90. Approaches to 1*H*-Cyclopropa[*l*]phenanthrenes. Eliminations with 1a,9b-Dihydro-1*H*-cyclopropa[*l*]phenanthrene Derivatives

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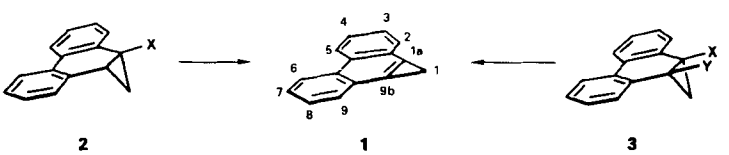
Base-induced elimination of the sulfonium salt **2i** in the presence of furan affords the addition products **7** and **8**, derived from 1*H*-cyclopropa[*l*]phenanthrene (**1**) and the isomeric cyclopropene **5a** *(Scheme 3)*. Upon oxidation, the selenide **2c** yields phenanthrene-9-methanol (**9**), presumably *via* **1**. No evidence for the intermediate **1** is obtained from sulfoxide pyrolysis with **2e**, which leads to products formed by radical pathways *(Scheme 5)*. Reductive elimination of the disulfone **3b** gives half-reduction to monosulfone **2g** and complete reduction to cyclopropane **2** as well as 9-methylphenanthrene (**15**), but no evidence for the intermediate **1**.

Introduction. – While a considerable number of cycloproparenes and derivatives thereof have been described over the past 20 years [1], 1*H*-cyclopropa[*l*]phenanthrene (**1**) remained elusive until very recently [2]. The successful synthesis of **1** due to a collaborative effort of the groups of *Vogel* and *Halton* prompts us to report our own research in this field.

Three unsuccessful approaches for **1** or dihalogenated derivatives of **1** have been reported in the literature [1–5], and the principal reason for the difficulties to isolate or trap them appears to be the inherent low kinetic stability of cycloproparenes. Our method is similar to one of these approaches [2] [3] and involves aromatization of a 1a-substituted and 1a,9b-disubstituted 1*H*-dihydrocyclopropa[*l*]phenanthrene **2** and **3**, respectively.

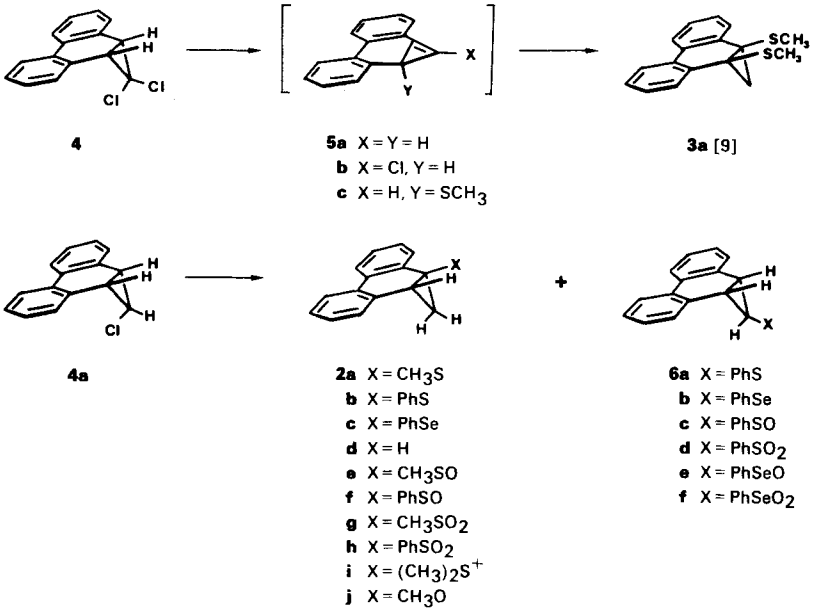
Scheme 1



2 **1** **3**

Substituted 1a,9b-Dihydro-1*H*-cyclopropa[*l*]phenanthrenes. – Compounds of structure **2** are in principle available *via* carbene addition to 9-substituted phenanthrenes [3] [6]. This approach was attempted, but abandoned when it was found impossible to effect dichlorocarbene addition to 9-bromophenanthrene under a variety of conditions. Similarly, the cyclopropan-forming procedure using diazomethane/CuBr which works for phenanthrene [7] afforded no addition product with the 9-bromo derivative. Alternatively, base-induced elimination of 1-halogenated dihydrocyclopropa[*l*]phenanthrenes in the presence of nucleophiles was investigated. Reaction of the dichlorocarbene adduct **4** [8] of phenanthrene with base in the presence of methanethiolate is known to afford the

Scheme 2



1a,9b-bis(methylthio) derivative **3a** *(Scheme 2)*, presumably *via* trapping of intermediary cyclopropenes [9]. The regioselectivity of this interception is surprising, since for reasons of stability of the intermediary carbanion, the opposite result would be expected [9].

Our results of the reaction of **4** with base in the presence of methanethiolate confirm those reported [9]; however, when methanethiolate was replaced by benzenethiolate, an untractable mixture was obtained, presumably owing to formation of several isomeric bis(phenylthio) derivatives. The latter hypothesis was confirmed by the behaviour of the half-reduction product of **4** [10], the 1-*'endo'*-chlorodihydrocyclopropa[*l*]phenanthrene **4a**. Although **4a** has the reputation of being unreactive towards base [9] [10], conditions were found (10 equiv. of *t*-BuOK in THF/DMSO 1:1, catalytic amount of [18]crown-6) so that elimination occurred within 3 days at r.t. Interception of the intermediate cyclopropene with methanethiolate produced the 1a-substituted sulfide **2a** in quantitative yield. With benzenethiolate, attack occurred preferentially at C(1a) (76%; →**2b**) and to the extent of 24% at C(1) (→**6a**), but benzeneselenolate produced reversed regioselectivity yielding 1- and 1a-substitution in 38 and 13% yields (→**6b** and **2c**), respectively.

