Synthesis of 1,2,3,4-Tetrahydro-1,2-dimethylidenenaphthalene: A Reactive s-*cis*-Butadiene Undergoing Highly Chemo- and Regioselective Cyclodimerization

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1,2,3,4-Tetrahydro-1,2-dimethylidenenaphthalene **11** has been derived in three steps from tetralone. In the condensed state and at $-80°$, it undergoes a highly chemo- and regioselective cyclodimerization to give 3,3′,4,4′-tetrahydro-2-methylidenespiro[naphthalene-1(2*H*),2′(1′*H*)-phenanthrene] (**14**), the structure of which has been established by single-crystal X-ray-diffraction analysis. Dimer **14** undergoes cycloreversion to diene **11** under flash-pyrolysis conditions. The reaction of diene **11** with SO_2 occurs without acid promoter at $-80°$ and gives a mixture of (±)-1,4,5,6-tetrahydronaphth[1,2-*d*][1,2]oxathiin 2-oxide (**23**; a single sultine), 1,3,4,5-tetrahydronaphtho[1,2-*c*]thiophene 2,2-dioxide (**25**), and dimer **14**. The high reactivity of diene **1** in its *Diels-Alder* cyclodimerization and its highly regioselective hetero-*Diels-Alder* addition with SO_2 can be interpreted in terms of the formation of relatively stable diradical intermediates or by concerted processes with transition states that can be represented as diradicaloids.

Introduction. – In a previous report, we described the reactions of sulfur dioxide to 2-phenylbuta-1,3-diene (**1**), 2-(β-naphthyl)- (**2**) and 2-(α-naphthyl)buta-1,3-diene (**3**) [1]. In the absence of acid promoter, **1** undergoes the hetero-*Diels-Alder* addition with SO_2 at $-80°$ to give small amounts of 4-phenylsultine **4** exclusively (*Scheme 1*). Above $-40°$, the concurrent cheletropic addition occurs to give sultine **5** at the expense of sultine **4**. In the presence of an acid promoter such as CF_3COOH, the hetero-*Diels-Alder* addition $\mathbf{1} + SO_2 \rightarrow \mathbf{4}$ is much faster. Under these conditions and at $-40°$, **4** is isomerized into the regioisomeric sultine **5** concurrently with the formation of sulfolene **6**. Similarly, 2-(β-naphthyl)buta-1,3-diene (**2**) undergoes a regioselective hetero-*Diels-Alder* addition of SO_2 at $-80°$ in the presence of CF_3COOH to afford sultine **7**. Above $-50°$, **7** undergoes the cycloreversion to diene **2** and SO_2, which then react in the cheletropic mode to give sulfolene **9**. Sultine **7** could not be isomerized to regioisomeric sultine **8**, in contrast with what is observed for the reactions of 2-phenylbuta-1,3-diene (**1**). Surprisingly, 2-(α-naphthyl)buta-1,3-diene (**3**) does not add to SO_2 in the hetero-*Diels-Alder* mode and undergoes a relatively slow cheletropic addition above $-30°$ to give sulfolene **10**. Because of the differences in behavior between dienes **1**–**3** toward SO_2, which probably originate in differences in their ground-state conformations, we decided to prepare 1,2-dimethylidene-1,2,3,4-tetrahydronaphthalene (**11**) that maintains a quasi-planarity of the benzene and s-*cis*-

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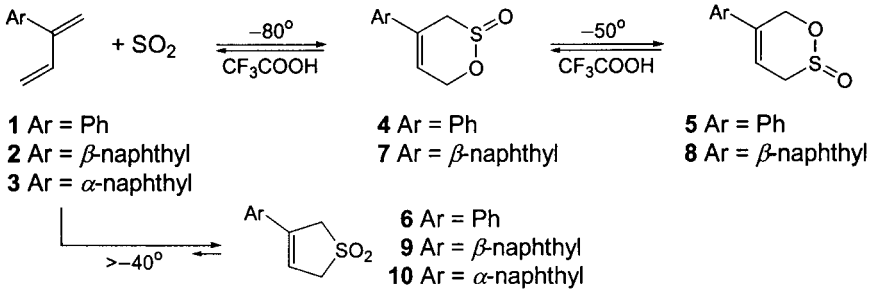
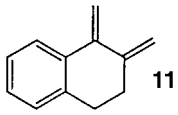
Scheme 1

