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Cycloallenes. Part 15:[1] 3δ^2-1*H*-Naphthalene (2,3-Didehydro-1,2-dihydronaphthalene) from 3-Bromo-1,2-dihydronaphthalene

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Dedicated to Professor Rolf Huisgen on the occasion of his 80th birthday

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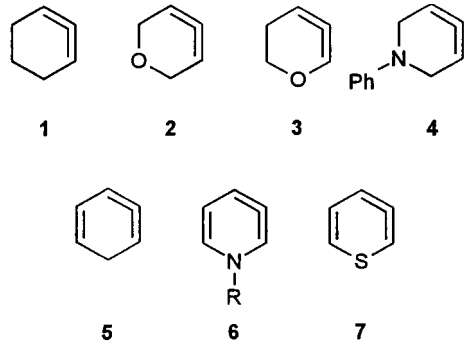
Abstract—As a test as to whether the title intermediate **13** can be liberated from 3-bromo-1,2-dihydronaphthalene (**19**), the latter was treated with potassium *tert*-butoxide (KO*t*Bu). Being the major products, naphthalene (**20**) and 3-*tert*-butoxy-1,2-dihydronaphthalene (**21**) provide unambiguous evidence for the intermediacy of **13**. When the reaction was carried out in the presence of furan, 2,5-dimethylfuran and spiro[2,4]hepta-4,6-diene, expected (**31**, **32**, **33**, **34**) and unexpected compounds (**30**, **35**–**37**) were formed, which either directly resulted from the cycloaddition of **13** or were consecutive products of cycloadducts. Performed in the presence of benzophenone, the generation of **13** gave, inter alia, naphth-2-yldiphenylmethanol (**27**). This product testifies the intermediacy of the naphth-2-yl anion (**24**), which emerged from the deprotonation of **13** and was trapped by benzophenone.

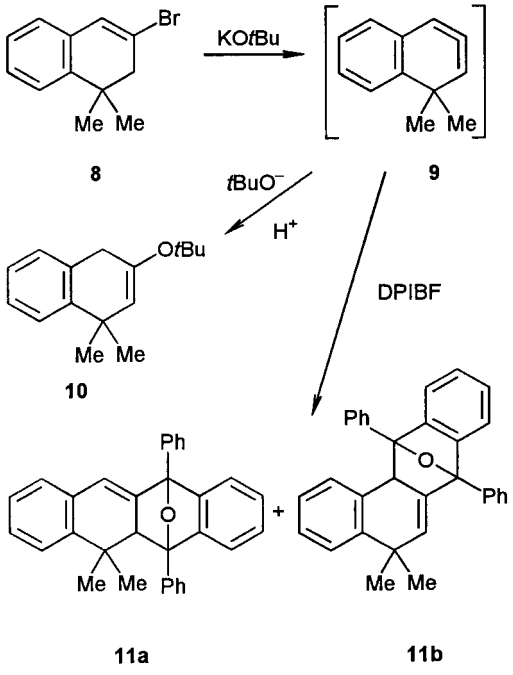
Introduction

Cyclohexa-1,2-diene (**1**)[2] and its oxa- and azaderivatives **2**,[3] **3**[4–7] and **4**[8] (Scheme 1) are extremely short-lived intermediates, which in spite of that may be intercepted in addition and cycloaddition reactions very efficiently. The introduction of a third double bond into the six-membered ring, being in conjugation with the allene system, was achieved in the case of cyclohexa-1,2,4-trienes for the first time.[2] Originally, the parent **5** (Scheme 1) of these was generated by Doering–Moore–Skattebøl reactions and intercepted by activated olefins.[5,9] Later, **5** was made accessible by two further routes.[10,11] Shevlin et al. provided evidence for the existence of 1-azacyclohexa-2,3,5-trienes **6**[12] and 1-thiacyclohexa-2,3,5-triene (**7**)[13] (Scheme 1).



Scheme 1.

The first benzo-annulated derivative of **5** (compound **9** in Scheme 2) was liberated from the bromonaphthalene **8** by



Scheme 2.

Keywords: allenes; cycloadditions; eliminations; rearrangements.

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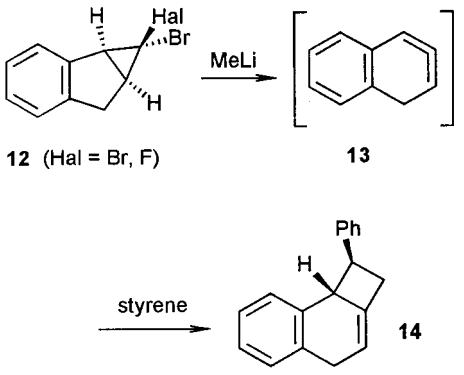
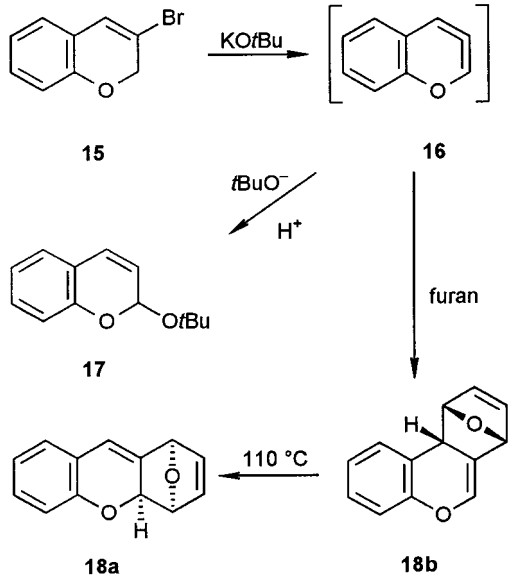


Scheme 3.

potassium *tert*-butoxide (KO*t*Bu) in a β-elimination reaction and trapped by KO*t*Bu as well as 1,3-diphenylisobenzofuran (DPIBF) furnishing the enol ether **10** and the cycloadducts **11**, respectively.[14]

The parent compound to **9**, i.e. the title cycloallene **13**, was shown to emerge from the dihalocarbene adducts **12** of indene in Doering–Moore–Skattebøl reactions (Scheme 3).[5,9] If the experiments are conducted in the presence of activated olefins, [2+2] cycloadducts of **13** result with styrene (see **14**),[5,9] α-methylstyrene, 2,3-dimethylbuta-1,3-diene[9] and buta-1,3-diene[9,15] and [4+2] cycloadducts with 2,3-dimethylbuta-1,3-diene[9], buta-1,3-diene[9,15] and cyclopenta-1,3-diene.[15]

Although methyllithium serves as reagent, the deprotonation of **13**, which would give rise to the naphth-2-yl anion (**24**), does not interfere. This is astounding, since the aromatic character of **24** causes an enormous driving force for this conversion. In the present work, we have revisited this problem and examined the possibility to generate **13** by a β-elimination as in the case of **9**. In addition to the reaction of **8** with KO*t*Bu,[14] the analogous transformations of 1-bromocyclohexa-1,4-diene to give **5**[11] and of 3-bromo-2*H*-chromene (**15**) to give the oxaderivative **16** of **13**[16] served as models. Apart from the interception of **16** by furan with formation of the [4+2] cycloadduct **18b**, which rearranges to **18a** on heating at 110°C, that by KO*t*Bu/HO*t*Bu is particularly remarkable (Scheme 4), since the resulting acetal **17** testifies a highly polar character of **16**.[16]



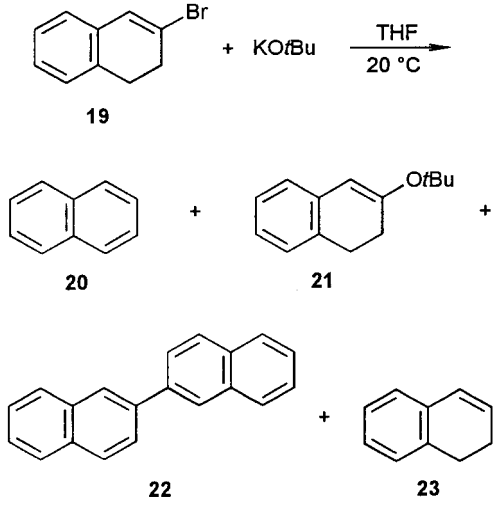
Scheme 4.

