180. Aromatization of Tetrahydrocyclopropa[*a*]naphthalenes: an Alternative Synthesis of 1*H*-Cyclopropa[*a*]naphthalene

by **Paul Müller***, **Gérald Bernardinelli**, and **Huong Can Godoy-Nguyen Thi**

Département de Chimie Organique, Université de Genève, 30, quai Ernest Ansermet, CH–1211 Genève 4

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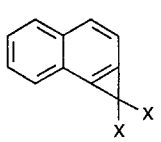
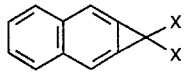
1*H*-Cyclopropa[*a*]naphthalene (**1a**) is accessible *via* reduction of the dichloro compound **1c** with $LiAlH_4$/$AlCl_3$. Several derivatives of tetrahydrocyclopropa[*a*]naphthalene were synthesized. However, contrary to their 1,1-dihalogeno analogues, they afforded no cycloproparenes upon attempted aromatization.

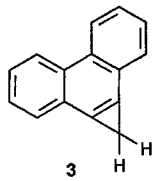
Introduction. – 1*H*-Cyclopropa[*a*]naphthalene (**1a**), unlike the more stable [*b*]-fused isomer **2**, has been synthesized only once, more than 10 years ago [1], and only two approaches to substituted derivatives of **1** have been reported [2][3]. An alternative access to **1a**, based on the benzocyclopropene synthesis by *Radlick* and *Crawford* [4] failed [5]. We intended to develop a new and simple access to this compound based on reactions previously applied for the synthesis of the dihalogenocyclopropa[*a*]naphthalenes **1b** and **1c** [3] and of 1*H*-cyclopropa[*l*]phenanthrenes **3** [6][7]. To this end, a series of substituted derivatives of tetrahydrocyclopropa[*a*]naphthalenes was synthesized and their base-induced aromatization investigated. It turned out that **1a** could not be obtained in this manner. However, **1a** was accessible *via* reduction of the dichloro derivative **1c**.



1a X = H
b X = F
c X = Cl



2 X = H



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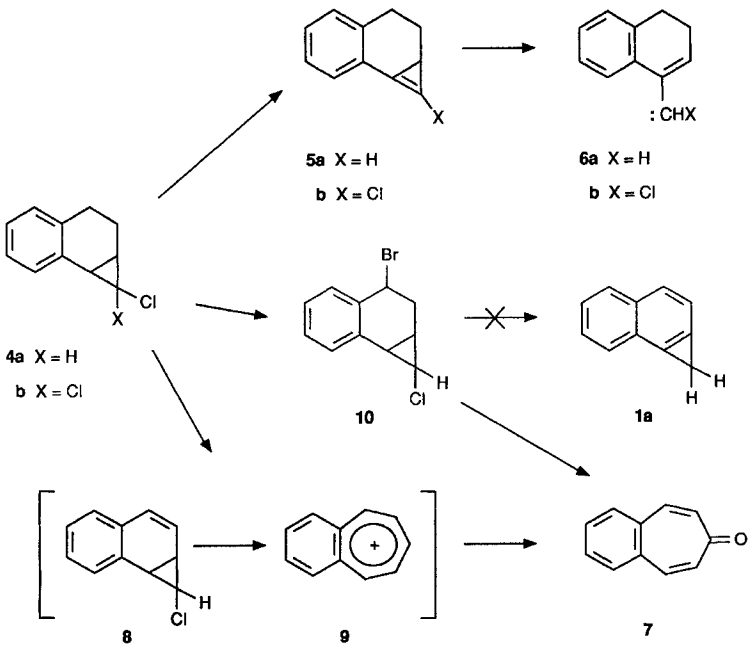
Synthesis and Trapping of 1*H*-Cyclopropa[*a*]naphthalene (1a). – Cyclopropa-[*b*]naphthalene **2** can easily be synthesized by base-induced aromatization of the CCl_2 adduct of 1,4-dihydronaphthalene [8], but this approach fails when applied to **1a**. Bis-dehydrochlorination of the CCl_2 adduct **4b** of 1,2-dihydronaphthalene [9] does not result in aromatization, because the intermediate chlorocyclopropene **5b** undergoes a ring opening leading to the vinylcarbene **6b** [10] (*Scheme 1*). We reasoned that the cyclopropene-vinylcarbene rearrangement was less likely to work with the cyclopropene **5a**, because the resulting carbene **6a** lacks the stabilizing Cl substituent. Accordingly, **4b** was reduced to the monochloride **4a**. Reaction of **4a** with DDQ produced 4,5-benzotropone

(**7**) in 24% yield [11] together with 28% of starting material. The formation of **7** from **4a** may involve electrocyclic ring opening of an intermediate dehydrogenation product **8** to the benzotropylium ion **9**, which is further oxidized to **7**. Reportedly, **7** is the principal oxidation product of **9** obtained using a variety of oxidants [12]. Similarly, **7** was formed in 18% yield, when **4a** was brominated with NBS, and the labile bromide **10** treated *in situ* with *t*-BuOK.

Scheme 1

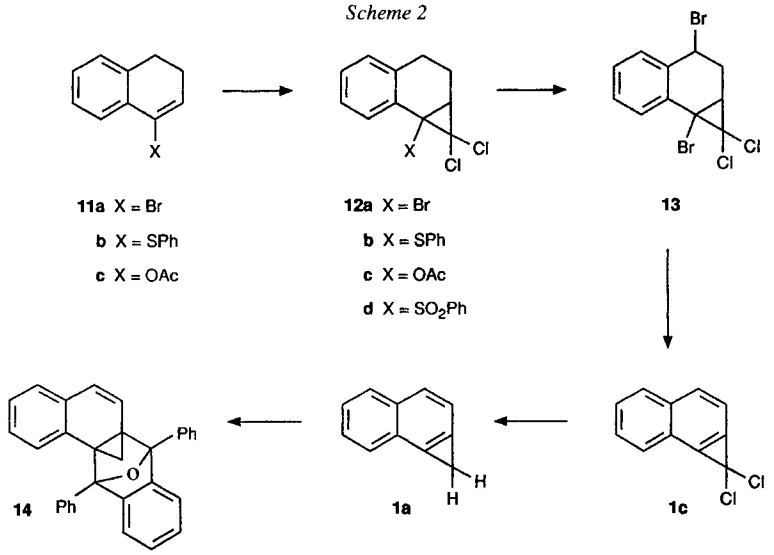


The failure of these aromatization experiments suggests the necessity of having both leaving groups of the precursor of **1a** bound to the cyclohexane C-atoms including the ring junction of the saturated rings rather than at the remote position of the cyclopropane. Several compounds meeting this criterion were synthesized (see below), but none of them could be aromatized. These negative results can be ascribed to the presence of H-atoms at C(1). Indeed, if these positions are blocked by halogens (F or Cl), aromatization to 1,1-dihalogenated **1b** and **1c** proceeds as expected [3]. Since we have previously found that 1,1-dihalogenocycloproparenes can be reduced to the parent hydrocarbons [13], **1c** appeared an obvious precursor of **1a**.

As previously reported [3], **1c** is accessible *via* CCl_2 addition to 4-bromo-1,2-dihydronaphthalene (**11a**) [14], bromination of the adduct **12a** with NBS, and bis-dehydrobromination of the dibromide **13** (*Scheme 2*). The phenyl sulfide **11b** [15] and the enol acetate **11c** [16] also underwent CCl_2 addition, but in this case the adducts, including the sulfone **12d**, obtained by oxidation of **12b**, resisted all attempt towards aromatization. Since **1c** is a very labile compound, it was not isolated, but it was reduced *in situ* to **1a** with $LiAlH_4/AlCl_3$ at low temperature (*ca.* 35% yield with respect to **13**). 1*H*-Cyclopropa[*a*]naphthalene (**1a**) proved to be much more delicate to handle than expected

on the grounds of reports [1], and in our hands, all purification procedures were accompanied by decomposition, which led to some difficulties for the detection of the resonance lines of the quaternary C-atoms in ^{13}C-NMR (for ^{1}H-NMR, see [1]).

