Synthesis of 9,10-Dihydro-9,10-propanoanthracene-12-ones from Anthracenes and Oxyallyl Cation Intermediates Generated by the BSA [*N,O*-Bis(trimethylsilyl)acetamide] Method

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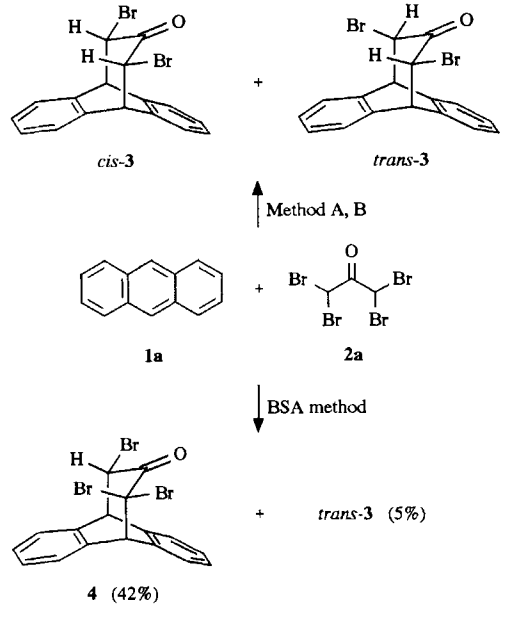
Sonication of a zinc/copper couple, *N,O*-bis(trimethylsilyl)-acetamide (BSA) and α,α'-oligobromo ketones in benzene gives rise to oxyallyl intermediates which cycloadd to anthracene. Starting from 1,1,3,3-tetrabromoacetone (**2a**) and anthracene (**1a**), we obtained 11,11,13-tribrominated adduct **4** as the major product (42%). The expected 11,13-dibrominated adduct *trans*-**3** was formed as a minor product (5%), but it became the main product when the known oxyallyl methodology was applied. Dibenzohomobarrelenes **9** and **17** were prepared by short routes.

Cycloadditions of oxyallyl cations to anthracenes have not yet been studied extensively[1], although a wide variety of tetracyclic ketones should be accessible. We have shown previously that sterically crowded ring systems containing up to four quaternary carbon centers[1b] can be prepared. Other 9,10-dihydro-9,10-propanoanthracenes substituted at one of the bridgehead carbon atoms are of medicinal interest[1d]. In this paper we describe the preparation of a series of the title tetracyclic ketones and consecutive reactions.

Results

Exploring procedures for adding the parent oxyallyl cation (or its synthetic equivalent) to anthracene, we studied the tetrabromoacetone **2a** in combination with BSA [*N,O*-bis(trimethylsilyl)acetamide] and a zinc/copper couple in benzene. Whereas the expected dibromo adduct (cf. *trans*-**3**) was isolated in low yield (5%), the unexpected tribromo adduct **4** was formed in good yield (42%). Other methods for generating oxyallyl cations gave only epimeric dibrominated *cis*-**3** and *trans*-**3**. Method B (zinc/copper couple, dioxane, ultrasound, 10–20°C) was superior to the trimethylsilyl chloride promoted reaction at 80°C (Method A). While parent anthracene is poorly soluble in benzene and other solvents, ultrasonication (35 kHz) helps to mediate the reaction.

Scheme 1



Method A: Zn/Cu, Me_3SiCl, dioxane, 80°C, 20 h, 15%. – Method B: Zn/Cu, dioxane, ultrasound, 10–20°C, 8 h, 28%.

Both *trans*-**3** and **4** were characterized further by reductive debromination to the desired 9,10-dihydro-9,10-propanoanthracen-12-one (**5**). Wolff-Kishner reduction of ketone **5** furnished parent tetracyclic hydrocarbon $C_{17}H_{16}$, i.e. 9,10-dihydro-9,10-propanoanthracene (**6**), whereas reduction of **5** with $NaBH_4$/methanol afforded secondary alcohol **7**.

Dibromo ketone *trans*-**3** also served as a starting material for the preparation of tetracyclic olefin **9**. Reduction with $NaBH_4$ in 2-propanol was chemoselective, leaving the two bromine atoms intact and producing secondary alcohol **8** as a racemic mixture. Subsequent elimination-debromination with a zinc/copper couple in weak acid (NH_4Cl, MeOH) gave dibenzohomobarrelene **9** directly.

Bisbenzoannulated benzylic ether **1b**[2] contains a methoxymethyl group which is sensitive to Lewis acids, including allyl cation intermediates generated from 2,4-dibromo-3-pentanone (**2b**) and a zinc/copper couple in dioxane (ultrasound 35 kHz, 10–20°C). Cycloadditions to **1b** under a variety of conditions failed. We found, however, that the milder BSA procedure afforded both *cis*-**10** and *trans*-**10** in one step.