The sulfides **2a**, **2b**, and **6a** were converted to the sulfoxides **2e**, **2f**, and **6c**, respectively, and to the sulfones **2g**, **2h**, and **6d**, respectively, using conventional methods, while formation of the sulfonium salt **2i** from **2a** failed with MeI. However, **2i** could be obtained upon treatment of **2a** with $Me_3O \cdot BF_4$ (2.5 h, r.t.). Treatment of the selenide **6b** with H_2O_2 afforded two products (M^+'s absent in MS). To one of them the structure of the selenoxide **6e** was tentatively assigned on the grounds of the similarity of the ^{1}H-NMR coupling pattern with that of the corresponding sulfoxide **6c**. (PhSO- and PhSeO- are both chiral substituents, hence H–C(1a) and H–C(9b) are diastereotopic and form an *ABX* system with H–C(1).) The other oxidation product is probably the selenone **6f**

(ν = 940 and 880 cm^{-1}; similar ^{1}H-NMR coupling pattern of the cyclopropane H-atoms for **6f** and sulfone **6d**). When treated with pyridine in the presence of benzeneselenol both **6e** and **6f** afforded the 1-*'exo'*-substituted phenylselenide **6b** *via* elimination to the cyclopropene **5a** and subsequent addition of benzeneselenol.

The structures of the addition products **2** and **6** and of their derivatives were assigned on the grounds of the ^{1}H-NMR spectra. The data for the cyclopropane H-atoms are collected in *Table 1*. Comparison of the vicinal coupling constants of the addition products **6a** and **6b** with the reported data for **2d** [7] and **4a** [10] shows that the substituents occupy the *'exo'*-position, which corresponds to *cis*-addition. The ^{1}H-NMR resonances of the aromatic moieties of the 1*H*-dihydrocyclopropa[*l*]phenanthrenes are collected in *Table 2* and the ^{13}C-NMR resonances of some representatives in *Table 3*.

Table 1. *NMR Data of the Cyclopropane Moiety of 1*H*-Dihydrocyclopropa[1]phenanthrenes*

	Substituent at				δ[ppm]				J[Hz]						Conditions
	C(1),) *'endo'*	C(1), *'exo'*	C(1a)	C(9b)	H_A	H_B	H_C	H_D	J_{AB}	J_{AC}	J_{AD}	J_{BC}	J_{BD}	J_{CD}	
2a	H_A	H_B	CH_3S	H_D	0.35	1.95	–	2.78	4.25	–	5.75	–	9.5	–	100 MHz
2b	H_A	H_B	PhS	H_D	0.54	2.11	–	2.97	4.50	–	6.0	–	9.25	–	100 MHz
2c	H_A	H_B	PhSe	H_D	0.59	2.14	–	3.08	4.75	–	5.75	–	9.75	–	100 MHz
2d	H_A	H_B	H_C	H_D	–0.05	1.45	2.38	(2.38)	–3.8	4.8	(4.8)	8.8	(8.8)	–	60 MHz [7]
2e	H_A	H_B	CH_3SO	H_D	0.55	2.05	–	3.16	4.50	–	6.0	–	10.25	–	100 MHz
2f	H_A	H_B	PhSO	H_D	0.56	2.18	–	3.08	4.5	–	6.0	–	10.5	–	100 MHz
2g	H_A	H_B	CH_3SO_2	H_D	0.64	2.44	–	3.25	4.0	–	6.0	–	10.0	–	100 MHz
2h	H_A	H_B	$PhSO_2$	H_D	0.78	2.65	–	3.54	4.75	–	6.75	–	10.5	–	100 MHz
2i	H_A	H_B	$(CH_3)_2S^+$	H_D	0.87	2.36	–	3.52	7.0	–	7.0	–	11.0	–	360 MHz
2j	H_A	H_B	CH_3O	H_D	0.4	1.86	–	2.75	4.5	–	5.5	–	10.5	–	360 MHz
3a	H_A	H_B	CH_3S	CH_3S	0.78	1.85	–	–	5.50	–	–	–	–	–	360 MHz
3b	H_A	H_B	CH_3SO_2	CH_3SO_2	1.68	3.44	–	–	6.50	–	–	–	–	–	360 MHz
4	Cl	Cl	H_C	H_D	–	–	3.30	(3.30)	–	–	–	–	–	–	60 MHz [4]
4a	Cl	H_B	H_C	H_D	–	3.77	2.98	(2.98)	–	–	–	8.0	(8.0)	–	360 MHz [10]
4b	Cl	Cl	CH_3O	H_D	–	–	–	3.37	–	–	–	–	–	–	360 MHz
6a	H_A	PhS	H_C	H_D	1.76	–	2.90	(2.90)	–	4.0	(4.0)	–	–	–	100 MHz
6b	H_A	PhSe	H_C	H_D	1.90	–	2.94	(2.94)	–	3.25	(3.25)	–	–	–	100 MHz
6c	H_A	PhSO	H_C	H_D	1.60	–	3.29	3.22	–	4.0	(4.0)	–	–	9.0	360 MHz
6d	H_A	$PhSO_2$	H_C	H_D	1.83	–	3.47	(3.47)	–	4.0	(4.0)	–	–	–	60 MHz
6e	H_A	PhSeO	H_C	H_D	1.74	–	3.26	3.03	–	4.0	(4.0)	–	–	9.0	360 MHz
6f	H_A	$PhSeO_2$	H_C	H_D	2.40	–	3.65	(3.65)	–	4.0	(4.0)	–	–	–	360 MHz

Table 2. *^{1}H-NMR Data for Aromatic Protons of 1*H*-Dihydrocyclopropa[1]phenanthrenes*[a])