Scheme 2



The signals of the primary C-atoms were unambiguously identified and tentatively assigned in analogy to those of **1b** [3] and **3** [7]. Three 'quaternary' signals appeared clearly in the APT mode, and an additional one, at 125.5 ppm, was covered by CH signals, attributed to impurities at 125.6 and 125.7 ppm. A comparison of the ^{13}C-NMR spectra of cyclopropa[*a*]naphthalenes is shown in *Fig. 1*. Comparison with the spectrum of 1,2-dimethylnaphthalene shows the characteristic upfield shift for the C-atom adjacent to the cyclopropene ring [17]. In **1a** and **1b**, resonances of C(2) at 114.9 and 112.4 ppm, respectively, were detected, while the signal of C(7a) is shifted to 123.6 in **1a** and 120.6 in **1b**. The signals corresponding to C(1) of **1a** are in the expected range for cycloproparenes at 22.04 ppm.

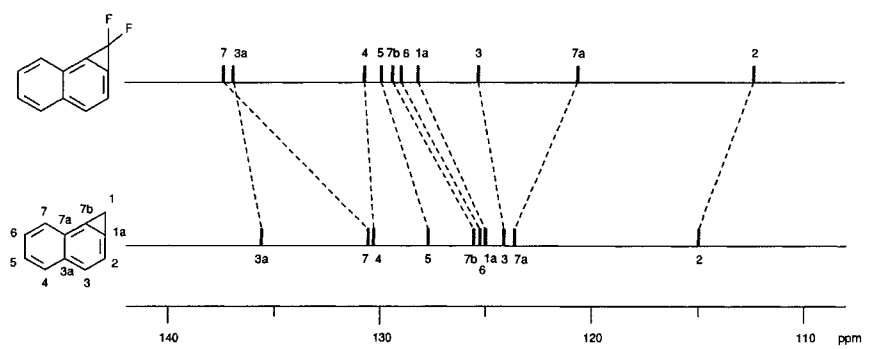
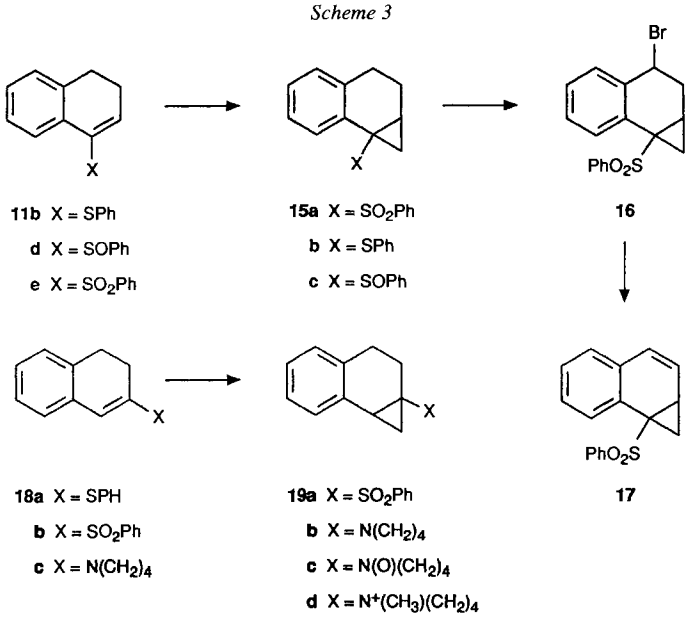


Fig. 1. *^{13}C-NMR Spectra of cyclopropa[a]naphthalenes*

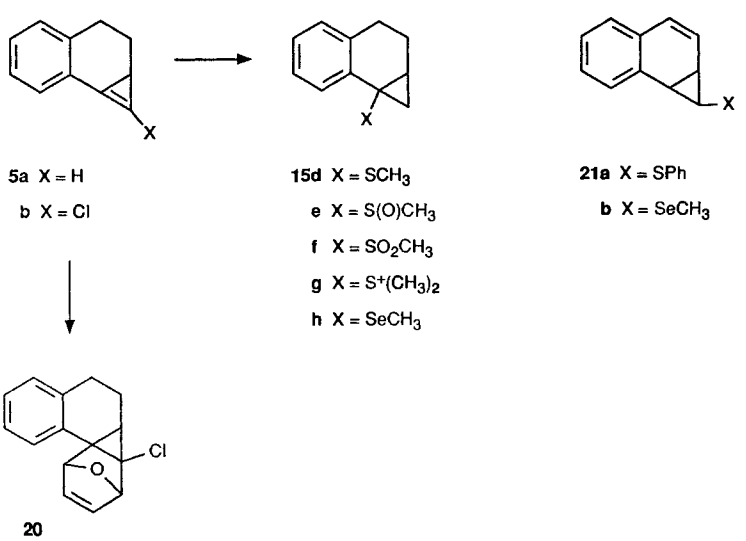
When diphenylisobenzofuran was added to a pentane solution containing the crude reduction products of **1c** (after hydrolysis of $LiAlH_4/AlCl_3$), the adduct **14** was formed in *ca.* 16% yield (with respect to **13**).

Synthesis and Characterization of Substituted Tetrahydrocyclopropa[*a*]-naphthalenes. – These compounds were synthesized either *via* methylene addition to 3- or 4-substituted 1,2-dihydronaphthalenes (*Scheme 3*) or, alternatively, *via* nucleophilic trapping of an appropriate cyclopropene (*Scheme 4*).

Scheme 3



Scheme 4



1,2-Dihydro-4-(phenylthio)naphthalene (**11b**) [15] was oxidized to the sulfone **11e**, which underwent methylene addition [18][19] to **15a**. Bromination of the latter with NBS afforded **16** which was converted to **17**. Aromatization of **17** to **1a** could not be accomplished. Contrary to expectation [20], the sulfoxide **11d** could not be cyclopropanated under the conditions used for **11e**, but **15c** could be obtained as a mixture of two separable diastereoisomers by reduction of **15a** to the sulfide **15b** with DIBAH [21] and selective re-oxidation. Partial reduction [22] of **15a** failed. An alternative synthesis of the skeleton of **17** has already been reported [23]. The ^{1}H-NMR spectra of **15a-c** are collected in *Table 1*.

Table 1. *^{1}H-NMR Data of 7b-Substituted Tetrahydro- and Dihydrocyclopropa[a]naphthalenes*

Compound	X	H–C(1) *exo* (*A*)	H–C(1) *endo* (*B*)	H–C(1a)	J_{AB} *gem*	J_{AC} *cis*	J_{BC} *trans*	H–C(2)	H–C(3)	Arom. H
15a	SO_2Ph	2.32–2.42	1.10	1.12–1.24	5.0	?	6.0	1.82–1.92	2.14–2.28	6.90–7.94 (9 H)
								2.14–2.28	2.32–2.42	
15b	SPh	1.41	1.48–1.54	1.90–2.06	5.2	9.0	?	1.90–2.06	2.50–2.64	7.06–7.25 (3 H)
								2.18–2.26	2.68–2.76	7.80–7.94 (H–C(7))
15c	SOPh	1.86	0.97	1.92–2.0	5.0	9.5	6.0	1.27–1.40	2.04–2.15	6.95–7.55 (8 H)
								1.52–1.65		7.66–7.72 (H–C(7))
15c'	SOPh	1.84–1.98	1.23	1.84–1.98	5	–	5	1.34–1.46	2.16 (*dt*, *J* = 5, 15)	6.85–7.40 (8 H)
								1.84–1.98	2.20–2.31	7.82–7.88 (H–C(7))
15d[a])	SCH_3	1.35	1.28	1.86–1.98	5.5	9.0	5.5	1.86–1.98	2.46–2.58	7.07–7.33 (3 H)
								2.10–2.20	2.66–2.74	8.08–8.12 (H–C(7))
15e[b])	$SOCH_3$	1.66	1.08	2.11–2.24	5.0	8.5	5.4	1.84–1.94	2.50–2.62	7.14–7.26 (3 H)
								2.11–2.24	2.70–2.80	7.40–7.44 (H–C(7))
15e'[c])	$SOCH_3$	1.66–1.82	1.26–1.31	1.66–1.82	–	–	–	1.66–1.82	2.50–2.58	7.14–7.3 (3 H)
								2.14–2.28	2.63–2.76	7.80–7.84 (H–C(7))
15f[d])	SO_2CH_3	2.16–2.30	1.10	2.16–2.30	4.5	–	5.5	1.46–1.58	2.59, (*dt*, ^2J=15, ^3J=5)	7.14–7.34 (3 H)
								2.44–2.50	2.76–2.86	8.00–8.03 (H–C(7))
15g[e])	$S^+(CH_3)_2$	2.11	1.40	1.47–1.60	7.0	10.0	7.0	2.40–2.50	2.54–2.66	7.26–7.42 (3 H)
								2.54–2.66	2.84–2.96	7.54–7.56 (H–C(7))
15h[f])	$SeCH_3$	1.38	1.26	1.95–2.0	5.5	9.0	5.5	1.95–2.00	2.45–2.57	7.00–7.26 (3 H)
								2.02–2.10	2.65–2.74	7.98–8.02 (H–C(7))
16	SO_2Ph 3-bromo	2.54	1.04	2.28–2.38	5.0	9.5	5.5	1.80–1.89 (^2J = 15, ^3J = 3.2)	4.88 (*t*) 6.0	7.08–7.60 (8 H) 8.29–8.34 (H–C(7))
								2.80–2.90 (^2J = 15, ^3J = 2.5,8.5)	(^3J = 3.0)	
17a	SO_2Ph 2,3-didehydro	2.57	0.56	2.90	4.5	10.5	6.5	6.18 (*dd*, ^3J = 10, 5)	6.26 (*d*, ^3J = 10) 8.32–8.40 (H–C(7))	6.95–7.80 (8 H)
17b[g])	$OSiMe_3$ 2,3-didehydro	1.78	–0.22	2.19	4.8	10.8	5.6	6.31 (*dd*, *J* = 3.1, 8)	6.33, (*dd*, *J* = 3.1, 8) 7.76 (H–C(7))	7.21–7.35 (3 H)
17c[h])	OTiPS 2,3-didehydro	1.84	–0.16	2.18–2.26	4.5	10.5	5.5	6.35 (*m*)	6.35 (*m*) 7.88–7.93 (H–C(7))	7.14–7.34 (3 H)

