Cycloaddition Reactions of 1,4-Dihydronaphthalene-1,4-epoxide with Cyclohexadiene and 7-(Methoxycarbonyl)cycloheptatriene: Selectivity in Additions

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Cycloaddition reactions of naphthalene-1,4-epoxide (**1**) with both 7-(methoxycarbonyl)cycloheptatriene (**2**) and cyclohexadiene (**4**) give adducts of type **3** and **5** exclusively. Selectivity was observed for the cycloaddition and bromination reactions, but neighboring group participation also occurrs in the latter. The formation of the products is discussed.

Introduction

1,4-Dihydronaphthalene-1,4-epoxide (**1**) is a reactive dienophile. It takes part in [2 + 4] cycloaddition reactions with dienes such as 2,3-dimethylbutadiene, α-pyrone, tropone derivatives, and tetrazine.[1] The epoxide **1** also takes part in 1,3-dipolar cycloaddition reactions with compounds such as nitryl oxide, phenyl azide, diazomethane, and diazoacetate.[2] Epoxide **1** and its derivatives are also intriguing, however, in terms of their photochemical rearrangement[3] and other versatile transformations.[4]

The aim of this study was to obtain adducts of epoxide **1** with 7-(methoxycarbonyl)cycloheptatriene (**2**) and cyclohexadiene (**4**), and to investigate the chemistry of these adducts. We synthesized these adducts and investigated the reactions of adduct **3**, which we obtained from the reaction of **1** with 7-(methoxycarbonyl)cycloheptatriene (**2**).

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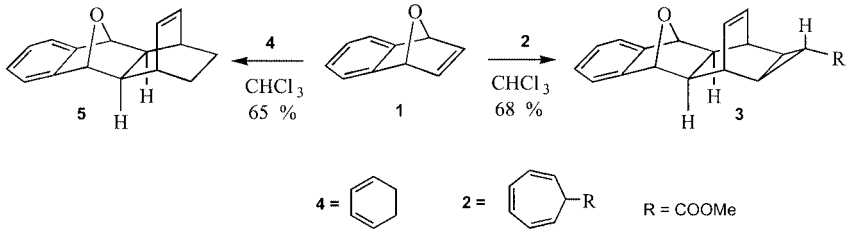
Results and Discussion

Epoxide **1** was obtained from the reaction of benzyne, which we generated from benzenediazonium-2-carboxylate hydrochloride,[5] with furan. Epoxide **1** was subjected to Diels−Alder cycloaddition with 7-(methoxycarbonyl)cycloheptatriene (**2**) in a chloroform solution at 65 ± 5 °C (in a sealed tube) for 3 weeks and only adduct **3** was isolated (Scheme 1). Careful examination of the ^{1}H NMR spectrum of the mixture revealed that other isomers not were present. The 200 MHz spectrum showed absorptions at δ = 7.17−7.05 (m, 4 H), 5.86 (m, 2 H) and 1.46 (t, 1 H) ppm, with relative intensities of 4:2:1, indicating the presence of one cyclopropane ring in adduct **3**. The resonances of the other protons and the eleven-lines ^{13}C NMR spectrum are in agreement with the proposed structure of adduct **3**, but, on the basis of these NMR spectra, it is not easy to establish the exact configuration. Compound **3** is the first norcaradiene-type adduct that has been formed from the reaction of a cycloheptatriene or cycloheptatriene derivative with a 1,4-epoxide.

In a similar manner, epoxide **1** was also reacted with 1,3-cyclohexadiene (**4**). In this cycloaddition reaction, adduct **5** was generated in high yield as the sole product (Scheme 1). Adduct **5** could be distinguished readily; it has a symmetri-



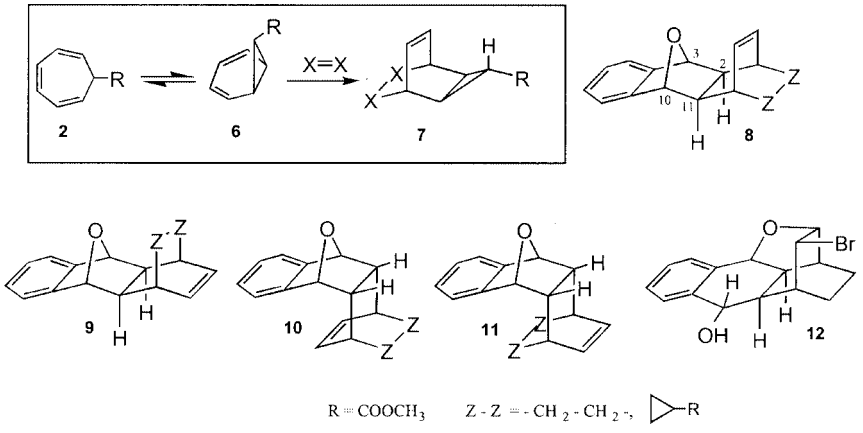
Scheme 1

cal structure and exhibits an AA′BB′ system for the methylene protons in its ^{1}H NMR spectrum. Also consistent with structure **5** is the eight-line ^{13}C NMR spectrum. On the basis of the NMR spectra of adduct **5**, however, it is not easy to establish the exact configuration of the molecule.