Results and Discussion

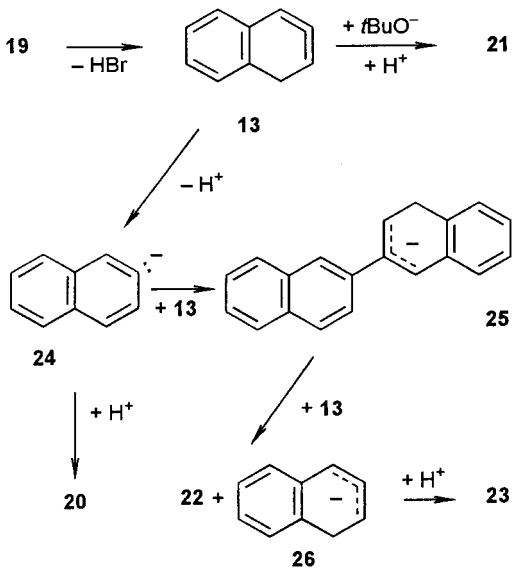
Treatment of 3-bromo-1,2-dihydronaphthalene (19) with KO*t*Bu in the absence and presence of benzophenone

As a precursor for **13**, we chose **19**, which is accessible from 1-tetralone in three steps with an overall yield of 50%.[17] The treatment of **19**, dissolved in anhydrous tetrahydrofuran (THF), with 2.3 equiv. of KO*t*Bu gave a 73:22:3:2 mixture of naphthalene (**20**), 3-*tert*-butoxy-1,2-dihydronaphthalene (**21**), 2,2′-binaphthyl (**22**) and 1,2-dihydronaphthalene (**23**) in a yield of 92% (Scheme 5). When less than 2 equiv. of KO*t*Bu were employed, **19** was not consumed completely. Five equivalents of KO*t*Bu changed the product ratio to 84:12:2:2. The identification of the known compounds **20**, **22** and **23** was trivial, whereas **21** revealed its structure by the characteristic NMR signals of the enol ether subunit.

The outcome of this reaction is best rationalised by assuming the β-elimination of HBr from **19** with formation of the desired intermediate **13**. There is no evidence for the alternative β-elimination, which would generate the isomeric cyclic alkyne. Since the yield of the products is close to quantitative, KO*t*Bu must interact with **13** efficiently in two ways. The nucleophilic attack at the central allene carbon atom and the protonation of the resulting allyl anion by HO*t*Bu leads to the enol ether **21** (Scheme 6). This pathway is analogous to that to **10**[14] or to 1-*tert*-butoxycyclohex-1-ene, the final product of the interception of **1** by tBuO^{-2}, but different to that to **17**, formed eventually after the addition of tBuO$^-$ to **16**.[16] The enol ether **21** on one side and the allyl ether (acetal) **17** on the other underline the different electronic character of **13** and **16**. While **16** is best described as a pyrylium ylide, the ground state of **13**



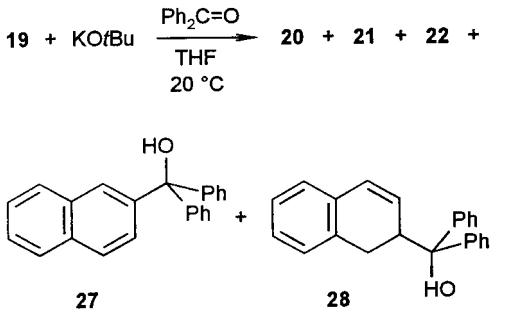
Scheme 5.



Scheme 6.

should be essentially nonpolar and should have an allene or an allyl diradical structure.

The second possibility for the interaction of KO*t*Bu with **13** is the deprotonation of the methylene group taking advantage of a strong thermodynamic preference due to the aromaticity of the arising naphth-2-yl anion (**24**), which is converted into **20** on protonation by HO*t*Bu. That the binaphthyl **22** appeared as a product may be a manifestation of the nucleophilicity of **24**. It could attack **13** in much the same way as $t\mathrm{BuO}^-$ and, in consequence, generate the allyl anion derivative **25**. Being a better stabilised anion than **24**, **25** seems not to accept a proton, but to transfer a hydride ion to **13**, the role of which as an electrophile is thus invoked a third time. The outcome would be **22** and the 1,2-dihydronaphth-2-yl anion (**26**), which should serve as the precursor to **23** (Scheme 6). Support for the intermediacy of the carbanions **24** and **26** was provided by the treatment of **19** with KO*t*Bu in the presence of benzophenone. Again, the major product was naphthalene (**20**) and also the enol ether **21** and the binaphthyl **22** were obtained, but the formation of the tertiary alcohols **27** and **28** (13 and 4% yield, respectively) could be demonstrated beyond doubt as well (Scheme 7). This was achieved by the synthesis of authentic samples of **27**[18] and **28** by reaction of benzophenone with naphth-2-yl magnesium bromide and 1,2-dihydronaphth-2-yl potassium,[19] respectively. Hence, **27** and **28** prove that the carbanions **24** and **26** emerge from **19** and are intercepted by benzophenone.

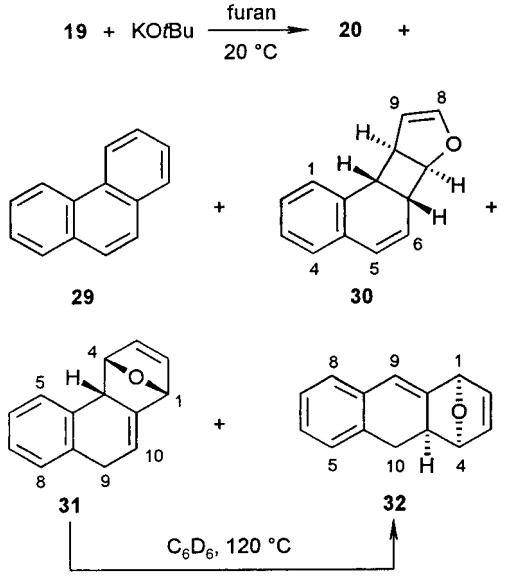


Scheme 7.

Treatment of 3-bromo-1,2-dihydronaphthalene (19) with KO*t*Bu in the presence of furan, 2,5-dimethylfuran and spiro[2,4]hepta-4,6-diene

Generated in the absence of any reaction partner, six-membered cycloallenes either dimerise to give derivatives of 1,2-bismethylenecyclobutane (**1**[2] and a number of derivatives thereof[20]), oligomerise (**1**[2]) or presumably polymerise, if dimers and oligomers are not formed in quantity (**2**, **3**, **4**, **5**, **13**). As mentioned in the Introduction, an outstanding property of many six-membered cycloallenes is their ability to undergo cycloadditions with activated olefins. Thus, a further indication for the fleeting existence of **13** on treatment of **19** with KO*t*Bu would be the observation of the respective cycloadducts. Relying on good experience, we chose furan,[2–4,6,8,9,11,16] 2,5-dimethylfuran[6,11,16] and spiro[2,4]hepta-4,6-diene[21] as trapping reagents for **13**. Spiro[2,4]hepta-4,6-diene was taken instead of cyclopenta-1,3-diene, which ranks first among activated olefins as to the cycloaddition rate with **1**[22] and which was successfully utilised also in the cases of **4**,[8] **5**[9] and **13**,[15] because KO*t*Bu is not compatible with cyclopenta-1,3-diene due to the acidity of the latter. Indeed, the isolation of two or three addition products in each case testified the intermediacy of **13**.