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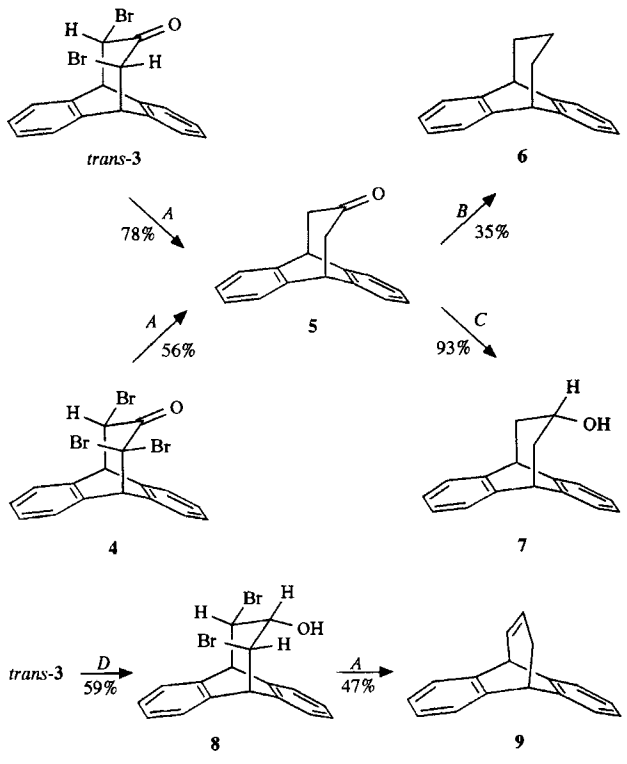
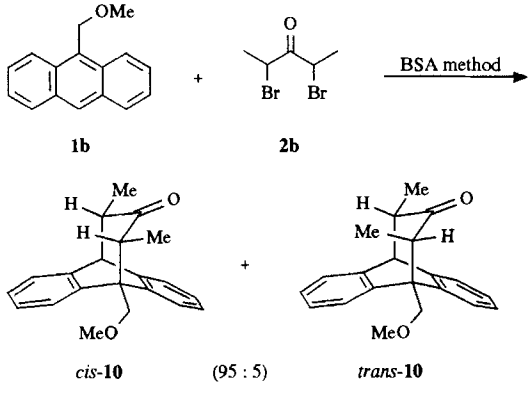
Scheme 2



A: Zn/Cu/NH_4Cl/MeOH, room temp. – *B*: NH_2NH_2/triethylene glycol/KOH. – *C*: $NaBH_4$/MeOH, room temp., 24 h. – *D*: $NaBH_4$/*i*PrOH, room temp., 24 h.

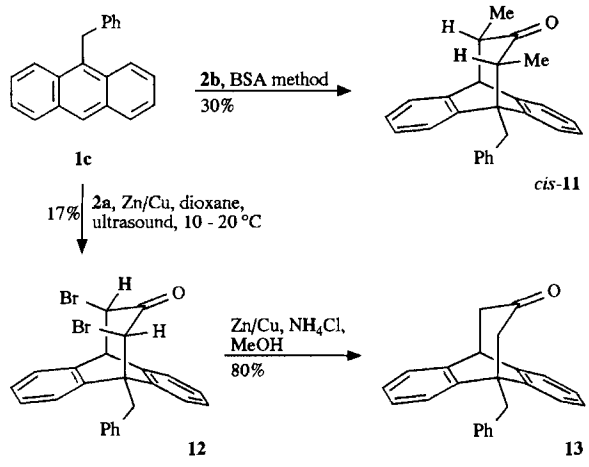
Scheme 3



9-Benzylanthracene (**1c**)[3] was also allowed to react with acyclic dibromo ketone **2b** in the presence of BSA and a zinc/copper couple, giving adduct *cis*-**11**.

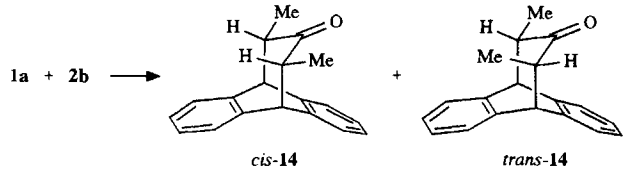
Intermolecular cyclodehalogenation of the tetrabromoacetone **2a** and **1c** by the standard ultrasound procedure in dioxane solvent gave *cis*-dibromo adduct **12**, which showed a long-range coupling ^4J(11-H,13-H) ≈ 2 Hz. Such coupling is usually found in planar chains H–C–C–C–H, which are *W*-configurated. Hence, the two bromine atoms adopt a *syn*-diaxial conformation. Reductive debromination of **12** furnished benzylated tetracyclic ketone **13** as colorless crystals.

Scheme 4



The two diastereomeric adducts *cis*-**14** and *trans*-**14** were prepared by two methods and separated by chromatography.

Scheme 5



	cis	*trans*	
Zn-Cu, dioxane, ultrasound	76	24	(29%)
BSA	82	18	(44%)

As before, the tetracyclic ketones were characterized by Wolff-Kishner reduction[4], giving dimethylated propano-bridged anthracene *cis*-**15** and *trans*-**15**. Dehydration of the epimeric alcohols **16α** and **16β**, obtained by $NaBH_4$ reduction of *cis*-**14**, afforded 9,10-dihydro-11,13-dimethyl-9,10-(prop-11-eno)anthracene (**17**).

Discussion

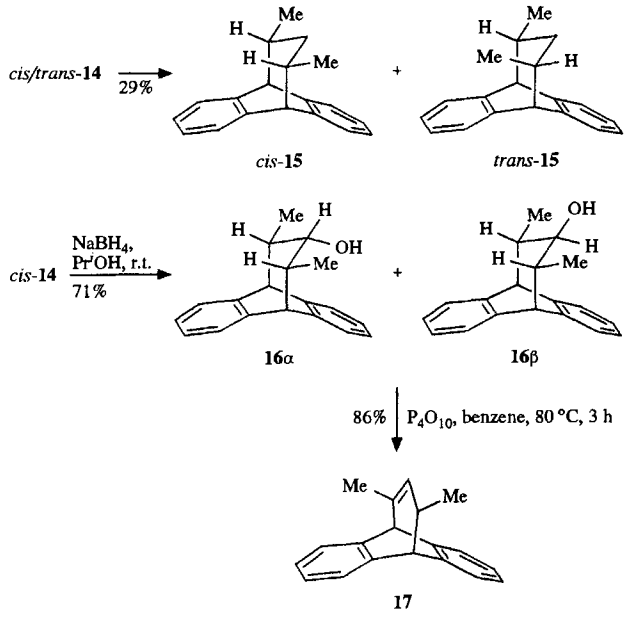
N,*O*-Bis(trimethylsilyl)acetamide (BSA) is a well-known acid trap and also displays oxophilic character. The formation of tribromo cycloadduct **4** points to a tribromooxyallyl cation **ii** as the key intermediate.

