

177. From Dichlorocyclopropanes to Furans and Cyclopentadienes *via* Vinylcarbenes

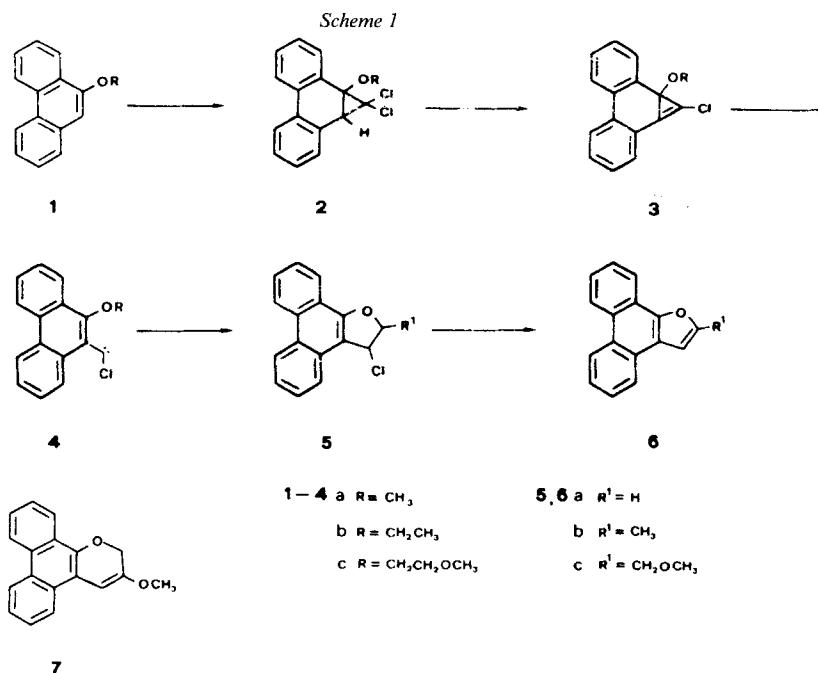
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Base-induced elimination of dichlorocarbene adducts **2** to 9-alkoxyphenanthrenes **1** leads to furans **6**, presumably *via* cyclopropenes **3** which undergo rearrangement to vinylcarbenes **4** and C–H insertion. By the same sequence, the 9-substituted alkylphenanthrene adducts **10** and **14** afford cyclopentadienes **11** and **15**. Carbene adducts of simple enol ethers, however, react differently and give preferentially 2-chloroalken-2-ones.

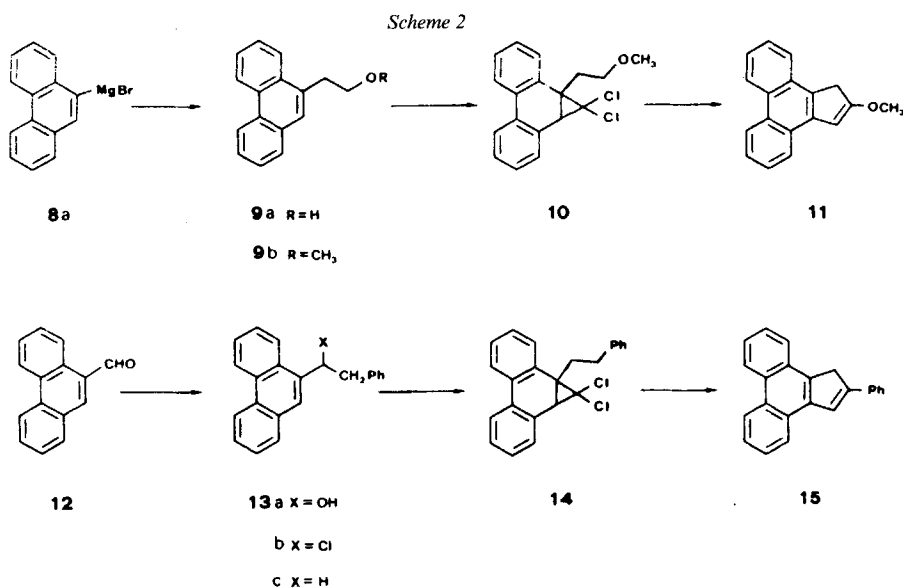
Introduction. – The cyclopropene-vinylcarbene rearrangement has been extensively investigated mechanistically over the recent years [1], but only few applications in synthesis are known. The synthetic potential of the reaction may be appreciated in the light of some recent examples, such as the ring opening of perchlorocyclopropene to perchlorovinylcarbene, and its subsequent addition and insertion reactions [2], and the 1,3-dipolar cycloadditions of cyclopropene ketals [3].



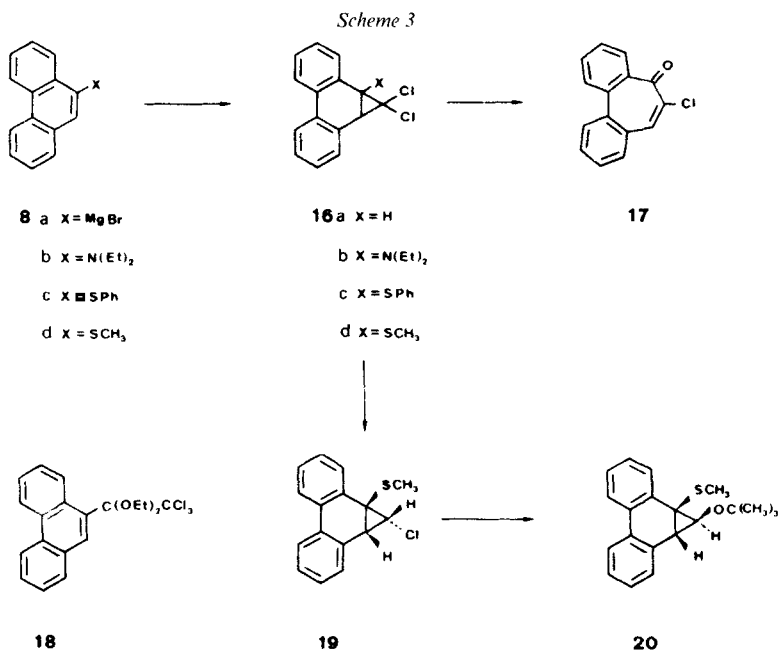
In connection with research directed towards synthesis of cyclopropa[1]-phenanthrenes [4], we reacted the dichlorocarbene adduct **2a** [5] of 9-methoxyphenanthrene (**1a**) with strong base and isolated phenanthro[9,10-*b*]furan (**6a**) in 80% yield [6]. The result was interpreted by the sequence shown in *Scheme 1*, which is formulated in analogy to known reactions of dichlorocarbene adducts of phenanthrene [7–9]: elimination of HCl from **2** leads to the chlorocyclopropene **3** which undergoes ring opening to the chlorovinylcarbene **4**. Insertion of the latter into one of the C–H bonds of the MeO group leads to **5**. Finally, furan **6** is formed upon dehydrohalogenation of **5** with base. Thus, the overall sequence consists in a transformation of a vinyl ether into a furan *via* dichlorocarbene addition. We felt that this procedure should have some synthetic value and investigated the scope of the reaction.