[a]) δ(SCH_3) = 2.12. [b]) δ($SOCH_3$) = 2.34 (major isomer). [c]) δ($SOCH_3$) = 2.47 (minor isomer). [d]) δ(SO_2CH_3) = 2.76. [e]) δ(S^+–CH_3) = 2.78 and 3.02. [f]) δ($SeCH_3$) = 2.04. [g]) Prepared according to [23]. δ($SiCH_3$) = 0.03. [h]) Prepared according to [23]. δ(TiPS) = 0.96–1.10.

Table 2. *^{1}H-NMR Data of* **19a–d**

Compound	X	H–C(1) *exo* (*A*)	H–C(1) *endo* (*B*)	H–C(7b) (*C*)	J_{AB}	J_{AC}	J_{BC}	H–C(2)	H–C(3)	Arom. H
19a	SO_2Ph	1.86–1.91	1.39	2.93	6.0	10.0	6.0	1.96–2.02 2.10–2.18	2.38–2.50 2.60–2.70	6.98–7.94 (9 H)
19b	$N(CH_2)_4$[a])		1.12	1.18	2.05	5.0	10.0	5.0 2.15 (*ddd*, ^2J = 13, ^3J = 6, 2.2)	1.93 (*dt*, ^2J = 13, ^3J = 5.5) 2.76 (*m*)	2.60 (*m*) 7.05–7.18 (3 H) 7.38 (H–C(7))
19c	$N(O)(CH_2)_4$[b])	2.14–2.24	1.24	3.00	5.5	10.5	5.5	2.14–2.24 2.44–2.60	2.70–2.77 2.85 (*ddd*, *J* = 16, 6.0, 2.5)	7.06–7.20 (3 H) 7.28–7.34 (H–C(7))
19d	$N(CH_3)(CH_2)_4$[c])	2.00–2.08	1.65	3.16	8.0	11.0	6.0	2.26–2.50 2.66–2.80	2.66–2.80 2.90–2.98	7.04–7.24 (3 H) 7.48–7.54 (H–C(7))

[a]) δ (CH_2N) = 2.80; δ (CH_2CH_2N) = 1.82. [b]) δ (CH_2N) = 3.15–3.70; δ (CH_2CH_2N) = 1.95–2.05; 2.44–2.60. [c]) δ (CH_3N^+) = 3.46 δ (CH_2N^+) = 3.60–4.02; δ ($CH_2CH_2N^+$) = 2.26–2.50.

Application of the same reactions to 1,2-dihydro-3-(phenylsulfonyl)naphthalene (**18b**), available from β-tetralone *via* the vinyl sulfide **18a**, afforded **19a**, which decomposed upon attempted bromination. The commercially available enamine **18c** of β-tetralone was cyclopropanated with CH_2N_2 in presence of CuCl [24] to **19b**, which was further transformed to the *N*-oxide **19c** and the ammonium salt **19d**. The ^{1}H-NMR data of **19a–d** are given in *Table 2*. Attempts towards aromatization of these precursors by a variety of methods failed invariably.

The CCl_2 adduct **4b** of 1,2-dihydronaphthalene is considered to react with base by loss of a benzylic proton to yield the conjugated cyclopropene **5b** [10]. The regioselectivity of the elimination was confirmed by trapping of **5b** with furan. The adduct **20** exhibits a *triplet* at 2.87–2.92 ppm (J = 5 Hz) assigned to H–C(1a), which is indicative for its structure. In the alternative regioisomer, the cyclopropane H-atom gave rise to a *singlet*. By analogy, the monochloride **4a** is expected to yield **5a** upon dehydrochlorination. Nucleophilic addition to **5a** may give rise to two regioisomers. However, if dehydrochlorination of **4a** is effected in presence of methyl thiolate, only the interception product **15d**, with the S-atom at the angular position C(7b) is obtained (84% yield). The structure can be assigned on the grounds of analogies in the ^{1}H-NMR spectrum with other carbene adducts to 4-substituted 1,2-dihydronaphthalenes, where the position of the substituent is known, particularly with **15b**. Oxidation of the sulfide **15d** with *m*-chloroperbenzoic acid leads to a mixture of sulfoxide **15e** (49%, two diastereoisomers) and sulfone **15f** (13%), while the sulfonium salt **15g** is formed upon treatment of **15d** with trimethyloxonium tetrafluoroborate. The ^{1}H-NMR of the derivatives **15a–h** together with those of **16** and **17** are summarized in *Table 1*. The spectra are assigned on the grounds of selective decoupling and, in some cases, COSY experiments. Whenever possible, the coupling constants of the cyclopropane H-atoms were extracted from the spectra, and assignments were made consistently.

On the other hand, when **4a** is dehydrochlorinated in the presence of phenylthiolate, only attack by the nucleophile at the less hindered position is observed, resulting in formation of **21a** in 92% yield. The ^{1}H-NMR of **21a** is very complex, even when recorded at 360 MHz. The structure was, therefore, established by X-ray analysis (*Fig. 2*), and once the structure was known, the ^{1}H-NMR could be assigned. As *Fig. 2* shows, the PhS substituent is oriented *exo* which corresponds to the expected *cis*-addition of thiophenol to **5a**. Interception of **5a** with methyl selenolate produces **15h** (3%) and **21b** (17%).

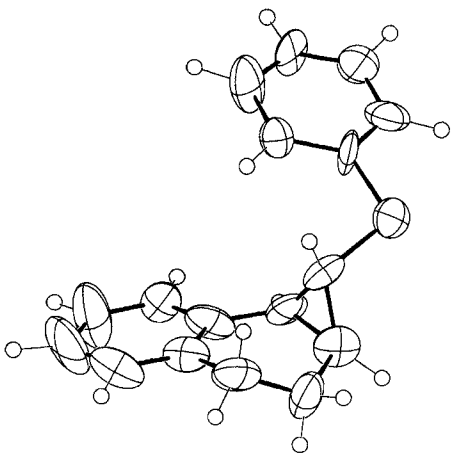


Fig. 2. *X-Ray structure of* **21a**

Experimental Part

1. *General.* See [25].