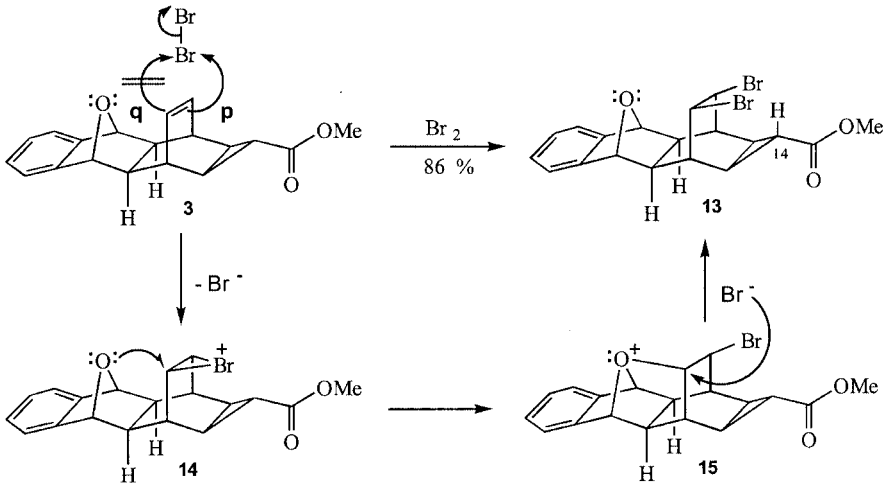
There is an equilibrium between cycloheptatriene (CHT) and norcaradiene (NOR). Electron-accepting substituents on the C-7 carbon atom, such as CHO, COOR, and CN, tend to shift the equilibrium toward NOR.[6] Cycloheptatrienes give, in most cases, norcaradiene-type adducts, such as **7**. Compound **3** is also a norcaradiene-type adduct. The structures of compounds **3** and **5** may be conceived as one of the four stereoisomeric structures, **8**−**11** (Scheme 2). The structures of adducts were eventually proved by complete analysis of the NMR spectra. Their oxygen bridgehead protons, C(3)−H and C(10)−H, give rise to sharp singlets (at δ = 4.96 and 5.02 ppm, respectively) with no vicinal coupling to C(2)−H and C(11)−H. Therefore, these protons [C(2)−H and C(11)−H] must be *endo* to the oxabenzonorbornene systems[7] and, thus, the structures **10** and **11** were ruled out. The exact configuration of compound **5** was determined from structure of product **12**, which was produced by the reaction of **5** with bromine.[8] The structure of product **12** has been published alone, as an X-ray crystallographic study, in a paper that does not include reaction details (especially experimental details) or spectroscopic data of compound **5**.[8] Investigation of the reactions of **5**, such as bromination, have not been completed yet. Therefore, the structures of adducts **3** and **5** were accepted to be similar to structure **8**.

Adduct **3** was reacted with Br_2 in $CHCl_3$ at room temperature for 2 h to give the dibromide **13** as almost the sole product (Scheme 3). Dibromide **13** has a symmetrical structure and exhibits an eleven-line ^{13}C NMR spectrum. According to the NMR spectra of adduct **13**, it is not easy to establish the exact configuration of the molecule. Therefore, the exact structure of compound **13** was determined by X-ray crystallographic analysis (Figure 1).[9]

As depicted in Figure 1, the bromine atoms are *cis*-configured and positioned towards the cyclopropane ring in the compound **13**. To rationalize the formation of compound **13**, we propose the following reaction mechanism. The intermediates, strongly bridged bromonium ions, are involved in the bromination of nonconjugated olefins, which give *anti* adducts. Bromine can attack the double bond in **3** from both the **p** and **q** faces. The oxygen atom of the epoxide and the cyclopropane ring will complicate any approach of bromine toward **3**. In the bromination and epoxidation of compound **16**, which is similar to **3**, reagents approach from the *endo* face because the cyclopropane ring in **16** prevents their approach.[10] The hinderance provided by the oxygen atom is greater than that of the cyclopropane unit in **3**, and so the bridged bromonium ion **14** is produced by the attack of bromine from the **p** face. The oxygen atom of the epoxide unit acts as a nucleophile to yield intermediate **15**, and then the bromide anion displaces the oxygen atom by a backside attack. Therefore, the bromine atoms have a cis configuration in compound **13**; i.e., neighboring group participation of the oxygen atom occurs in the formation of this dibromide.