	Substituent at				H–C(2)	H–C(3), H–C(4), H–C(7), H–C(8)	H–C(9)	H–C(5), H–C(6)	Substituent (Ph or CH_3)	Conditions
	C(1), *'endo'*	C(1), *'exo'*	C(1a)	C(9b)						
2a	H	H	CH_3S	H	7.24–7.51		8.22–8.32	7.95–8.08	2.07	100 MHz
2b	H	H	PhS	H	7.24–7.55		8.20–8.32	8.0–8.16	7.13	100 MHz
2c	H	H	PhSe	H	7.25–7.53		8.21–8.30	8.0–8.11	7.12–7.53	100 MHz
2d	H	H	H	H	7.43–7.47/7.30–7.33		7.43–7.47	7.98–8.01		360 MHz
2e	H	H	CH_3SO	H		7.26–7.69		7.93–8.18	2.41	100 MHz

Table 2 (continued)

	Substituent at				H–C(2)	H–C(3), H–C(4), H–C(7), H–C(8)	H–C(9)	H–C(5), H–C(6)	Substituent (Ph or CH_3)	Conditions
	C(1), *'endo'*	C(1), *'exo'*	C(1a)	C(9b)						
2f	H	H	PhSO	H	7.33–7.48		7.80–8.04	7.80–8.04	7.26–7.48	100 MHz
2g	H	H	CH_3SO_2	H	7.28–7.53		8.50–8.60	7.95–8.15	2.84	100 MHz
2h	H	H	$PhSO_2$	H	7.24–7.40		8.56–8.66	7.80–7.96	7.24–7.96	100 MHz
2i	H	H	$(CH_3)_2S^+$	H	7.63–7.68/7.30–7.47		8.05–8.10	7.85–7.98	2.83, 2.98	360 MHz
2j	H	H	CH_3O	H	7.24–7.54		7.80–7.90	8.0–8.14	3.28	100 MHz
3a	H	H	CH_3S	CH_3S	8.37–8.42/7.32–7.42		8.37–8.42	8.05–8.10	2.15	360 MHz
3b	H	H	CH_3SO_2	CH_3SO_2	8.25–8.30/7.33–7.48		8.25–8.30	7.93–8.0	3.37	360 MHz
4	Cl	Cl	H	H			7.23–7.67	7.92–8.23		60 MHz
4a	Cl	H	H	H			7.32–7.47	8.05–8.10		360 MHz
4b	Cl	Cl	CH_3O	H	7.35–7.54		7.83–7.87	8.08–8.14	3.34	360 MHz
6a	H	PhS	H	H	7.20–7.40			8.0–8.10	7.20–7.56	100 MHz
6b	H	PhSe	H	H	7.20–7.56			7.94–8.10	7.20–7.56	100 MHz
6c	H	PhSO	H	H	7.15–7.72			7.93–8.0	7.15–7.72	360 MHz
6d	H	$PhSO_2$	H	H	7.23–7.40			7.95–8.0	7.57–7.70 7.95–8.0	360 MHz
6e	H	PhSeO	H	H	7.30–7.74			7.92–8.0	6.90–7.74	360 MHz
6f	H	$PhSeO_2$	H	H	7.28–7.47			7.98–8.06	7.65–7.73 7.98–8.06	360 MHz

[a]) All signals are *m*'s, except CH_3 substituent.

Table 3. *^{13}C-NMR Spectra of Selected 1*H*-Dihydrocyclopropa[l]phenanthrenes*[a])

	2e (X = CH_3SO)	**2j** (X = CH_3O)	**3b** (X = Y = CH_3SO_2)	**4**	**4a**	**4b**	**6a** (X = PhS)	**6d** (X = $PhSO_2$)
C(1)	14.34	26.63	20.32	58.95	28.86	68.53	30.56	42.67
C(1a)	41.86	63.01	56.18	36.57	24.88	63.26	26.54	26.65
C(1b)	130.69	130.36	127.73	127.96	129.39	128.13	133.31	130.40
C(2)	129.92	129.16	131.04	131.02	130.46	130.69	129.64	129.63
C(3)	128.45	128.17	129.35	128.27	127.74	128.77	128.13	128.33
C(4)	128.28	127.21	127.57	128.12	127.28	128.13	127.07	127.71
C(5)	124.10	123.68	124.00	123.07	122.67	123.09	123.38	123.41
C(5a)	133.45	136.78	130.99	131.30	132.02	132.87	138.36	140.54
C(5b)	130.89	134.64	130.99	131.30	132.02	130.56	138.36	140.54
C(6)	123.39	123.53	124.00	123.07	122.67	122.75	123.38	123.41
C(7)	127.11	126.51	127.57	128.12	127.28	127.10	127.07	127.71
C(8)	127.16	126.51(?)	129.35	128.27	127.74	128.03	128.13	128.33
C(9)	127.72	128.11	131.04	131.02	130.46	128.22	129.64	129.63
C(9a)	128.84	129.34	127.73	127.96	129.39	127.87	133.31	130.40
C(9b)	36.74	20.64	56.18	36.57	24.88	40.86	26.54	26.65
CH_3X'	16.87	55.75	41.83	–	–	56.07	–	–
C(1′) of PhS							?	?
C(2′)/C(6′) of PhS							126.75	127.40
C(3′)/C(5′) of PhS							128.64	129.39
C(4′) of PhS							125.21	133.57
MHz	50	90.56	50	50	50	90.56	50	50