2. *Reactions with 1-*endo*-Chloro-1a,2,3,7b-tetrahydro-1*H*-cyclopropa[a]naphthalene* (**4a**). *Synthesis of* **4a**. To a suspension of $LiAlH_4$ (11.5 g, 0.3 mol) in Et_2O (100 ml) and under N_2, a soln. of **4b** [10] (5.09 g, 23.9 mmol) in Et_2O (80 ml) was added dropwise within 1.5 h. After 3.5 d at reflux, the mixture was decomposed by successive addition of H_2O (6.5 ml), 15% aq. NaOH (6.5 ml), and H_2O (19.5 ml) at –15°, and filtered. The filtrate was evaporated and the crude product (4.04 g) purified by CC (SiO_2, $CHCl_3$/hexane 1:20): **4a** (1.24 g; 29%) as a colorless oil. IR ($CHCl_3$): 3070*w*, 3025*m*, 2940*m*, 2865*w*, 2845*w*, 1495*s*, 1455*m*, 1440*m*, 1290*m*, 1285*m*, 1280*m*, 680*m*. ^{1}H-NMR: 1.73–1.82 (*m*, ^3J = 4.0, 7.5, 7.6, 9.5, 1 H); 2.02–2.12 (*m*, ^2J = 14, ^3J = 4.0, 6.9, 1 H); 2.12–2.25 (*m*, ^2J = 14.0, ^3J = 6.9, 7.5, 1 H); 2.29 (*dd*, ^3J = 7.6, 9.5, 1 H); 2.80 (*t*, ^3J = 6.9, 2 H); 3.55 (*t*, ^3J = 6.9, 1 H); 7.10–7.35 (*m*, 4 H). MS: 178/180 (20, 3:1, M^+), 143 (100), 128 (50), 115 (23).

Reaction of **4a** *with DDQ. 1,2-Benzocyclohepta-1,3,6-trien-5-one* (**7**). The chloride **4a** (53.5 mg, 0.3 mmol) was heated with DDQ (0.14 g, 0.6 mmol) in dioxane (2.0 ml) to reflux for 2.5 d. After filtration of the precipitate, the filtrate was evaporated, and the residue was purified by prep. TLC (SiO_2, $CHCl_3$): 15 mg (28%) of **7**. M.p. 66° [11]. UV (cyclohexane): 235 (4.35), 261 (4.33), 269 (4.34), 312 (3.41), 324 (3.28), 338 min. (3.08). IR ($CHCl_3$): 3000*s*, 1630*vs*, 1605*s*, 1588*vs*,1550*s*, 1486*m*, 1415*m*, 1335*s*, 1290*s*, 862*s*, 655*m*. ^{1}H-NMR: 6.76–6.85 (*BB'* of *AA'BB'*, ^3J = 12.5, 2 H); 7.42–7.52 (*AA'* of *AA'BB'*, ^3J = 12.5, 2 H); 7.55–7.73 (*AA'BB'*, 4 H). ^{13}C-NMR: 130.5 (CH); 134.0 (CH); 135.0 (CH); 136.0 (CC); 141.5 (CH); 188.4 (C=O). MS: 156 (8, M^+), 129 (10), 128 (100), 127 (12), 102 (14), 75 (10), 63 (13), 51(18), 50 (16).

*3-Bromo-1-*endo*-chloro-1a,2,3,7b-tetrahydro-1*H*-cyclopropa[a]naphthalene* (**10**). A mixture of **4a** (0.34 g, 1.9 mmol), NBS (0.35 g, 2.1 mmol), and AIBN (17.3 mg, 0.1 mmol) in CCl_4 (4.0 ml) was heated to

reflux for 20 min. After filtration and concentration of the filtrate, crude **10** was obtained as light-brown oil in quant. yield. The product decomposed rapidly at 0° and was used without further purification. ^{1}H-NMR: 1.93–2.0 (*m*, 1 H); 2.32–2.40 (*ddd*, *J* = 3.2, 5.5, 15.0, 1 H); 2.45 (*dd*, ^3J = 7.5, 9.0, 1 H); 2.77–2.88 (*m*, 1 H); 3.63 (*t*, ^3J = 7.5, 1 H); 5.24 (*t*, ^3J = 3, 1 H); 7.20–7.35 (*m*, 3 H); 7.48 (*m*, 1 H).

Compound **7** *from* **4a** via **10**. A mixture of **4a** (84.1 mg, 0.5 mmol), NBS (94.8 mg, 0.5 mmol), and AIBN (15.6 mg, 0.06 mmol) in CCl_4 (1 ml) was heated to reflux for 15 min. The mixture was cooled to –15°, and DBN (0.7 mmol) was added dropwise. After 1 h of stirring from –15 to 0°, it was poured onto sat. aq. NaCl (5 ml). The precipitate was washed with CCl_4. After usual workup, the crude product was purified by prep. TLC (SiO_2, $CHCl_3$) to give **7** in an overall yield of 5%.

3. *Synthesis of 1*H*-cyclopropa[*a*]naphthalene* (**1a**). *Addition of* CCl_2 *to* **11a–c**. *7b-Bromo-1,1-dichloro-1a,2,3,7b-tetrahydro-1*H*-cyclopropa[*a*]naphthalene* (**12a**). See [3].

*1,1-Dichloro-1a,2,3,7b-tetrahydro-7b-(phenylthio)-1*H*-cyclopropa[*a*]naphthalene* (**12b**). A mixture of **11b** (0.5 g, 2.1 mmol) and $PhHgCCl_3$ (1.30 g, 3.3 mmol) was heated to reflux in benzene for 14 h. The resulting precipitate was removed by filtration and washed with pentane. The filtrate was evaporated, and the crude product was purified by FC (SiO_2, toluene/petroleum ether 1:5) to yield **12b** (0.36 g, 53%) as a yellow oil. IR ($CHCl_3$): 3068*m*, 3025*m*, 2945*m*, 2875*w*, 2850*w*, 1585*w*, 1480*m*, 1452*m*, 1440*s*, 1117*w*, 1070*m*, 1055*m*, 1025*s*, 820*s*, 690*s*. ^{1}H-NMR: 1.72–1.85 (*m*, 1 H); 2.15–2.25 (*m*, 1 H); 2.30–2.43 (*m*, 3 H); 6.92–6.97 (*m*, 1 H); 7.12–7.18 (*m*, 1 H); 7.20–7.35 (*m*, 6 H); 7.50–7.55 (*m*, 1 H). MS ($C_{17}H_{14}Cl_2S$): 320/322 (2, 3:2, M^+), 285, 287 (52), 249 (42), 175 (73), 159 (71), 141 (65), 139 (78), 128 (86), 115 (100).

Compound **12b** was also obtained from **11b** with CCl_3COONa (82%) or CCl_3COOEt (88%).

*1,1-Dichloro-1a,2,3,7b-tetrahydro-1*H*-cyclopropa[*a*]naphthalen-7b-yl Acetate* (**12c**). A mixture of **11c** [19] (1.0 g, 5.3 mmol) and $PhHgCCl_3$ (2.61 g, 6.6 mmol) in benzene (5.0 ml) was heated to reflux under N_2 for 45 h. The soln. was cooled to r.t. and filtered. Evaporation of the filtrate and CC (SiO_2, CH_2Cl_2) yielded **12c** (1.40 g, 97%) as colorless oil. IR ($CHCl_3$): 3000*w*, 2900*w*, 1740*s*, 1490*w*, 1450*m*, 1430*m*, 1365*m*, 1296*w*, 1210v*s*, 1125*m*, 1080*m*, 1050*s*, 1030*s*, 835*m*. ^{1}H-NMR: 2.08 (*s*, 3 H); 1.97–2.10 (*m*, 1 H); 2.29 (*dd*, ^3J = 4.5, 9, 1 H); 2.47–2.63 (*m*, 2 H); 3.05–3.17 (*m*, 1 H); 7.07–7.10 (*m*, 1 H); 7.19–7.27 (*m*, 2 H); 7.47–7.50 (*m*, 1 H). MS ($C_{13}H_{12}Cl_2O_2$): 270, 272, 274 (1, 9:6:1, M^+), 228, 230, 232 (42), 194, 196 (16), 193, 195 (100), 190, 192 (12), 175 (21).