Scheme 2



Scheme 3

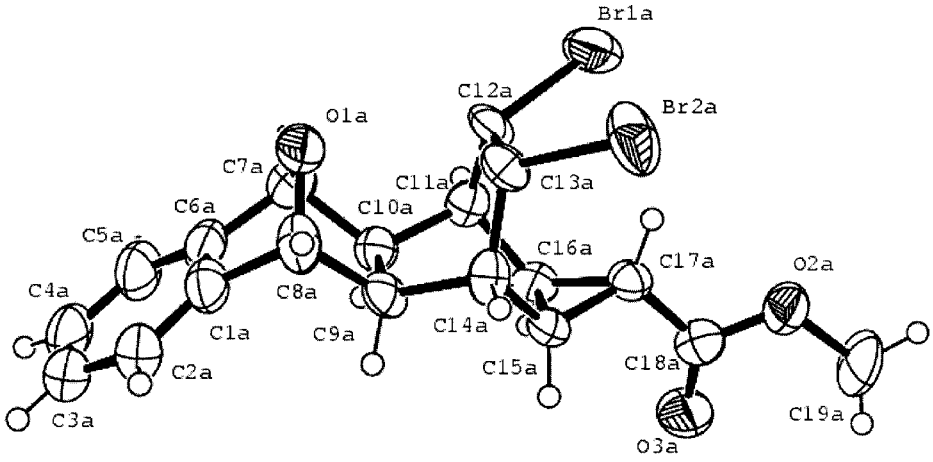
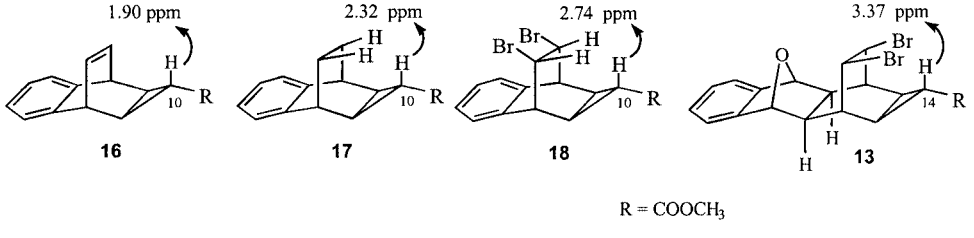


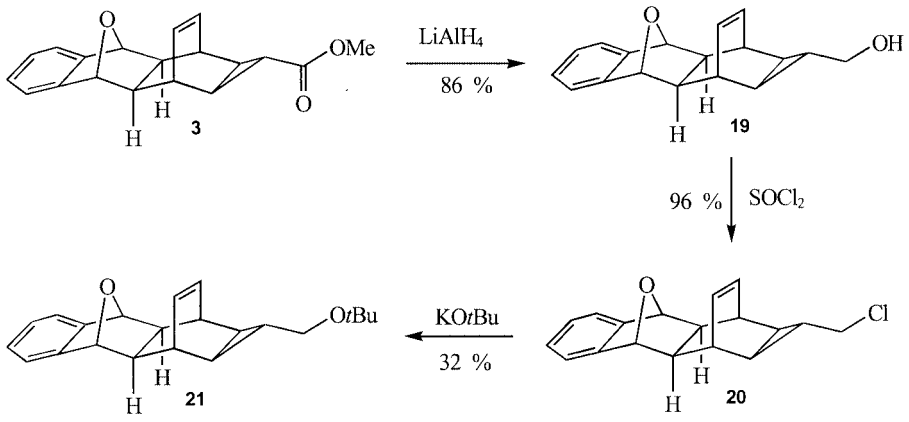
Figure 1. Molecular structure of **13**

As is observed in some molecules,[11] there is the γ gauche effect in dibromide **13** that is due to steric compression. The cyclopropane hydrogen atom, C(14)−H, in the dibromide **13** resonates at δ = 3.37 ppm. As shown in Scheme 4, the C(10)−H hydrogen atoms in compounds **16**,[10] **17**,[11] and **18**[10a], which are similar to the C(14)−H hydrogen atoms in **13**, resonate at δ = 1.90, 2.32, and 2.74 ppm, respectively. We attribute this extraordinary shift to steric compression between this proton and the bromine atoms in dibromide **13**. This steric compression may also be estimated from the C(14)H···Br bond lengths, 2.659 Å and 2.660 Å.