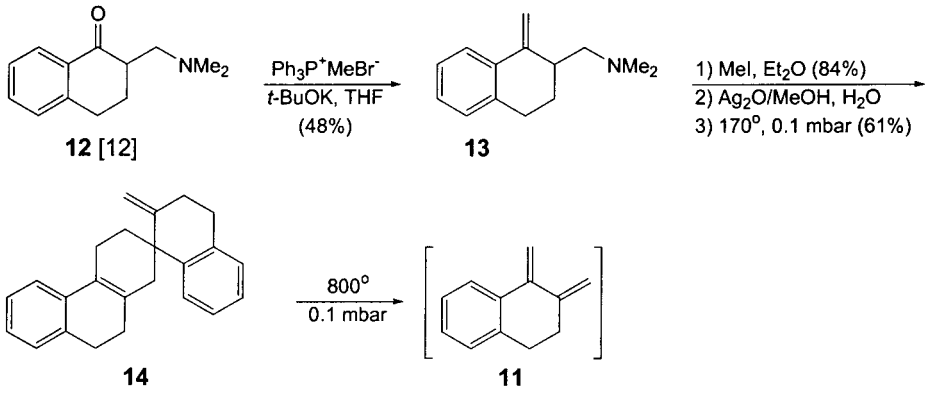


butadiene moieties. We have found that diene **11** undergoes very fast reactions with SO_2 at $-80°$ in the absence of acidic promoter to give mixtures of a single regioisomeric sultine and the corresponding sulfolene, concurrently with its *Diels-Alder* cyclodimerization to a single cyclodimer. The latter undergoes cycloreversion to diene **11** under high-vacuum flash-pyrolysis conditions. A thermochemical calculation indicates that diradical intermediates might be involved in cycloadditions of diene **11**. The latter as well as other hypotheses explain the high chemo- and regioselectivity of the cyclodimerization of diene **11** and of its hetero-*Diels-Alder* addition with SO_2.



Results and Discussion. – *Synthesis. Mannich* condensation of α-tetralone with Et_2NH_2Cl and formaldehyde provided **12** in 60% yield [2]. *Wittig* olefination of **12** with methyl(triphenyl)phosphonium bromide and *t*-BuOK gave **13** in 48% yield. Amine quaternization of **13** with MeI, and subsequent *Hoffmann* elimination with Ag_2O in aqueous MeOH [3] furnished the cyclodimer **14** of diene **11** in 51% yield (*Scheme 2*). The structure of **14** was established by single-crystal X-ray-diffraction studies (*Fig.* and *Table* in *Exper. Part*).

