (4s; C1, 3*i*-C); as far as specified, the assignment is based on the comparison with the spectra of *endo*- and *exo*-**10**; IR (KBr): $\tilde{\nu} = 3070$, 3045, 3020, 2915, 2855, 2835, 1595, 1490, 1440, 1030, 770, 755, 695 cm^{-1}; elemental analysis calcd (%) for $C_{26}H_{24}$: C 92.81, H 7.19; found: C 93.32, H 7.53.

(4aα,4bβ,9aβ)-3,4,4a,4b,9,9a-Hexahydro-1-phenyl-2*H*-benzo-[3,4]cyclobuta[1,2-*a*]indene (12): Under nitrogen, a stirred solution of **5** (1.97 g, 6.23 mmol) in indene (10 mL) was cooled to −3 °C and was treated dropwise with methyllithium (9.8 mmol, 10 mL of 0.98 M in DEE) in a manner so that the temperature remained at −3 °C. After removal of the cooling bath, the temperature was allowed to rise to 20 °C, and the mixture was then cautiously hydrolysed (20 mL). The layers were separated, the aqueous layer was extracted with CH_2Cl_2 (2 × 5 mL), and the combined organic phases were dried with $MgSO_4$ and concentrated in vacuo (15 mbar). From the remaining oil, the excess of indene was distilled off in a kugelrohr (45 °C/0.03 mbar). The residue, a light brown oil, was purified by flash chromatography (silica gel; PE/EA, 100:1) to give almost pure **12** (124 mg, 7 %) as a colourless oil. Another fraction (433 mg, 44 %) consisted mainly of the trimer **17** of **2** and products that may be other oligomers of **2**. ^{1}H NMR (600 MHz, C_6D_6): $\delta = 1.23$ (dtd, $J_{3\alpha,4\beta} = 13.5$ Hz, $J_{4\alpha,4\beta} = 11.3$ Hz, $J_{4\beta,4a} = 10.7$ Hz, $J_{3\beta,4\beta} = 2.4$ Hz, 1H; H4$^{\beta}$), 1.33 (tddd, $J_{3\alpha,4\beta} = 13.5$ Hz, $J_{3\alpha,3\beta} = 13.3$ Hz, $J_{2\beta,3\alpha} = 10.8$ Hz, $J_{2\alpha,3\alpha} = 5.9$ Hz, $J_{3\alpha,4\alpha} = 2.6$ Hz, 1H; H3$^{\alpha}$), 1.78 (ddddd, $J_{3\alpha,3\beta} = 13.3$ Hz, $J_{2\beta,3\beta} = 6.5$ Hz, $J_{3\beta,4\alpha} = 3.4$ Hz, $J_{3\beta,4\beta} = 2.4$ Hz, $J_{2\alpha,3\beta} = 1.4$ Hz, 1H; H3$^{\beta}$), 1.82 (dddd, $J_{4\alpha,4\beta} = 11.3$ Hz, $J_{4\alpha,4a} = 6.2$ Hz, $J_{3\beta4\alpha} = 3.4$ Hz, $J_{3\alpha,4\alpha} = 2.6$ Hz, 1H; H4$^{\alpha}$), 2.17 (dddt, $J_{2\alpha,2\beta} = 16.9$ Hz, $J_{2\alpha,3\alpha} = 5.9$ Hz, $J_{2\alpha,4a} = 2.5$ Hz, $J_{2\alpha,3\beta} = J_{2\alpha,9a} = 1.4$ Hz, 1H; H2$^{\alpha}$), 2.53 (ddddd, $J_{2\alpha,2\beta} = 16.9$ Hz, $J_{2\beta,3\alpha} = 10.8$ Hz, $J_{2\beta,3\beta} = 6.5$ Hz, $J_{2\beta,4a} = 3.6$ Hz, $J_{2\beta,9a} = 1.4$ Hz, 1H; H2$^{\beta}$), 2.80 (≈dtq, $J_{4\beta,4a} = 10.7$ Hz, $J_{4\alpha,4a} = 6.2$ Hz, $J_{4a,4b} = 5.7$ Hz, $J_{2\beta,4a} = 3.6$ Hz, $J_{4a,9a} = 2.9$ Hz, $J_{2\alpha,4a} = 2.5$ Hz, 1H; H4a), 3.20 (dd, $J_{9\alpha,9\beta} = 16.7$ Hz, $J_{9\beta,9a} = 10.7$ Hz, 1H; H9$^{\beta}$), 3.31 (dd, $J_{9\alpha,9\beta} = 16.7$ Hz, $J_{9\alpha,9a} = 5.3$ Hz, 1H; H9$^{\alpha}$), 3.41 (≈t, $J_{4b,9a} = 6.8$ Hz, $J_{4a,4b} = 5.7$ Hz, 1H; H4b), 3.67 (ddddt, $J_{9\beta,9a} = 10.7$ Hz, $J_{4b,9a} = 6.8$ Hz, $J_{9\alpha,9a} = 5.3$ Hz, $J_{4a,9a} = 2.9$ Hz, $J_{2\alpha,9a} = J_{2\beta,9a} = 1.4$ Hz, 1H; H9a), 7.06–7.17 (m, 4H; H5, H6, H7,