The reaction of **19** with KO*t*Bu in pure furan furnished the dihydrofuran derivatives **30**–**32**, albeit in yields of only 2, 11 and 8%, respectively. Major products were naphthalene (**20**, 41%) and phenanthrene (**29**, 26%). On heating in C_6D_6 at 120°C, **31** rearranged to **32** with high efficiency (Scheme



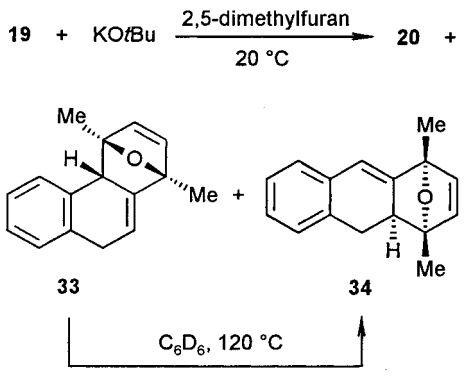
Scheme 8.

8). This kind of isomerisation was discovered in the case **18b** (Scheme 4) and two of its methyl derivatives.[16]

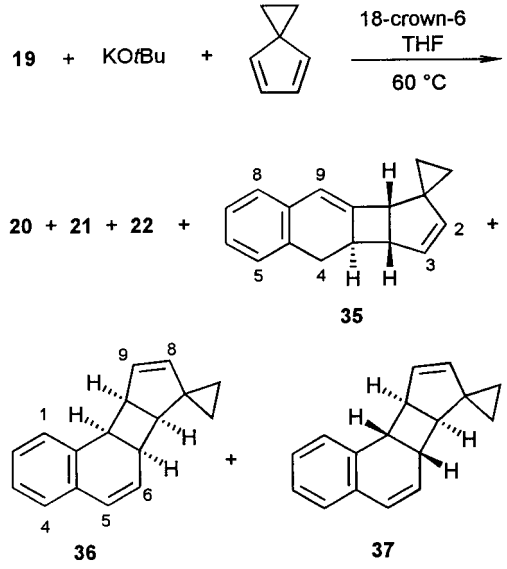
2,5-Dimethylfuran behaved like furan and gave rise to the [4+2] cycloadducts **33** and **34** of **13**. Since again **20** was the dominating product (46%), only poor yields of **33** (8%) and **34** (<1%) could be obtained. The virtually quantitative transformation of **33** to **34** by heating a solution in C_6D_6 at 120°C proved to be the best source for **34** (Scheme 9).

In the solution of **19** in pure spiro[2,4]hepta-4,6-diene, KO*t*Bu did not cause the elimination to happen. Only on dilution of the mixture with THF, addition of 18-crown-6 and heating at 60°C, **19** was consumed to produce **20**, **21** and **22** as well as the pentacyclic adducts **35**–**37**, which were isolated in yields of only 3, 2, 1, 9, 4 and 7%, respectively (Scheme 10).

Constitution and configuration of **31**–**34** were established by the typical NMR spectroscopic data in comparison to those of the furan adducts of other six-membered cycloallenes, which are [4+2] cycloadducts with no exception and have the *endo*-configuration either exclusively (**2**–**5**, **16**) or predominantly (**1**). Conclusive evidence for the



Scheme 9.



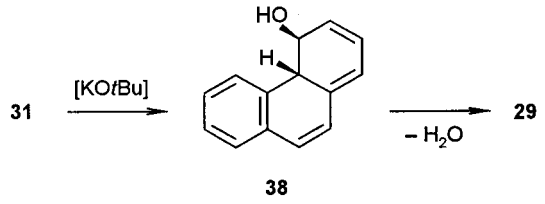
Scheme 10.

endo-configuration is provided by the coupling constants $J_{4,4a}$=4.2 Hz in **31** and **32**. If 4a-H occupied the *endo*-position at the oxanorbornane skeleton, the value of this coupling constant should be close to zero according to the Karplus–Conroy relationship. Although this criterion is not applicable to **33** and **34**, we assign them the *endo*-configuration due to the similarity of their data to those of **31** and **32**. As to the structure of **30**, the deciding pieces of information originate from the enol ether moiety. The proposed configuration rests on the magnitude of the interproton coupling constants of the cyclobutane subunit, whereas the relative orientation of the furan and naphthalene entities was determined by a H,H COSY spectrum. By employing these tests, the structures of **35**–**37** could also be elucidated completely. Even if we did not succeed in isolating **30**, **36** and **37** in a pure state, no doubts remain as to their structures due to extremely characteristic ^{1}H and ^{13}C NMR spectroscopic data.

Striking features of these cycloadditions of **13** are low yields of all the adducts accompanied by good yields of naphthalene (**20**), apart from the case of spiro[2,4]hepta-4,6-diene. There, 18-crown-6 probably enhances the nucleophilicity of the intermediate naphth-2-yl anion (**24**) so strongly that it causes most of the material to polymerise. In comparison to the Doering–Moore–Skattebøl route to **13**, the urgent question arises as to why there, the formation of **20** is negligible and here it proceeds predominantly. For two reasons, the β-elimination route starting from **19** may be put at a disadvantage with respect to the trapping of **13** by activated olefins. Firstly, the elimination of HBr takes place slowly and, in consequence, the intermediate **13** formed is exposed to a large excess of base, which deprotonates **13** and thus produces **24**, the precursor of naphthalene (**20**). Activated olefins have to compete for **13** against the base. This obstacle plays hardly any part in the generation of **13** from the dihalocyclopropane derivatives **12** by methyllithium, since the bromine–lithium exchange as well as the α-elimination of lithium halide are rapid steps.[23] Therefore, **13** never faces a large concentration of base, if methyllithium is slowly added to a solution of **12**. The second reason may have its origin in the different nature of the bases. It is well known that at a given p*K* value hetero atom bases react considerably more rapid than carbon atom bases.[24] If these characteristics hold for KO*t*Bu on one side and methyllithium on the other, the rate constant for the deprotonation of **13** by KO*t*Bu could be the larger one.

The [4+2] cycloadducts **31**–**34** meet the expectation as to the intermediacy of **13**, but the appearance of phenanthrene (**29**) and the enol ether **30** throw new light on the mechanism of interception of strained allenes by furan and on the behaviour of certain furan adducts. Most probably, **29** is a consecutive product of **31**, which just has to eliminate one molecule of water. This is assumed to occur under the catalytic influence of KO*t*Bu, which could deprotonate the rather acidic methylene group of **31**, via the cyclohexadienol **38** as shown in Scheme 11.

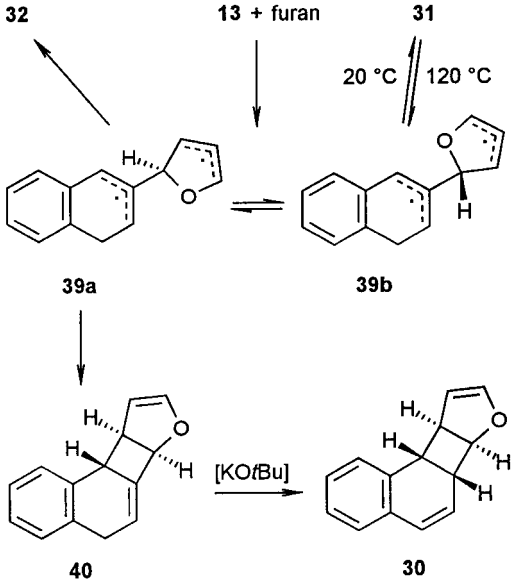
The enol ether **30** seems to emerge from the [2+2] cycloadduct **40** of **13** with furan. Heretofore, no such products from furan and six-membered cycloallenes are known and



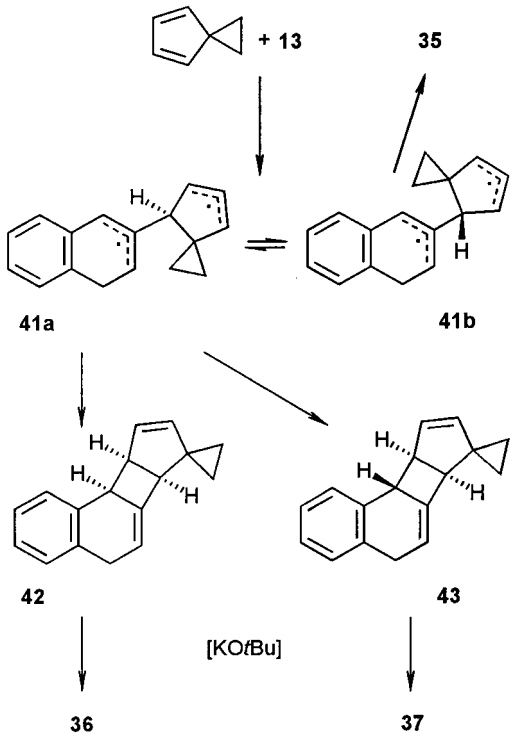
Scheme 11.