Scheme 2



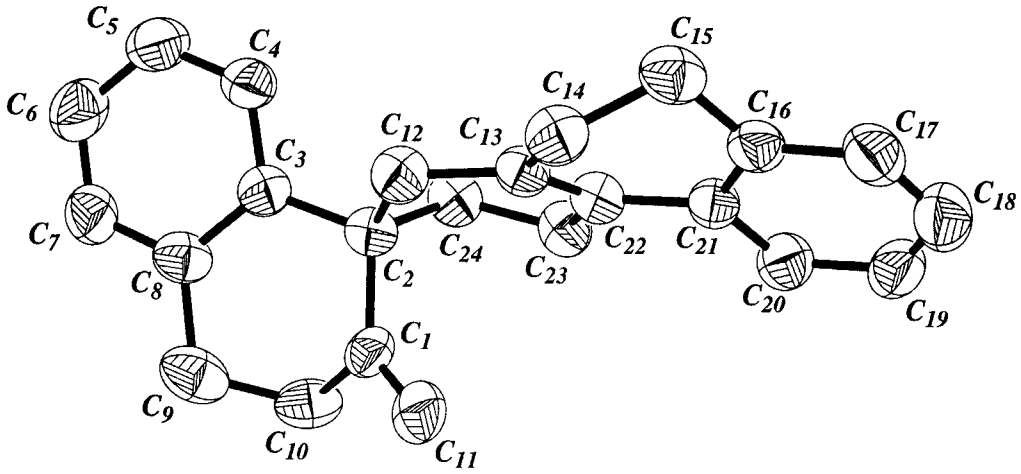
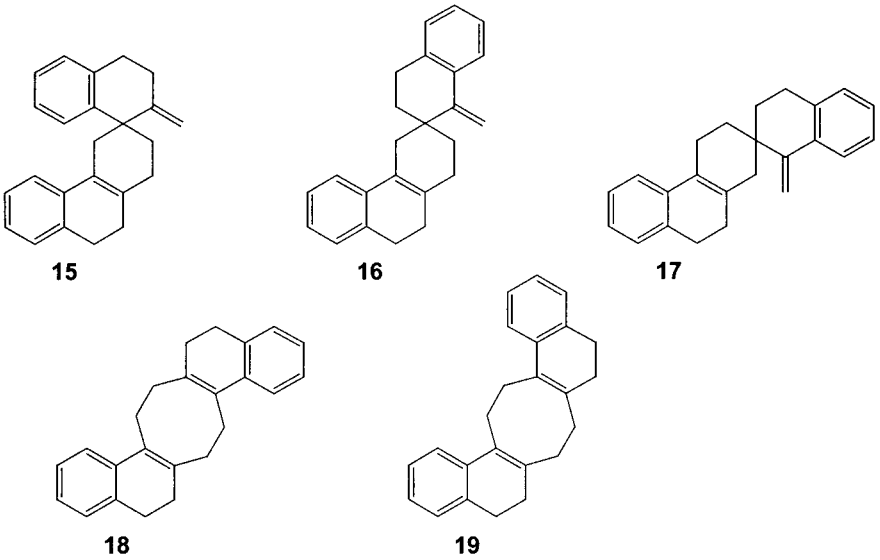
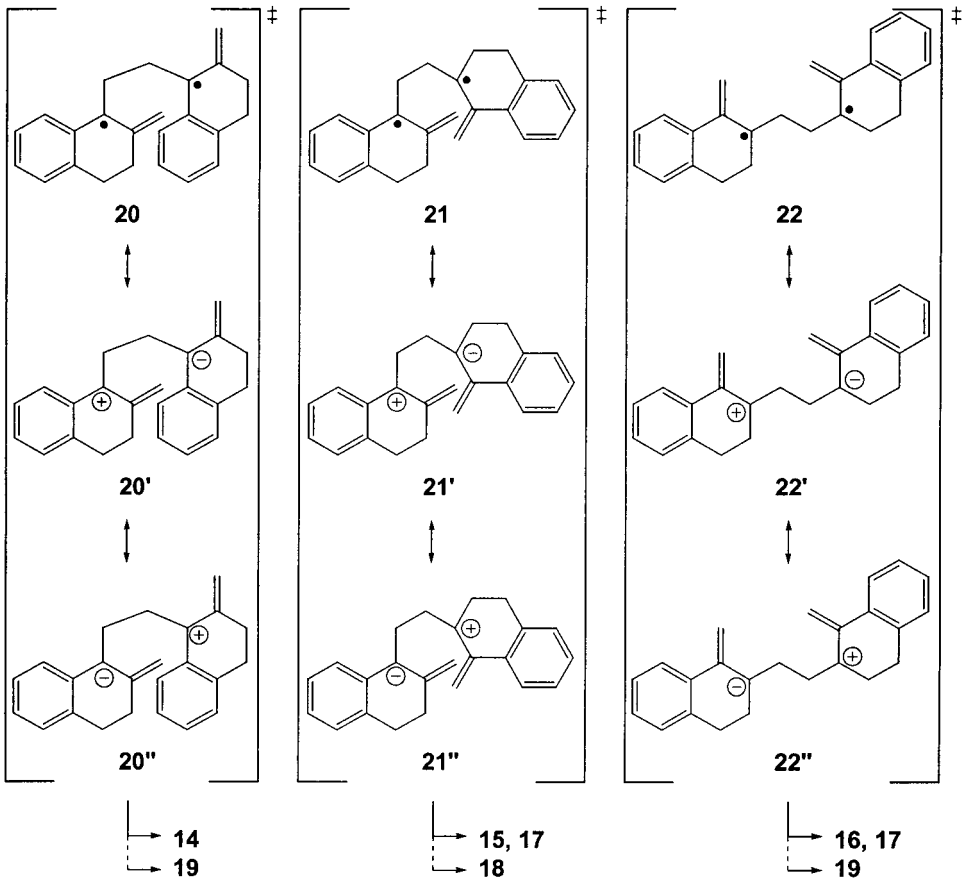


Figure. *ORTEP Representation of Compound* **14**. The C-atoms are represented at the 50% probability level; arbitrary numbering.