Another functional group present in compound **3** is the ester group, which is substituted in the cyclopropane ring. To investigate the chemical reactions, such as rearrangements, of this group in **3**, we reacted it with $LiAlH_4$ to give alcohol **19** (Scheme 5). Alcohol **19** is a (cyclopropyl)methanol derivative; (cyclopropyl)methanols generally rearrange to corresponding homoallylic compounds.[13] The reaction of alcohol **19** with $SOCl_2$ gave the non-rearranged chloride **20**. The reaction of chloride **20** with KO*t*Bu gave a substitution product **21** in the case of the corresponding alkene. The approach of KO*t*Bu to the corresponding hydrogen atom and the conformation of the molecule are probably not conducive for HCl elimination in compound **20** by an E_2 mechanism. Similar reactions have been described in the literature.[13d,14]



Scheme 4



Scheme 5

Conclusion

There is a selectivity in the cycloaddition reactions of epoxide **1** with 7-substituted cycloheptatriene (**2**) and cyclohexadiene (**4**) and in the addition of bromine to compound **3**. However, neighboring group participation was also observed for the addition of bromine to compound **3**. The reaction of alcohol **19**, formed from **2**, gave the non-rearranged chloride **20**. Substitution product **21**, in the case of the corresponding alkene, was obtained from the reaction of chloride **20** with KO*t*Bu.

Experimental Section

General Methods: All chemicals and solvents are commercially available and were used after distillation or treatment with drying agents. M.p.: Determined using a Thomas−Hoover capillary melting point apparatus; they are uncorrected. IR spectra were obtained from solutions in 0.1-mm cells using a Perkin−Elmer spectrophotometer. The ^{1}H (^{13}C) NMR spectra were recorded with a 200 (50) MHz Varian spectrometer; δ in ppm, Me_4Si as the internal standard. Mass spectra were determined using a VG ZabSpec, range 1000 EI, 10000 for HRMS. Elemental analyses were performed using a Carlo−Erba 1106 apparatus. All column chromatography was performed on silica gel (60 mesh, Merck). Preparative thick-layer chromatography (PLC) was performed on glass plates coated with 1 mm of silica gel 60 PF (Merck).

Cycloaddition Reaction of Epoxide 1 with 7-(Methoxycarbonyl)cycloheptatriene (2): A solution of the 1,4-epoxide **1** (1.5 g, 10.4 mmol) and 7-(methoxycarbonyl)cycloheptatriene (1.92 g, 12.8 mmol) in $CHCl_3$ (3 mL) was placed into a constricted test tube, sealed under vacuum, and heated at 65 ± 5 °C for 3 weeks. After cooling to room temperature, the reaction solution was filtered through silica gel (3−4 g, in a small column), eluting with $CHCl_3$. The solvent was evaporated and the addition product **3** (2.04 g, 6.94 mmol) was crystallized from ethyl acetate as white crystals.

***exo*-[1*S*(*R*),2*R*(*S*),3*R*(*S*),10*S*(*R*),11*S*(*R*),12*R*(*S*),13*R*(*S*),15*S*(*R*)]-14-(Methoxycarbonyl)-3,10-epoxypentacyclo[10.3.2.0^{2,11}.0^{4,9}.0^{13,15}]-heptadeca-4,6,8,16-tetraene (3):** Yield 68% (2.04 g); m.p. 172−174 °C. ^{1}H NMR (200 MHz, $CDCl_3$): δ = 1.46 [t, *J* = 2.87 Hz, 1 H, C(14)−H], 1.54−1.57 [m, 2 H, C(13)−H and C(15)−H], 2.11 [br. s, 2 H, C(1)−H and C(12)−H], 3.16 [m, 2 H, C(2)−H and C(11)−H], 3.60 (s, 3 H, OCH_3), 4.96 [s, 2 H, C(3)−H and C(10)−H], 5.86 [m, 2 H, C(16)−H and C(17)−H], 7.05−7.17 [m, 4 H, C(5)−H, C(6)−H, C(7)−H, and C(8)−H] ppm. ^{13}C NMR (50 MHz, $CDCl_3$): δ = 21.2 (CH), 23.9 (CH), 36.1 (CH), 50.1 (CH), 53.3 (OCH_3), 83.6 (CH−O), 120.4 (CH), 128.3 (CH), 129.6 (CH), 149.0 (C), 175.3 (CO) ppm. IR (KBr): $\tilde{\nu}$ = 3080, 3004, 2927, 1727, 1446, 1421, 1370, 1293, 1242, 1191, 961, 936 cm^{-1}. $C_{19}H_{18}O_3$ (294.34): calcd. C 77.53, H 6.16; found C 77.49, H 6.18.

Bromination of Compound 3: Excess bromine was added to a solution of compound **3** (400 mg, 1.36 mmol) in $CHCl_3$ (150 mL), and the mixture was stirred at room temperature for 2 h. The solvent and excess Br_2 were evaporated. Reaction product **13** (531 mg, 1.17 mmol) was crystallized from ethyl acetate as white crystals.