only [4+2] cycloadducts have been described.[2–4,6,8,9,11,16] Recently, Tolbert et al.[25] presented convincing theoretical evidence that even [4+2] cycloadducts of **1** with conjugated dienes such as furan proceed in two steps via a diradical intermediate. Since the Woodward–Hoffmann rules favour the stepwise formation of [2+2] cycloadducts, the diradical **39** should be the common intermediate en route to the products **30**–**32** (Scheme 12). On closure of the four-membered ring, conformer **39a** furnishes **40**, which isomerises to give **30** by deprotonation of the methylene group by KO*t*Bu and reprotonation by HO*t*Bu of the resulting allyl anion at the terminus belonging to the cyclobutane moiety. The energetic preference of **30** over **40** originates from the special strain of the methylenecyclobutane subunit of **40** and the resonance energy of the styrene subunit of **30**. An alternative ring closure of **39a** leads to the [4+2] cycloadduct **32**. Being engaged in the extremely mobile equilibrium with **39a**, conformer **39b** seems to collapse to the [4+2] cycloadduct **31** exclusively. Probably owing to its conjugated double bond, **32** is more stable than **31**. For the rearrangement of **31** to **32** at 120°C, we again invoke the diradical **39** (Scheme 12).

As trapping products of **13** by spiro[2,4]hepta-4,6-diene, the cyclobutane derivatives **35**–**37** came as a surprise, since the only previous reaction of this kind, i.e. the interception of **3** by that diene led to a [4+2] cycloadduct in 53% yield.[21] The diradical **41** is assumed to be the common intermediate for all products **35**–**37** (Scheme 13). Why no [4+2] cycloadduct was observed may have two reasons. Either the



Scheme 12.



Scheme 13.

collapse of **41** to give a six-membered ring is kinetically unfavourable because of the steric hindrance exerted by the cyclopropane subunit or the [4+2] cycloadducts are thermodynamically unstable and maintain a mobile equilibrium with **41** even under the reaction conditions (60°C).

Resulting from the attack of the central allene carbon atom of **13** at a terminus of the diene moiety of spiro[2,4]hepta-4,6-diene, the conformer **41b** furnishes the [2+2] cycloadduct **35**, which was isolated, on the conrotatory ring closure. In contrast, no isolable compound emerges directly from conformer **41a**. As we infer from the products **36** and **37**, it may collapse in either way, disrotatorily or conrotatorily, and bring about the [2+2] cycloadducts **42** and **43**, respectively, which are converted into **36** and **37** by [1,3] hydrogen migration, probably catalysed by KO*t*Bu as discussed for the pathway proposed for the formation of **30** (see Scheme 12).

Conclusions

We have demonstrated that the title intermediate **13** can be generated from 3-bromo-1,2-dihydronaphthalene (**19**) by β-elimination of HBr with KO*t*Bu. In line with the behaviour of other six-membered cycloallenes, **13** is subject to trapping by KO*t*Bu and conjugated dienes. Particularly interesting are the products **30** and **35**–**37**, which give evidence for [2+2] cycloadditions of a strained cycloallene with furan and spiro[2,4]hepta-4,6-diene for the first time. However, produced on the above route, **13** preferably isomerises to naphthalene (**20**). This process is initiated by KO*t*Bu by deprotonation of **13** to furnish the naphth-2-yl anion (**24**) and takes advantage of a substantial driving force due to the aromatic character of **24**. In consequence, the

access to **13** via **19** has mechanistic importance, although it is inferior to the one-pot procedure starting from indene[9] for the preparation of cycloadducts of **13** in quantity.

Experimental

^{1}H and ^{13}C NMR spectra were recorded with Bruker AC 200, AC 250 and DMX 600 instruments. As internal standards served $CHCl_3$ (δ 7.26) for ^{1}H NMR and $CDCl_3$ (δ 77.0) for ^{13}C NMR spectroscopy. *J* values are given in Hz. The multiplicities of the signals in the ^{1}H NMR spectra are abbreviated by s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet), br (broad) and combinations thereof. The multiplicities in the ^{13}C NMR spectra were determined by a DEPT sequence or by C,H COSY spectra. IR spectra were recorded on a Perkin–Elmer 1605 FT-IR spectrometer. Mass spectra were recorded on Finnigan MAT 8200 (EI mode, 70 eV) and MAT 90 instruments (CI mode and high resolution MS). Elemental analyses were obtained from a LECO CHNS 932 Elemental Analyzer. Melting points were determined by using a Kofler hot stage from C. Reichert, Optische Werke A. G., Wien, Austria. For the separation by HPLC, a Bruker-Franzen instrument LC 21C was used.

All reactions were conducted in anhydrous solvents in an atmosphere of dry nitrogen. The progress was monitored by thin layer chromatography on pre-coated plastic sheets Polygram® SIL G/UV_{254} or ALOX N/UV_{254} (Macherey–Nagel, Düren) having 0.25 and 0.2 mm layers, respectively, and a fluorescent indicator. Flash chromatography was performed on SiO_2 (0.040–0.063 mm). The eluants were light petroleum (LP, referring to the fraction with bp 30–50°C) and diethyl ether (E). Whereas the former had to be distilled for purification, the latter was used as obtained from the supplier.

Reaction of 3-bromo-1,2-dihydronaphthalene (19) with potassium *tert*-butoxide (KO*t*Bu)

To a solution of **19** (1.614 g, 7.72 mmol) in THF (40 cm^3) was added KO*t*Bu (1.970 g, 17.6 mmol). The mixture was stirred at 20°C and turned brown within 24 h. It was then cautiously treated with water (5 cm^3). Diethyl ether was admixed until two layers resulted, which were separated. The aqueous layer was extracted with diethyl ether (3×10 cm^3). The combined organic layers were dried with $MgSO_4$ and concentrated in vacuo to give a somewhat gummy solid (1.147 g), which was shown to consist mainly of a 73:22:3:2 mixture of naphthalene (**20**), 3-*tert*-butoxy-1,2-dihydronaphthalene (**21**), 2,2′-binaphthyl (**22**) and 1,2-dihydronaphthalene (**23**) by ^{1}H NMR spectroscopy. By using diethyl malonate as internal standard the yield was determined to be 92%. On employing a molar ratio of **19**: KO*t*Bu=1:5 instead of 1.0:2.3 (see above), the product ratio changed to 84:2:2:2.

The crude product obtained from 2.55 g of **19** (12.2 mmol) was subjected to flash chromatography (SiO_2, LP for the first 1140 cm^3 of eluate and finally LP–E 20:1). The enol ether **21** (160 mg, 6%) was eluted after the hydrocarbons.