The Chemo- and Regioselective Cyclodimerization of 1,2,3,4-Tetrahydro-1,2-dimethylidenenaphthalene. No trace of isomeric cyclodimers **15**, **16**, **17**, **18**, or **19** could be detected in the crude reaction mixture. This demonstrates the high chemoselectivity ([4 + 2] rather than [4 + 4] or [2 + 2] cycloadditions) and the high regioselectivity of the *Diels-Alder* cyclodimerization. The latter can be explained (PMO theory [4]) considering the eigenvectors of the LUMO and HOMO of 2-phenylbutadiene [5] that are the largest at C(1) of the buta-1,3-diene moiety. Alternatively (*Scheme 3*), the [4 + 2] cyclodimerization of **11** could involve the formation of a 1,4-diradical intermediate **20** [6], which cyclizes into the most stable product, the cyclohexene



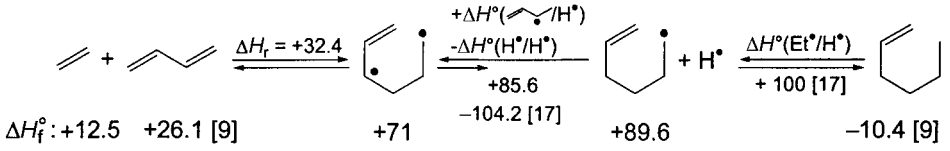
Scheme 3. *Diradical Models for* Diels-Alder *Transition Structures*



derivative **14**. Diradical intermediate **20** could, in fact, profit from some electron exchange, thus being a diradicaloid [7] **20** ↔ **20′**, which is expected (allyl + benzyl conjugation, twice) to be significantly more stable than isomeric diradicaloids **21** ↔ **21′** (allyl + benzyl + allyl conjugation) and **22** ↔ **22′** (allyl conjugation, twice) [8].

An estimate for the heat of reaction **11** + **11** ⇌ **20** (diradical) is given by correcting the heat of equilibrium ethylene + butadiene ⇌ hex-5-ene-1,4-diyl diradical by the allylic-conjugation-stabilization effect and twice the benzylic-conjugation-stabilization effect on radicals due to the diphenyl substitution (*Scheme 4*). Taking − 11 kcal/mol for the vinyl substitution effect on the stability of a secondary radical (ΔH^0(i-Pr$^{\bullet}$/H$^{\bullet}$) = 96.3 kcal/mol *vs.* ΔH^0(CH_2=CH−C$^{\bullet}$H−Me/H$^{\bullet}$) = 85.6 kcal/mol) and − 12 kcal/mol for the Ph substitution effect on the stability of a radical (ΔH^0($CH_3CH_2^{\bullet}$/H$^{\bullet}$) = 100 kcal/mol *vs.* ΔH^0($PhCH_2^{\bullet}$/H$^{\bullet}$) = 88 kcal/mol [8]), one obtains for ΔH_r^0 (**11** + **11** ⇌ **20**) = 32.4 − 33 = − 0.6 kcal/mol. The entropy of condensation ΔS_r^0 (**11** + **11** ⇌ **20**) = − 41 kcal K^{-1} mol^{-1} (translation entropy, no degree of freedom for the rotations in **20**!), thus giving an estimated ΔG_r^0 (**11** + **11** ⇌ **20**) ≤ 12 kcal/mol at 25°. This

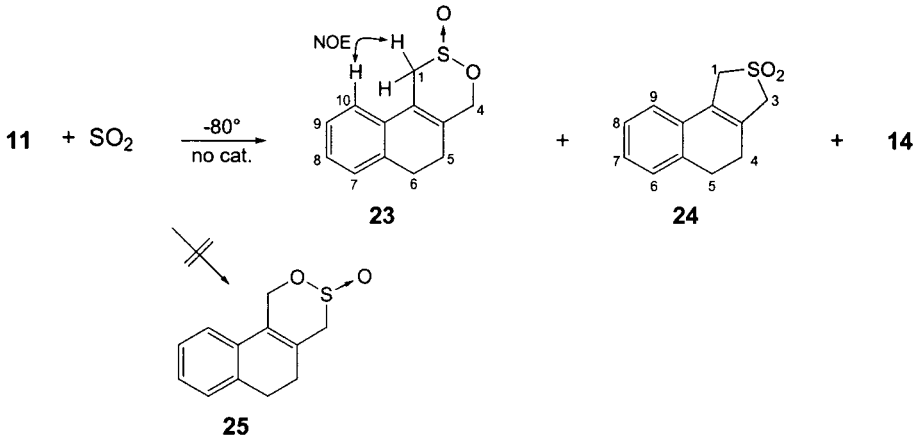
Scheme 4. *Thermochemical Analysis* (in kcal/mol)