Results and Discussion. – In the first part of this investigation, the alcohol moiety of the enol ether was varied from Me (**1a**) to Et (**1b**) and MeOEt (**1c**). The compounds were prepared from 9-bromophenanthrene by Cu(I)-catalyzed substitution according to a known procedure [10]. The dichlorocarbene adducts **2b** and **2c** were obtained in 66 and 60% yield, respectively, with $\text{Cl}_3\text{COEt}/\text{MeONa}$ [5]. Treatment of **2b** and **2c** with 2 equiv. of *t*-BuOK in THF in presence of dicyclohexano(18-crown-6) afforded the furans **6b** (52%) and **6c** (66%). In the case of **1c**, two sites are available for insertion; however, only **6c** was obtained and none of the dihydropyran **7**, which might also be expected.

The sequence can also be realized when the activating ether function lies further away from the phenanthrene, so that a substituted cyclopentadiene is formed, as shown for **10** (*Scheme 2*). Compound **10** was synthesized from (9-phenanthryl)magnesium bromide **8a** [11] and ethylene oxide, and subsequent methylation of the addition product **9a** with NaH/MeI [12] yielded **9b**.



When the carbene adduct **10** was subjected to dehydrohalogenation under standard conditions, the ring-expanded product **11** (2-methoxy-1*H*-cyclopenta[*l*]phenanthrene) was formed in moderate yield (35%). The spectroscopic data of **11** are given in the *Exper. Part*. The structural assignment is essentially based on the presence of *singlets* at 3.84 (2H) and 3.93 (3H) ppm in the ¹H-NMR, corresponding to the CH₂ group of the cyclopentadiene and the CH₃ of the enol-ether moieties. The corresponding resonances in the ¹³C-NMR are found at δ 37.78 (*t*) and 57.47 (*q*) ppm. Similarly, 9-(2-phenylethyl)-phenanthrene (**13c**), prepared from 9-phenanthrenecarbaldehyde (**12**) via alcohol **13a** and chloride **13b**, when subjected to the same sequence, gave the 2-phenyl-substituted cyclopentadiene **15** in 44.5% yield, together with 55.5% of unreacted **14**. The spectral data of the known 3-phenyl isomer of **15** [13] were useful for establishing the structure.



Attempts to prepare other heterocyclic molecules by this route were unsuccessful. For example, when dichlorocarbene was added to 9-(diethylamino)phenanthrene (**8b**; synthesized from 9-bromophenanthrene by reaction with Li-diethylamide [14] [15]; *Scheme 3*), the expected adduct **16b** could not be isolated, but rather the chlorotropone **17** in max. 8% yield. Compound **17** is also generated from **2a** under solvolytic conditions [5]. The occurrence of **17** from **8b** implies that at least some of the desired adduct **16b** had been formed. Analogous ring expansions of dihalocarbene adducts of enamines are known [16]. Another complication arose, when it was attempted to replace the ether function in **1** by thioether. Although 9-(phenylthio)phenanthrene (**8c**) adds dichlorocarbene normally under phase-transfer conditions [17] to yield **16c**, addition to the methyl derivative **8d**,

which is readily available from (9-phenanthryl)magnesium bromide (**8**) and dimethyl disulfide [18], takes a different course and leads to the rearranged product **18**. The intriguing pathway connecting **8d** with **18** is currently under investigation in our laboratory [19]. Nevertheless, a methylthio analogue **19** of **1a** albeit with only one Cl substituent on the cyclopropane ring could be synthesized from **16a** [20], by dehydrohalogenation with 1 equiv. of *t*-BuOK in presence of methanethiol [4] [7–9]. The regioselectivity of the elimination-addition sequence of **16a** with thiolate is known [7] [8]. The vicinal coupling constant of 7 Hz indicates *cis*-configuration for the cyclopropane H-atoms, while the Cl substituent adopts 'endo'-orientation. This corresponds to *cis*-addition of MeSH, which is the rule for such systems [4]. Compound **19** was found very resistant towards treatment with base. Under standard conditions, most of the starting material (60%) was recovered, and only a *ca.* 10% yield of a new product of structure **20** could be isolated. Compound **20** must originate from addition of *t*-BuOH to an intermediate cyclopropene. The position of the *t*-BuO group in **20** was deduced by comparison of the ¹H-NMR spectrum with spectra of other dihydro-1*H*-cyclopropa[*I*]phenanthrenes [4]. The cyclopropane H-atoms are *trans*-oriented, with ³*J* = 4 Hz, which corresponds again to *cis*-addition to the cyclopropene. The formation of **20** from **19** implies that the presence of two geminal Cl substituents on the cyclopropane ring is required for ring opening to occur in the desired sense under our reaction conditions. In the absence of the carbene stabilizing halogen, addition to the cyclopropene becomes competitive with ring opening even with rather poor nucleophiles such as *t*-BuO.