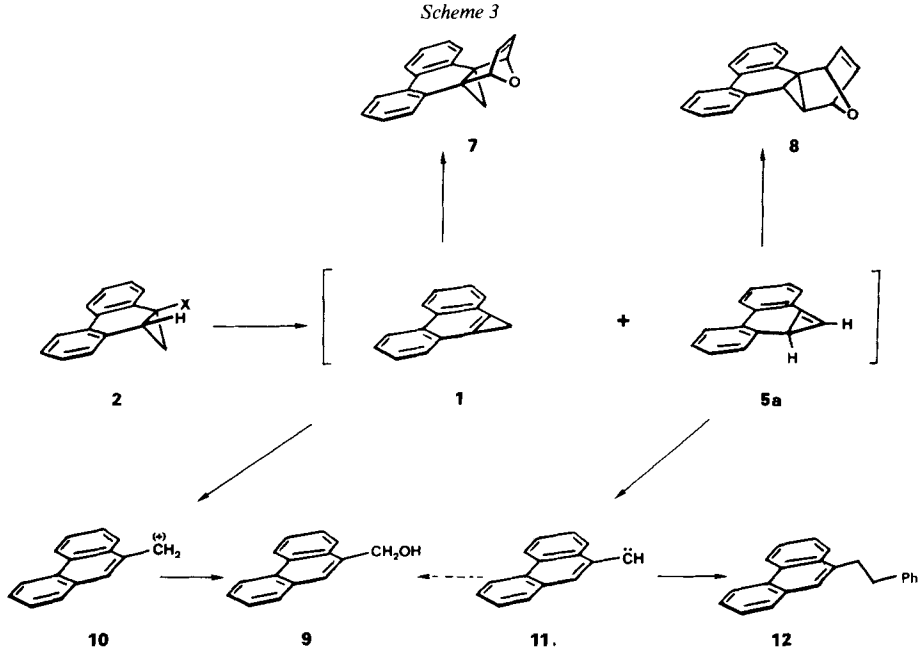
[a]) Tentative assignments, based on [25] [26].

Eliminations. – Base-induced, pyrolytic, or reductive eliminations of HX from the substituted dihydrocyclopropa[*l*]phenanthrenes **2** and **3** produced invariably complex product mixtures from which, after elaborate purification procedures, only the main components could be isolated and identified.

The only reaction giving conclusive evidence for formation of **1** is that of the dimethylsulfonium salt **2i** which, upon treatment with *t*-BuOK at −78° in the presence of furan, afforded a mixture containing the addition products **7** and **8** in a 2:1 ratio (30%) and the sulfide **2a** (37%; *Scheme 3*). In addition, trace amounts of **2d** and 9-methylphenanthrene (see below, **15**) were also formed. Elimination of HX from **2i** with 6 equiv. of $Li(i\text{-}Pr)_2N$ yielded only **2a** (26%) and **2d** (3%), but no addition products to furan were observed.

The other eliminination products could originate either from **1** or **5a**. Thus, oxidation of the phenylselenide **2c** with *m*-chloroperbenzoic acid led to a 50% yield of phenanthrene-9-methanol (**9**), the structure of which was confirmed by independent synthesis (reduction of the commercially available aldehyde [12]). The formation of **9** is best rationalized by an elimination in the intermediate selenoxide to give **1** and subsequent acid-catalyzed ring opening to the carbenium ion **10**, followed by trapping. This sequence has been demonstrated for the selenoxide elimination leading to 1,1-dichloro-1*H*-cyclopropa[*l*]phenanthrene (1,1-Cl_2-**1**) [3]. However, in our case, an alternative pathway is possible involving formation of the cyclopropene **5a** followed by rearrangement to the carbene **11**. The alcohol could be formed *via* reaction of **11** with *m*-chlorobenzoic acid to give an ester and hydrolysis of the latter during workup. This second possibility seems, however, less likely. Although the chlorocyclopropene **5b** undergoes the cyclopropene/vinylcarbene rearrangement already at 0° [9], this reaction has not been reported for the unsubstituted cyclopropene **5a** [11]. Since the (calculated) heats of formation of **5a** and **11**

Scheme 3

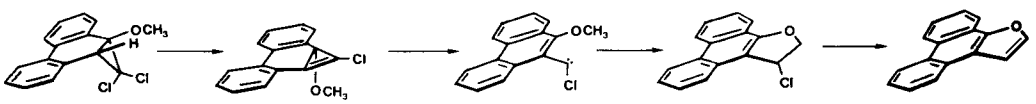


are relatively close [13], interconversion should be possible but might require higher temperature. Indeed, in the flash pyrolysis of the sulfoxide **2e**, in the presence of toluene, we found a product **12** which could be derived from carbene insertion of **11** into the CH(α) bond of toluene. However, **12** could as well be formed *via* a radical pathway (see below).

The methoxy derivative **2j** (obtained from **4b**, see *Exper. Part*), could not be forced to eliminate MeOH, even under violent reaction conditions, *i.e.* 10 equiv. of *t*-BuOK in the presence of [18]crown-6 in refluxing THF or Li(i-Pr)$_2$N in refluxing THF in the presence of furan.

Treatment of the sulfone **2h** with Li(i-Pr)$_2$N or lithium tetramethylpiperidide afforded none of the desired **1** or derivatives thereof, but rather the isomeric sulfone **6d**, which must have been formed by addition of phenylsulfinic acid to **5a**.

Scheme 4

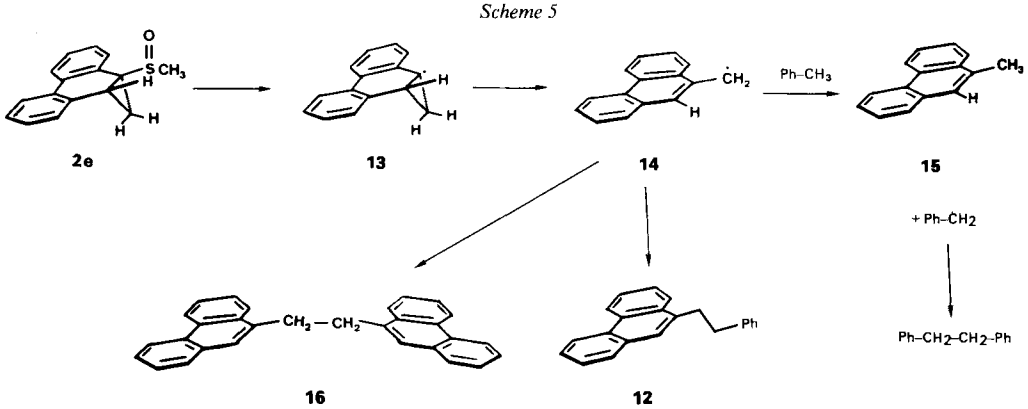


4b **5d** **17**

Not unexpectedly, the dichlorocarbene adduct **4b** of 9-methoxyphenanthrene reacted with base *via* elimination of HCl to **5d** and, finally, to phenanthro[9,10-*b*]furan (**17**) [16] [17] by the sequence outlined in *Scheme 4* which is formulated in analogy to the behavior of **5b** [9]. Intermolecular insertion of a chlorocarbene into a C–H bond adjacent to an ether function has been reported for chloro-9-phenanthryl carbene, where intramolecular insertion is impossible [9] [11].