H8), 7.15 (tt, 1H; *p*-H), 7.30 (m, 2H; *m*-H), 7.39 ppm (m, 2H; *o*-H); the assignment is based on H,H COSY and NOESY spectra; ^{13}C NMR (151 MHz, C_6D_6): δ=23.0 (C3), 27.0 (C2), 27.8 (C4), 38.3 (C9), 49.4 (C9a), 51.8 (C4a), 53.1 (C4b), 123.7 (C5), 125.4 (C8), 125.5 (C1), 126.4 (*o*-C of Ph), 126.6 (*p*-C of Ph), 126.77, 126.83 (C6, C7), 128.5 (*m*-C of Ph), 140.1 (*i*-C of Ph), 141.9 (C9b), 145.6 (C8a), 147.4 ppm (C4c); the assignment is based on HSQC and HMBC spectra; UV (hexane): λ_{max} ($\log\varepsilon$)=275 (3.89), 266 (sh, 4.09), 260 (4.15), 255 (4.15), 250 (4.07), 233 (sh, 4.56), 218 (4.95), 209 nm (sh, 4.91); MS (70 eV, EI): *m*/*z* (%): 272 (100) $[M]^+$, 257 (22), 244 (20), 229 (64), 228 (22), 216 (23), 215 (58), 181 (69), 173 (23), 168 (52), 167 (33), 165 (22), 157 (32), 155 (22), 153 (26), 144 (26), 142 (26), 141 (37), 129 (32), 128 (49), 116 (28), 115 (72), 91 (56), 77 (26); HRMS (70 eV, EI): *m*/*z*: calcd for $C_{21}H_{20}$ $[M]^+$: 272.1560; found 272.1557.

Preparation of (1α,4α,4aα)-1,4-dimethyl-4a-phenyl-1,4,4a,5,6,7-hexahydro-1,4-epoxynaphthalene (14)

From **7**: Under nitrogen, a stirred solution of **7** (1.10 g, 4.31 mmol) in 2,5-dimethylfuran (6 mL) was cooled to −30 °C and was treated dropwise with methyllithium (8.0 mmol, 10 mL of 0.8 M in DEE) in a manner so that the temperature remained at −30 °C (20 min). After removal of the cooling bath, the temperature was allowed to rise to 0 °C, and the mixture was then cautiously hydrolysed (10 mL). The layers were separated, the aqueous layer was extracted with DEE (3×10 mL), and the combined organic phases were dried with $MgSO_4$ and concentrated in vacuo. The residue was purified by flash chromatography (silica gel; PE/EA, 20:1) to give pure **14** (237 mg, 22%) as a colourless oil. ^{1}H NMR (600 MHz, C_6D_6): δ=0.70 (≈td, $J_{5\alpha,5\beta}=J_{5\beta,6\alpha}$=12.2 Hz, $J_{5\beta,6\beta}$=6.0 Hz, 1H; H5$^{\beta}$), 1.20 (s, 3H; 4-Me), 1.35–1.46 (m, 2H; H6$^{\alpha}$, H6$^{\beta}$), 1.63 (s, 3H; 1-Me), 1.72–1.83 (m, 2H; H7$^{\alpha}$, H7$^{\beta}$), 2.24 (ddd, $J_{5\alpha,5\beta}$=12.2 Hz, $J_{5\alpha,6\alpha}$ and $J_{5\alpha,6\beta}$=4.2, 3.0 Hz, 1H; H5$^{\alpha}$), 5.39 (dd, $J_{7\alpha,8}$ and $J_{7\beta,8}$=4.6, 3.1 Hz, 1H; H8), 5.81 (d, $J_{2,3}$=5.3 Hz, 1H; H3), 5.94 (d, $J_{2,3}$=5.3 Hz, 1H; H2), 7.10 (tt, 1H; *p*-H), 7.21 (m, 2H; *m*-H), 7.30 ppm (m, 2H; *o*-H); the assignment is based on NOESY and HMQC spectra; ^{13}C NMR (151 MHz, D_6D_6): δ=15.0 (1-Me), 16.5 (4-Me), 19.9 (C6), 23.6 (C7), 32.3 (C5), 54.1 (C4a), 86.6 (C1), 90.8 (C4), 117.6 (C8), 126.0 (*p*-C), 127.6 (broad, *m*-C), 130.0 (very broad, *o*-C), 136.1 (C3), 140.2 (C2), 142.9 (*i*-C), 151.0 ppm (C8a); the assignment is based on HMQC and HMBC spectra; UV (methanol): λ_{max} ($\log\varepsilon$)=270 (2.18), 266 (2.31), 263 (sh, 2.31), 259 (2.41), 253 (2.39), 248 (2.36), 215 nm (3.88); MS (70 eV, EI): *m*/*z* (%): 252 (7) $[M]^+$, 210 (21), 209 (100), 181 (27), 179 (12), 178 (11), 167 (18), 165 (15), 129 (11), 117 (10), 115 (18), 105 (18), 91 (30), 77 (13), 43 (37); HRMS (70 eV, EI): *m*/*z*: calcd for $C_{18}H_{20}O$ $[M]^+$: 252.1509; found 252.1507.