The dehydrohalogenation of dichlorocarbene adducts of monocyclic and acyclic enol ethers takes a different course and cannot be diverted to furan formation. Monocyclic enol ethers [21] [22] react *via* ring expansion to 2-chlorocycloalkenones, in analogy to adducts of cyclic enamines [16] [23], or, under more vigorous conditions, to aromatic ethers [19]. Similarly, adducts of acyclic enol ethers [24] give preferentially 2-chloroalkenones or the corresponding acetals which may react further to 2-alkynones. Most likely, these reactions do not involve cyclopropenes as intermediates. In cases where the intermediacy of cyclopropenes could be established by trapping with diphenylisobenzofuran, no products could be isolated when the reaction was carried out in the absence of trapping agent.

Conclusion. – From our present understanding of the reaction, it appears that the ring expansion of dichlorocarbenes to furans or cyclopentadienes is restricted to the phenanthrene skeleton. In simple systems, other pathways predominate in such a way that cyclopropene formation does not occur, or else, the cyclopropenes, if formed, decompose instead of undergoing ring opening to vinylcarbenes. Further work will be directed towards isolable cyclopropenes which are expected to open under flash-pyrolysis conditions.

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Experimental Part

General. See [25].

Synthesis of 2-Substituted Phenanthro[9,10-*b*]furans. – 9-Methoxyphenanthrene (**1a**), 1,1-Dichloro-1a,9b-dihydro-1a-methoxy-1H-cyclopropa[1]phenanthrene (**2a**), Phenanthro[9,10-*b*]furan (**6a**). See [4].

9-Ethoxyphenanthrene (**1b**) [10]. Collidine (10 ml) and CuI (0.77 g) was added to 9-bromophenanthrene (2.00 g, 7.78 mmol) in EtONa/EtOH, prepared from 0.80 g of Na in 40 ml of EtOH. The soln. was heated to reflux during 18 h, then allowed to cool to r.t. and poured on ice. After addition of 2N HCl (100 ml), it was extracted with Et₂O and worked up as usual. The crude product was purified by column chromatography (silica gel, petroleum ether/CH₂Cl₂ 5:1) and recrystallized from EtOH to yield 1.63 g (94%) of **1b**. M.p. 104–105° ([10]: 104.5–105.5°). IR (CHCl₃): 3090w, 3070w, 3020m, 2990m, 2940w, 1630s, 1605s, 1580w, 1530m, 1500s, 1480m, 1455s, 1430m, 1410w, 1390s, 1315s, 1285w, 1240s, 1200s, 1165m, 1160m, 1150s, 1120s, 1095s, 1040m, 900m, 865m, 820m, 660m. ¹H-NMR: 1.63 (*t*, ³*J* = 7, 3 H); 4.33 (*q*, ³*J* = 7, 2 H); 7.00 (*s*, 1 H); 7.50–7.60 (*m*, 2 H); 7.62–7.73 (*m*, 2 H); 7.77–7.83 (*m*, 1 H); 8.45–8.50 (*m*, 1 H); 8.60–8.65 (*m*, 1 H); 8.67–8.73 (*m*, 1 H). MS (C₁₆H₁₄O): 222 (100, *M*⁺), 194 (93), 165 (90), 139 (6).

9-(2-Methoxyethoxy)phenanthrene (**1c**). Same procedure as described for **1b**, using NaOCH₂CH₂OCH₃/HOCH₂CH₂OCH₃. The crude product was purified by FC (silica gel; CHCl₃) and recrystallized from EtOH. Yield 88%. M.p. 68–69°. IR (CHCl₃): 3080w, 3070w, 3010m, 2940m, 2890m, 2820w, 1630s, 1600s, 1580w, 1530w, 1500m, 1455s, 1430m, 1390m, 1370m, 1315s, 1280w, 1240s, 1200m, 1165m, 1160m, 1150m, 1120s, 1095s, 1040m, 905m, 865m, 825m. ¹H-NMR: 3.57 (*s*, 3 H); 3.95–4.00 (*m*, 2 H); 4.40–4.45 (*m*, 2 H); 7.00 (*s*, 1 H); 7.48–7.58 (*m*, 2 H); 7.60–7.72 (*m*, 2 H); 7.75–7.80 (*m*, 1 H); 8.43–8.47 (*m*, 1 H); 8.60–8.63 (*m*, 1 H); 8.65–8.70 (*m*, 1 H). MS (C₁₇H₁₆O₂): 252 (50, *M*⁺), 194 (100), 176 (7), 165 (35), 59 (35).

1,1-Dichloro-1a,9b-dihydro-1a-ethoxy-1H-cyclopropa[1]phenanthrene (**2b**). To a soln. of MeONa (0.57 g, 10.56 mmol) and **1b** (1.06 g, 4.77 mmol) in dry pentane (20 ml) was added, at –5°, Cl₃COOEt (1.6 ml, 11.4 mmol). The mixture was stirred for one night at 4°, then 4 h at r.t. After addition of H₂O and usual workup, the crude product was purified by FC (silica gel; petroleum ether/CH₂Cl₂ 2:1) to afford **2b** (0.96 g; 66%). M.p. 119–120°. IR (CHCl₃): 3080w, 3010m, 2990m, 2940w, 2890w, 1490m, 1450s, 1400w, 1375m, 1355w, 1310m, 1285m, 1140s, 1080s, 1060s, 1020w, 950w, 915m, 885m, 830m. ¹H-NMR: 1.28 (*t*, ³*J* = 7, 3 H); 3.35 (*s*, 1 H); 3.54 (*qAB*, ²*J* = 8, ³*J* = 7, 2 H); 7.35–7.53 (*m*, 5 H); 7.87–7.95 (*m*, 1 H); 8.05–8.13 (*m*, 2 H). MS (C₁₇H₁₄Cl₂O): 304/306 (20, *M*⁺), 269/271 (100), 241/243 (81), 212/214 (35), 194 (14), 178 (24), 177 (37), 176 (35), 165 (28), 151 (11), 88 (11), 75 (7).