Benzene as the solvent appears to be essential for this reaction. Oxygen-containing solvents such as dioxane were not successful. The role of the zinc/copper couple in the BSA procedure is not yet clear. The formation of dibromo cycloadduct **3b** as the minor product suggests that some $ZnBr_2$ is generated in situ, which assists the S_N1 ionization of allylic bromide **i** to the postulated allylic cation **ii**.

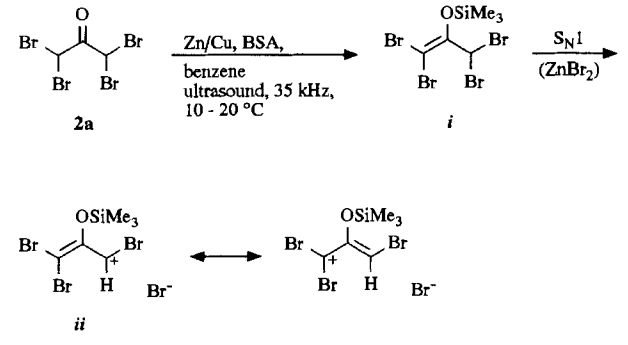
In conclusion, the BSA method is currently the only method for preparing tribrominated cycloadduct **4**, which together with dibrominated cycloadducts *trans*-**3**, is formed in 47% yield. The BSA method also tolerates a methoxymethyl group at C-9 of anthracene, thus allowing the preparation of tetracyclic ketone *cis*-**10** and *trans*-**10** and comp-

lementing the standard ultrasound/dioxane[1c,d] and other procedures[5,6]. Dibenzohomobarrelene (**9**) and derivatives such as **17** are directly accessible[7].

Scheme 6



Scheme 7



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Experimental

Column chromatography (silica gel, 0.02–0.63 mm, Merck) was carried out under weak positive pressure. – TLC: Precoated plates, Macherey-Nagel, Merck. – Gas chromatography: FID, N_2, Varian A 1400; glass capillary column (25 m, type OV 1 CB) and SE 54 CB (25 m fused silica, widebore). – Melting points: Büchi apparatus. – IR: Electrophotometer 580 and FT spectrometer 1710, Perkin-Elmer. – ^{1}H NMR: WP 80, WH 90, WP 200 SY and AM 300, Bruker. – ^{13}C NMR: WP 200 SY, AM 300, Bruker; APT (*a*ttached *p*roton *t*est): spin-echo-based selection of multiplicities of ^{13}C signals; quaternary C and CH_2 carbon atoms give positive signals (+), while CH and CH_3 give negative signals (–). – MS: Spectrometer MAT 312, Finnigan. – Elementary analyses: Microanalytical laboratory of the Department of Organic Chemistry. – PE: petroleum ether; E: diethyl ether; CH: cyclohexane; DCM: dichloromethane.

General Methods for Cycloaddition of Metal Oxyallyl Cations to Anthracenes. – Method A: Cycloaddition with Zn/Cu/Me$_3$SiCl at 80°C: **1a** (5.5 mmol) was dissolved in a minimum amount of dry dioxane (30 ml) with stirring at 80°C in a 100-ml three-necked flask fitted with a reflux condenser, drying tube, and a pressure-equalizing dropping funnel. Commercial zinc dust (2.0 g, 31 mmol) and CuCl (0.32 g, 3.2 mol) were added from a powder funnel, and the hot mixture was stirred for several minutes. A solution of **2a** (11 mmol) and Me_3SiCl (12 mmol) was then added dropwise over a 0.5-hour period. After the hot reaction mixture had been stirred continuously at 80°C for 20 h under nitrogen, it was suction-filtered through a No. 2 sintered glass funnel to remove the Zn/Cu couple, and the reaction flask was subsequently washed with several portions of DCM. The combined filtrates were concentrated in a rotary evaporator, and the residue was washed with a saturated NH_4Cl solution and water. The aqueous phases were extracted with DCM, and the combined organic extracts were dried ($MgSO_4$ or $CaCl_2$), filtered, and the filtrate was concentrated to give a reddish-brown solid. The crude product was chromatographed on silica gel 60 (Macherey and Nagel, 0.05–0.2 mm).

Method B: Cycloaddition with the Zn/Cu Couple Method Under Ultrasonic Conditions: A mixture of zinc powder (4 mmol), CuCl (0.4 mmol) and **1a** (1 mmol) in dry dioxane (20 ml) was sonicated under nitrogen in an ultrasonic bath [ELMA (480 H2), 35 kHz]. The reaction mixture was sonicated, while a solution of dibromo ketone (2 mmol) was added dropwise over a period of 0.5 h. The bath temperature was maintained below 20°C for the first hour, then allowed to slowly reach room temperature, and the reaction mixture was sonicated for a further 6–8 h. It was subsequently filtered through silica gel, washed several times with DCM and worked up as in method A.

Method C: BSA Method: A mixture of zinc dust (4 mmol), CuCl (0.4 mmol) and **1a** (1 mmol) was sonicated in dry benzene (20 ml) under nitrogen in an ultrasonic bath below 10°C. The reaction mixture was sonicated for a few minutes, and a solution of di- or tetrabromo ketone (2.0 mmol) and *N,O*-bis(trimethylsilyl)acetamide (BSA) (1.0 mmol) in a minimum amount of dry benzene was added dropwise over a period of 0.5 h. The bath temperature was maintained below 20°C with continuous sonication (5 h). The reaction mixture was filtered, the residue was washed several times with $CHCl_3$ or DCM and the filtrate dried in vacuo to remove the benzene. The residue was washed with water, extracted with $CHCl_3$ or DCM, the extract was dried ($CaCl_2$) and chromatographed (silica gel) to give the corresponding cycloadducts.