Since the base-induced eliminations of derivatives of **2** afforded only indirect evidence for the formation of **1**, some thermal eliminations [14] were also investigated. Flash pyrolysis of the sulfoxide **2e** required 500°; at lower temperature, unreacted **2e** was recovered. Since the vapor pressure of **2e** is very low, we found it convenient to effect pyrolysis by dropping the compound dissolved in toluene *via* a cooled condenser into the pyrolysis tube. Pyrolysis of **2e** *(Scheme 5)* at 500° produced 9-methylphenanthrene (**15**;

Scheme 5



2e **13** **14** **15**

16 **12**

24%), **12** (30%), and dimer **16** (48%) together with dibenzyl (9%). Experiments of trapping **1** or **5a** in the pyrolysate with diphenylisobenzofuran or MeOD/$AgNO_3$ [15] failed.

The phenyl sulfoxide **2f** could be pyrolyzed in the range of 300–400°. The reaction mixture was not analyzed in detail when it was found that it consisted essentially of the same products as obtained from **2e**.

Although the formation of **12** can be rationalized by a carbene mechanism *(Scheme 3)*, we believe that the results of the pyrolysis are best interpreted by a radical pathway, inasmuch as the temperatures required for our reactions are much higher than those usually used for sulfoxide elimination [18]. Homolytic cleavage of the C–S bond could lead to a cyclopropyl radical **13**, which, under these conditions, rearranges to a benzylic radical **14** [19]. H-Abstraction from the solvent leads to 9-methylphenanthrene (**15**) and benzyl radical. The other products, **12**, **16**, and dibenzyl, would then be formed by radical recombination. Apparently, this mechanism is more favorable than the concerted pathway leading to the strained compounds **1** and **5a**.

Recently, *Halton et al.* and *Vogel et al.* [2] have completed the synthesis of cyclopropa[*l*]phenanthrene (**1**) by *Alder-Rickert* cleavage. Compound **1** is very unstable decomposing in solution at −70°. The authors also describe that base-induced elimination of the 1a-dimethylselenium derivative of **2** in the presence of furan affords addition products derived from **1** and **5a**. Our results provide additional evidence for the observation that 1a-substituted dihydrocyclopropa[*l*]phenanthrenes eliminate towards C(1) as well as C(9b). Apparently, the energy gain due to conjugation of the 1a,9b-double bond is insufficient to overrule the easier accessibility of the H-atom at C(1). The failure to observe **1** under our reaction conditions is undoubtedly due to our overestimation of its kinetic stability.

The formation of **5a** on elimination can be suppressed if the reaction is forced to proceed at C(1a) and C(9b) by appropriate substitution. The *Alder-Rickert* cleavage used by *Halton* and *Vogel* [2] is a typical example of this approach. With the same objective, we attempted reductive bis-desulfonation [20] of the disulfone **3b** (see **3**, X=Y=CH_3SO_2; obtained from **3a**, see *Exper. Part*) with Na amalgam in MeOH. However, only the monosulfone **2g** was formed in quantitative yield. Similarly, **2g** was formed upon treatment of **3b** with Mg/MeOH [21], while reaction with Mg/THF and Li/*t*-BuOH gave only unreacted starting material. Monodesulfonation occurred also upon reaction with sublimed Mg [22] at −120° in the presence of cyclopentadiene or furan under a variety of conditions, while treatment of **3b** with lithium naphthalenide [23] afforded 9-methylphenanthrene (**15**); (26%) and the reduced hydrocarbon **2d** (32%).

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Experimental Part

1. *General.* See [24].

2. *1a,9b-Dihydro-1a-methoxy-1*H*-cyclopropa[l]phenanthrene* (**2j**). The dichlorocarbene adduct **4b** [6] of 9-methoxyphenanthrene [8] (1.0 g, 3.4 mmol) in Et_2O was added rapidly to Li (0.6 g, 86 mmol) in 100 ml of Et_2O and 10 ml of *t*-BuOH. After 18 h of reflux, excess Li was filtered. After usual workup, the crude product (0.8 g) was repeatedly chromatographed (silica gel column, CH_2Cl_2) to give **2j** in 35% yield. M.p. 58–60°. IR ($CHCl_3$): 3065*w*, 3005*m*, 2935*w*, 2830*w*, 1485*s*, 1450*s*, 1325*w*, 1280*w*, 1075*s*, 1035*s*, 910*m*. MS: 222 (81, M^+), 209 (31), 191 (62), 179 (100), 178 (62).

3. *Eliminations of 1-*'endo'*-Chloro-1a,9b-dihydro-1*H*-cyclopropa[l]phenanthrene in Presence of Nucleophiles. 1a,9b-Dihydro-1a-(methylthio)-1*H*-cyclopropa[l]phenanthrene* (**2a**). A soln. of **4a** (1.07 g, 4.7 mmol) in 20 ml of DMSO/THF 3:1 was added dropwise to a soln. containing MeSH (5 g, 0.1 mol), *t*-BuOK (23.0 g, 0,21 mol), and [18]crown-6 (0.21 g) in 320 ml of DMSO/THF 1:1 at –15°. The mixture was stirred at 4° for 20 h, then at r.t. for 4 d, and then poured into 1.2 l of ice/H_2O. After usual workup, the crude product was purified by chromatography (alox column, petroleum ether/CH_2Cl_2 5:1): 1.13 g (100%) of **2a**, m.p. 57–59°. IR: 3070*m*, 3030*w*, 2910*m*, 1485*s*, 1440*s*, 1048*m*. MS: 238 (33, M^+), 191 (100).