1,1-Dichloro-1a,9b-dihydro-1a-(2-methoxyethoxy)-1H-cyclopropa[1]phenanthrene (**2c**). To a soln. of **1c** (1.50 g, 5.94 mmol) and MeONa (6.12 g, 113 mmol) in dry Et₂O (70 ml) was added, at –5°, Cl₃COOEt (21.93 g, 0.155 mol). After 2 h at 10°, the mixture was stirred at r.t. overnight, then decomposed with H₂O, and worked up. Compound **2c** (1.20 g, 60%) was obtained after double FC (silica gel, CHCl₃) and recrystallization from MeOH. M.p. 105.5–106.5°. IR (CHCl₃): 3080w, 3010m, 2930m, 2880m, 2820w, 1490m, 1450s, 1360w, 1310m, 1270m, 1230–1200m, 1130m, 1110m, 1080s, 1060m, 1035m, 950m, 910s, 890w, 830m. MS (C₁₈H₁₆Cl₂O₂): 334 (2, *M*⁺), 299/301 (25), 241/243 (21), 212 (11), 176 (9), 59 (100).

2-Methylphenanthro[9,10-*b*]furan (**6b**). To a soln. of *t*-BuOK (0.18 g, 1.6 mmol) and dicyclohexano(18-crown-6) (30 mg) in dry THF (10 ml) was added, at –50° and under N₂, **2b** (0.20 g, 0.66 mmol) in THF (5 ml) within 15 min. After 30 min, the soln. was allowed to warm up slowly to r.t. After addition of H₂O and extraction with CH₂Cl₂ followed by usual workup, the crude product was purified by FC (silica gel; petroleum ether/CH₂Cl₂ 2:1) to give 80 mg (52%) of **6b**. M.p. 124–125° ([26]: 127.5–128°; [27]: 123–124°). IR (CHCl₃): 3070m, 3010m, 2960w, 2930m, 2860w, 1635w, 1615m, 1605w, 1585s, 1520m, 1450s, 1350s, 1330m, 1260m, 1235w, 1180w, 1160m, 1115w, 1100s, 1050w, 1040w, 1030w, 990w, 950m, 940m, 800m. ¹H-NMR: 2.63 (*s*, 3 H); 6.88 (*s*, 1 H); 7.58–7.72 (*m*, 4 H); 8.08–8.13 (*m*, 1 H); 8.32–8.37 (*m*, 1 H); 8.70–8.77 (*m*, 2 H). MS (C₁₇H₁₂O): 232 (100, *M*⁺), 231 (41), 202 (22).

2-(Methoxymethyl)phenanthro[9,10-*b*]furan (**6c**). The procedure used for **6b**, when applied to **2c**, afforded **6c** (66%), after recrystallization from MeOH. M.p. 97–98°. UV (EtOH): 354 (3.16), 338.2–337.5 (3.08), 306.8 (3.14), 294.2 (4.07), 281.8 (4.17), 257.3 (4.83), 250.0 (4.73), 240.4 (4.58), 205.2 (4.28). IR (CHCl₃): 3070w, 3000w, 2940w, 2900m, 2860w, 2830w, 1635w, 1620w, 1520w, 1455m, 1380m, 1360m, 1350w, 1330w, 1260w, 1240w, 1190w, 1160m, 1105s, 1090s, 1045w, 950m, 820m, 795w. ¹H-NMR: 3.52 (*s*, 3 H); 4.72 (*s*, 2 H); 7.22 (*s*, 1 H); 7.60–7.73 (*m*, 4 H); 8.10–8.17 (*m*, 1 H); 8.38–8.42 (*m*, 1 H); 8.72–8.77 (*m*, 2 H). ¹³C-NMR: 58.4 (*q*); 67.2 (*t*); 105.8 (*d*); 120.68 (*s*); 120.73 (*d*); 122.4 (*s*); 123.4 (*d*); 123.6 (*d*); 125.2 (*d*); 125.9 (*d*); 127.0 (*d*); 127.4 (*s*); 128.2 (*s*); 129.1 (*s*); 149.6 (*s*); 153.6 (*s*). MS (C₁₆H₁₄O₂): 262 (50, *M*⁺), 231 (100), 202 (22), 189 (6), 131 (7), 116 (10), 101 (14), 88 (6).

2-Substituted 1H-Cyclopenta[1]phenanthrenes. – 2-Methoxy-1H-cyclopenta[1]phenanthrene (**11**). 2-(9-Phenanthryl)ethanol (**9a**). (9-Phenanthryl)magnesium bromide (**8a**) was prepared by addition of 9-bromophenanthrene (3.71 g, 14.4 mmol) in dry THF (60 ml) to Mg turnings (0.36 g, 14.8 mg · atom) in THF (20 ml). After 3 h at

reflux, the mixture was cooled to -10° , and ethylene oxide (1.15 g, 26 mmol) in THF (30 ml) was added. After stirring at 0° during 30 min, then at 40° during 30 min, the soln. was refluxed for 1 h, then cooled to r.t. and concentrated. Addition of 1N HCl (40 ml) was followed by usual workup. The crude product was recrystallized from CCl_4 and yielded 1.91 g of **9a** (60%). M.p. $87-88^{\circ}$. IR (CHCl_3): 3660m, 3090m, 3020s, 2970m, 2900m, 1630w, 1610w, 1530w, 1500m, 1450m, 1430m, 1390m, 1250m, 1150w, 1120w, 1050s, 950w, 890m, 870w, 840m. $^1\text{H-NMR}$: 1.53 (s, 1 H); 3.42 (t, $^3J = 7$, 2 H); 4.07 (t, $^3J = 7$, 2 H); 7.58–7.72 (m, 5 H); 7.84–7.90 (m, 1 H); 8.11–8.16 (m, 1 H); 8.66–8.72 (m, 1 H); 8.74–8.80 (m, 1 H). MS ($\text{C}_{16}\text{H}_{14}\text{O}$): 222 (29, M^+), 191 (100), 189 (26), 165 (23), 94 (6).