*1,1-Dichloro-1a,2,3,7b-tetrahydro-7b-(phenylsulfonyl)-1*H*-cyclopropa[*a*]naphthalene* (**12d**). To *m*-chloroperbenzoic acid (0.83 g, 4.3 mmol) in $CHCl_3$ (8.5 ml), **12b** (0.6 g, 1.9 mmol) in $CHCl_3$ was added dropwise at 0°. After 30 min at 0°, the mixture was stirred at r.t. for 1 h and filtered. After usual workup, crude **12d** (0.57 g, 85%) was obtained. M.p. 178–179° (dec.). IR ($CHCl_3$): 1459*m*, 1325*s*, 1310*s*, 1152*s*, 1087*s*, 686*s*. ^{1}H-NMR: 1.65 (*tdd*, ^2J = 4.5, ^3J = 6.5, 14.5, 1 H); 2.03 (*td*, ^2J = 4.5, ^3J = 14.5, 1 H); 2.25–2.33 (*m*, 1 H); 2.48–2.57 (*m*, 1 H); 3.25 (*dd*, ^3J = 6.5, 10.0, 1 H); 6.82–6.87 (*m*, 1 H); 7.13–7.20 (*m*, 1 H); 7.20–7.30 (*m*, 1 H); 7.30–7.37 (*m*, 2 H); 7.47–7.53 (*m*, 1 H); 7.57–7.67 (*m*, 3 H). MS ($C_{17}H_{14}Cl_2O_2S$): 352/354/356 (35, 9:6:1, M^+), 211, 213 (56), 176, 178 (74), 175, 177 (100), 141 (46).

*1,1-Dichloro-1*H*-cyclopropa[*a*]naphthalene* (**1c**). To a soln. of **13** [3] (1.01 g, 2.7 mmol) in THF (6.0 ml), *t*-BuOK (1.02 g, 9.1 mmol) in THF (9.0 ml) was added dropwise at –78°. The soln. was stirred at –78° for 15 min, then at –40° for 1 h. After evaporation *in vacuo* at –35°/1 Torr for 3 h, the residue was taken up with Et_2O (30 ml). The ^{1}H-NMR of **1c**: see [3].

*1*H*-Cyclopropa[*a*]naphthalene* (**1a**). To $AlCl_3$ (1.05 g, 7.9 mmol) in Et_2O (12 ml), $LiAlH_4$ (0.60 g, 18.8 mmol) was added at 0°. The suspension was stirred at r.t. for 1 h. After dilution with Et_2O (10 ml), it was slowly added to crude **1c** at –78°. After stirring for 15 h at –20°, the mixture was decomposed at –10° with 15% aq. NaOH (1.15 ml), followed by H_2O (1.7 ml). After 30 min, the precipitate was filtered, and the filtrate was evaporated. The crude product (1.19 g) was purified by CC at –10° (basic Al_2O_3 (100 g), pentane), and the collected fractions were immediately cooled to –20°. Yield: 0.14 g (*ca.* 37% based on **13**), white solid at –10°, transparent oil at r.t. ^{1}H-NMR ($CDCl_3$, 360 MHz): 3.45 (*s*, 2 H–C(1)); 7.45–7.65 (*m*, H–C(5), H–C(6)); 7.55 (*B* of *AB*, ^3J = 7, H–C(2)); 7.81 (*A* of *AB*, ^3J = 7, H–C(3)); 7.83–7.86 (*m*, 1 H); 7.98–8.00 (*m*, 1 H). ^{13}C-NMR ($CDCl_3$, 50 MHz): 22.04 (C(1)); 114.88 (C(2)); 123.6 (C(7a)); 124.07 (C(3)); 124.9 (C(1a)); 125.23 (C(5)); 125.5 (C(7b?)); 127.72 (C(6)); 130.26 (C(4)); 130.49 (C(7)); 135.6 (C(3a)).

Trapping of **1a** *with Diphenylisobenzofuran. 3,4;9,10-Dibenzo-1,8-diphenyl-12-oxatetracyclo[6.2.1.1*^{2,7}*.0*^{2,7}*]dodeca-3,9-diene* (**14**). A soln. of crude **1a** prepared from **13** (0.51 g, 1.4 mmol) in Et_2O was washed rapidly with sat. NaCl at –5° and dried ($MgSO_4$) at –10°. After cooling to –20°, 1,3-diphenylisobenzofuran (0.41 g, 1.5 mmol) was added. The soln. was stirred at –20° for 2 h, then at 4° for 5 h. After addition of CH_2Cl_2 (10 ml) to dissolve the remaining diphenylisobenzofuran, stirring was continued at 4° for 20 h. The mixture was evaporated and the residue purified by FC (SiO_2, CH_2Cl_2/pentane 1:1): 92.7 mg

(16%) of **14**. ^{1}H-NMR ($CDCl_3$, 360 MHz): 0.97 (*d*, ^2J = 4.4, H–C(1)); 3.36 (*d*, ^2J = 4.4, H–C(1)); 6.09 (*B* of *AB*, ^3J = 9.4); 6.23 (*A* of *AB* , ^3J = 9.4, 1 H); 6.92–7.10 (*m*, 8 H); 7.42–7.57 (*m*, 8 H); 7.84–7.90 (*m*, 2 H); 8.02–8.08 (*m*, 1 H). MS: 410 (54, M^+), 305 (100), 270 (28), 228 (27), 105 (55), 77 (32). Anal. calc. for $C_{31}H_{22}O$ (410.51): C 90.70, H 5.40; found: C 89.00, H 5.44.

4. *Methylene Addition to* **11e**. *1,2-Dihydro-4-(phenylsulfinyl)naphthalene* (**11d**). To **11b** [15] (1.05 g, 4.4 mmol) in $CHCl_3$ (5 ml), a soln. of *m*-chloroperbenzoic acid (85%, 0.99 g; 4.9 mmol) in $CHCl_3$ was added dropwise at 0° in 30 min. After 12 h of stirring at r.t., the white precipitate (*m*-chlorobenzoic acid) was removed by filtration. The filtrate was worked up, and the crude product was purified by FC (SiO_2, $CHCl_3$) to afford **11d** (1.20 g, 100%). M.p. 73–76°. IR ($CHCl_3$): 3070*w*, 3025*w*, 2950*w*, 2895*w*, 2840*w*, 1490*w*, 1478*w*, 1452*m*, 1445*s*, 1218*m*, 1072*s*, 1042v*s*, 1020*m*, 687*s*. ^{1}H-NMR: 2.45–2.65 (*m*, 2 H); 2.75–2.82 (*m*, 2 H); 7.02–7.06 (*m*, 1 H); 7.06–7.16 (*m*, 3 H); 7.38–7.46 (*m*, 4 H); 7.70–7.76 (*m*, 2 H). MS: 254 (3, M^+), 143 (71), 128 (100), 115 (39).

1,2-Dihydro-4-(phenylsulfonyl)naphthalene (**11e**). To *m*-chloroperbenzoic acid (85%, 5.39 g; 26.6 mmol) in $CHCl_3$ (55 ml), a soln. of **11b** [15] (3.08 g, 12.9 mmol) in $CHCl_3$ (8.0 ml) was added dropwise at 0°. The mixture was stirred at 0° for 1.5 h, then at r.t. for 3.5 h. The *m*-chlorobenzoic acid formed was separated by filtration, and the filtrate was worked up. The crude product was purified by recrystallization (EtOH) to give **11e** (2.6 g, 75%). M.p. 117–118°. IR ($CHCl_3$): 3075*w*, 2953*w*, 2900*w*, 2940*w*, 1450*s*, 1310*s*, 1280*m*, 1150v*s*, 1120*m*, 1088*s*, 975*w*, 783*m*, 687*s*, 622*s*, 602*m*. ^{1}H-NMR: 2.53–2.60 (*m*, 2 H); 2.75–2.82 (*m*, 2 H); 7.12–7.20 (*m*, 3 H); 7.47–7.58 (*m*, 4 H); 7.83–7.88 (*m*, 1 H); 7.92–7.98 (*m*, 2 H). MS: 270 (75, M^+), 145 (19), 129 (100), 128 (93).

*1a,2,3,7b-Tetrahydro-7b-(phenylsulfonyl)-1*H*-cyclopropa[*a*]naphthalene* (**15a**) [18][19]. A suspension of NaH (55–60%, 1.01 g; 23.1 mmol), washed with hexane, in DMSO (26 ml) was treated with trimethyloxosulfonium iodide (5.24 g, 23.8 mmol) in small portions. After 30 min of stirring, **11e** (3.02 g, 11.2 mmol) in DMSO (35 ml) was added dropwise, and the mixture was stirred at r.t. for 17 h. It was then poured into cold H_2O and worked up. The crude product was recrystallized (EtOH) and gave 2.46 g (77%) of **15a**. M.p. 99–100°. IR ($CHCl_3$): 3075*w*, 3032*w*, 2952*w*, 2870*w*, 2850*w*, 1490*w*, 1450*m*, 1305*s*, 1290*m*, 1185*m*, 1150*s*, 1091*m*, 1070*m*, 790*s*, 688*s*, 612*s*. ^{1}H-NMR: see *Table 1*. MS: 284 (14, M^+) 143 (100), 141 (52), 128 (60).