Enol ether 21. Colourless oil, bp 100°C (kugelrohr)/0.01 mbar; *m/z* (EI) 202 (M^+, 5%), 147 (12), 146 (100), 145 (29), 131 (14), 128 (11), 127 (11), 117 (24), 116 (23), 115 (25), 41 (18), 39 (11) [Found (EI): M^+, 202.1352. $C_{14}H_{18}O$ requires for M^+, 202.1358]; $\tilde{\nu}_{max}$ (thin film)/cm^{-1} 3013 (m), 2976 (s), 2934 (s), 2887 (s), 2833 (m), 1631 (s), 1602 (m), 1570 (s), 1486 (s), 1452 (m), 1436 (m), 1426 (m), 1391 (m), 1367 (s), 1320 (m), 1270 (m), 1253 (s), 1172 (s), 1149 (s), 1106 (m), 1036 (m), 1001 (m), 907 (s), 860 (m), 821 (m), 746 (s), 670 (m); δ_H (600 MHz, $CDCl_3$) 1.48 (9H, s, *t*Bu), 2.36 (2H, pseudo-t of d, line distance of pseudo-t=8.1, $J_{2,4}$=0.9 Hz, 2-CH_2), 2.89 (2H, br pseudo-t, line distance=8.1, 1-CH_2), 5.82 (1H, br s, 4-H), 6.96 (1H, br d, *J*=7.4 Hz) and 7.13 (1H, tdt, *J*=7.4,1.4 and 0.7 Hz) (5-H, 6-H or 8-H, 7-H), 7.02 (1H, td, *J*=7.4 and 1.3 Hz) and 7.09 (1H, dm, *J*=7.4 Hz) (7-H, 8-H or 6-H, 5-H); as far as specified, the assignment is based on a H,H COSY spectrum; δ_C (151 MHz, $CDCl_3$) 28.76, 78.1 (*t*Bu), 28.79 (C-1), 29.4 (C-2), 105.2 (C-4), 124.5, 126.9 (C-6, C-5 or C-7, C-8), 124.8, 126.4 (C-8, C-7 or C-5, C-6), 132.2, 135.8 (C-4a, C-8a), 155.9 (C-3).

2,2′-Binaphthyl (22). See next experiment.

1,2-Dihydronaphthalene (23). The ^{1}H NMR signals were the same of those of a commercial sample.

Reaction of 19 with KO*t*Bu in the presence of benzophenone—formation of naphth-2-yldiphenylmethanol (27) and 1,2-dihydronaphth-2-yldiphenylmethanol (28)

To a solution of **19** (2.55 g, 12.2 mmol) and benzophenone (4.44 g, 24.4 mmol) in THF (40 cm^3) was added KO*t*Bu (6.85 g, 61.0 mmol). The mixture was stirred at room temperature for 2 h and then treated with water (50 cm^3) and diethyl ether, until two layers resulted. These were separated and the aqueous layer was extracted with diethyl ether (3×30 cm^3). The combined organic layers were dried with $MgSO_4$ and concentrated in vacuo. The residue was purified by flash chromatography (SiO_2, LP–E 20:1 for the first 260 cm^3 of eluate, 10:1 for the next 220 cm^3, 5:1 for the next 100 cm^3 and finally 2:1) to give, in the order of elution, naphthalene **20** (800 mg, 51%), a 1:2 mixture (120 mg) of **20** (2%) and **21** (4%), **22** (120 mg, 4%), a 3:1 mixture (190 mg) of **28** (4%) and benzophenone and **27** (500 mg, 13%).

2,2′-Binaphthyl (22). Colourless crystals, mp 187°C (Ref. 26, 187–189°C); δ_H (600 MHz, $CDCl_3$) 7.51, 7.53 (2×1H, 2×ddd, $J_{6,7}$=6.8 Hz, *J*=8.0 and 1.4 Hz, 6-H, 7-H), 7.893 (1H, dd, $J_{3,4}$=8.4 Hz, $J_{1,3}$=1.8 Hz, 3-H), 7.895, 7.95 (2×1H, 2×br d, $J_{5,6}$=$J_{7,8}$=8.0 Hz, 5-H, 8-H), 7.97 (1H, br d, $J_{3,4}$=8.4 Hz, 4-H), 8.18 (1H, br d, $J_{1,3}$=1.8 Hz, 1-H); δ_C (151 MHz, $CDCl_3$) 125.7, 127.7, 128.2 (C-3, C-5, C-8), 126.0, 126.3 (C-6, C-7), 126.1 (C-1), 128.5 (C-4), 132.7, 133.7 (C-4a, C-8a), 138.4 (C-2); in Ref. 26, two carbon signals are missing and that at 148.5 does not originate from **22**.

Alcohol 27. Colourless solid, mp 115°C (Ref. 18, 115.5°C); we prepared an authentic sample by the reaction of naphth-2-yl magnesium bromide with benzophenone; δ_H (600 MHz, $CDCl_3$) 2.90 (1H, br s, OH), 7.27–7.35 (10H,

m, C_6H_5), 7.44–7.50 (3H, m, 3-H, 6-H, 7-H), 7.70 (1H, br d, $J_{1,3}$=1.5 Hz, 1-H), 7.75, 7.83 (2×1H, 2×br d, J=7.4 Hz, 5-H, 8-H), 7.79 (1H, br d, $J_{3,4}$=8.8 Hz, 4-H); δ_C (151 MHz, $CDCl_3$) 82.2, 126.1, 126.2, 126.3, 126.5, 127.4 (high intensity), 127.5, 127.7, 127.9, 128.0 (very high intensity), 128.4, 132.5 and 132.8 (C-4a, C-8a), 144.2 (C-2), 146.7 (C-1′).

Alcohol 28. The NMR signals were the same as those of a pure authentic sample, which was prepared by reaction of 1,2-dihydronaphth-2-yl potassium in liquid ammonia[19] with benzophenone. The crude product was submitted to flash chromatography (SiO_2, LP–E 10:1 for the first 750 cm^3 of eluate and finally 5:1) to give a mixture of naphthalene, benzophenone and **28**, which was separated by HPLC (PROGIDY 5u ODS3 100A, 250×21.2 mm, methanol–water 9:1). Alcohol **28** (12% yield) was eluted as the last component, yellowish crystals, mp 116–118°C; *m/z* (EI) 294 (M^+–H_2O, 5%), 215 (6), 184 (15), 183 (100), 130 (7), 129 (10), 128 (18), 127 (6), 106 (8), 105 (100), 78 (5), 77 (43), 51 (10), 40 (7) [Found (CI, CH_4): $M+H^+$, 313.1594. $C_{23}H_{20}O$ requires for $M+H^+$, 313.1592]; δ_H (600 MHz, $CDCl_3$) 2.22 (1H, s, OH), 2.65 (1H, dd, $J_{1,1}$=16.0 Hz, $J_{1,2}$=7.2 Hz) and 2.91 (1H, dd, $J_{1,1}$=16.0 Hz, $J_{1,2}$=11.7 Hz) (1-CH_2), 3.81 (1H, ddt, $J_{1,2}$=11.7 and 7.2 Hz, average of $J_{2,3}$ and $J_{2,4}$=2.8 Hz, 2-H), 5.77 (1H, dd, $J_{3,4}$=9.8 Hz, J=3.1 Hz) and 6.58 (1H, dd, $J_{3,4}$=9.8 Hz, J=2.4 Hz) (3-H, 4-H), 6.99 (1H, br d, J=7.1 Hz) and 7.03 (1H, dd, J=7.2 and 1.3 Hz) (5-H, 8-H), 7.11 (1H, td, average of two ^3J=7.3 Hz, J=1.5 Hz) and 7.13 (1H, br t, average of two ^3J=7.3 Hz) (6-H, 7-H), 7.219, 7.222 (2×1H, 2×tt, 2×*p*-H of C_6H_5), 7.323, 7.334 (2×2H, 2×m, 2×*m*-H of C_6H_5), 7.50, 7.56 (2×2H, 2×m, 2×*o*-H of C_6H_5); δ_C (151 MHz, $CDCl_3$) 28.8 (C-1), 42.7 (C-2), 80.0 (COH), 125.6, 126.0 (2×*o*-C of C_6H_5), 126.1 (C-5 or C-8), 126.5, 127.6 (C-6, C-7), 126.6, 126.8 (2×*p*-C of C_6H_5), 127.8, 127.9 (C-8 or C-5 and C-3 or C-4), 128.3, 128.4 (2×*m*-C of C_6H_5), 131.0 (C-4 or C-3), 133.1, 135.0 (C-4a, C-8a), 145.3 (C-2), 145.9 (2×*i*-C of C_6H_5).