General Method for Debromination of the Brominated Cycloadducts: A mixture of zinc powder (100 mmol), CuCl (10 mmol), and NH_4Cl (2.0 g) was stirred in dry methanol (20 ml) at room temperature. The dibromo cycloadduct (10 mmol) in dry methanol (50 ml) was added slowly with continuous stirring. The reaction mixture was stored for ca. 12 h, filtered through silica gel, and the methanol was removed from the filtrate under reduced pressure. The residue was dissolved in DCM, washed with water (2×), the organic layer was separated by means of a separating funnel and dried ($MgSO_4$). The crude product was chromatographed (silica gel) to give the debrominated cycloadducts.

cis,trans-11,13-Dibromo-9,10-dihydro-9,10-propanoanthracen-12-one (**3**). – *Method A:* **2a** (7.48 g, 20 mmol) and **1a** (1.78 g, 10 mmol) were allowed to react, giving after chromatography [E/CH (1:6)] 1.7 g (15%) of **3** (*cis*-**3**: <10%; *trans*-**3**: >90%) as colorless crystals. Pure *trans*-**3** was separated as needles by crystallization (E/

PE), m.p. 249°C. – *Method B: cis*-**3** and *trans*-**3**: combined yields 28%. – IR (KBr): $\tilde{\nu}$ = 2959 cm^{-1}, 2931, 1723, 1477, 1457, 1284, 1166, 1139, 759. – ^1H NMR (CD_2Cl_2): *cis*-**3**: δ = 4.61 (d, *J* = 5 Hz, 2H, 9-H, 10-H), 5.52 (d, *J* = 5 Hz, 2H, 11-H, 13-H), 7.22–7.52 (m, 8H, arom. H); *trans*-**3**: δ = 4.40 (d, *J* = 5 Hz, 2H, 9-H, 10-H), 4.71 (d, *J* = 5 Hz, 2H, 11-H, 13-H), 7.22–7.52 (m, 8H, arom. H). – ^{13}C NMR (APT, CD_2Cl_2), *cis/trans*-**3**: δ = 50.61, 51.93 (–, C-9, C-10), 52.61, 57.16 (–, C-11, C-13), 127.26–129.46 (–, complex arom. C), 138.10, 138.37, 138.58, 138.67 (+, arom. C), 194.44, 198.53 (+, 2 C=O); *trans*-**3** ($CDCl_3$): δ = 50.61 (–, C-9, C-10), 52.29 (–, C-11, C-13), 127.58, 128.00, 129.22, 129.47 (–, arom. C), 138.10, 138.68 (+, arom. C), 198.55 (+, C=O). – MS: *m/z* (%) = 392 (8) [M^+], 312 (72), 310 (69), 295 (3), 267 (7), 233 (31), 232 (100), 215 (9), 203 (32), 191 (72), 178 (77), 165 (14), 152 (7), 149 (5), 125 (8), 111 (9), 101 (29), 88 (15), 76 (10), 57 (20), 45 (6). – $C_{17}H_{12}Br_2O$ (392.1): calcd. C 52.07, H 3.08; found C 51.96, H 3.20. – Cycloadducts *cis*-**3** and *trans*-**3** could not be separated by standard chromatographic methods, but pure *trans*-**3** was obtained by crystallization (E/PE or E/CH). – ^1H NMR of *trans*-**3** in various solvents: See Table 1.

Table 1. ^1H-NMR data of *trans*-**3** (solvents $CDCl_3$, CD_2Cl_2, [D_6]DMSO)

$CDCl_3$	CD_2Cl_2	[D_6]DMSO
δ = 4.47 (d, *J* = 5 Hz, 2H, 9-H, 10-H), 4.70 (d, *J* = 5 Hz, 2H, 11-H, 13-H), 7.20–7.50 (m, 8H, arom. H)	δ = 4.51 (d, *J* = 5 Hz, 2H, 9-H, 10-H), 4.73 (d, *J* = 5 Hz, 2H, 11-H, 13-H), 7.30–7.50 (m, 8H, arom. H)	δ = 4.70 (d, *J* = 5 Hz, 2H, 9-H, 10-H), 5.08 (d, *J* = 5 Hz, 2H, 11-H, 13-H), 7.30–7.60 (m, 8H, arom. H)

11,11,13-Tribromo-9,10-dihydro-9,10-propanoanthracen-12-one (**4**). – *Method C:* A mixture of **1a** (0.5 g, 2.8 mmol) in dry benzene (15 ml), Zn (1.0 g, 15 mmol), and CuCl (0.16 g, 1.6 mmol) was sonicated under nitrogen at ca. 10°C for a few minutes, and a mixture of **2a** (2.09 g, 5.6 mmol) and BSA (0.57 g, 2.8 mmol) in dry benzene (15 ml) was added dropwise over a period of 20 min. The reaction mixture was sonicated at 10–25°C under nitrogen for 6 h, worked up and chromatographed [silica gel, E/PE (1:10)] to give, after removal of anthracene, colorless crystalline needles of **4**, yield 0.55 g (42%), m.p. 164°C, followed by 55 mg (5%) of *trans*-**3**. – Data of **4**: IR (KBr): $\tilde{\nu}$ = 3030 cm^{-1}, 1718, 1477, 1269, 1115, 1034, 850, 779, 761. – ^1H NMR (C_6D_6): δ = 4.00 (d, *J* = 4 Hz, 1H, 9-H), 4.83 (d, *J* = 4 Hz, 1H, 13-H), 4.87 (s, 1H, 10-H), 6.70–7.20 (m, 8H, arom. H). – ^{13}C NMR (APT, $CDCl_3$): δ = 52.0 (–, C-9), 54.11 (–, C-10), 61.26 (–, C-13), 70.10 (+, C-11), 126.76–130.27 (–, arom. C), 136.72–138.42 (+, arom. C), 190.19 (+, C=O). – MS: *m/z* (%) = 473 (4) [M^+ + 2], 471 (7) [M^+], 469 (6) [M^+ – 2], 426 (3), 391 (75), 347 (3), 311 (22), 269 (28), 233 (8), 232 (27), 231 (48), 202 (57), 189 (43), 178 (100), 165 (10), 152 (10), 116 (13), 101 (45), 88 (26), 80 (8), 76 (10), 63 (10). – $C_{17}H_{11}Br_3O$ (471.0): calcd. C 43.36, H 2.35; found C 43.33, H 2.41.