From ***8***: A stirred mixture of **8** (197 mg, 0.83 mmol), 2,5-dimethylfuran (2.26 g, 23.5 mmol), THF (2.5 mL) and KO*t*Bu (110 mg, 0.98 mmol) was heated at 70 °C for 5 h. It was hydrolysed (5 mL) after it had adopted room temperature and the layers were separated. The aqueous layer was extracted with DEE (2×3 mL). The combined organic layers were dried with $MgSO_4$ and concentrated in vacuo to give a yellow oil (46 mg), the ^{1}H NMR spectrum of which proved it to be essentially a 1.0:1.5 mixture of **14** (9%) and **8**.

From ***9***: A stirred mixture of **9** (228 mg, 0.96 mmol), 2,5-dimethylfuran (4.50 g, 46.8 mmol), THF (2.5 mL), dimethyl sulfoxide (2.5 mL) and KO*t*Bu (124 mg, 1.10 mmol) was heated at 70 °C for 5 h. It was hydrolysed (5 mL) after it had adopted room temperature and the layers were separated. The aqueous layer was extracted with DEE (2×3 mL). The combined organic layers were dried with $MgSO_4$ and concentrated in vacuo to give a yellow oil (58 mg), the ^{1}H NMR spectrum of which proved that **14** was the major component.

(1α,4α,4aα)-4a-Phenyl-1,4,4a,5,6,7-hexahydro-1,4-epoxynaphthalene (3): A stirred mixture of **8** and **9** (1.7:1.0, 500 mg, 2.11 mmol), furan (2.81 g, 41.3 mmol), dimethyl sulfoxide (3 mL) and KO*t*Bu (272 mg, 2.42 mmol) was heated at 60 °C for 5 h. It was hydrolysed (4 mL) after it had adopted room temperature and the layers were separated. The aqueous layer was extracted with DEE (2×3 mL). The combined organic layers were dried with $MgSO_4$ and concentrated in vacuo to give a yellow oil (227 mg), the ^{1}H NMR spectrum for which, in comparison with the published data,[4] indicated the presence of **3** as component of a mixture with dimethyl sulfoxide and impurities. As estimated on the basis of the integrals, the content of **3** was about 70 mg (15%). In view of the previous characterisation of **3**,[4] we did not carry out its isolation.