1a,9b-Dihydro-1a-(phenylthio)- and 1a,9b-Dihydro-1-'exo'*-phenylthio-1*H*-cyclopropa[l]phenanthrene* (**2b** and **6a**, resp.). The procedure described above starting from **4a** (0.50 g, 2.2 mmol) in presence of PhSH (44 mmol) afforded, after chromatography (*Alox* column, petroleum ether/CH_2Cl_2 5:1), 0.50 g (76%) of **2b** and 0.16 g (24%) of **6a**. **2b**: Viscous oil. IR: 3075*m*, 3030*m*, 1735*m*, 1585*s*, 1485v.*s*, 1445v.*s*, 1220*m*, 1095*s*, 1050*s*, 1025*s*, 615*m*. MS: 300 (34, M^+), 218 (45), 192 (45), 191 (100).

6a: M.p. 126–128°. IR: 3080*m*, 3040*w*, 3015*s*, 1585*s*, 1490*s*, 1482*s*, 1455*s*, 1450*s*, 1442*s*, 1160*w*, 1090*m*, 1025*s*, 1000*m*, 890*w*, 865*w*, 825*w*, 690*s*, 615*w*. MS: 300 (3, M^+), 221 (5), 192 (13), 191 (100), 189 (14), 178 (8), 165 (7).

1a,9b-Dihydro-1a-(phenylseleno)- and 1a,9b-Dihydro-1-'exo'*-phenylseleno-1*H*-cyclopropa[l]phenanthrene* (**2c** and **6b**, resp.). The procedure described for **2a** starting with 0.20 g (0.9 mmol) of **4a** in presence of PhSeH (3.0 g, 19.4 mmol) afforded, after column chromatography (*Alox* basic, petroleum ether/CH_2Cl_2 5:1) followed by prep. TLC (*Alox*, petroleum ether), 40.5 mg (13%) of **2c** and 120 mg (38%) of **6b**. **2c**: Viscous oil. MS: 346, 348 (weak, M^+), 191 (100). **6b**: Clear yellow crystals. M.p. 96–108°. MS: 346, 348 (weak, M^+), 191 (100).

4. *Oxidations. 1a,9b-Dihydro-1a-(methylsulfinyl)-1*H*-cyclopropa[l]phenanthrene* (**2e**). To a soln. of **2a** (0.20 g, 0.8 mmol) in 1 ml of $CHCl_3$, *m*-chloroperbenzoic acid (90%; 0,18 g, 0.9 mmol) in 1.6 ml of $CHCl_3$ was added dropwise at 0°. The mixture was stirred at r.t. for 21 h. The crude product obtained after usual workup was purified by column chromatography (silica gel, AcOEt): 0.18 g (89%) of **2e**. White crystals, m.p. 129–131°. IR: 3080*w*, 1490*m*, 1450*m*, 1080*w*, 1067*s*, 1052*s*, 1045*m*, 962*m*. MS: 254 (3, M^+), 221 (6), 192 (17), 191 (100), 190 (14), 189 (22), 165 (16).

*1a,9b-Dihydro-1a-(phenylsulfinyl)-1*H*-cyclopropa[l]phenanthrene* (**2f**). Oxidation of **2b** (200 mg) by the procedure used for **2e** afforded sulfoxide **2f** (170 mg, 77%) and sulfone **2h**, which were separated by column chromatography (silica gel, $CHCl_3$/AcOEt 20:1). **2f**: M.p. 146–148°. IR ($CHCl_3$): 3085*w*, 1490*m*, 1448*s*, 1087*s*, 1052*s*, 1035v.*s*, 690*m*. MS: 300 (weak, $M^+ - 0$), 191 (100). Anal. calc. for $C_{21}H_{16}SO$ (316.43): C 79.71, H 5.10; found: C 79.82, H 4.95.

*1a,9b-Dihydro-1a-(methylsulfonyl)-1*H*-cyclopropa[l]phenanthrene* (**2g**). To a soln. of *m*-chloroperbenzoic acid (90%; 0.16 g, 0.8 mmol) in $CHCl_3$ (1.6 ml), **2a** (0.10 g, 0.4 mmol) in $CHCl_3$ (0.5 ml) was added dropwise at – 10°. After stirring for 25 h at r.t. and usual workup, 150 mg of **2g** was obtained as a viscous liquid which was used without further purification. IR: 3070*w*, 3030*w*, 1490*m*, 1450*m*, 1320*s*, 1300*s*, 1260*m*, 1215*m*, 1180*m*, 1145*s*, 1132*s*, 1050*m*, 960*m*, 790*m*. MS: 270 (3, M^+), 191 (100).

*1a,9b-Dihydro-1a-(phenylsulfonyl)-1*H*-cyclopropa[l]phenanthrene* (**2h**). Oxidation of **2b** (150 mg) by the procedure described for **2g** afforded 135 mg (81%) of **2h**. Clear yellow crystals, m.p. 162–163°. IR ($CHCl_3$): 3070*m*, 1490*m*, 1447*s*, 1320*s*, 1300v.*s*, 1290*s*, 1180*m*, 1170*m*, 1150v.*s*, 1140*s*, 1090*s*, 1047*m*, 835*m*, 787*s*, 625*s*, 612*m*. MS: 332 (7, M^+), 191 (100).

*[1a,9b-Dihydro-1*H*-cyclopropa[l]phenanthr-1a-yl]dimethylsulfonium Tetrafluoroborate* (**2i**). To a soln. of Me_3OBF_4 (0.17 g, 1.1 mmol) in nitromethane (1.1 ml), **2a** (167 mg, 0.7 mmol) in nitromethane (1 ml) was added dropwise at 0°. After stirring for 30 min at 0°, then 2.5 h at r.t., the soln. was concentrated (25°/12 Torr, then at 0.5 Torr for 2 h). The salt **2i** was used without purification.