*1a,2,3,7b-Tetrahydro-7b-(phenylthio)-1*H*-cyclopropa[*a*]naphthalene* (**15b**). To **15a** (1.44 g, 5.1 mmol) in toluene (10 ml), a 1M soln. of DIBAH in toluene (26 ml, 26 mmol) was added dropwise and heated to reflux for 3.5 d. After cooling to 0°, EtOH (2.0 ml) was added slowly, followed by H_2O (8 ml) and 6N HCl (4.0 ml). After usual workup, the product was purified by FC (SiO_2, CH_2Cl_2) and yielded 1.20 g (93%) of **15b** as colorless oil. IR ($CHCl_3$): 3070*w*, 3010*w*, 2930*m*, 2860*m*, 1585*m*, 1480*s*, 1450*m*, 1440*m*, 1035*m*, 1025*m*, 780*m*, 695*s*. ^{1}H-NMR: see *Table 1*. MS: 252 (50, M^+), 219 (45), 175 (19), 161 (15), 143 (60), 142 (32), 141 (56), 129 (29), 128 (60), 127 (26), 115 (100), 91 (78).

*1a,2,3,7b-Tetrahydro-7b-(phenylsulfinyl)-1*H*-cyclopropa[*a*]naphthalene* (**15c**). To **15b** (0.56 g, 2.2 mmol) in $CHCl_3$ (10 ml), a soln. of *m*-chloroperbenzoic acid (0.43 g, 90%, 2.2 mmol) in $CHCl_3$ (5 ml) was added at –10°. After 1 h of stirring at 0°, the mixture was washed with 10% Na_2CO_3 (2 × 15 ml) and worked up as usual. The crude product was purified by FC (SiO_2, CH_2Cl_2/AcOEt 10:1) to give **15a** (19%) and two diastereoisomeric sulfoxides **15c** (m.p. 72–73°, 37%) and **15c'** (m.p. 80–82°, 16%). Further oxidation of the diastereoisomers produced **15a** quantitatively.

Data of **15c**: IR ($CHCl_3$): 3075*w*, 3025*w*, 2945*w*, 2863*w*, 1488*w*, 1444*m*, 1088*m*, 1040*s*. ^{1}H-NMR: see *Table 1*. MS: 144 (12), 143 (100), 142 (52), 141 (23), 129 (11), 128 (91), 127 (17), 126 (11), 115 (28). Anal. calc. for $C_{17}H_{16}OS$ (268.37): C 76.08, H 6.01, S 11.95; found: C 75.98, H 6.06, S 11.87.

Data of **15c'**: IR ($CHCl_3$): 3063*m*, 3000*w*, 2948*s*, 2868*w*, 1734*w*, 1489*m*, 1450*s*, 1269*w*, 1125*w*, 1093*s*, 1048v*s*, 1000*w*, 931*m*. ^{1}H-NMR: see *Table 1*. MS: 144 (12), 143 (100), 142 (51), 141 (22), 129 (12), 128 (95), 127 (18), 126 (10), 115 (27). Anal. calc. for $C_{17}H_{16}OS$ (268.37): C 76.08, H 6.01 S 11.95; found: C 75.90, H 5.95, S 11.83.

*3-Bromo-1a,2,3,7b-tetrahydro-7b-(phenylsulfonyl)-1*H*-cyclopropa[*a*]naphthalene* (**16**). A mixture of **15** (2.45 g, 8.6 mmol), NBS (1.77 g, 9.9 mmol), and AIBN (0.16 g, 1 mmol) in CCl_4 (35 ml) was heated to reflux for 16 h. After cooling and filtration, the filtrate was evaporated and the residue purified by FC (SiO_2, $CHCl_3$) to yield 4.56 g of **16**, contaminated with the elimination product **17**.

Data of **16**: IR ($CHCl_3$): 3075*m*, 3030*s*, 1482*m*, 1450*s*, 1320v*s*, 1198*m*, 1180*m*, 1170*m*, 1150v*s*, 1090*s*, 1055*m*, 923*m*, 687*s*, 654*s*. ^{1}H-NMR: see *Table 1*.

*1a,7b-Dihydro-7b-(phenylsulfonyl)-1*H*-cyclopropa[*a*]naphthalene* (**17**). To **16** (2.27 g, 6.3 mmol) in THF (19 ml), a soln. of freshly sublimed *t*-BuOK (1.51 g, 13.5 mmol) in THF (15 ml) was added dropwise at –78° under N_2. The mixture was slowly warmed up to r.t., stirred for 3.5 h, and evaporated *in vacuo*. The residue was

extracted with Et_2O. After workup of the org. layer, the crude product was purified by FC (SiO_2, $CHCl_3$) and afforded **17** (1.72 g, 97%). M.p. 80–82°. IR ($CHCl_3$): 3030*w*, 1450*w*, 1318*m*, 1303*m*, 1290*w*, 1170*m*, 1162*m*, 1145*s*, 1089*m*, 686*m*, 654*m*, 600*s*. ^{1}H-NMR: see *Table 1*. MS: 288 (6, M^+), 215 (10), 141 (100), 115 (20). Anal. calc. for $C_{17}H_{14}O_2S$ (282.36): C 72.31, H 5.00, S 11.36; found: C 72.07, H 5.13, S 11.13.

5. *Methylene Addition to 3-Substituted 1,2-Dihydronaphthalenes. 1,2-Dihydro-3-(phenylthio)naphthalene* (**18a**). A mixture of β-tetralone (1.97 g, 14.1 mmol) and PhSH [15][26] (2.93 ml, 28.6 mmol) was sat. with HCl for 1 h and stirred at r.t. overnight. It was diluted with Et_2O (10 ml) and treated with H_2O. The org. layer was worked up. Distillation of the crude product afforded **18a** (3.14 g, 94%) as a yellow oil. B.p. 171–173°/1.2 Torr. IR ($CHCl_3$): 3070*m*, 3020*w*, 2940*w*, 2890*w*, 2840*w*, 1616*w*, 1585*m*, 1570*w*, 1487*s*, 1480*s*, 1440*s*, 1025*s*, 730*m*, 700*m*, 690*s*. ^{1}H-NMR ($CDCl_3$, 200 MHz): 2.40–2.45 (*m*, 2 H–C(2)); 2.81–2.86 (*m*,2 H–C(1)); 6.50 (s, H–C(4)); 7.05–7.50 (*m*, 9 arom. H). MS: 238 (100, M^+), 205 (36), 129 (68), 128 (89).

1,2-Dihydro-3-(phenylsulfonyl)naphthalene (**18b**). To **18a** (2.68 g, 11.3 mmol) in $CHCl_3$ (6.0 ml), *m*-chloroperbenzoic acid (85%, 4.71 g, 23.2 mmol) in $CHCl_3$ (48 ml) was added dropwise at 0°. After stirring overnight at 4°, the *m*-chlorobenzoic acid was filtered off, and the filtrate was worked up. The crude product was purified by FC (SiO_2, hexane/CH_2Cl_2 1:1, followed by CH_2Cl_2) and yielded 2.14 g (70%) of **18b** as a white solid. M.p. 125–126°. IR ($CHCl_3$): 3075*w*, 3030*w*, 2950*w*, 2900*w*, 2840*w*, 1660*w*, 1450*m*, 1340*m*, 1307*s*, 1150*vs*, 1088*s*, 685*s*, 628*s*. ^{1}H-NMR ($CDCl_3$, 360 MHz): 2.44–2.52 (*m*, 2 H–C(2)); 2.82–2.90 (*m*, 2 H–C(1)); 7.10–7.20 (*m*, 1 H); 7.20–7.30 (*m*, 3 H); 7.51–7.58 (*m*, 2 H); 7.58–7.65 (*m*, 2 H); 7.92–7.98 (*m*, 2 H). MS: 270 (48, M^+), 129 (56), 128 (100).