1,2,3,4,6,7,8,8a-Octahydro-8a-phenyltriphenylene (16): KO*t*Bu (325 mg, 2.90 mmol) was added to a solution of **8** (596 mg, 2.51 mmol) in anhydrous THF (10 mL) at 20 °C. The mixture was vigorously stirred at 60 °C for 7 h and then cooled to 20 °C. Water (30 mL) and CH_2Cl_2 (30 mL) were admixed and the layers were separated. The aqueous layer was extracted with CH_2Cl_2 (30 mL). The combined organic layers were dried with Na_2SO_4 and concentrated in vacuo to give an oily residue. Purification by chromatography (silica gel, pentane) afforded pure **16** (122 mg, 31%) as colourless crystals. M.p. 141–142 °C; ^{1}H NMR (600 MHz, C_6D_6): δ=1.25 (m, 1H; H2), 1.36–1.46 (m, 3H; 2H7, H3), 1.49 (m, 1H; H2), 1.62 (m, 1H; H3), 1.85 (br dt, ^2J=16.9 Hz, average of $2\,^3J$=4.5 Hz, 1H; H1), 2.04 (apparent dt, line distances=8.1, 4.4 Hz, 2H; 2H6), 2.12 (td, (average of ^2J and ^3J)=12.5 Hz, ^3J=3.4 Hz, 1H; H8), 2.12–2.24 (m, 2H; H1, H4), 2.33 (ddd, ^2J=12.5 Hz, ^3J=4.5, 2.8 Hz, 1H; H8), 2.53 (br dt, ^2J=16.9 Hz, average of $2\,^3J$=5.0 Hz, 1H; H4), 5.99 (t, line distance 4.2 Hz, 1H; H5), 6.94 (*p*-H of Ph), 7.08 (*m*-H of Ph), 7.11 (dd, $J_{11,12}$=7.7 Hz, $J_{10,12}$=1.5 Hz, 1H; H12), 7.16 (td, (average of $J_{10,11}$ and $J_{11,12}$)=7.5 Hz, $J_{9,11}$=1.3 Hz, 1H; H11), 7.22 (td, (average of $J_{9,10}$ and $J_{10,11}$)=7.5 Hz, $J_{10,12}$=1.5 Hz, 1H; H10), 7.28 (*o*-H of Ph), 7.59 ppm (dd, $J_{9,10}$=7.7 Hz, $J_{9,11}$=1.3 Hz, 1H; H9); the assignment is based on a H,H COSY spectrum and NOE measurements; ^{13}C NMR (151 MHz, $CDCl_3$): δ=18.3, 22.5, 22.9 (C2, C3, C7), 25.5, 25.9 (C1, C6), 27.0 (C4), 36.4 (C8), 45.9 (C8a), 122.4 (C11), 125.1 (C9), 125.4 (*p*-C of Ph), 125.5 (C5), 125.7 (C10), 126.3 (C12), 127.2 (*m*-C of Ph), 127.6 (*o*-C of Ph), 128.2, 131.8, 135.7, 139.0, 142.2, 147.3 ppm (C4a, C4b, C8b, C12a, C12b, *i*-C of Ph); as far as specified, the assignment is based on a C,H COSY spectrum; UV (CH_3CN): λ_{max} ($\log\varepsilon$)=304 nm (3.98); MS (70 eV, EI): *m*/*z* (%): 312 (100) $[M]^+$, 284 (19), 269 (19), 241 (17), 236 (21), 235 (85), 234 (17), 208 (19), 195 (19), 193 (26), 191 (20), 179 (24), 178 (29), 167 (22), 165 (26), 157 (45), 141 (15), 129 (18), 128 (16), 115 (19), 91 (50); elemental analysis calcd (%) for $C_{24}H_{24}$: C 92.26, H 7.74; found: C 92.03, H 7.71.