3-(2-Methoxyethyl)phenanthrene (9b). To a soln. of **9a** (1.82 g, 8.19 mmol) in DME (30 ml) under Ar, was added MeI (0.6 ml, 9.64 mmol), followed by NaH (0.25 g, 10.4 mmol) in small portions. After the last addition of NaH, more MeI (0.2 ml, 3.2 mmol) was added. After 2 h of stirring, sat. NaCl (30 ml) was added, and the mixture was worked up. After FC (silica gel, CHCl_3), a yellow oil was obtained which crystallized at 4° . After washing of the crystals with MeOH, 1.63 g (84%) of **9b** was obtained. M.p. $42-43^{\circ}$. IR (CHCl_3): 3080m, 3030m, 3010s, 2930s, 2880s, 2830m, 1630m, 1610m, 1530w, 1500s, 1480m, 1450s, 1430m, 1385m, 1310w, 1245m, 1190m, 1180m, 1145m, 1110s, 1070m, 1040m, 1020w, 1000m, 960m, 950m, 920w, 890s, 860w, 850w, 820m. $^1\text{H-NMR}$: 3.35 (s, 3 H); 3.36 (t, $^3J = 7$, 2 H); 3.76 (t, $^3J = 7$, 2 H); 7.52–7.66 (m, 5 H); 7.78–7.84 (m, 1 H); 8.08–8.14 (m, 1 H); 8.62–8.66 (m, 1 H); 8.70–8.76 (m, 1 H). MS ($\text{C}_{17}\text{H}_{16}\text{O}$): 236 (63, M^+), 203 (10), 191 (100), 176 (7), 165 (38), 101 (8).

1,1-Dichloro-1a,9b-dihydro-1a-(2-methoxyethyl)-1H-cyclopropa[1]phenanthrene (10). To **9b** (1.13 g, 4.78 mmol) and MeONa (5.56 g, 102.9 mmol) in dry petroleum ether (130 ml) was added, at -5° under N_2 , Cl_3COOEt (13.5 ml, 97.5 mmol) dropwise. The mixture was stirred at 4° during 24 h, then at r.t. during 5 h. The precipitate was filtered and washed with petroleum ether. The filtrate was worked up and the crude product filtered through silica gel with CHCl_3 . Compound **10** crystallized after evaporation of the solvent and adjunction of pentane and afforded 0.82 g (54%) of pure product. M.p. $131-132^{\circ}$. IR (CHCl_3): 3110w, 3080w, 3040w, 3010m, 2970w, 2935m, 2880m, 2840w, 2820w, 1490s, 1450s, 1395w, 1385w, 1115s, 1080w, 1050w, 1025w, 1005w, 970w, 950m, 910m, 875w, 860w, 820w, 655w, 635w, 615w. $^1\text{H-NMR}$: $ABMN$ system: 2.09 (H_A), 3.03 (H_B), 3.32 (H_M), 3.43 (H_N) ($^2J_{AB} = 15$, $^2J_{MN} = 10$, $^3J_{AM} = 7$, $^3J_{AN} = 9$, $^3J_{BM} = 9$, $^3J_{BN} = 5$); 3.00 (s, 1 H); 3.16 (s, 3 H); 7.32–7.48 (m, 5 H); 7.60–7.64 (m, 1 H); 7.90–8.06 (m, 2 H). $^{13}\text{C-NMR}$: 35.42 (t); 35.88 (s); 41.04 (d); 58.72 (q); 64.52 (s); 70.62 (t); 122.99 (d); 123.04 (d); 127.86 (d); 127.99 (d); 128.05 (d); 128.19 (d); 128.25 (s); 130.36 (s); 130.72 (s); 130.79 (d); 132.78 (s). MS ($\text{C}_{18}\text{H}_{16}\text{Cl}_2\text{O}$): 318/320 (15, M^+), 259/261 (57), 251/253 (63), 238/240 (70), 225/227 (37), 215 (59), 202 (100), 191 (75), 176 (18), 165 (44), 150 (9), 108 (30), 101 (22), 95 (25), 88 (13), 75 (11), 59 (20), 51 (10).

2-Methoxy-1H-cyclopenta[1]phenanthrene (11). The procedure described for **6b**, applied to **10** (0.36 mmol), gave **11** (35%), which was purified by FC (silica gel; petroleum ether/ CH_2Cl_2 3:1) and recrystallized from cyclohexane. M.p. $154-155^{\circ}$. IR (CHCl_3): 3080w, 3065w, 3030w, 3026m, 3018m, 3010m, 2960m, 2935m, 2856w, 2834w, 1735m, 1637w, 1600s, 1567s, 1535m, 1451m, 1437m, 1430m, 1380m, 1353m, 1340s, 1326m, 1284m, 1253m, 1235m, 1219m, 1205m, 1172m, 1153m, 1037m, 1014s. $^1\text{H-NMR}$: 3.84 (s, 2 H); 3.93 (s, 3 H); 6.25 (s, 1 H); 7.48–7.68 (m, 4 H); 7.82–7.88 (m, 1 H); 8.02–8.08 (m, 1 H); 8.68–8.70 (m, 2 H). $^{13}\text{C-NMR}$: 37.78 (t); 57.47 (q); 96.88 (d); 122.89 (d); 123.27 (d); 123.32 (d); 123.89 (d); 124.30 (d); 125.55 (d); 126.07 (d); 126.67 (d); 127.18 (s); 127.70 (s); 129.41 (s); 130.18 (s); 139.53 (s); 168.29 (s). MS ($\text{C}_{18}\text{H}_{14}\text{O}$; M_{obs} 246.1049; M_{calc} 246.1044): 246 (55, M^+), 231 (39), 203 (100), 202 (82), 189 (5), 176 (5), 149 (4), 123 (6), 101 (36), 88 (11), 75 (11), 69 (8), 57 (10).