*1a,2,3,7b-Tetrahydro-1a-(phenylsulfonyl)-1*H*-cyclopropa[a]naphthalene* (**19a**). A suspension of NaH (50–60%, 0.35 g, 8.0 mmol), washed with hexane in DMSO (9.0 ml) under N_2, was treated with trimethyloxosulfonium iodide (1.75 g, 8.0 mmol) in small portions. A soln. of **18b** (1.0 g, 3.7 mmol) in DMSO (12 ml) was added dropwise at r.t., and the mixture was stirred for 19 h. It was poured onto cold H_2O (20 ml) and worked up. The crude product (0.96 g) was purified by FC (SiO_2, CH_2Cl_2), followed by recrystallization (EtOH): 0.63 g (60%) of **19a** as a white solid. M.p. 120–142°. IR ($CHCl_3$): 1300*s*, 1150*s*. ^{1}H-NMR: see *Table 2*. MS: 284 (34, M^+), 159 (24), 144 (38), 143 (78), 142 (100), 141 (62), 131 (44), 129 (29), 128 (79), 127 (42), 115 (69). Anal calc. for $C_{17}H_{16}O_2S$ (284.37): C 71.80, H 5.67, S 11.28; found: C 71.60, H 5.68, S 11.34.

*1a,2,3,7b-Tetrahydro-1a-(pyrrolidin-1-yl)-1*H*-cyclopropa[a]naphthalene* (**19b**). CH_2N_2, prepared from (*p*-toluenesulfonyl)methylnitrosamide (21.69 g, 0.10 mol) according to *De Boer* and *Backer* [27] in Et_2O (150 ml) and dried over KOH pellets at –30° for 3 h, was added slowly to a suspension of commercial (*Aldrich*) *1,2-dihydro-3-(pyrrolidin-1-yl)naphthalene* (**18c**; 0.48 g, 2.4 mmol) and CuCl [28] (0.24 g, 2.4 g · atom) in Et_2O (40 ml) at –30°. After stirring overnight at r.t., the mixture was evaporated to 100 ml, then filtered, and the filtrate was evaporated to dryness. The crude product was purified by FC (first with SiO_2, AcOEt, followed by SiO_2, AcOEt/MeOH 1:1) and afforded 244 mg (48%) of **19b** as a brown-transparent oil. IR ($CHCl_3$): 3072*w*, 3025*m*, 2975*s*, 2935*s*, 2880*s*, 2860*s*, 2830*s*, 1495*s*, 1467*s*, 1449*s*, 1435*m*, 1382*s*, 1362*m*, 1260*m*, 1195*m*, 1170*m*, 1140*m*, 1118*m*, 1052*w*, 640*m*. ^{1}H-NMR: see *Table 2*. MS: 213 (55, M^+), 212 (30), 198 (100).

*1a,2,3,7b-Tetrahydro-1a-(*N*-oxydopyrrolidin-1-yl)-1*H*-cyclopropa[a]naphthalene* (**19c**). To a soln. of **19b** (200 mg, 0.9 mmol) in MeOH (1.0 ml), H_2O_2 (30%, 0.3 ml; 2.9 mmol) was added dropwise at 0°. After 2 h of stirring at 0°, another portion of H_2O_2 (2.9 mmol) was added. The soln. was stirred at r.t. overnight. It was treated with $CHCl_3$ (2.0 ml), washed with a 10% soln. of $Na_2S_2O_3$ and sat. NaCl, and dried. The *N*-oxide **19c** (0.24 g) was not further purified. IR ($CHCl_3$): 3025*w*, 2970*m*, 1492*s*,1450*s*, 1217*s*, 640*s*. ^{1}H-NMR: see *Table 2*. MS: 229 (1, M^+), 211 (21), 196 (100), 182 (3), 168 (6), 157 (7), 141 (21), 128 (36), 115 (44)

*1-(1a,2,3,7b-Tetrahydro-1*H*-cyclopropa[a]naphthalen-1-yl)-*N*-methylpyrrolidinium Iodide* (**19d**) [29]. To a suspension of **19b** (260 mg, 1.2 mmol) in Et_2O (5.0 ml) and THF (5.0 ml), MeI (5.0 ml) was added at –25°. After 2.5 h of stirring at r.t., an oil separated from the orange mixture. The soln. was evaporated and gave 0.39 g (91%) of crude **19d** as a yellow solid. ^{1}H-NMR: see *Table 2*. MS: 355 (8, M^+), 228 (14), 213 (38), 198 (65), 196 (38), 143 (48), 142 (65), 141 (36), 129 (47), 128 (54), 127 (46), 115 (55), 91 (32), 69 (45), 57 (100).

6. *Generation and Interception of Cyclopropenes. Reaction of 1-Chloro-2,3-dihydro-1a*H*-cyclopropa[a]-naphthalene* (**5b**) *with Furan. 3,4-Benzo-8-chloro-2-oxatetracyclo[7.2.1.0^{2,7}.0^{2,8}]dodeca-3,10-diene* (**20**). To a soln. of diisopropylamide, prepared by reaction of *i*-PrNH (0.8 ml, 5.6 mmol) and MeLi (5.6 mmol) in Et_2O (5.0 ml), furan (2.0 ml) was added at –78° and, dropwise, **4b** (0.30 g, 1.4 mmol) in Et_2O (6.0 ml). After stirring for 12 h at –25°, the mixture was decomposed with ice-water and worked up. The crude product was purified by FC (SiO_2, toluene/petroleum ether 1:1) to yield **20** (64%) as a brown-clear oil. IR: 3075*w*, 3015*s*, 2940*s*, 2865*m*, 1607*w*, 1498*s*, 1455*s*, 1440*m*, 1302*s*, 1096*m*, 1081*m*, 1056*m*, 1042*m*, 1030*s*, 977*m*, 960*m*, 950*s*, 915*s*, 890*m*, 882*m*, 869*m*, 855*s*, 710*vs*. ^{1}H-NMR (360 MHz, $CDCl_3$) [28]: 2.05–2.13 (*m*, 2 H-C(6)); 2.72–2.82 (*m*, H–C(5)); 2.87–2.92 (*t*, ^3J = 5, H–C(7)); 2.95–3.07 (*m*, H–C(5)); 4.92–5.0 (*m*, H–C(1), H–C(9)); 6.77–7.83 (*m*, 1 H);

7.10–7.25 (*m*, 5 H). MS: 244/246 (2, 3:1, M^+), 215, 217 (75), 209 (22), 181 (82), 180 (73), 179 (100), 178 (50), 166 (35), 165 (69),152 (28).

Generation and Interception of **5a**. *1a,2,3,7b-Tetrahydro-7b-(methylthio)-1*H*-cyclopropa[*a*]naphthalene* (**15d**) *and Derivatives* **15e–h**. To a soln. of methyl thiolate, prepared from MeSH (0.68 g, 14.2 mmol) and *t*-BuOK (3.65 g, 32.6 mmol) in THF (22 ml) and DMSO (22 ml) and 18-crown-6 (40 mg) at –30°, **4a** (0.39 g, 2.2 mmol) in THF (2.2 ml) and DMSO (6.6 ml) was added dropwise at 0°. After 3.5 d of stirring at r.t., the mixture was poured into cold H_2O (150 ml) and worked up as usual. FC (SiO_2, $CHCl_3$/hexane 1:5) of the crude product afforded **15d** (0.35 g, 84%) as colorless oil. IR ($CHCl_3$): 3070*w*, 3020*m*, 2920*s*, 2860*m*, 1602*w*, 1485*s*, 1448*s*, 1437*m*, 1424*m*, 1270*m*, 1180*w*, 1035*s*, 970*m*, 775*s*. ^{1}H-NMR: see *Table 2*. ^{13}C-NMR: 15.2 (CH_3S); 19.5 (C(1)); 20.5 (C(2)); 26.7 (C(3)); 27.6 (C(7b)); 27.8 (C(1a)); 125.5 (C(5)); 126.6 (C(6)); 128.1 (C(4)); 128.8 (C(7)); 134.7 (C(3a)); 138.0 (C(7a)). MS: 190 (39, M^+), 175 (67), 162 (66), 143 (73), 142 (63), 141 (72), 128 (100), 115 (97).

*1a,2,3,7b-Tetrahydro-7b-(methylsulfinyl)-1*H*-cyclopropa[*a*]naphthalene* (**15e**) *and 1a,2,3,7b-Tetrahydro-7b-(methylsulfonyl)-1*H*-cyclopropa[*a*]naphthalene* (**15f**). To a soln. of **15d** (0.27 g, 1.4 mmol) in $CHCl_3$ (1 ml), *m*-chloroperbenzoic acid (55%; 0.45 g, 1.4 mmol) in $CHCl_3$ (4 ml) was added at –15°. After 2 h at –15°, the precipitate was filtered, and the filtrate was washed with aq. Na_2CO_3 (10%). After usual workup, the crude product was purified by CC (SiO_2, AcOEt) to yield **15e** as two diastereoisomers (49% and 9%) and **15f** (13%) as clear transparent oils.