9,10-Dihydro-9,10-propanoanthracen-12-one (**5**): **5** was prepared by debromination of **3** (78%). Furthermore, **4** was debrominated to give after chromatography [silica gel, E/CH (1:5)] **5** as colorless crystalline needles (58%), m.p. 220°C. For spectroscopic data see ref.[1c].

9,10-Dihydro-9,10-propanoanthracene (**6**): A mixture of **5** (0.234 g, 1.0 mmol), KOH (0.15 g, 2.7 mmol), hydrazine hydrate (0.36 g, 72 mmol, 80% solution) and triethylene glycol was stirred at 150°C for 7 h. The water was removed by means of a Dean-Stark separator, and the reaction mixture was heated for a further 8 h to 200–210°C. After cooling to room temperature, the pH of the mixture was adjusted to 2 by addition of dil. HCl. The aqueous layer was extracted several times with toluene, and the combined organic extracts were washed with brine. After drying ($MgSO_4$) and removal of the solvent, the crude product was purified by chromatography [silica gel, E/CH (1:5)] to give white crystals of **6**, yield 76 mg (35%), m.p. 91–93°C. – IR (KBr): $\tilde{\nu}$ = 3020 cm^{-1}, 2922, 2855, 1624, 1455, 1298, 754. – ^1H NMR ($CDCl_3$): δ = 1.25–1.40 (m, 2H, 12-H), 1.70–1.85 (m, 4H, 11-H, 13-H), 3.90–4.00 (t, *J* = 4 Hz, 2H, 9-H, 10-H), 7.10–7.30 (m, 8H, arom. H). – ^{13}C NMR (APT, $CDCl_3$): δ = 22.24 (+, C-12), 29.88 (+, C-11, C-13), 46.21 (–, C-9, C-10), 125.52, 126.03 (–, arom. C), 143.22 (+, arom. C). – MS: *m/z* (%) = 220 (100) [M^+], 205 (12), 191 (69), 178 (85), 165 (9), 152 (9), 139 (3), 130 (4), 116 (4), 101 (5), 95 (6), 89 (12), 76 (6), 69 (8), 57 (3), 51 (2). – $C_{17}H_{16}$ (220.3): calcd. C 92.68, H 7.32; found C 92.35, H 7.53.

9,10-Dihydro-9,10-propanoanthracen-12-ol (**7**): A mixture of **5** (15 mg, 0.064 mmol) and $NaBH_4$ (40 mg) was stirred in methanol (10 ml) at room temperature for 24 h under nitrogen. The reaction mixture was worked up and chromatographed [silica gel, E/CH (1:3)] to afford colorless crystals of **7**, yield 16 mg (93%), m.p. 114–116°C. – IR (KBr): $\tilde{\nu}$ = 3309 cm^{-1}, 3069, 3020, 2925, 2855, 1474, 1456, 1105, 1042, 763, 748. – ^1H NMR ($CDCl_3$): δ = 1.25–1.40 (m, 3H, OH, 11-H, 13-H), 2.40 (m, 2H, 11-H, 13-H), 3.27 (m, 1H, C*H*OH), 4.10 (d, *J* = 7 Hz, 2H, 9-H, 10-H), 7.32–7.50 (m, 8H, arom. H). – ^{13}C NMR (APT, $CDCl_3$): δ = 39.26 (+, C-11, C-13), 43.98 (–, C-9, C-10), 68.26 (–, C-12), 125.36, 125.56, 126.33, 126.42 (–, arom. C), 140.60, 144.24 (+, arom. C). – MS: *m/z* (%) = 236 (39) [M^+], 218 (100), 203 (26), 191 (54), 178 (80), 165 (10), 152 (8), 139 (4), 129 (4), 115 (5), 101 (5), 95 (6), 89 (7), 83 (8), 76 (5), 69 (9). – $C_{17}H_{16}O$: calcd. C 236.1199, found 236.1201 (MS).

11,13-Dibromo-9,10-dihydro-9,10-propanoanthracen-12-ol (**8**): A mixture of *trans*-**3** (0.20 g, 0.51 mmol) and $NaBH_4$ (22 mg, 0.58 mmol) was stirred in dry *i*PrOH (10 ml) at room temperature for 24 h. The reaction mixture was diluted with ice-cold water, extracted with DCM, and the extract was dried ($MgSO_4$). The crude product was chromatographed [silica gel, E/CH (1:3)] to give colorless crystals of **8**, yield 118 mg (59%), m.p. 192°C. – IR (KBr): $\tilde{\nu}$ = 3499 cm^{-1}, 3033, 2937, 1627, 1493, 1455, 1322, 1284, 1083, 867, 767. – ^1H NMR ($CDCl_3$): δ = 2.60 (d, *J* = 12 Hz, 1H, OH), 3.44 (m, 1H, 12-H), 4.46 (d, *J* = 6 Hz, 2H, 9-H, 10-H), 4.72 (dd, *J* = 6 Hz, *J* = 1.5 Hz, 2H, 11-H, 13-H), 7.20–7.40 (m, 8H, arom. H). – ^{13}C NMR (APT, $CDCl_3$): δ = 51.37 (–, C-9, C-10), 57.36 (–, C-11, C-13), 67.17 (–, C-12), 126.56, 126.67, 128.03, 128.94 (–, arom. C), 138.71, 139.01 (+, arom. C). – MS: *m/z* (%) = 396 (10) [M^+ + 2], 394 (19) [M^+], 392 (9) [M^+ – 2], 348 (2), 314 (24), 312 (23), 296 (5), 269 (7), 251 (3), 233 (39), 216 (61), 215 (35), 202 (13), 191 (100), 178 (84), 165 (14), 152 (5), 128 (2), 115 (3), 101 (6), 95 (6), 80 (7), 57 (3), 51 (1). – $C_{17}H_{14}Br_2O$ (394.1): calcd. C 51.81, H 3.58; found C 52.46, H 3.70.