Reaction of 19 with KO*t*Bu in furan—formation of (1α,4α,4aα)-1,4,4a,9-tetrahydro-1,4-epoxyphenanthrene (31), (1α,4α,4aα)-1,4,4a,10-tetrahydro-1,4-epoxyanthracene (32) and (6aα,6bβ,9aβ,9bα)-6a,6b,9a,9b-tetrahydronaphtho[1′,2′:3,4]cyclobuta[1,2-*b*]furan (30)

To a stirred solution of **19** (4.00 g, 19.1 mmol) in freshly distilled furan (60 cm^3) was added KO*t*Bu (7.69 g, 68.5 mmol) in small portions over a period of 1 h at 20°C. After stirring had been continued for 3 h, more furan (20 cm^3) was added to the mixture, which was now stirred for 24 h. Then the treatment with water (30 cm^3) ensued, followed by the separation of the layers and extraction of the aqueous layer with diethyl ether (3×30 cm^3). The combined organic layers were dried with $MgSO_4$ and concentrated in vacuo. The residue was purified by flash chromatography (SiO_2, deactivated by ammonia, LP for the first 640 cm^3 of eluate, LP–E 20:1 for the next 400 cm^3 and finally 5:1) to give, in the order of elution, naphthalene (**20**) (1.00 g, 41%), phenanthrene (**29**) (890 mg, 26%), **30** (85 mg, 2%), **31** (410 mg, 11%), and **32** (300 mg, 8%).

Compound 30. Green fluorescing oil, containing impurities to the extent of 10–20%; *m/z* (EI) 196 (M^+, 2%), 195 (1), 165 (5), 129 (10), 128 (100), 127 (7), 102 (7), 63 (5), 51 (6), 39 (7) [Found (EI): $(M–H)^+$, 195.0810. $C_{14}H_{12}O$ requires for $(M–H)^+$, 195.0810]; δ_H (600 MHz, $CDCl_3$) 3.52 (1H, dddt, $J_{6a,9b}$=10.7 Hz, $J_{6,6a}$=5.4 Hz, $J_{6a,6b}$=4.0 Hz, average of $J_{5,6a}$ and $J_{6a,9a}$=1.4 Hz, 6a-H), 3.57 (1H, dtt, $J_{6b,9a}$=7.6 Hz, average of $J_{9a,9b}$ and $J_{9,9a}$=3.1 Hz, average of $J_{8,9a}$ and $J_{6a,9a}$=1.4 Hz, 9a-H), 3.65 (1H, br dd, $J_{6a,9b}$=10.7 Hz, $J_{9a,9b}$=3.4 Hz, 9b-H), 4.88 (1H, ddd, $J_{6b,9a}$=7.6 Hz, $J_{6a,6b}$=4.0 Hz, $J_{6b,9b}$=0.8 Hz, 6b-H), 5.34 (1H, t, $J_{8,9}$=$J_{9,9a}$=2.8 Hz, 9-H), 5.85 (1H, dd, $J_{5,6}$=9.8 Hz, $J_{6,6a}$=5.4 Hz, 6-H), 6.33 (1H, br d, $J_{5,6}$=9.8 Hz, 5-H), 6.43 (1H, dd, $J_{8,9}$=2.8 Hz, $J_{8,9a}$=1.5 Hz, 8-H), 6.97 (1H, dd, J=7.3 and 1.5 Hz) and 7.00 (1H, dm, J=6.9 Hz) (1-H, 4-H), 7.10 (1H, tm, J=7.4 Hz) and 7.13 (1H, td, J=7.4 and 1.6 Hz) (2-H, 3-H); δ_C (151 MHz, $CDCl_3$) 41.2 (C-9b), 42.8 (C-6a), 55.8 (C-9a), 86.6 (C-6b), 106.0 (C-9), 125.2 (C-6), 126.7, 127.9 (C-2, C-3), 127.2 (C-5), 127.3, 128.1 (C-1, C-4), 131.5, 135.8 (C-4a, C-9c), 146.7 (C-8).

Compound 31. Brownish crystals, mp 90–92°C (Found 85.24; H, 6.45. $C_{14}H_{12}O$ requires C, 85.68; 6.16%); *m/z* (EI) 196 (M^+, 58%), 195 (68), 181 (23), 179 (56), 178 (44), 177 (20), 167 (100), 166 (36), 165 (100), 153 (21), 152 (72), 128 (48), 115 (27); δ_H (600 MHz, $CDCl_3$) 3.28 (1H, ddd, $J_{9,9}$=18.5 Hz, $J_{9,10}$=6.4 Hz, $J_{4a,9}$=1.7 Hz, 9β-H), 3.37 (1H, ddm, $J_{9,9}$=18.5 Hz, $J_{4a,9}$=6.5 Hz, 9α-H), 3.47 (1H, m, 4a-H), 5.26 (1H, br d, $J_{1,2}$=1.9 Hz, 1-H), 5.61 (1H, ddt, $J_{4,4a}$=4.2 Hz, $J_{3,4}$=1.6 Hz, average of $J_{1,4}$ and $J_{4,10}$=0.7 Hz, 4-H), 5.85 (1H, dddt, $J_{9,10}$=6.4 and 2.0 Hz, $J_{4a,10}$=2.6 Hz, average of $J_{1,10}$ and $J_{4,10}$=0.9 Hz, 10-H), 6.18 (1H, dd, $J_{2,3}$=5.7 Hz, $J_{3,4}$=1.6 Hz, 3-H), 6.27 (1H, dd, $J_{2,3}$=5.7 Hz, $J_{1,2}$=1.9 Hz, 2-H), 7.08 (1H, dm, $J_{5,6}$=7.7 Hz, 5-H), 7.13–7.19 (3H, m, 6-H, 7-H, 8-H), the assignment is based on a H,H COSY spectrum; δ_C (151 MHz, $CDCl_3$) 32.1 (C-9), 44.4 (C-4a), 80.0 (C-1), 80.4 (C-4), 113.7 (C-10), 124.0 (C-5), 125.9, 126.0, 127.0 (C-6, C-7, C-8), 131.5 (C-3), 135.3 (C-2), 137.7, 138.4, 141.3 (C-4b, C-8a, C-10a).

Compound 32. Brownish crystals, mp 86°C; *m/z* (EI) 196 (M^+, 61%), 195 (64), 181 (20), 179 (47), 178 (32), 167 (100), 166 (31), 165 (93), 153 (21), 152 (70), 128 (40), 115 (21) [Found (EI): $(M–H)^+$, 195.0812. $C_{14}H_{12}O$ requires for $(M–H)^+$, 195.0810]; δ_H (600 MHz, $CDCl_3$) 2.25 (1H, br dd, $J_{4a,10}$=16.9 Hz, $J_{10,10}$=14.4 Hz, 10β-H), 2.85 (1H, dd, $J_{10,10}$=14.4 Hz, $J_{4a,10}$=5.9, 10α-H), 3.10 (1H, dddd, $J_{4a,10}$=16.9 and 5.9 Hz, $J_{4,4a}$=4.2 Hz, $J_{4a,9}$=2.5 Hz, 4a-H), 5.15 (1H, br d, $J_{1,2}$=1.9 Hz, 1-H), 5.23 (1H, br d, $J_{4,4a}$=4.2 Hz, 4-H), 6.21 (1H, dd, $J_{2,3}$=5.7 Hz, $J_{3,4}$=1.6 Hz, 3-H), 6.31 (1H, d, $J_{4a,9}$=2.5 Hz, 9-H), 6.73 (1H, dd, $J_{2,3}$=5.7 Hz, $J_{1,2}$=1.9 Hz, 2-H), 6.98 (2H, br d, $J_{5,6}$=$J_{7,8}$=7.4 Hz, 5-H, 8-H), 7.05 (1H, td, J=7.4 and 1.4 Hz) and 7.10 (1H, tt, J=7.4 and 1.2 Hz) (6-H, 7-H); δ_C (151 MHz, $CDCl_3$) 33.3 (C-10), 40.8 (C-4a), 79.9 (C-1), 81.7 (C-4), 116.7 (C-9), 126.4, 128.0 (C-5, C-8), 126.9 (2 C, C-6, C-7), 133.6 (C-3), 139.1 (C-2), 134.1, 135.3 (C-8a, C-10a), 146.3 (C-9a).