***exo*-[1*S*(*R*),1*S*(*R*),3*R*(*S*),10*S*(*R*),11*R*(*S*),12*R*(*S*),13*R*(*S*),15*S*(*R*),16*R*(*S*),17*S*(*R*)]-16,17-Dibromo-14-methoxycarbonyl-3,10-epoxypentacyclo[10.3.2.0^{2,11}.0^{4,9}.0^{13,15}]heptadeca-4,6,8-triene (13):** Mol. mass 451.15; yield 86% (531 mg); m.p. 245−247 °C. ^{1}H NMR (200 MHz, $CDCl_3$): δ = 1.53 [br. s, 2 H, C(13)−H and C(15)−H], 2.12 [br. s, 2 H, C(1)−H and C(12)−H], 2.94 [br. s, 2 H, C(2)−H and C(11)−H], 3.37 [t, *J* = 3.22 Hz, 1 H, C(14)−H], 3.71 (s, 3 H, OCH_3), 4.88 [s, 2 H, C(16)−H and C(17)−H], 5.20 [s, 2 H, C(3)−H and C(10)−H], 7.12−7.24 [m, 4 H, C(5)−H, C(6)−H, C(7)−H, and C(8)−H] ppm. ^{13}C NMR (50 MHz, $CDCl_3$): δ = 26.0 (2CH), 40.6 (CH), 49.0 (CH), 49.9 (CH), 53.7 (OCH_3), 82.3 (CH−O), 121.1 (CH), 128.9 (CH), 147.4 (C), 174.7 (CO) ppm. IR (KBr): $\tilde{\nu}$ = 3106, 3055, 3004, 2953, 2930, 1753, 1472, 1370, 1319, 1217, 1165, 1089, 1038, 961, 859, 782, 680 cm^{-1}. HRMS: found 453.976928, calcd. for $C_{19}H_{20}Br_2O_3$ 453.977917.

X-ray Crystal Structure Analysis of 13:[9] Empirical formula $C_{19}H_{15}Br_2O_3$, *M* = 451.63, colorless crystal of size 0.25 × 0.21 × 0.12 mm, *a* = 12.1847(7), *b* = 22.2895(14), *c* = 13.0241(8) Å, α = 90, β = 90.912(3), γ = 90°, *V* = 3536.8(4) Å^3 $\delta_{calcd.}$ = 1.696 gcm^{-3}, μ = 4.598 cm^{-1}, *F*(000) = 1788, absorption correction none (0.969 ≤ *T* ≤ 991), *Z* = 8, monoclinic, space group $P2_1/n$ (No. 14), λ = 0.71073 Å, *T* = 293(2) K, θ range for data collection 1.81 to 28.05°, Φ and ω-scans, 19045 reflections collected (−16 ≤ *h* ≤ 14, −28 ≤ *k* ≤ 29, −14 ≤ *l* ≤ 17), 7836 independent (R_{int} = 0.0631) and 2855 observed reflections [$I > 2\sigma(I)$], 433 refined parameters, *R* = 0.0397, wR^2 = 0.0499, goodness-of-fit on F^2 = 0.722, max. residual electron density 0.54 (−0.45) e·Å^{-3}, hydrogen atoms calculated and refined as riding atoms.

Reduction of 3 with $LiAlH_4$: $LiAlH_4$ (60 mg, 1.56 mmol) was added in portions over a period of 15 min at −15 °C (salt-ice) to a stirred solution of **3** (111 mg, 0.38 mmol) in dry THF (15 mL). After stirring at the same temperature for 1 h, the cold-water bath was removed and the mixture was stirred at room temperature for 20 h. The gray mixture was cooled to 0 °C and hydrolyzed by the addition of methanol and water (1:1). The mixture was filtered (inorganic salts) and the solvent evaporated. The residue was filtered through silica gel [4.3 g, in a small column (gravity column, length ca. 33 cm, joint 16.5/23)] eluting with $CHCl_3$. Alcohol **19** (86 mg, 0.32 mmol) was crystallized from diethyl ether as white crystals.