9,10-Dihydro-9,10-(prop-11-eno)anthracene (**9**): A mixture of **8** (60 mg, 0.15 mmol), zinc powder (0.1 g, 1.5 mmol), CuCl (15 mg, 0.15 mmol), and NH_4Cl (80 mg) was stirred at room temperature for 24 h under nitrogen. The reaction mixture was worked up to furnish after chromatography [silica gel, E/CH (1:5)] white crystals of **9**, yield 12 mg (47%), m.p. 165–168°C. – IR (KBr): $\tilde{\nu}$ = 3011 cm^{-1}, 2948, 2877, 2814, 1476, 1455, 1112, 1030, 761, 728. – ^1H NMR ($CDCl_3$): δ = 2.50 (m, 2H, 13-H), 4.03 (t, *J* = 4 Hz, 1H, 9-H), 4.13 (d, *J* = 8 Hz, 1H, 10-H), 5.05 (m, 1H, 12-H), 6.25 (m, 1H, 11-H), 7.07–7.40 (m, 8H, arom. H). – ^{13}C NMR (APT,

$CDCl_3$): δ = 33.72 (+, C-13), 45.97, 46.06 (−, C-9, C-10), 123.97−131.93 (−, complex arom. C, C-11, C-12), 141.21, 146.15 (+, arom. C). − MS: *m/z* (%) = 218 (100) [M^+], 203 (64), 191 (19), 178 (12), 165 (7), 152 (6), 139 (3), 125 (4), 108 (13), 101 (12), 94 (10), 85 (11), 83 (11), 76 (6), 71 (16), 67 (5). − $C_{17}H_{14}$: calcd. 218.1095, found 218.1096 (MS).

cis,trans-9,10-Dihydro-9-(methoxymethyl)-11,13-dimethyl-9,10-propanoanthracen-12-one (**10**). − *Method C:* A mixture of Zn (0.35 g, 5.4 mmol) and CuCl (55 mg, 0.55 mmol) was sonicated in a minimum amount of dry benzene at ca. 10°C in a three-necked flask fitted with two separate dropping funnels. A mixture **2b** (0.66 g, 2.7 mmol) and BSA (0.28 g, 1.4 mmol) in dry benzene (10 ml) (from one dropping funnel) and a solution of **1b** (0.30 g, 1.35 mmol) in benzene (10 ml) (from the other dropping funnel) were added slowly at the same rate over a period of 20 min. The reaction mixture was sonicated for another 5 h, kept for ca. 12 h with stirring at room temperature, worked up and chromatographed [silica gel, E/CH (1:8)] to give 0.10 g (24%) of impure cycloadducts *cis*-**10** and *trans*-**10**. Paper chromatography gave the *cis/trans* mixture of **10** as a colorless oil (*cis/trans* = >95:<5; ^{1}H NMR analysis). − IR (film): ṽ = 3070 cm^{-1}, 2978, 2930, 2874, 2812, 1695, 1601, 1477, 1456, 1374, 1306, 1288, 1140, 1110, 1057, 760. − ^{1}H NMR ($CDCl_3$): *cis*-**10**: δ = 0.86 (d, *J* = 8 Hz, 3H, CH_3), 1.05 (d, *J* = 8 Hz, 3H, CH_3), 2.85 (m, 2H, 11-H, 13-H), 3.54 (s, 3H, OCH_3), 3.96 (d, *J* = 5 Hz, 1H, 10-H), 4.25 (dd-like q, *J* = 9 Hz, *J* = 12 Hz, 2H, C*H*$_2$OCH$_3$), 7.13−7.55 (m, 8H, arom. H); *trans*-**10**: δ = 0.75 (d, *J* = 8 Hz, 3H, CH_3), 1.21 (d, *J* = 8 Hz, 3H, CH_3), 2.72 (m, 2H, 11-H, 13-H), 3.55 (s, 3H, OCH_3), 3.87 (d, *J* = 1 Hz, 1H, 10-H), 4.25 (dd-like q, *J* = 9 Hz, *J* = 12 Hz, 2H, C*H*$_2$OCH$_3$), 7.13−7.55 (m, 8H, arom. H). − ^{13}C NMR (APT, $CDCl_3$): δ = 15.27, 15.39, 16.02, 18.78 (−, 4 × CH_3), 48.18 (+, C-9), 48.78, 49.89, 51.24, 52.74 (−, C-10, C-11, C-13), 59.11 (−, OCH_3), 71.92 (+, OCH_2), 124.97−128.47 (−, complex arom. C), 139.07, 142.07, 143.13 (+, arom. C), 212.02, 215.17 (+, 2 × C=O). − MS: *m/z* (%) = 306 (7) [M^+], 305 (22), 291 (3), 275 (4), 261 (10), 249 (5), 233 (10), 221 (76), 207 (27), 191 (69), 178 (34), 165 (12), 152 (16), 141 (32), 123 (10), 113 (13), 95 (15), 83 (100), 76 (11), 73 (20), 65 (8). − $C_{21}H_{22}O_2$: calcd. 306.1630, found 306.1620 (MS).