Rearrangement of 31 to 32

A solution of a 60:40 mixture of **32** and **31** (50 mg) in C_6D_6 (0.7 cm^3), contained in an NMR tube, was degassed by

several freeze–pump–thaw cycles. The NMR tube was then sealed and heated at 120°C for 4 d. Analysed by ^{1}H NMR spectroscopy, the ratio of mixture had turned to 95:5 in favour of **32**. By using the signals of the aromatic protons as internal standard, the yield was determined to be close to quantitative.

Reaction of 19 with KO*t*Bu in 2,5-dimethylfuran—formation of (1α,4α,4aα)-1,4,4a,9-tetrahydro-1,4-dimethyl-1,4-epoxyphenanthrene (33) and (1α,4α,4aα)-1,4,4a,10-tetrahydro-1,4-dimethyl-1,4-epoxyanthracene (34)

A mixture of **19** (2.00 g, 9.57 mmol) and KO*t*Bu (4.00 g, 35.6 mmol) in 2,5-dimethylfuran (30 cm^3) was stirred at room temperature for 20 h. Water (30 cm^3) was then cautiously added to the mixture with continued stirring. The resulting two layers were separated and the aqueous layer was extracted with diethyl ether (3×30 cm^3). After drying with $MgSO_4$, the combined organic layers were concentrated in vacuo. By flash chromatography (SiO_2, LP for the first 50 cm^3 of eluate, LP–E 20:1 for the next 340 cm^3 and finally 10:1), the residue was purified to give, in the order of elution, naphthalene (**20**) (560 mg, 46%), **33** (160 mg, 8%) and a 3:1 mixture (20 mg, 1%) of **33** and **34**.

Compound 33. Yellow oil; *m*/*z* (EI) 224 (M$^+$, 4%), 209 (9), 182 (16), 181 (100), 179 (8), 178 (10), 167 (10), 166 (59), 165 (62), 153 (10), 152 (11), 141(8), 128 (12), 115 (10), 89 (7), 63 (8), 43 (43) [Found (EI): M$^+$, 224.1200. $C_{16}H_{16}O$ requires for M$^+$, 224.1201]; δ_H (600 MHz, $CDCl_3$) 1.68 (3H, s, 1-CH_3), 2.03 (3H, s, 4-CH_3), 3.21 (1H, br d, $J_{4a,9}$=6.2 Hz, 4a-H), 3.29 (1H, ddd, $J_{9,9}$=18.3 Hz, $J_{9,10}$=6.2 Hz, $J_{4a,9}$=1.6 Hz, 9β-H), 3.34 (1H, br dd, $J_{9,9}$=18.3 Hz, $J_{4a,9}$=6.2 Hz, 9α-H), 5.73 (1H, dt, $J_{9,10}$=6.2 and 2.4 Hz, $J_{4a,10}$=2.4 Hz, 10-H), 6.01, 6.10 (2×1H, 2×d, $J_{2,3}$=5.4 Hz, 2-H, 3-H), 7.12–7.19 (3H, m) and 7.25 (1H, br d, *J*=7.5 Hz) (5-H, 6-H, 7-H, 8-H), as far as specified, the assignment is based on a H,H COSY spectrum; δ_C (151 MHz, $CDCl_3$) 15.4 (1-CH_3), 20.3 (4-CH_3), 32.4 (C-9), 51.2 (C-4a), 85.9, 87.4 (C-1, C-4), 112.1 (C-10), 123.0 (C-5 or C-8), 125.8, 125.9, 127.2 (C-6, C-7, C-8 or C-5), 135.7, 138.80 (C-2, C-3), 138.3, 138.76, 148.2 (C-4b, C-8a, 10a).

Compound 34. See next experiment.

Rearrangement of 33 to 34

A solution of a 87:13 mixture of **33** and **34** (50 mg) in C_6D_6 (0.7 cm^3), contained in an NMR tube, was degassed by several freeze–pump–thaw cycles. The NMR tube was then sealed and heated at 120°C for 4 d. As analysed by ^{1}H NMR spectroscopy, **33** had converted into **34**. By using the signals of the aromatic protons as internal standard, the yield was determined to be close to quantitative. The concentration of the solution in vacuo led to virtually pure **34** as a yellow oil; *m*/*z* (EI) 224 (M$^+$, 7%), 209 (7), 182 (16), 181 (100), 179 (10), 178 (10), 167 (10), 166 (63), 165 (70), 164 (7), 163 (7), 153 (12), 152 (11), 141 (8), 128 (7), 127 (7), 115 (10), 89 (7), 82 (7), 63 (7), 43 (26) [Found (EI): M$^+$, 224.1202. $C_{16}H_{16}O$ requires for M$^+$, 224.1201]; δ_H (600 MHz, $CDCl_3$) 1.66, 1.72 (2×3H, 2×s, 1-CH_3, 4-CH_3), 2.28 (1H, dd, $J_{4a,10}$=16.0 Hz, $J_{10,10}$=14.4 Hz, 10β-H), 2.80 (1H, dd, $J_{10,10}$=14.4 Hz, $J_{4a,10}$=5.9 Hz, 10α-H), 2.88 (1H, ddd, $J_{4a,10}$=16.0 and 5.9 Hz, $J_{4a,9}$=2.4 Hz, 4a-H), 6.00, 6.50 (2×1H, 2×d, $J_{2,3}$=5.5 Hz, 2-H, 3-H), 6.18 (1H, d, $J_{4a,9}$=2.4 Hz, 9-H), 7.00 (2H, br d, *J*=7.4 Hz, 5-H, 8-H), 7.05 (1H, td, *J*=7.4 and 1.3 Hz) and 7.10 (1H, tt, *J*=7.4 and 1.1 Hz) (6-H, 7-H); δ_C (151 MHz, $CDCl_3$) 14.7, 17.9 (1-CH_3, 4-CH_3), 32.9 (C-10), 48.1 (C-4a), 86.7, 88.5 (C-1, C-4), 115.0 (C-9), 126.3, 126.8, 126.9, 128.0 (C-5, C-6, C-7, C-8), 134.1, 135.1, (C-8a, C-10a), 137.6, 142.8 (C-2, C-3), 152.7 (C-9a).

Reaction of 19 with KO*t*Bu in the presence of spiro-[2,4]hepta-4,6-diene—formation of (3aα,3bβ,9bα)-3a,3b,4,9b-tetrahydrospiro[cyclopenta[1,2]cyclobuta[3,4-*b*]naphthalene-1,1′-cyclopropane] (35), (6aα,6bα,9aα,9bα)-6a,6b,9a,9b-tetrahydrospiro[cyclopenta[1,2]cyclobuta[3,4-*a*]naphthalene-7,1′-cyclopropane] (36) and (6aα,6bβ,9aβ,9bα)-6a,6b,9a,9b-tetrahydrospiro[cyclopenta[1,2]-cyclobuta[3,4-*a*]naphthalene-7,1′-cyclopropane] (37)

A stirred mixture of **19** (1.90 g, 9.09 mmol), spiro[2,4]-hepta-4,6-diene (5 cm^3), KO*t*Bu (3.00 g, 26.7 mmol) and 18-crown-6 (2.39 g, 9.04 mmol) in THF (50 cm^3) was heated at 60°C. After 2 h and after 4 h, further KO*t*Bu (1.00 g, 8.9 mmol each time) was added. After 6 h, the mixture was hydrolysed (50 cm^3) cautiously and diethyl ether was added until two layers resulted. The aqueous layer was extracted with diethyl ether (3×30 cm^3), the combined organic layers were dried with $MgSO_4$ and concentrated in vacuo. The residue was purified by flash chromatography (SiO_2, LP–E 20: 1 for the first 640 cm^3 of eluate and finally 15:1) to give, in the order of elution, **37** (140 mg, 7%), **35** (170 mg, 8%), **20** (30 mg, 3%) and a fourth fraction, which, for its part, was submitted to flash chromatography (SiO_2, LP–E 10:1). It afforded **21** (30 mg, 2%) and **22** (30 mg, 1%) as the second and third fraction, whereas the first fraction gave **36** (80 mg, 4%) in third flash chromatography step (SiO_2, LP).