(4a*R,8b*R**,1′*R**)-2,3,4,4a,8b,9,10,11-Octahydro-8b-phenyl-4a-(3-phenylcyclohex-2-en-1-yl)triphenylene (17)**: Under nitrogen, a stirred solution of **5** (2.00 g, 6.33 mmol) in anhydrous *tert*-butyl methyl ether (20 mL), cooled to −30 °C, was treated dropwise with methyllithium (6.3 mmol, 4.2 mL 1.5 M in DEE) within 15 min. The mixture was then allowed to warm to 0 °C and was cautiously hydrolysed. The layers were separated, the organic layer was extracted with water (20 mL), dried with $MgSO_4$ and concentrated in vacuo. The residue was purified by chromatography (silica gel; PE/EA, 13:1) to give a colourless material (390 mg), which was dissolved in pentane at room temperature. This solution was kept at −30 °C. After 14 d, a solid (m.p. 121–122 °C, 180 mg, 18%) had precipitated, which turned out to be almost pure **17**. ^{1}H NMR (600 MHz, $CDCl_3$): δ=1.41–1.53 (m, 2H), 1.56 (m, 1H), 1.72 (m, 1H), 1.75–1.88 (m, 3H), 1.89–1.95 (m, 2H), 1.98 (td, J=12.7, 4.7 Hz, 1H), 2.02–2.19 (m, 4H), 2.20–2.29 (m, 2H), 2.35 (br d, J=16.5 Hz, 1H), 2.53 (m, 1H, H1′), 2.69 (≈dt, J=12.5, 3.9 Hz, 1H), 5.70 (t, J=4.0 Hz, 1H), 5.80 (t, J=4.0 Hz, 1H), 6.19 (br s, 1H), 7.06 (1H; *p*-H of Ph), 7.11–7.20 (m, 5H), 7.22–7.28 (m, 4H), 7.31 (m, 1H), 7.36 (2H; *o*-H of Ph), 7.38 ppm (m, 1H); ^{13}C NMR (151 MHz, $CDCl_3$): δ=18.8, 19.8, 23.6, 24.3, 25.0, 25.2, 27.5, 31.3, 36.1 (C2, C3, C4, C9, C10, C11, C4′, C5′, C6′), 44.9. 47.2 (C4a, C8b), 48.3 (C1′), 124.0, 124.6, 125.2, 125.3, 125.9, 126.4, 126.5, 127.6, 129.2 (C1, C5, C6, C7, C8, C12, C2′, 2*p*-C of Ph), 125.1, 127.5, 127.7, 128.1 (2*m*-C, 2*o*-C of Ph), 137.0, 142.1, 142.9, 143.4 (double intensity), 143.7, 148.3 (C4b, C8a, C12a, C12b, C3′, 2*i*-C of Ph); as far as specified, the assignment is based on a C,H COSY spectrum; MS (70 eV, EI): *m*/*z* (%): 468 (1) $[M]^+$, 312 (34), 311 (100) $[M-C_{12}H_{13}]^+$, 233 (25), 193 (10), 157 (44) $[C_{12}H_{13}]^+$, 129 (11), 91 (30); elemental analysis calcd (%) for $C_{36}H_{36}$: C 92.26, H 7.74; found: C 92.08, H 7.82.

The ^{1}H NMR spectrum of the crude product (before submission to chromatography) showed that 50% of the aromatic proton signals originated from **17**, as determined by comparison of the integral with that of an olefinic proton signal of **17**. Crystals for the X-ray structure analysis were obtained by dissolving the almost pure **17** (see above) in hexane heated to reflux, which took several hours, and allowing only a very slow cooling of the solution to room temperature. Yield: colourless prisms, m.p. 159–

160 °C. As evidenced by ^{1}H NMR signals at $\delta = 5.81$, 5.83 and 6.28 ppm, for which the shapes are the same as those of the signals of **17** at $\delta =$ 5.70, 5.80 and 6.19 ppm, even this crystalline solid held an impurity of about 5%, which may well be a diastereomer of **17.**

X-ray crystal-structure determination of ***17***: The data were collected from a shock-cooled crystal using a Bruker Smart APEX II diffractometer with a D8 goniometer (graphite-monochromated $Mo_{K\alpha}$ radiation, $\lambda =$ 71.073 pm) equipped with a low-temperature device operating at 100(2) K.[26] An empirical absorption correction with the program SADABS 2004/1 was employed.[27] The structure was solved by direct methods (SHELXS-97[28]) and refined by full-matrix least squares methods against F^2 (SHELXL-97[29]). R values: $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$, $wR_2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2]^{0.5}$, $w = [\sigma^2(F_o^2) + (g_1P)^2 g_2P]^{-1}$, $P = {}^1/_3[\max(F_o^2,0) + 2F_c^2]$; $C_{36}H_{36}$; $M_r = 468.65$; monoclinic; space group $P2_1/n$; $a = 1665.41(8)$, $b = 971.16(5)$, $c = 1726.45(8)$ pm; $\beta = 113.6120(10)°$; $V = 2.5585(2)$ nm^3; $Z = 4$; $\rho_{calcd} = 1.217$ Mg m^{-3}; 28736 reflections measured, 6004 unique; R_1 $[I > 2\sigma(I)] = 0.0465$; wR_2 (all data) $= 0.1516$; $g_1 = 0.0959$, $g_2 = 0.3554$ for 335 parameters and 12 restraints; GOF $= 1.124$; residual density (max/min) $= 0.468/-0.389$ e Å^{-3}.

All non-hydrogen atoms were refined with anisotropic displacement parameters. Hydrogen atoms were assigned ideal positions and refined isotropically by using a riding model with U_{iso} constrained to 1.2 times the U_{eq} of the parent atom. The disorder of the methylene group of position 17 was refined using similarity restraints. Site occupation factors of 0.845 and 0.155 have been obtained.

CCDC-724091 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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