2-Phenyl-1H-cyclopenta[1]phenanthrene (15). **2-(9-Phenanthryl)-1-phenylethanol (13a)**. PhCH_2Cl (5.5 ml, 47.7 mmol) in dry THF (10 ml) was added dropwise to Mg turnings (1.17 g, 48 mg-atom) in THF (8 ml) at r.t. After 3 h at reflux, the mixture was cooled to 5° and 9-phenanthrenecarbaldehyde (**12**, 4.85 g, 23.5 mmol) was added in THF (10 ml). After 10 h of stirring at r.t., the soln. was treated with dil. HCl and worked up. Recrystallization with cyclohexane gave 3.26 g (46%) of **13a**. M.p. $121.5-122.5^{\circ}$. IR (CHCl_3): 3600m, 3060m, 3010s, 2930w, 1610m, 1500s, 1450m, 1080s, 700s. $^1\text{H-NMR}$: 2.18 (s, 1 H); 3.12 (dAB, $^2J = 14$, 1 H); 3.38–3.46 (dAB, $^2J = 14$, $^3J = 3.5$, 1 H); 5.73 (dAB, $^3J = 9$, $^3J = 3.5$, 1 H); 7.37 (m, 5 H); 7.60–7.76 (m, 4 H); 7.90–7.96 (m, 1 H); 8.00 (s, 1 H); 8.24–8.30 (m, 1 H); 8.69–8.74 (m, 1 H); 8.78–8.86 (m, 1 H). MS ($\text{C}_{22}\text{H}_{18}\text{O}$): 298 (6, M^+), 280 (33), 207 (100), 179 (62), 151 (6), 91 (10).

9-(1-Chloro-2-phenylethyl)phenanthrene (13b). To **13a** (0.66 g, 2.21 mmol) in dry CHCl_3 (20 ml) was added SOCl_2 (7.34 g, 62 mmol) in CHCl_3 (40 ml) during 30 min. After stirring at r.t. overnight, followed by refluxing during 5 h, part of the CHCl_3 and SOCl_2 were distilled off. The mixture was then decomposed with ice and sat. Na_2CO_3 , and worked up. The crude product was recrystallized from benzene, and the crystals were washed with pentane to yield 0.65 g (93%) of **13b**. M.p. $143.5-144.5^{\circ}$. IR (CHCl_3): 3070m, 3030m, 3010m, 1605w, 1530w, 1500m, 1455m, 1435w, 1270w, 1250m, 890m, 700s, 615m. $^1\text{H-NMR}$: 3.62–3.80 (m, 2 H); 5.88–5.96 (m, 1 H); 7.26–7.38 (m, 5 H); 7.62–7.76 (m, 4 H); 7.92–7.96 (m, 1 H); 7.98–8.08 (s, 1 H); 8.24–8.34 (s, 1 H); 8.68–8.74 (m, 1 H); 8.78–8.84 (m, 1 H). MS ($\text{C}_{22}\text{H}_{17}\text{Cl}$): 316/318 (12, M^+), 280 (9), 225 (100), 203 (27), 189 (29), 176 (6), 165 (10), 138 (5), 126 (7), 91 (15).

9-(2-Phenylethyl)phenanthrene (13c). To NaBH₄ (2.5 g, 66.1 mmol) in dry DMSO (40 ml) was added, at 50°, **13b** (1.39 g; 4.92 mmol) in DMSO (30 ml). The soln. was heated to 80° overnight, then treated with H₂O, and worked up. After chromatography (silica gel; petroleum ether/CHCl₃ 2:1), 0.99 g (71 %) of **13c** was obtained. M.p. 80–81°. ¹H-NMR: 3.14–3.22 (m, 2 H); 3.44–3.50 (m, 2 H); 7.26–7.42 (m, 5 H); 7.58–7.76 (m, 5 H); 7.82–7.88 (m, 1 H); 8.20–8.26 (m, 1 H); 8.70–8.74 (m, 1 H); 8.78–8.84 (m, 1 H). MS (C₂₂H₁₈): 282 (24, M⁺), 191 (100), 165 (14), 83 (8), 69 (13), 57 (22). Calc. C 93.58, H 6.42; found: C 93.47, H 6.56.

1,1-Dichloro-1a,9b-dihydro-1a-(2-phenylethyl)-1H-cyclopropa[1]phenanthrene (14). The dichlorocarbene addition was carried out as described for **2b** starting with 0.285 g (1 mmol) of **13c**. The product was purified by FC (silica gel; toluene/hexane 1:1) and crystallized from pentane: 0.258 g (71 %) of **14**. M.p. 113–114°. IR (CHCl₃): 3112w, 3070w, 3030m, 3010m, 2960m, 2930m, 2870w, 1604m, 1493s, 1433s, 1138w, 1110m, 1084w, 1005w, 948m, 911m, 832w, 813w, 775m, 756m, 730m, 721m. ¹H-NMR: ABMN system: 2.02 (H_A), 2.53 (H_B), 2.73 (H_M), 3.13 (H_N) (²J_{AB} = 7.5, ²J_{MN} = 4.5, ³J_{AM} = 10, ³J_{AN} = 14, ³J_{Bm} = 14, ³J_{BN} = 9.5); 2.65 (s, 1 H); 6.69–7.02 (m, 2 H); 7.08–7.16 (m, 3 H); 7.26–7.34 (m, 3 H); 7.36–7.46 (m, 3 H); 7.64–7.70 (m, 1 H); 7.98–8.04 (m, 1 H); 8.04–8.10 (m, 1 H). ¹³C-NMR: 33.18 (t); 37.48 (s); 37.82 (t); 41.36 (d); 64.82 (s); 122.91 (d); 123.07 (d); 125.96 (d); 127.81 (d); 127.82 (d); 128.07 (d); 128.27 (d); 128.30 (d); 128.32 (d); 128.39 (s); 130.60 (s); 130.70 (d); 130.74 (s); 133.12 (s); 140.84 (s). MS (C₂₃H₁₈Cl₂): 364, 366 (6, M⁺), 329/331 (24), 259 (50), 202 (67), 189 (44), 176 (10), 165 (21), 105 (32), 91 (100), 77 (9), 65 (22).