thermochemical analysis demonstrates that diradical **20** might well be an intermediate on the hypersurface of the *Diels-Alder* cyclodimerization of diene **11** and explains its instability in dilute solution at $-80°$ (see below).

The Hetero-Diels-Alder *Addition with SO_2*. The hetero-*Diels-Alder* addition of SO_2 to diene **11** occurs at $-80°$ without catalyst to give sultine **23**. The formation of sulfolene **24** and of the diene cyclodimer **14** takes place concomitantly at this temperature (*Scheme 5*). No trace of isomeric sultine **25** could be detected after 15 h at $-80°$. Instead, diene **11** was completely converted into a 100:15:40 mixture **23**/**24**/dimer **14**. This demonstrates that the energy barrier for the isomerization **23** $\rightleftharpoons$ **25** is higher than both the energy barriers of the cheletropic addition **11** + SO_2 → **24** and of the cyclodimerization **11** + **11** → **14**. The extremely high reactivity of diene **11** compared with that of the other 2-aryl-substituted buta-1,3-dienes **1**–**3** can be attributed to the nearly s-*cis*-conformation of its diene moiety and its coplanarity with the aromatic ring. The structure of **23** was inferred from its 2D-NOESY ^{1}H-NMR spectrum that showed a significant cross-peak for the signal pairs H_a–C(1) (3.73 ppm, ^2J = 16.6 Hz)/H–C(10) (7.05 ppm) and H_e–C(1) (3.23 ppm, ^2J = 16.6 Hz)/H–C(10). Because of several long-range-coupling constants involving the sultine protons H–C(1) and H–C(4), and those (H–C(5), H–C(6)) of the cyclohexa-1,3-diene ring, complicated *multiplets* (in fact, broad *doublets*) were observed for the four signals of H–C(1) and H–C(4). This does not allow one to comment on the conformation of sultine **23**. Distinction between sultines **23** and its isomeric sulfolene **24** is obvious from their ^{1}H-NMR spectra, as the former do not share a mirror plane of symmetry.

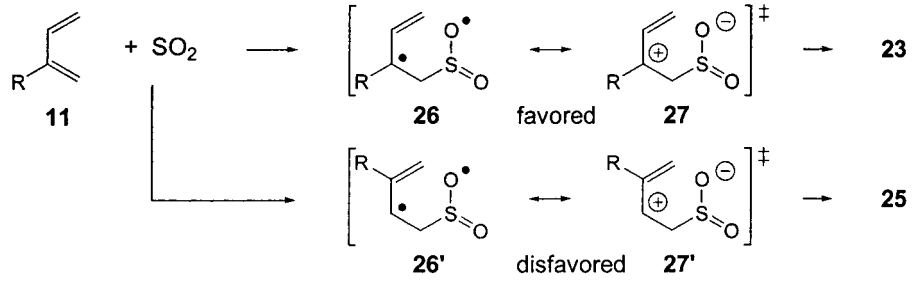
Scheme 5



The PMO theory [4][10] predicts that the hetero-*Diels-Alder* additions of SO_2 to 2-substituted buta-1,3-dienes should be regioselective under conditions of kinetic control and give preferentially the corresponding 4-substituted sultines, as observed for the reactions of isoprene [11], 2-(triethylsilyl)buta-1,3-diene, and 2-arylbuta-1,3-dienes **1**–**3** [1]. The theory of the diradicaloids [7] leads to the same prediction when one assumes the C–S bond of the sultines to be formed earlier than the C–O bond in the transition states. This hypothesis will be confirmed by kinetic and thermodynamic deuterium isotope effects [12]. Accordingly (*Scheme 6*), the hetero-*Diels-Alder* addition **11** + SO_2 → **23** should be preferred over **11** + SO_2 → **25** under conditions of kinetic control as the stabilizing Ph group [8] operates in **26** → **26′** and not in **27** ↔ **27′** (*Scheme 6*).