9-Benzyl-9,10-dihydro-11,13-dimethyl-9,10-propanoanthracen-12-one (**11**). − *Method C:* **1c** (0.20 g, 0.75 mmol) was allowed to react with **2b** (0.37 g, 1.5 mmol) to give after chromatography [silica gel, E/PE (1:10)] *cis*-**11** as a colorless oil, yield 81 mg (30%). − IR (KBr): ṽ = 3028 cm^{-1}, 2976, 2930, 1692, 1603, 1497, 1454, 1080, 1032, 762, 747, 726. − ^{1}H NMR ($CDCl_3$): δ = 1.12 (d, *J* = 8 Hz, 3H, CH_3), 1.19 (d, *J* = 8 Hz, 3H, CH_3), 2.90 (dq, *J* = 8 Hz, *J* = 1.5 Hz, 1H, 13-H), 3.05 (m, 1H, 11-H), 3.90 (d, *J* = 19 Hz, 1H, C*H*HPh), 4.26 (d, *J* = 5 Hz, 1H, 10-H), 4.38 (d, *J* = 19 Hz, 1H, CH*H*Ph), 6.92−7.98 (m, 13H, arom. H). − MS: *m/z* (%) = 352 (47) [M^+], 318 (7), 295 (25), 281 (16), 268 (75), 252 (16), 239 (11), 231 (7), 217 (10), 208 (51), 191 (26), 180 (53), 165 (20), 152 (26), 139 (11), 126 (15), 105 (44), 91 (100), 84 (88), 76 (34), 73 (63), 65 (25), 61 (35). − $C_{26}H_{24}O$: calcd. 352.1822, found 352.1827 (MS).

cis-9-Benzyl-11,13-dibromo-9,10-dihydro-9,10-propanoanthracen-12-one (**12**). − *Method B:* **1c** (1.34 g, 5 mmol) and **2a** (3.74 g, 10 mmol) were allowed to react to afford after chromatography [silica gel, DCM/CH (1:5)] white crystals of *cis*-**12**, yield 0.41 g (17%), m.p. 112−114°C. − IR (KBr): ṽ = 3060 cm^{-1}, 3024, 2924, 1704, 1600, 1476, 1452, 1316, 1180, 724. − ^{1}H NMR ($CDCl_3$): δ = 3.80 (d, *J* = 19 Hz, 1H, C*H*HPh), 4.46 (d, *J* = 2 Hz, 1H, 13-H), 4.50 (d, *J* = 19 Hz, 1H, CH*H*Ph), 4.59 (d, *J* = 6 Hz, 1H, 10-H), 4.62 (dd, *J* = 6 Hz, *J* = 2 Hz, 1H, 11-H), 6.70−7.52 (m, 13H, arom. H). − ^{13}C NMR ($CDCl_3$): δ = 30.37 (t, CH_2), 48.10 (s, C-9), 49.00 (d, C-11), 60.00 (d, C-13), 69.00 (d, C-10), 125.71−129.97 (d, arom. C), 135.72−137.66 (s, arom. C), 198.18 (s, C=O). − MS: *m/z* (%) = 484 (6) [M^+ + 2], 482 (15) [M^+], 480 (7) [M^+ − 2], 437 (11), 403 (40), 401 (40), 392 (7), 357 (21), 321 (37), 300 (11), 281 (25), 268 (53), 267 (53), 252 (12), 231 (54), 215 (27), 203 (100), 191 (27), 178 (28), 165 (9), 152 (9), 115 (11), 103 (18), 91 (60), 77 (6), 56 (21).

9-Benzyl-9,10-dihydro-9,10-propanoanthracen-12-one (**13**): **12** (0.50 g, 1.04 mmol) was debrominated to afford colorless crystals of **13**, yield 0.27 g (80%), m.p. 204−205°C. − IR (KBr): ṽ = 3064 cm^{-1}, 3024, 2908, 2856, 1692, 1592, 1496, 1452, 1300, 1028, 712. − ^{1}H NMR ($CDCl_3$): δ = 2.74 (s, 2H, CH_2C=O), 2.80 (d, *J* = 4 Hz, 2H, CH_2C=O), 3.94 (s, 2H, C*H*$_2$Ph), 4.38 (t, *J* = 4 Hz, 1H, 10-H), 6.77−7.42 (m, 13H, arom. H). − ^{13}C NMR ($CDCl_3$): δ = 39.95 (t, *C*H$_2$Ph), 43.55 (d, C-10), 43.77 (s, C-9), 50.61 (t, C-11), 62.52 (t, C-13), 125.34−127.33 (d, arom. C), 130.13−141.27 (s, arom. C), 209.15 (s, C=O). − MS: *m/z* (%) = 325 (26) [M^+ + 1], 323 (100) [M^+ − 1], 281 (22), 265 (15), 252 (6), 233 (14), 215 (8), 208 (24), 191 (30), 180 (19), 165 (6), 152 (17), 139 (2), 126 (4), 103 (2), 91 (11), 76 (9), 65 (2), 57 (5), 50 (3). − $C_{24}H_{20}O$ (324.4): calcd. C 88.85, H 6.21; found C 88.85, H 6.21.

cis,trans-9,10-Dihydro-11,13-dimethyl-9,10-propanoanthracene (**15**): *cis*- and *trans*-**14** (0.30 g, 1.1 mmol) were reduced according to the Wolff-Kishner method[4] to give after chromatography [silica gel, E/PE (1:7)] a white precipitate of *cis*-**15** and *trans*-**15**, yield 83 mg (29%). − IR (KBr): ṽ = 3019 cm^{-1}, 2952, 2909, 2874, 1474, 1455, 1373, 1173, 1032. − ^{1}H NMR ($CDCl_3$): *cis*-**15**: δ = 0.85 (d, *J* = 8 Hz, 6H, 2 CH_3), 1.00 (t, *J* = 6 Hz, 2H, CH_2), 2.00 (m, 2H, 11-H, 13-H), 3.70 (d, *J* = 4 Hz, 2H, 9-H, 10-H), 7.05−7.26 (m, 8H, arom. H); *trans*-**15**: δ = 0.93 (d, *J* = 8 Hz, 6H, 2 CH_3), 1.00 (t, *J* = 6 Hz, 2H, CH_2), 1.80 (m, 2H, 11-H, 13-H), 3.60 (s, 2H, 9-H, 10-H), 7.05−7.26 (m, 8H, arom. H). − ^{13}C NMR (APT, $CDCl_3$): δ = 20.65, 22.80 (−, CH_3), 30.85, 34.73 (−, C-11, C-13), 38.33, 40.28 (+, C-12), 52.60, 53.11 (−, C-9, C-10), 125.29−128.14 (−, arom. C), 138.87, 139.69, 143.67, 144.32 (+, arom. C). − MS: *m/z* (%) = 250 (6) [M^+ + 2], 249 (27) [M^+ + 1], 234 (2), 219 (1), 207 (17), 191 (2), 178 (100), 165 (3), 152 (6), 139 (1), 126 (1), 89 (3), 76 (2), 55 (1). − $C_{19}H_{20}$ (248.4): calcd. C 91.88, H 8.11; found C 91.68, H 8.07.