2-Phenyl-1H-cyclopenta[1]phenanthrene (15). To a soln. of *t*-BuOK (0.1609 g, 1.43 mmol) and dicyclohexano-(18-crown-6) (50 mg) in dry THF (15 ml) was added dropwise, at –50° and under N₂, **14** (0.1529 g, 0.42 mmol) in THF (10 ml) during 20 min. After 10 min at –50°, the soln. was allowed to reach r.t. slowly. After addition of H₂O, the mixture was worked up by extraction with CHCl₃. The crude product was purified by FC (silica gel; hexane/CHCl₃ 3:1) to give a mixture of **15** (45%) and **14** (55%). Pure **15** (36%) was obtained after recrystallization with CCl₄. M.p. 175–176°. UV (EtOH): 356.3 (4.35), 293.9 (4.28), 281.9 (4.48), 251.9 (4.61), 209.2 (4.5). IR (CHCl₃): 3080w, 3025w, 3016w, 3010w, 2960w, 2932w, 2856w, 1600w, 1503w, 1491w, 1454w, 1436w, 1388w, 1224w, 1206w, 915w, 854w, 793m, 788s, 775s, 758s, 752s, 745s, 739s, 733m. ¹H-NMR: 4.28 (ds, ⁴J = 1, 2 H); 7.30–7.36 (m, 1 H); 7.44–7.50 (m, 2 H); 7.58–7.74 (m, 4 H); 7.78–7.88 (m, 3 H); 8.03–8.10 (m, 1 H); 8.24–8.30 (m, 1 H); 8.72–8.82 (m, 2 H). MS (C₂₃H₁₆; M_{calc} 292.1252, M_{obs} 292.1236): 292 (100, M⁺), 215 (27), 145 (21), 132 (16), 77 (10), 51 (13).

9-(Diethylamino)phenanthrene (8b). To a soln. of PhLi (32 mmol) in dry benzene (16 ml) and Et₂O (16 ml) was added Et₂NH (4.2 ml, 40 mmol). After 60 min of stirring at r.t., 9-bromophenanthrene (6.00 g, 23.3 mmol) in Et₂O was added. Stirring was continued during 19 h, then H₂O was added. After usual workup, the crude product was purified by FC (basic aluminum oxide, petroleum ether) and furnished 2.78 g (48%) of **8b**. M.p. 71–72°. IR (CHCl₃): 3080w, 3060w, 3010m, 2980s, 2930m, 2870m, 2820m, 1620m, 1600s, 1525w, 1495s, 1450s, 1425m, 1370s, 1330m, 1315m, 1300m, 1280w, 1260w, 1230–1200s, 1170m, 1070s, 1040m, 995w, 875m, 845m. ¹H-NMR: 1.09 (t, ³J = 7, 6 H); 3.30 (q, ³J = 7, 4 H); 7.33 (s, 1 H); 7.53–7.69 (m, 4 H); 7.77–7.83 (m, 1 H); 8.41–8.45 (m, 1 H); 8.61–8.67 (m, 1 H); 8.69–8.75 (m, 1 H). MS (C₁₈H₁₉N): 249 (37, M⁺), 234 (100), 220 (6), 204 (51), 191 (6), 178 (37), 165 (15), 151 (13), 125 (11), 109 (11), 102 (15), 88 (18), 56 (39).

Addition of Dichlorocarbene to 8b: 6-Chloro-5H-dibenzo[a,c]cyclohepten-5-one (17). To **8b** (0.172 g, 0.69 mmol) in dry petroleum ether (10 ml), cooled with ice/NaCl, was added MeONa (0.74 g, 13.7 mmol) followed by Cl₃COOEt (1.9 ml, 13.7 mmol). After stirring overnight at 4°, the precipitate was filtered and extracted with petroleum ether. The filtrate and the extract were combined and worked up. After filtration through a silica-gel column (petroleum ether/CH₂Cl₂ 4:1) and prep. TLC (same solvent), **17** was isolated (13.6 mg, 8%). IR (CHCl₃): 3081w, 3046m, 3023m, 2953w, 2907w, 2837w, 1666s, 1655s, 1619m, 1607m, 1571w, 1559w, 1448m, 1440m, 1381m, 1321w, 1298m, 1238m, 1119m, 1059m, 874m, 855m, 836s. ¹H-NMR: 7.52–7.66 (m, 4 H); 7.70–7.80 (m, 2 H); 7.88–8.00 (m, 3 H). MS (C₁₅H₉ClO): 240, 242 (35, M⁺), 212 (95), 176 (100), 151 (30), 126 (7), 106 (19), 88 (80), 75 (39), 63 (18).

1'-endo'-Chloro-1a,9b-dihydro-1a-(methylthio)cyclopropa[1]phenanthrene (19). To a soln. of *t*-BuOK (0.301 g, 2.68 mmol) in dry DMSO (5.5 ml) under Ar was added MeSH (0.114 g, 2.37 mmol) in DMSO (4.5 ml) and, subsequently, 1,1-dichloro-1a,9b-dihydro-1H-cyclopropane[1]phenanthrene (**16a**) [20] (0.700 g, 2.68 mmol) in DMSO (25 ml) within 45 min. After stirring overnight at 4°, H₂O was added, and the soln. was extracted with CHCl₃. The crude product obtained after usual workup was purified by column chromatography (150 g of silica gel; toluene/petroleum ether 1:1) followed by recrystallization with hexane to yield 0.442 g (68% with respect to MeSH) of **19**. M.p. 103.5–104.5°. ¹H-NMR: 2.01 (s, 3 H); 3.10 (d, ³J = 7, 1 H); 4.00 (d, ³J = 7, 1 H); 7.30–7.46 (m, 5 H); 8.04–8.10 (m, 2 H); 8.18–8.24 (m, 1 H). ¹³C-NMR: 14.52 (q); 19.76 (s); 35.14 (d); 36.23 (d); 122.38 (d); 122.51 (d); 127.65 (d); 127.60 (d); 127.77 (d); 128.04 (d); 129.07 (s); 129.74 (s); 129.92 (d); 130.07 (d); 131.29 (s); 132.85 (s). MS (C₁₆H₁₃SCl): 272, 274 (3, M⁺), 237 (100), 225 (43), 221 (21), 189 (42), 178 (21), 165 (28), 111 (11), 88 (6).