The model of the diradicaloids of the transition structures of the hetero-*Diels-Alder* additions of SO_2 predicts also that these reactions are catalyzed by *Brønsted* and *Lewis*

Scheme 6



acids, as observed, and as predicted also by high-level quantum calculations of these reaction hypersurfaces [13][14]. It can be applied to predict the regioselectivity of the hetero-*Diels-Alder* additions of SO_2 to 1-substituted buta-1,3-dienes. In agreement with experiments [15] and high-level quantum calculations [16], these cycloadditions generate 6-substituted sultines, rather than their 3-substituted isomers under conditions of kinetic control.

Conclusions. – The very reactive 1,2,3,4-tetrahydro-1,2-dimethylidenenaphthalene (**11**) has been derived from α-tetralone. It undergoes very fast chemo- and regioselective cyclodimerization to give a single *Diels-Alder* cycloadduct **14**. Toward SO_2, diene **11** is much more reactive than other 2-arylbuta-1,3-dienes. It adds to SO_2 in the hetero-*Diels-Alder* mode without acidic promoter at $-80°$ to give 1,4,5,6-tetrahydronaphth[1,2-*d*][1,2]oxathiin 2-oxide (**23**, regioselectivity similar to the reactions of SO_2 with the other 2-arylbuta-1,3-dienes **1** and **2**), together with the corresponding sulfolene **24** and the *Diels-Alder* cyclodimer **14**. Sultine **23** could not be isomerized to its regioisomer **25** before its complete conversion to **24** and **14**. If the hetero-*Diels-Alder* additions of SO_2 are concerted reactions, their regioselectivity under kinetic control can be predicted by the diradicaloid model assuming that the C–S bonds in sultines are formed earlier than the C–O bonds. Alternatively, the cycloadditions could involve the formation of diradical intermediates; the relative stability of these, given by the known substituent effects on radical stability, defines the

regioselectivity of the reactions under conditions of kinetic control. The same applies for the cyclodimerization of diene **11**.

We thank the *Swiss National Science Foundation* (Grant No. 20-63677.001) and the *Office Fédéral de l'Education et de la Science* (COST D13/010/00), the *Fonds Herbette* (Lausanne) for financial support. We are grateful also to Mr. *R. Estoppey*, *M. Rey*, and *F. Sepulveda* for their technical help.

Experimental Part

General. See [1][16][17].

1,2,3,4-Tetrahydro-1,2-dimethylidenenaphthalene (**11**). The spiro compound **14** (0.5 g, 1.6 mmol) in a 10-ml *Pyrex* flask connected to a quartz tube was placed in a oven and mounted on a trap connected to a vacuum pump. The oven was heated to 800°, and the *Pyrex* flask was heated (electric heating mantle) to 300° under 0.1 mbar. The product of pyrolysis was condensed in the trap cooled by a liq. N_2 bath. Yield: 125 mg (25%), a yellowish oil, which dimerized instantly at 20°. Thus, a soln. of **11** had to be prepared by adding cold solvent to frozen **11** in the trap. Yellowish oil. IR (film): 2930, 2845, 2360, 1485, 1455, 1260, 890, 775, 755, 715. ^{1}H-NMR (400 MHz, $CDCl_3$): 7.72 (*m*, 1 arom. H); 7.54–7.12 (*m*, 3 arom. H); 5.61 (br. *s*, 1 H, C(1)=CH_2); 5.55 (br. *s*, 1 H, C(1)=CH_2); 5.44 (br. *s*, 1 H, C(2)=CH_2); 4.96 (*m*, 1 H, C(1)=CH_2)); 2.89 (*dd*, ^3J(3,4) = 6.4, 6.4, CH_2(4)); 2.58 (*dd*, ^3J(3,4) = 6.3, 6.4, CH_2(3)). ^{13}C-NMR (100.6 MHz, $CDCl_3$): 146.5, 142.9, 138.0, 134.6 (4*s*); 129.0 (*d*, ^1J(C,H) = 158, 1 arom. C); 127.9 (*d*, ^1J(C,H) = 160, 1 arom. C); 126.7 (*d*, ^1J(C,H) = 160, 1 arom. C); 124.3 (*d*, ^1J(C,H) = 162, 1 arom. C); 108.6 (*t*, ^1J(C,H) = 157, CH_2=); 107.5 (*t*, ^1J(C,H) = 158, CH_2=); 32.6 (*t*, ^1J(C,H) = 125); 31.7 (*t*, ^1J(C,H) = 129). CI-MS (NH_3): 157 (100, $[M+1]^+$), 141 (77), 128 (51), 115 (63), 102 (12), 89 (13).