Compound 35. Colourless crystals, mp 74°C; *m*/*z* (EI) 220 (M$^+$, 74%), 219 (29), 205 (57), 204 (31), 203 (34), 202 (27), 192 (46), 191 (51), 190 (24), 189 (32), 179 (26), 178 (35), 165 (38), 142 (22), 141 (100), 128 (40), 91 (23) [Found (EI): M$^+$, 220.1252. $C_{17}H_{16}$ requires for M$^+$, 220.1252]; $\tilde{\nu}_{max}$ (KBr)/cm^{-1} 3067 (w), 2991 (w), 2937 (m), 2927 (m), 2873 (m), 1664 (w), 1596 (w), 1476 (w), 1450 (w), 1428 (w), 968 (w), 938 (m), 892 (m), 845 (w), 838 (w), 778 (m), 743 (s), 698 (m), 669 (m), 601 (w), 573 (w), 544 (w), 456 (w); δ_H (600 MHz, $CDCl_3$) 0.63–0.71 (2H, m, 2′-H, 3′-H), 0.85–0.93 (2H, m, 2′-H, 3′-H), 2.72–2.82 (2H, m, 3b-H, 4-H), 2.84 (1H, m, 4-H), 3.21 (1H, ddd, $J_{3a,9b}$=6.7 Hz, $J_{3a,3b}$=3.9 Hz, $J_{3,3a}$=2.7 Hz, 3a-H), 3.42 (1H, br d, $J_{3a,9b}$= 6.7 Hz, 9b-H), 5.34 (1H, d, $J_{2,3}$=5.5 Hz) and 5.90 (1H, dd, *J*=5.5 and 2.7 Hz) (2-H, 3-H), 6.12 (1H, br s, 9-H), 7.01 (1H, br d, *J*=7.3 Hz) and 7.12 (1H, br t, *J*=7.3 Hz) (5-H, 6-H or 8-H, 7-H), 7.04 (1H, br td, *J*=7.3 and 1.2 Hz) and 7.07 (1H, br d, *J*=7.3 Hz) (7-H, 8-H or 6-H, 5-H), the assignment is based on a H,H COSY spectrum; δ_C (151 MHz, $CDCl_3$) 10.8, 15.7 (C-2′, C-3′), 32.5 (C-1), 34.0 (C-4), 45.7 (C-3b), 50.2 (C-3a), 51.4 (C-9b), 117.6 (C-9), 125.6, 126.6 (C-5, C-6 or C-8 or C-7), 125.9, 128.0

(C-7, C-8 or C-6, C-5), 131.5, 140.1 (C-2, C-3), 135.3, 135.5 (C-4a, C-8a), 146.4 (C-9a).

Compound 36. Yellow crystals, mp 72°C, containing impurities to the extent of 10–20%; *m/z* (EI) 220 (M^+, 22%), 205 (16), 192 (10), 191 (14), 165 (11), 141 (26), 129 (14), 128 (100), 92 (56), 91 (52) [Found (EI): M^+, 220.1247. $C_{17}H_{16}$ requires for M^+, 220.1252]; δ_H (600 MHz, $CDCl_3$) 0.48 (1H, ddd, J_{cis}=9.6 Hz, J_{trans}=6.3 Hz, J_{gem}=4.3 Hz) and 0.52 (1H, ddd, J_{cis}=9.2 Hz, J_{trans}=6.2 Hz, J_{gem}=4.3 Hz) (2′-CH_2 or 3′-CH_2), 0.84 (1H, ddd, J_{cis}=9.2 Hz, J_{trans}=6.3 Hz, J_{gem}=4.9 Hz) and 0.94 (1H, ddd, J_{cis}=9.6 Hz, J_{trans}=6.2 Hz, J_{gem}=4.9 Hz) (3′-CH_2 or 2′-CH_2), 3.00 (1H, dd, $J_{6a,9b}$=9.0 Hz, $J_{9a,9b}$=6.9 Hz, 9b-H), 3.53 (1H, dddt, $J_{6a,6b}$=10.9 Hz, $J_{6a,9b}$=9.0 Hz, $J_{6,6a}$=4.2 Hz, average of $J_{5,6a}$ and $J_{6a,9a}$=1.9 Hz, 6a-H), 3.82 (1H, ddq, $J_{6b,9a}$=8.8 Hz, $J_{9a,9b}$=6.9 Hz, average of $J_{6a,9a}$ and $J_{8,9a}$ and $J_{9,9a}$=1.9 Hz, 9a-H), 3.97 (1H, dd, $J_{6a,6b}$=10.9 Hz, $J_{6b,9a}$=8.8 Hz, 6b-H), 5.28 (1H, br d, $J_{8,9}$=5.5 Hz) and 5.36 (1H, dd, J=5.5 and 2.4 Hz) (8-H, 9-H), 5.96 (1H, dd $J_{5,6}$=10.0 Hz, $J_{6,6a}$=4.2 Hz, 6-H), 6.17 (1H, dd, $J_{5,6}$=10.0 Hz, $J_{5,6a}$=2.1 Hz, 5-H), 6.87, 6.88 (2×1H, 2×dd, J=ca. 7 and 2.1 Hz, 1-H, 4-H), 7.03–7.08 (2H, m, 2-H, 3-H), the assignment is based on a H,H COSY spectrum; δ_C (151 MHz, $CDCl_3$) 11.0, 13.5 (C-2′ C-3′), 30.7 (C-7), 37.6 (C-6a), 39.0 (C-6b), 52.1 (C-9b), 54.7 (C-9a), 126.4, 127.8 (C-2, C-3), 126.7, 127.4 (C-1, C-4), 127.0 (C-5), 130.0, 140.7 (C-8, C-9), 130.1 (C-6), 133.0, 133.8 (C-4a, C-9c).

Compound 37. Yellow crystals, mp 64°C, containing impurities to the extent of 10–20%; *m/z* (EI) 220 (M^+, 2%), 205 (4), 191 (3), 141 (4), 129 (11), 128 (100), 127 (6), 93 (4), 92 (60), 91 (50), 65 (4) [Found (EI): M^+, 220.1253. $C_{17}H_{16}$ requires for M^+, 220.1252]; δ_H (600 MHz, $CDCl_3$) 0.62 (1H, m) and 0.70–0.77 (2H, m) and 0.82 (1H, m) (2′-CH_2, 3′-CH_2), 2.53 (1H, t, average of $J_{6a,6b}$ and $J_{6b,9a}$=6.5 Hz, 6b-H), 3.19 (1H, br dt, $J_{6a,9b}$=10.2 Hz, average of $J_{6,6a}$ and $J_{6a,6b}$=5.5 Hz, 6a-H), 3.48 (1H, dd, $J_{6a,9b}$=10.2 Hz, $J_{9a,9b}$=3.4 Hz, 9b-H), 3.56 (1H, m, 9a-H), 5.34 (1H, d, $J_{8,9}$=5.4 Hz) and 5.97 (1H, dd, J=5.4 and 2.5 Hz) (8-H, 9-H), 5.73 (1H, dd, $J_{5,6}$=9.7 Hz, $J_{6,6a}$=5.3 Hz, 6-H), 6.22 (1H, d, $J_{5,6}$=9.7 Hz, 5-H), 6.95, 7.01 (2×1H, 2×br d, J=7.3 Hz, 1-H, 4-H), 7.09, 7.11 (2×1H, 2×tm, J=7.3 Hz, 2-H, 3-H), the assignment is based on a H,H COSY spectrum; δ_C (151 MHz, $CDCl_3$) 8.4, 15.6 (C-2′, C-3′), 35.1 (C-7), 37.7 (C-6a), 40.6 (C-9b), 53.6 (C-6b), 57.9 (C-9a), 125.3 (C-5), 126.3, 127.7 (C-2, C-3), 126.9, 128.1 (C-1, C-4), 129.0 (C-6), 132.1, 137.2 (C-4a, C-9c), 132.5, 138.3 (C-8, C-9).

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