*1a,9b-Dihydro-1a,9b-bis(methylsulfonyl)-1*H*-cyclopropa[l]phenanthrene* (**3b**). To a soln. of **3a** [9] (200 mg, 0.7 mmol) in $CHCl_3$ (1.1 ml) at 0°, a soln. of *m*-chloroperbenzoic acid (90%; 0.68 g, 3.53 mmol) in $CHCl_3$ (6.5 ml) was added dropwise. After 72 h of stirring at r.t., the mixture was worked up and **3b** purified by recrystallization from EtOH: 0.21 g (86%). M.p. 257–258°. IR ($CHCl_3$): 3020*w*, 1320*m*, 1295*m*, 1155*s*, 1140*s*, 970*w*. MS: 348 (6, M^+), 269 (100), 206 (53), 189 (89), 178 (98).

1a,9b-Dihydro-1-'exo'*-(phenylsulfinyl)-1*H*-cyclopropa[l]phenanthrene* (**6c**). Sulfide **6a** (200 mg) was oxidized by the procedure described for **2e**. Upon flash chromatography of the crude product (silica gel, $CHCl_3$), 180 mg (81%) of **6c** and 10 mg of **6d** were isolated. **6c**: M.p. 190–191°. IR: 3080*w*, 2970*w*, 2940*w*, 1490*w*, 1456*m*, 1448*m*, 1087*m*, 1046*s*. MS: 316 (1, M^+), 299 (30), 221 (30), 191 (100), 189 (48), 178 (39), 165 (43). Anal. calc. for $C_{21}H_{16}OS$ (316.43): C 79.71, H 5.10, S 10.13; found: C 79.62, H 5.17, S 10.32.

1a,9b-Dihydro-1-'exo'*-(phenylsulfonyl)-1*H*-cyclopropa[l]phenanthrene* (**6d**). Sulfide **6a** (160 mg) was oxidized to **6d** with *m*-chloroperbenzoic acid as described for **2g**. The crude sulfone was purified by column chromatography (silica gel, $CHCl_3$/AcOEt 20:1) to furnish 150 mg (88%) of **6d**, m.p. 209–210° (dec.). IR ($CHCl_3$): 1490*w*, 1455*m*, 1500*m*, 1320*s*, 1310*s*, 1150v*s*, 1090*s*, 1000*w*, 830*s*, 685*m*, 605*s*. MS: 332 (6, M^+), 192 (18), 191 (100), 190 (17), 189 (3).

5. *Eliminations of 1a-Substituted 1a,9b-Dihydro-1*H*-cyclopropa[l]phenanthrenes. Elimination of* **2i**. Crude **2i** (from 167 mg (0.7 mmol) of **2a**) was dissolved in THF (3.5 ml) and furan (2 ml). A soln. of *t*-BuOK (0.68 g, 6.1 mmol) in THF (7 ml) was added dropwise at –78°. After 14 h at –78°, the mixture was concentrated (25°/12 Torr), then taken up in $CHCl_3$ (10 ml), filtered, and concentrated. The crude product was purified by flash chromatography (silica gel, hexane/$CHCl_3$ 5:1). The first fraction contained 62 mg (37%) of **2a**. Exhaustive elution with $CHCl_3$ (300 ml) afforded a mixture containing **7** [2] and **8** [2] in a 2:1 ratio (total yield 67 mg, *ca.* 30%), which were partially separated by prep. TLC and identified by comparison of their NMR spectra with those reported.

Elimination of **2c**. To a soln. of **2c** (16.3 mg, 0.05 mmol) in $CDCl_3$ (0.5 ml), *m*-chloroperbenzoic acid (19 mg, 0.099 mmol) was added. Usual workup after 24 h at r.t., column chromatography (silica gel, $CHCl_3$), and subsequent prep. TLC (silica gel, $CHCl_3$/AcOET 5:1) afforded 5.1 mg of *phenanthrene-9-methanol* (**9**; 52%), identified by comparison with a sample prepared by $NaBH_4$ reduction of the corresponding carboxaldehyde [12].

Elimination of **2h**. To a soln. of lithium 2,2,6,6-tetramethylpiperidide prepared from 0.15 ml of amine and BuLi (0.9 mmol) in THF (1 ml), **2h** (0.10 g, 0.3 mmol) in THF (1 ml), was added dropwise at –78°. After 30 min at –78°, the mixture was warmed to r.t. and worked up as usual. The crude product was purified by prep. TLC (silica gel) first with CH_2Cl_2, then with CH_2Cl_2/AcOEt 50:1. The crude **6d** (12.7 mg) was further purified by column chromatography (silica gel, AcOEt/CH_2Cl_2 1:200) and identified by spectral comparison with independently prepared **6d** (by oxidation of **6a**).

*Phenanthro[9,10-*b*]furan* (**17**) *from* **4b** [17]. Dichloride **4b** (100 mg, 0.7 mmol) in THF (50 ml) was reacted at –50° with *t*-BuOK (1.5 mmol) in presence of dicyclohexano[18]crown-6 (20 mg). After slow warmup to r.t. and workup as usual, the crude furan **17** was purified by column chromatography (silica gel, CH_2Cl_2). Yield 80%. M.p. 114–116° [16]. IR ($CHCl_3$): 3060, 3000*m*, 1630, 1610, 1590*m*, 1505v.*s*, 1450*s*, 1345*s*, 1320*s*, 1270*m*, 1160, 1140v.*s*, 1115*w*, 1090*m*, 1050*w*, 1035v.*s*, 940*s*, 885v.*s*. ^{1}H-NMR (360 MHz, CD_2Cl_2): 7.30 (*d*, ^3J = 2, H–C(3)); 7.62–7.2 (*m*, H–C(5), H–C(6), H–C(9), H–C(10)); 7.84 (*d*, ^3J = 2, H–C(2)); 8.16 (*m*), 8.35 (*m*, H–C(4), H–C(11)); 8.72 (*m*, H–C(7), H–C(8)). ^{13}C-NMR: 106.2 (*d*, C(3)); 120.0 (*s*, C(11a)); 120.5 (*d*, C(7), C(8)); 122.5 (*s*, C(3b)); 123.4 (*d*, C(4)); 123.5 (*d*, C(5)); 123.9 (*d*, C(6)); 125.1 (*d*, C(9)); 125.8 (*d*, C(10)); 126.9 (*d*, C(11)); 127.4 (*s*, C(3a)); 128.1 (*s*, C(7a)); 129.0 (*s*, C(7b)); 143.7 (*d*, C(2)); 149.1 (*s*, C(11b)). MS: 218 (100, M^+), 189 (58), 187 (14), 163 (7), 109 (9), 95 (9), 94 (18). Anal. calc. for $C_{16}H_{10}O$ (208.86): C 88.05, H 4.62; found: C 87.80, H 4.47.