N,N-*Dimethyl(1,2,3,4-tetrahydro-1-methylidenenaphthalen-2-yl)methanamine* (**13**). In a flame-dried 100-ml three-necked flask, $Ph_3P^+MeBr^-$ (17.8 g, 50 mmol) was suspended in THF (30 ml) under N_2. *t*-BuOK (5.6 g, 50 mmol) and 18-crown-6 (10 mg, 0.04 mmol) were added to the suspension, and the mixture was stirred for 15 min at 25°, then cooled to 0°. A soln. of **12** [2] (9 g, 44 mmol) in dry THF (20 ml) was slowly added, and the mixture was stirred at 25° for 4 h. The precipitate was filtered off, the solvent was evaporated under reduced pressure, and the residue was extracted several times with Et_2O and light petroleum ether. The combined org. extracts were evaporated, and the residue was purified by bulb-to-bulb distillation (180°/0.1 mbar): 4.3 g (48%) of **13**. Dense, pale yellow oil. UV (MeCN): 249 (11900), 213 (16300). IR (film): 2940, 2765, 1680, 1625, 1455, 1265, 1035, 885, 775, 735, 690. ^{1}H-NMR (400 MHz, C_6D_6): 7.67 (*m*, 1 arom. H); 7.10 (*m*, 2 arom. H); 7.00 (*m*, 1 arom. H); 5.05 (br. *s*, 1 H, CH_2=); 5.57 (br. *s*, 1 H, CH_2=); 2.87 (*ddd*, ^2J = 16.8, ^3J(3,4) = 9.8, 5.0, H–C(4)); 2.68 (*dddd*, ^3J(2,HCN) = 10.2, 5.9, ^3J(2,3) = 10.1, 5.3,H–C(2)); 2.62 (*ddd*, ^2J = 16.8, ^3J(3,4) = 5.3, 5.2, H–C(4)); 2.41 (*dd*, ^2J = 12.2, ^3J(2,HCN) = 10.2, 1 H, CH_2N); 2.16 (*dd*, ^2J = 12.2, ^3J(2,HCN) = 5.9, 1 H, CH_2N); 2.07 (*s*, Me_2N); 1.95 (*m*, CH_2(3)). ^{13}C-NMR (100.6 MHz, $CDCl_3$): 145.9, 136.5, 134.4 (3*s*); 128.9 (*d*, ^1J(C,H) = 157, 1 arom. C); 127.5 (*d*, ^1J(C,H) = 161, arom. C); 125.9 (*d*, ^1J(C,H) = 153, arom. C); 124.8 (*d*, ^1J(C,H) = 163, arom. C); 108.8 (*t*, ^1J(C,H) = 157, *C*=C(1)); 62.4 (*t*, ^1J(C,H) = 131, CH_2N); 45.8 (*q*, 2 C, ^1J(C,H) = 133, Me_2N); 38.8 (*d*, ^1J(C,H) = 124, C(2)); 26.4 (*t*, ^1J(C,H) = 129, C(4)); 25.9 (*t*, ^1J(C,H) = 127, C(3)). CI-MS (NH_3): 202 (100, $[M+1]^+$), 159 (20), 128 (30), 115 (45), 102 (10), 84 (70).