Dehydrohalogenation of 19: 1'-exo'-(tert-butoxy)-1a,9b-dihydro-1a-(methythio)cyclopropa[1]phenanthrene (20). To *t*-BuOK (39 mg, 0.35 mmol) and dicyclohexano(18-crown-6) (20 mg) in dry THF (5 ml) was added, at -50° , **19** (94 mg, 0.34 mmol) in THF (5 ml). After 30 min stirring, the temp. was allowed to reach r.t. The solvent was evaporated, the residue decomposed with H_2O and worked up. Column chromatography (silica gel, benzene) afforded 10.2 mg (10%) of **20** and 56.2 mg (60%) of unreacted **19**.

Data of 20: IR (CHCl₃): 3070w, 2977s, 2933s, 2870m, 2843m, 1600w, 1480m, 1440s, 1395m, 1364s, 1262s, 1240m, 1177m, 1137s, 1128s, 1098s, 1049m, 1018s, 942w, 893m, 867m, 858m, 813m. ¹H-NMR: 1.20 (s, 1 H); 2.01 (s, 3 H); 2.77 (d, ³J = 4, 1 H); 2.97 (d, ³J = 4, 1 H); 7.26–7.44 (m, 5 H); 7.90–7.94 (m, 1 H); 7.94–8.00 (m, 1 H); 8.10–8.14 (m, 1 H). MS (C₂₀H₂₂OS): 310 (absent, M⁺), 263 (10), 225 (46), 207 (100), 178 (100), 57 (41).

REFERENCES

- [1] W. M. Jones, U. H. Brinker, in 'Pericyclic Reactions', Eds. A. P. Marchand and R. E. Lehr, Academic Press, New York, 1977, Vol. 1, p. 110–198.
- [2] W. Weber, A. de Meijere, *Chem. Ber.* **1985**, *118*, 2450.
- [3] D. L. Boger, C. E. Brotherton, *J. Am. Chem. Soc.* **1986**, *108*, 6695.
- [4] P. Müller, H. C. Godoy-Nguyen Thi, J. Pfyffer, *Helv. Chim. Acta* **1986**, *69*, 855.
- [5] R. G. R. Bacon, S. C. Rennison, *Chem. Ind.* **1966**, 812; W. E. Parham, D. A. Bolon, E. E. Schweizer, *J. Am. Chem. Soc.* **1961**, *83*, 603.
- [6] P. Müller, J. Pfyffer, *Chimia* **1984**, *38*, 79.
- [7] W. E. Billups, L. P. Lin, W. Y. Chow, *J. Am. Chem. Soc.* **1974**, *96*, 4026.
- [8] W. E. Billups, L. E. Reed, E. W. Casserly, P. Lin, *J. Org. Chem.* **1981**, *46*, 1326.
- [9] B. Halton, D. L. Officer, *Austr. J. Chem.* **1983**, *36*, 1167; B. Halton, D. L. Officer, *Tetrahedron Lett.* **1981**, *22*, 3687.
- [10] R. G. R. Bacon, S. C. Rennison, *J. Chem. Soc. (C)* **1969**, 312.
- [11] C. A. Dornfeld, G. H. Coleman, *Org. Synth. Coll. Vol.* **1955**, *3*, p. 701.
- [12] U. E. Diner, F. Sweet, R. K. Brown, *Can. J. Chem.* **1966**, *44*, 1591.
- [13] H. Dürr, A. Hackenberger, *Synthesis* **1978**, 594.
- [14] J. D. Roberts, D. A. Semenow, H. E. Simmons, Jr., L. A. Carlsmith, *J. Am. Chem. Soc.* **1956**, *78*, 601.
- [15] T. Kauffmann, H. Fischer, R. Nürnberg, R. Wirthwein, *Liebigs Ann. Chem.* **1970**, *731*, 23.
- [16] M. Ohno, *Tetrahedron Lett.* **1963**, 1753; T. C. Shields, W. E. Billups, A. N. Kurtz, *Angew. Chem. Int. Ed.* **1968**, *7*, 209.
- [17] B. R. Dent, B. Halton, *Austr. J. Chem.* **1986**, *39*, 1789.
- [18] F. G. Bordwell, P. J. Boutan, *J. Am. Chem. Soc.* **1957**, *79*, 717.
- [19] P. Müller, N. Pautex, *Tetrahedron Lett.*, accepted for publication.
- [20] G. C. Joshi, N. Singh, L. M. Pande, *Synthesis* **1972**, 317.
- [21] A. Johannissian, E. Akunian, *Chem. Abstr.* **1931**, *25*, 921, 922; W. Parham, W. Soeder, J. R. Throckmorton, K. Kuncel, R. M. Dodson, *J. Am. Chem. Soc.* **1965**, *87*, 321.
- [22] R. A. Wohl, *Synthesis* **1974**, 38.
- [23] J. Wolinsky, D. Chan, R. Novak, *Chem. Ind.* **1965**, 720; T. C. Shields, W. E. Billups, A. N. Kurtz, *Angew. Chem. Int. Ed.* **1968**, *7*, 209; U. K. Pandit, S. A. G. De Graaf, *J. Chem. Soc., Chem. Commun.* **1970**, 381.
- [24] A. Ledwith, H. J. Woods, *J. Chem. Soc. (B)* **1967**, 973; L. Skattebol, *J. Org. Chem.* **1966**, *31*, 1554.
- [25] P. Müller, M. Rey, *Helv. Chim. Acta* **1982**, *65*, 1157.
- [26] D. T. Anderson, W. M. Horspool, *J. Chem. Soc., Perkin Trans. I* **1972**, 536.
- [27] F. R. Japp, F. Klingemann, *Chem. Ber.* **1888**, *21*, 2932.