Data of **15e** (major isomer): IR ($CHCl_3$): 3070*w*, 3020*w*, 3000*w*, 2940*m*, 2860*w*, 1490*m*, 1455*w*, 1444*m*, 1418*m*, 1406*w*, 1292*w*, 1050*s*, 1035*s*, 1023*s*, 1018*s*, 960*m*, 779*m*, 648*m*. ^{1}H-NMR: see *Table 1*. MS: 206 (1, M^+), 143 (100), 142 (40), 128 (88), 115 (20).

Data of **15e'** (minor isomer): IR ($CHCl_3$): 3000*s*, 2940*m*, 2860*w*, 1642*w*, 1487*m*, 1450*m*, 1443*m*, 1045*s*, 1035*s*, 1017*s*. ^{1}H-NMR: see *Table 1*. MS: 206 (1, M^+), 143 (100), 142 (40), 128 (88), 115 (20).

Data of **15f**: IR ($CHCl_3$): 2940*w*, 1490*w*, 1452*w*, 1440*w*, 1300*s*, 1272*w*, 1183*w*, 1140*s*, 1121*m*, 960*w*, 940*w*, 795*m*. MS: 222 (25, M^+), 143 (100), 128 (68), 115 (24).

*Dimethyl(1a,2,3,7b-Tetrahydro-1*H*-cyclopropa[*a*]naphthalen-7b-yl)sulfonium Tetrafluoroborate* (**15g**). To **15d** (0.31 g, 1.6 mmol) in CH_2Cl_2 (35 ml), trimethyloxonium tetrafluoroborate (0.52 g, 3.5 mmol) was added at 0°. After 1 h of stirring at 0° and 14 h at r.t., the mixture was filtered and the filtrate evaporated. Crude **15g** (0.52 g) was isolated and characterized by ^{1}H-NMR (*Table 1*).

1a,2,3,7b-Tetrahydro-1-exo-*(phenylthio)-1*H*-cyclopropa[*a*]naphthalene* (**21a**). To phenylthiolate, prepared from thiophenol (2.3 ml, 22.4 mmol) and *t*-BuOK (4.91 g, 43.8 mmol) in THF (47 ml) and DMSO (47 ml), 18-crown-6 (50 mg) and then dropwise, at –13°, a soln. of **4a** (0.78 g, 4.4 mmol) in THF (4.4 ml) and DMSO (13.1 ml) were added. After 3 d of stirring at r.t., the mixture was poured into cooled H_2O (265 ml) and worked up. The crude product was purified by FC (SiO_2, $CHCl_3$/hexane 1:5) and gave **21a** (1.02 g, 92%) as colorless crystals. M.p. 78° (from MeOH). IR ($CHCl_3$): 3080*w*, 3068*w*, 3025*m*, 2935*m*, 2862*m*, 1586*m*, 1586*m*, 1495*s*, 1482*s*, 1461*m*, 1440*m*, 1093*m*, 1025*m*, 800*w*, 690*s*. ^{1}H-NMR: 1.44 (*dd*, ^3J = 5.0, 9.0, 1 H); 1.53 (*t*, ^3J = 6.0, 1 H); 1.94–2.02 (*m*, 1 H); 2.02–2.10 (*m*, 1 H); 2.20–2.30 (*m*, 1 H); 2.54–2.66 (*m*, 1 H); 2.70–2.80 (*m*, 1 H); 7.06–7.26 (*m*, 8 H); 7.90–7.96 (*m*, 1 H). MS: 252 (35, M^+), 175 (15), 143 (100), 128 (46), 115 (27).

Crystallographic Data of **21a**. Data were collected at r.t. on a *Philips PW1100* diffractometer (Mo$K\alpha$). The structure was solved by direct method (MULTAN 80) and refined by full-matrix least-squares analysis (XRAY-76) [31]. All coordinates of the H-atoms were calculated. The structure can be considered as slightly disordered. Most of the atoms are affected by important atomic displacement parameters that led to a poor number of observed reflections and to a relatively high value of the final *R* factor ($R = \omega R = 0.10$; $\omega = 1$; for 631 observed reflections with $|Fo| > 4\sigma(Fo)$ and $|Fo| > 8.0$). The crystals (MeOH) are orthorhombic, $a = 20.297(4)$, $b = 8.0745(14)$, $c = 8.4760(17)$ Å; space group $Pca2_1$, $Z = 4$, $\mu = 0.203$ mm^{-1}, $F_{000} = 536$, $d_c = 1.21$ g · cm^{-3}. Crystallographic data have been deposited with the *Cambridge Data Centre*, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW, England.

*1a,2,3,7b-Tetrahydro-1-(methylseleno)-1*H*-cyclopropa[*a*]naphthalene* (**21b**) *and 1a,2,3,7b-Tetrahydro-7b-(methylseleno)-1*H*-cyclopropa[*a*]naphthalene* (**15h**) [32]. To Se (0.66 g, 8.4 g · atom) in THF (14 ml), MeLi, 1.6M in Et_2O (6.5 ml, 10.4 mmol), was added dropwise at 10°. After successive addition of *t*-BuOK (1.0 g, 8.9 mmol), DMSO (15 ml), and 18-crown-6 (0.01 g), the mixture was cooled to 0°, and a soln. of **4a** (0.30 g, 1.7 mmol) in THF (1.7 ml) and DMSO (5.0 ml) was added dropwise. The temp. was raised to r.t. within 3 h, and stirring was continued for 24 h. The mixture was poured into cold water (150 ml) and worked up. The crude product was purified by FC (SiO_2, $CHCl_3$/hexane 1:3) and gave **15h** (10.4 mg, 3%) and **21b** (70 mg, 17%).

Data of **15h** (yellow oil): IR ($CHCl_3$): 3075*w*, 3010*w*, 2930*s*, 1472*m*, 1448*m*, 1270*w*, 1030*m*, 770*s*, 663*m*. ^{1}H-NMR: see *Table 1*. MS: 236/238 (3, 1:2, M^+), 221, 223 (5), 144 (18), 143 (43), 142 (29), 141 (45), 129 (59), 128 (100), 127 (23), 115 (82).

Data of **21b** (colorless oil): IR ($CHCl_3$): 3020*m*, 2930*s*, 2860*m*, 1490*s*, 1460*m*, 1445*m*, 1430*w*, 1420*w*, 1272*w*, 1220*w*, 1212*m*, 1200*w*, 1135*m*, 978*w*, 800*m*, 790*m*, 780*m*. ^{1}H-NMR: 1.72–1.83 (*m*, 1 H); 1.83–1.93 (*m*, 1 H); 2.13 (*s*, 3 H); 2.18–2.30 (*m*, 2 H); 2.40–2.46 (*m*, 1 H); 2.47–2.57 (*m*, 1 H); 2.60–2.70 (*m*, 1 H); 7.05–7.08 (*m*, 1 H); 7.08–7.22 (*m*, 2 H); 7.32–7.35 (*m*, 1 H). MS: 236/238 (weak, 1:2, M^+), 143 (100), 128 (80), 115 (55).

Reduction of **15a**. *1a,2,3,7b-Tetrahydro-7b-(phenylthio)-1*H*-cyclopropa[a]naphthalene* (**15b**). To **15a** (1.44 g, 5.1 mmol) in toluene (10 ml), a 1M soln. of DIBAH in toluene (26 ml, 26 mmol) was added dropwise and heated to reflux for 3.5 d. After cooling to 0°, EtOH (2.0 ml) was added slowly, followed by H_2O (8 ml) and 6N HCl (4.0 ml). After usual workup, the product was purified by FC (SiO_2, CH_2Cl_2) and yielded 1.20 g (93%) of **15b** as colorless oil. IR ($CHCl_3$): 3070*w*, 3010*w*, 2930*m*, 2860*m*, 1585*m*, 1480*s*, 1450*m*, 1440*m*, 1035*m*, 1025*m*, 780*m*, 695*s*. ^{1}H-NMR: see *Table 2*. MS: 252 (50, M^+), 219 (45), 175 (19), 161 (15), 143 (60), 142 (32), 141 (56), 129 (29), 128 (60), 127 (26), 115 (100), 91 (78).

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