***exo*-[1*S*(*R*),2*R*(*S*),3*R*(*S*),10*S*(*R*),11*S*(*R*),12*R*(*S*),13*R*(*S*),15*S*(*R*)]-14-Hydroxymethyl-3,10-epoxypentacyclo[10.3.2.0^{2,11}.0^{4,9}.0^{13,15}]heptadeca-4,6,8,16-tetraene (19):** Yield 86% (86 mg); m.p. 160−162 °C. ^{1}H NMR (200 MHz, $CDCl_3$): δ = 0.82 [m, 2 H, C(13)−H and C(15)−H], 1.00 [tt, *J* = 7.25, 3.10 Hz, 21 H, C(14)−H], 1.53 (br. s, 1 H, OH), 2.04 [br. s, 2 H, C(1)−H and C(12)−H], 3.08 [m, 2 H, C(2)−H and C(11)−H], 3.39 (d, *J* = 7.25 Hz, 2 H, OCH_2), 4.99 [s, 2 H, C(3)−H and C(10)−H], 5.84 [s, 2 H, C(16)−H and C(17)−H], 7.07−7.20 [m, 4 H, C(5)−H, C(6)−H, C(7)−H, and C(8)−H] ppm. ^{13}C NMR (50 MHz, $CDCl_3$): δ = 19.1, 21.7, 36.1, 50.2, 66.5, 83.9 (CH−O), 120.4 (CH), 128.2 (CH), 130.0 (CH), 149.2 (C) ppm. IR (KBr): $\tilde{\nu}$ = 3530, 3400, 2984, 2923, 2181, 1438, 1369, 1253, 1100, 1030, 930, 946, 769, 653 cm^{-1}. $C_{18}H_{18}O_2$ (266.33): calcd. C 81.17, H 6.81; found C 81.16, H 6.79.

Reduction of Alcohol 19 with $SOCl_2$: $SOCl_2$ (3 mL) was added in one portion to a stirred solution of alcohol **19** (245 mg, 0.92 mmol) in $CHCl_3$ (8 mL) at room temperature. Gas evolution was observed. After stirring for 3 h, the solvent and excess $SOCl_2$ were removed by evaporation. Chloride **20** (250 mg, 0.88 mmol) was crystallized from diethyl ether as white crystals.

***exo*-[1*S*(*R*),2*R*(*S*),3*R*(*S*),10*S*(*R*),11*S*(*R*),12*R*(*S*),13*R*(*S*),15*S*(*R*)]-14-Chloromethyl-3,10-epoxypentacyclo[10.3.2.0^{2,11}.0^{4,9}.0^{13,15}]heptadeca-4,6,8,16-tetraene (20):** Yield 96% (250 mg); m.p. 124−126 °C. ^{1}H NMR (200 MHz, $CDCl_3$): δ = 0.92 [m, 2 H, C(13)−H and C(15)−H], 1.12 [tt, *J* = 7.41, 2.93 Hz, 1 H, C(14)−H], 2.03 [br. s, 2 H, C(1)−H and C(12)−H], 3.12 [m, 2 H, C(2)−H and C(11)−H], 3.37 (d, *J* = 7.41 Hz, 1 H, $ClCH_2$), 4.96 [s, 2 H, C(3)−H and C(10)−H], 5.86 [m, 2 H, C(16)−H and C(17)−H], 7.04−7.18 [m, 4 H, C(5)−H, C(6)−H, C(7)−H, and C(8)−H] ppm. ^{13}C NMR (50 MHz, $CDCl_3$): δ = 21.6, 21.8, 36.2, 49.2, 50.1, 83.7 (CH−O), 120.3 (CH), 128.2 (CH), 130.0 (CH), 149.2 (C) ppm. IR (KBr): $\tilde{\nu}$ = 3053, 2938, 1730, 1653, 1453, 1376, 1269 1207, 1030, 923, 876, 746 cm^{-1}. $C_{18}H_{17}ClO$ (284.78): calcd. C 75.92, H 6.02, Cl 12.45; found C 75.88, H 6.03, Cl 12.44.

Reduction of Chloride 20 with KO*t*Bu: Potassium *tert*-butoxide (745 mg, 6.48 mmol) was added to a stirred solution of chloride **20** (230 mg, 0.81 mmol) in dry THF (40 mL) at room temperature. The mixture was heated under reflux for 3 days, and then it was cooled to room temperature. After evaporation of the solvent, water (100 mL) was added. The mixture was neutralized by the addition of solid NH_4Cl and then it was extracted with $CHCl_3$ (3 × 40 mL). The combined organic phases were dried ($CaCl_2$) and the solvent was evaporated. The residue was submitted to PLC, eluting with EtOAc/hexane (3:7). The product (**21**; 85 mg, 0.26 mmol) was obtained and crystallized from $CHCl_3$/hexane as to yield white crystals.