Pyrolysis of **2e**. The pyrolysis apparatus consisted of a vertical quartz tube (∅ 2.5 cm, *l* = 60 cm) passing through an oven at 500°. The pyrolysate passed through a glass-wool plug supporting solid Na_2CO_3 (for neutralization of methanesulfonic acid) and was collected in a trap cooled to –78°. A soln. of **2e** (52.3 mg, 0.21 mmol) in toluene (4.0 ml) was added dropwise into the quartz tube at 100 Torr. After the addition, the toluene was evaporated (25°/12–0.5 Torr) to yield 30 mg of crude viscous product. Additional 20.9 mg of product with the same composition was contained in the lower part of the pyrolysis tube. The composition of the mixture was determined from the ^{1}H-NMR, giving *dimethyl disulfide* (9%), *9-methylphenanthrene* (**15**; 24%), *1-(9-phenanthryl)-2-phenylethane* (**12**; 30%), *1,2-di(9-phenanthryl)ethane* (**16**; 48%), and *1,1'-ethylenedibenzene* (9%). Repeated prep. TLC (silica gel, petroleum ether/$CHCl_3$ 2:1) allowed isolation of pure samples of **12** and **16**. Compound **15** was identified by comparison with a sample prepared from 9-bromophenanthrene [4]. **12**: Yellow oil. ^{1}H-NMR (360 MHz): 3.12–3.18 (*m*, 2 H); 3.42–3.48 (*m*, 2 H); 7.30–7.38 (*m*, 5 H); 7.58–7.72 (*m*, 5 H); 7.80–7.85 (*m*, 1 H); 8.18–8.22 (*m*, 1 H); 8.68–8.72 (*m*, 1 H); 8.75–8.80 (*m*, 1 H). MS: 282 (14, M^+), 191 (100), 189 (19), 165 (21), 91 (16).

16: Yellow solid. ^{1}H-NMR (360 MHz): 3.67 (*s*, 4 H); 7.60–7.77 (*m*, 10 H); 7.85–7.88 (*m*, 2 H); 8.23–8.28 (*m*, 2 H); 8.70–8.83 (*m*, 4 H). MS: 382 (14, M^+), 191 (100), 165 (14).

6. *Oxidation of* **6b** *to Selenoxide* **6e** *and Selenone* **6f**. Selenide **6b** (31.2 mg, 0.09 mmol) in CH_2Cl_2 (0.5 ml) was oxidized with H_2O_2 (30%; 30 µl, *ca.* 0.80 mmol). After 15 h at r.t., the white precipitate was dissolved by addition of CH_2Cl_2 (3 ml). After usual workup and column chromatography (silica gel, AcOEt), **6e** (9.5 mg) and **6f** (6.3 mg) were isolated. *1a,9b-Dihydro-1-(phenylseleninyl)-1*H*-cyclopropa[l]phenanthrene* (**6e**): M.p. 215–217°. IR: 3075*w*,

2990*w*, 2960*m*, 2855*w*, 1490*m*, 1480*w*, 1452*s*, 1442*s*, 998*m*, 823*s*, 685*m*, 657*w*. MS: 347 (8, $M^+ - OH$), 269 (10), 191 (100), 189 (31), 178 (15), 165 (19).

*1a,9b-Dihydro-1-(phenylselenonyl)-1*H*-cyclopropa[l]phenanthrene* (**6f**): M.p. 248–250° (dec.). IR ($CHCl_3$): 3005*m*, 1453*w*, 1447*m*, 1065*w*, 985*w*, 940*s*, 880*s*, 685*w*. MS: 348 (19, $M^+ - O_2$), 269 (71), 267 (79), 265 (46), 252 (25), 206 (63), 191 (100), 178 (19), 165 (13).

7. *Reaction of* **6e** *and* **6f** *with PhSeH and Pyridine.* Selenoxide **6e** (9.53 mg) in CH_2Cl_2 (1 ml) was reacted with PhSeH (100 mg, 0.6 mmol) and pyridine (10 µl, *ca.* 0.1 mmol) for 70 h at r.t. The soln. was evaporated and the residue purified by column chromatography (silica gel, $CHCl_3$) to yield 6.6 mg of **6b**.

The same procedure with selenone **6e** (6.3 mg) afforded 2.4 mg of **6b**.

8. *Reduction of* **3b**. To lithium naphthalenide prepared from naphthalene (0.46 g, 3.6 mmol) and Li (0.02 g, 3.6 mmol) in HMPA (5.0 ml) [23], a soln. of **3b** (0.6 mmol) in furan (80 ml) was added at −70°. The soln. was stirred 3 h at −70°, then 5 h at −50° and 10 h at r.t. After decomposition with EtOH (2.0 ml) at 0°, the mixture was worked up as usual. Two successive purifications by flash chromatography (silica gel, AcOEt, then $CHCl_3$/hexane 1:10) afforded **2d** (26%) [7] and **15** (22%) [4], both identified by comparison of their ^{1}H-NMR with those reported.

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