(12α,β)-9,10-Dihydro-11,13-dimethyl-9,10-propanoanthracen-12-ol (**16α,β**): *cis*-**14** (0.237 g, 0.9 mmol) was stirred with $NaBH_4$ (0.07 g, 1.9 mmol) in dry *i*PrOH (20 ml) under nitrogen at room temperature. The reaction mixture was kept for ca. 12 h, diluted with water, extracted with $CHCl_3$, the extract was dried ($CaCl_2$) and chromatographed [silica gel, E/CH (1:10)] to give colorless crystals of **16α** [110 mg (46%), m.p. 105−106°C] in the early fractions, followed by colorless crystals of **16β** [60 mg (25%), m.p. 144°C (decomp.)]. − Data of **16α**: IR (film): ṽ = 3544 cm^{-1}, 3022, 2965, 2926, 1475, 1455, 1285, 1042, 766, 749. − ^{1}H NMR ($CDCl_3$): δ = 1.14 (d, *J* = 7 Hz, 6H, 2 CH_3), 2.15 (m, 2H, 11-H, 13-H), 3.45 (m, 1H, 12-H), 3.68 (d, *J* = 2 Hz, 2H, 9-H, 10-H), 7.08−7.37 (m, 8H, arom. H). − ^{13}C NMR (APT, $CDCl_3$): δ = 18.16 (−, 2 CH_3), 41.05 (−, C-11, C-13), 51.60 (−, C-9, C-10), 76.26 (−, C-12), 125.25, 126.21, 126.57, 127.36 (−, arom. C), 140.68, 143.60 (+, arom. C). − MS: *m/z* (%) = 264 (12) [M^+], 246 (32), 231 (19), 206 (14), 191 (20), 178 (100), 166 (6), 149 (6), 139 (12), 123 (83), 109 (5), 91 (7), 76 (8), 65 (5). − $C_{19}H_{20}O$ (264.4): calcd. C 86.32, H 7.62; found C 85.69, H 7.63. − Data of **16β**: IR ($CHCl_3$): ṽ = 3444 cm^{-1}, 3072, 3000, 2960, 2912, 2872, 1612, 1472, 1452, 1116, 1096, 1028, 908. − ^{1}H NMR ($CDCl_3$): δ = 0.68 (d, *J* = 7 Hz, 3H, CH_3), 1.18 (d, *J* = 7 Hz, 3H, CH_3), 1.60 (m, 1H, OH), 1.70 (m, 1H, 11-H or 13-H), 2.35 (m, 1H, 13-H or 11-H), 2.85 (m, 1H, 12-H), 3.69 (s, 1H, 9-H or 10-H), 3.95 (d, *J* = 6 Hz, 1H, 9-H or 10-H), 7.08−7.30 (m, 8H,

arom. H). – MS: *m/z* (%) = 264 (8) [M^+], 246 (13), 231 (10), 206 (7), 191 (11), 178 (39), 165 (3), 152 (4), 139 (2), 121 (3), 115 (3), 101 (2), 99 (2), 91 (3), 87 (74), 83 (100), 76 (3), 65 (2).

9,10-Dihydro-11,13-dimethyl-9,10-(prop-11-eno)anthracene (**17**): A mixture of **16α** (0.331 g, 0.125 mmol) in dry benzene (or dry cyclohexane) (20 ml) and P_4O_{10} (0.3 g) was stirred in an oil bath under nitrogen at 80°C for 3 h. The reaction mixture was filtered and the benzene removed in vacuo. The residue was dissolved in $CHCl_3$, the resulting solution washed with water, separated, dried ($CaCl_2$) and chromatographed [silica gel, E/PE (1:10)] to give colorless crystals of **17**, yield 263 mg (86%), m.p. 102–103°C. – IR (KBr): $\tilde{\nu}$ = 3018 cm^{-1}, 2963, 2924, 1474, 1453, 1140, 749. – ^1H NMR ($CDCl_3$): δ = 0.93 (d, *J* = 7 Hz, 3H, CH_3), 1.82 (dd-like t, *J* = 2 Hz, *J* = 0 Hz, 3H, CH_3), 2.48 (m, 1H, 13-H), 3.75 (dd, *J* = 2 Hz, *J* = 1 Hz, 1H, 9-H), 3.85 (s, 1H, 10-H), 4.50 (m, 1H, 12-H). – ^{13}C NMR ($CDCl_3$): δ = 20.02 (q, CH_3), 25.80 (q, CH_3), 36.50 (d, C-13), 51.86 (d, C-9), 52.12 (d, C-10), 123.66–128.28 (d, C-12, arom. C), 137.84, 138.07, 141.75, 144.09, 145.54 (s, C-11, arom. C). – MS: *m/z* (%) = 246 (100) [M^+], 231 (78), 225 (49), 217 (95), 202 (39), 189 (11), 178 (58), 165 (7), 152 (14), 139 (5), 123 (5), 123 (6), 108 (13), 101 (16), 89 (9), 76 (9), 63 (10). – $C_{19}H_{18}$ (246.4): calcd. C 92.46, H 7.36; found C 92.02, H 7.34; calcd. 246.1411, found 246.1409 (MS).

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