***exo*-[1*S*(*R*),2*R*(*S*),3*R*(*S*),10*S*(*R*),11*S*(*R*),12*R*(*S*),13*R*(*S*),15*S*(*R*)]-14-*tert*-Butoxymethyl-3,10-epoxypentacyclo[10.3.2.0^{2,11}.0^{4,9}.0^{13,15}]heptadeca-4,6,8,16-tetraene (21):** Yield 32% (85 mg); m.p. 80−82 °C. ^{1}H NMR (200 MHz, $CDCl_3$): δ = 0.75−0.79 [m, 2 H, C(13)−H and C(15)−H], 0.82−0.98 [m, 1 H, C(14)−H], 1.13 (s, 9 H, CH_3), 2.02 [br. s, 2 H, C(2)−H and C(11)−H], 3.08 [m, 2 H, C(1)−H and C(12)−H], 3.14 (d, *J* = 6.47 Hz, 2 H, OCH_2], 4.95 [s, 2 H, C(3)−H and C(10)−H], 5.86 [m, 2 H, C(16)−H and C(17)−H], 7.03−7.16 [m, 4 H, C(5)−H, C(6)−H, C(7)−H, and C(8)−H] ppm. ^{13}C NMR (50 MHz, $CDCl_3$): δ = 19.2, 19.7, 29.6, 36.4, 50.4, 65.0, 74.2 (C), 83.8 (OCH), 120.2 (CH), 128.0 (CH), 130.0 (CH), 149.4 (C) ppm. IR ($CHCl_3$): $\tilde{\nu}$ = 3024, 2402, 1543, 1430, 1220, 1072, 915, 758, 675 cm^{-1}. $C_{22}H_{26}O_2$ (322.44): calcd. C 81.95, H 8.13; found C 81.96, H, 8.12.

Cycloaddition Reaction of Epoxide 1 with Cyclohexadiene (4): A solution of the 1,4-epoxide **1** (2.0 g, 13.89 mmol) and 1,3-cyclohexadiene (**4**; 3.0 g, 37.5 mmol) in $CHCl_3$ (5 mL) was placed into a constricted test tube, sealed under vacuum, and heated at 65 ± 5 °C for 28 days. After cooling to room temperature, the solvent was evaporated. The residue was submitted to column chromatography (silica gel, 50 g; diethyl ether/$CHCl_3$/hexane, 1:3:16). An unknown compound (probably a dimer of cyclohexadiene), adduct **5** (2.0 g, 8.93 mmol), and 1,4-epoxide **1** were isolated. Adduct **5** was crystallized from hexane to yield white crystals.

[1*R*(*S*),2*R*(*S*),3*R*(*S*),10*S*(*R*),11*S*(*R*),12*S*(*R*)]-3,10-Epoxytetracyclo-[10.2.2.0^{2,11}.0^{4,9}]hexadeca-4,6,8,13-tetraene (5): Yield 65% (2.0 g); m.p. 104−105 °C. ^{1}H NMR (200 MHz, $CDCl_3$): δ = 1.19−1.23 [m, AA′ part of AA′BB′ system, 2 H, C(15)−H and C(16)−H], 1.40−1.44 [m, BB′ part of AA′BB′ system, 2 H, C(15)−H and C(16)−H], 1.88 [br. s, 2 H, C(2)−H and C(11)−H], 2.82 [m, 2 H, C(1)−H and C(12)−H], 5.02 [s, 2 H, C(3)−H and C(10)−H], 6.24 [m, 2 H, C(13)−H and C(14)−H], 7.07−7.19 [m, 4 H, C(5)−H, C(6)−H, C(7)−H, and C(8)−H] ppm. ^{13}C NMR (50 MHz, $CDCl_3$): δ = 27.2, 35.3, 48.4, 84.7 (CHO), 120.3 (CH), 128.1 (CH), 134.0 (CH), 149.0 (C) ppm. IR ($CHCl_3$): $\tilde{\nu}$ = 3055, 3029, 2953, 1472, 1268, 1217, 1191, 1063, 966, 757 cm^{-1}. MS: *m*/*z* (%) = 226.1/224.1 (0.5/4), 207.1/206.1 (1/5), 195.1 (1), 179.1/178.0 (6/26), 167.1/165.0 (1/6), 154.1/152.0 (1/5), 128.0 (5), 119.0/117.9/115.0 (14/100/15), 91.0/90.0/89.0/88.0 (4/8/9/1). $C_{16}H_{16}O$ (224.12): calcd. C 85.68, H 7.19; found C 85.65, H 7.20.

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[1] [1a] F. Fieser, M. J. Haddadin, *Can. J. Chem.* **1965**, *43*, 1599−1606. [1b] L. F. Fieser, M. Fieser, *Reagents for Organic Synthesis*, John Wiley & Sons, New York, **1967**, vol. 1, p. 255 and 521. [1c]T. Sasaki, K. Kanemetsu, K. Hakayawa, A. Kondo, *J. Org. Chem.* **1973**, *38*, 4100−4106. [1d] R. N. Warraner, *J. Am. Chem. Soc.* **1971**, *93*, 2346−2348. [1e] T. Sasaki, K. Kanemetsu, K. Hakayawa, *J. Chem. Soc., Perkin Trans. 1* **1972**, 1951−1954.
[2] [2a] L. Fisera, D. Pavlovic, *Coll. Czech. Chem. Commun.* **1983**, *48*, 1590−2000. [2b] L. Fisera, L. Stripranyi, V. Oremus, *Chem. Zvesti* **1984**, *38*, 557−565. [2c] E. Jedlovska, L. Fisera, J. Kovac, *Chem. Zvesti* **1988**, *42*, 823−833. [2d] T. Sasaki, K. Kanemetsu, K. Hakayawa, M. Uchide, *J. Chem. Soc., Perkin Trans. 1* **1972**, 2750−2754.

[3] [3a] G. R. Ziegler, G. S. Hammond, *J. Am. Chem. Soc.* **1968**, *90*, 513−514. [3b] G. R. Ziegler, *J. Am. Chem. Soc.* **1969**, *91*, 446−449. [3c] A. Altundaş, Y. Kara, H. Seçen, N. Akbulut, *J. Chem. Res., Synop.* **2002**, 361−362.
[4] [4a] R. Caple, M. S. Chen, J. D. Nelson, *J. Am. Chem. Soc.* **1971**, *90*, 2874−2876. [4b] A. Altudaş, A. Daştan, M. McKee, M. Balcı, *Tetrahedron* **2000**, *56*, 6115−6120. [4c] M. Lautens, T. Rovis, *Tetrahedron* **1999**, *55*, 8967−8976.
[5] H. Hart, A. Oku, *J. Org. Chem.* **1972**, *37*, 4269−4274.
[6] [6a] M. Balcı, *Turk. J. Chem.* **1992**, *16*, 42−90. [6b] G. Maier, *Angew. Chem. Int. Ed. Engl.* **1967**, *6*, 402−413. [6c] R. Abbasoğlu, A. Menzek, M. Balcı, *Turk. J. Chem.* **1998**, *22*, 201−207. [6d] A. Menzek, M. Balcı, *Tetrahedron* **1993**, *49*, 6071−6078.
[7] J. D. Slee, E. LeGoff, *J. Org. Chem.* **1970**, *35*, 3897−3901.
[8] U. Çoruh, S. Garcia-Granda, A. Menzek, A. Altundaş, N. Akbulut, A. Erdönmez, *Acta Crystallogr. E58* **2002**, *11*, O1234−O1236.
[9] Data sets were collected with a Bruker SMART CCD diffractometer using a fine-focus sealed tube and a graphite monochromator. Programs used: data collection, SMART (Bruker SMART and SAINT; Bruker AXS Inc., Madison, Wisconsin, USA, **1998**); data reduction, SAINT (Bruker SMART and SAINT; Bruker AXS Inc., Madison, Wisconsin, USA, **1998**); structure solution, SHELXS-97 (G. M. Sheldrick, Universität Göttingen, **1997**); structure refinement, SHELXL-97 (G. M. Sheldrick, University of Göttingen, **1997**); graphics, ORTEP-3 for Windows (L. J. Farrugia, *J. Appl. Cryst.* **1997**, *30*, 565). CCDC-218398 (**9**) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; Fax: (internat.) +44-1223-336-033; E-mail: deposit@ccdc.cam.ac.uk].
[10] [10a] A. Menzek, N. Saracoğlu, A. Daştan, M. Balcı, R. Abbasoğlu, *Tetrahedron* **1997**, *53*, 14451−14462. [10b] D. Ülkü, M. N. Tahir, A. Menzek, M. Balcı, *Acta Crystallogr., Sect. C* **1995**, *51*, 2714−2715. [10c] M. Balcı, A. Menzek, C. Kazaz, *Turk. J. Chem.* **1994**, *18*, 205−214.
[11] A. Menzek, M. Gökmen, *J. Chem. Res., Synop.* **2002**, *10*, 475−476.
[12] [12a] A. Menzek, N. Saracoğlu, M. Krawiec, W. H. Watson, M. Balcı, *J. Org. Chem.* **1995**, *60*, 829−832. [12b] M. Christl, H. Leininger, E. Brunn, *J. Org. Chem.* **1982**, *47*, 661−666. [12c] M. D. Gheorghiu, E. Olteanu, *J. Org. Chem.* **1987**, *52*, 5158−5166. [12d] O. Cakmak, M. Balcı, *J. Org. Chem.* **1989**, *54*, 181−187.
[13] [13a] M. Julia, S. Julia, R. Guegan, *Bull. Soc. Chim. Fr.* **1960**, 1072−1079. [13b] P. D. McCormik, D. L. Barton, *J. Org. Chem.* **1980**, *45*, 2566−2570. [13c] P. D. McCormik, A. S. Fitterman, D. L. Barton, *J. Org. Chem.* **1981**, *46*, 4708−4712. [13d] A. Menzek, *Tetrahedron* **2000**, *56*, 8505−8512. [13e] A. Menzek, M. Gökmen, *Helv. Chim. Acta* **2003**, *86*, 324−329.
[14] U. Stampfli, M. Neuenschwander, *Helv. Chim. Acta* **1988**, *71*, 2022−2025.

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