N,N,N-*Trimethyl(1,2,3,4-tetrahydro-1-methylidenenaphthalen-2-yl)methanammonium Iodide*. A mixture of MeI (2.60 g, 18 mmol, 1.1 ml) and **13** (1.6 g, 8 mmol) in dry Et_2O (20 ml) was stirred overnight at 25°. The white solid was collected and washed with Et_2O to afford 2.3 g (84%) of a white solid. M.p. 165–166°. UV (MeCN): 245 (18400), 214 (16700). IR (film): 3000, 2935, 1625, 1485, 1440, 1410, 915, 740, 705, 465. ^{1}H-NMR (400 MHz, $CDCl_3$): 7.42 (*m*, 1 arom. H); 7.25 (*m*, 1 arom. H); 7.20 (*m*, 1 arom. H); 7.11 (*m*, 1 arom. H); 5.48 (br. *s*, 1 H, C(1)=CH_2); 5.32 (br. *s*, 1 H, C(1)=CH_2); 4.25 (*dd*, ^2J = 13.1, ^3J(2,HCN) = 2.9, HCN); 3.43 (*s*, Me_3N); 3.37 (*m*, H–C(2)); 3.22 (*dd*, ^2J = 13.1, ^3J(2,HCN) = 10.2, 1 H, CH_2N); 2.93 (*m*, CH_2(4)); 2.31 (*dm*, ^2J = 13.8, H–C(3)); 2.11 (*m*, H–C(3)). ^{13}C-NMR (100.6 MHz, $CDCl_3$): 145.3, 135.0, 132.6 (3*s*); 129.4 (*d*, ^1J(C,H) = 160, arom. C); 128.9 (*d*, ^1J(C,H) = 161, arom. C); 126.8 (*d*, ^1J(C,H) = 160, arom. C); 125.7 (*d*, ^1J(C,H) = 156, arom. C); 112.8 (*t*, ^1J(C,H) = 158, C=C(1)); 67.8 (*t*, ^1J(C,H) = 143, CH_2N); 54.3 (*q*, ^1J(C,H) = 144, Me_3N); 36.9 (*d*, ^1J(C,H) = 130, C(2)); 28.2 (*t*, ^1J(C,H) = 131, C(4)); 24.5 (*t*, ^1J(C,H) = 127, C(3)). Anal. calc. for $C_{15}H_{22}NI$ (343.25): H 6.46, C 52.49; found: H 6.36, C 52.10.

*3,3′,4,4′-Tetrahydro-2-methylidenespiro[naphthalene-1(2*H*),2′(1′*H*)-phenanthrene]* (**14**). Ag_2O (4.4 g, 19 mmol) was added to a soln. of *N,N,N*-trimethyl(1,2,3,4-tetrahydro-1-methylidenenaphthalen-2-yl)methanammonium iodide (5.9 g, 17 mmol) in MeOH/H_2O 3:1 (70 ml), and the suspension was stirred for 4 h at 25°. The mixture was filtered (*Celite*), and the solvent was evaporated *in vacuo* at 35°. The residue was distilled *in vacuo* (170–175°/0.1 mbar): 1.6 g (61%) of **14** as a pale yellow oil, which was crystallized from dry MeOH to

give a white solid. M.p. 92–93°. UV (MeCN): 271 (13900), 214 (20600). IR (film): 3010, 2900, 2830, 1650, 1485, 1450, 1430, 905, 765, 755, 695, 670, 615, 475. ^{1}H-NMR (400 MHz, $CDCl_3$): 7.77–7.10 (*m*, 8 arom. H); 4.93 (br. *s*, H–C(2)); 4.64 (br. *s*, H–C=C(2)); 2.89 (*m*, 5 H); 2.60 (*m*, 1 H); 2.32 (*m*, 6 H); 2.03 (*m*, 2 H). ^{13}C-NMR (100.6 MHz, $CDCl_3$): 150.5, 145.3, 137.3, 136.2, 135.1, 133.7 (6*s*); 128.7 (*d*, ^1J(C,H) = 159, arom. C); 127.1 (*d*, ^1J(C,H) = 161, arom. C); 126.9 (*d*, ^1J(C,H) = 158, arom. C); 126.3 (*d*, ^1J(C,H) = 160, arom. C); 126.2 (*d*, ^1J(C,H) = 159, arom. C); 125.8 (*s*); 125.7 (*d*, ^1J(C,H) = 161, arom. C); 125.6 (*d*, ^1J(C,H) = 160, arom. C); 121.6 (*d*, ^1J(C,H) = 156, arom. C); 109.1 (*t*, ^1J(C,H) = 150, CH_2=C(2)); 43.2 (*s*); 42.3 (*t*, ^1J(C,H) = 125); 35.7 (*t*, ^1J(C,H) = 129); 33.1 (*t*, ^1J(C,H) = 128); 30.8 (*t*, ^1J(C,H) = 125); 28.7 (*t*, ^1J(C,H) = 128); 28.3 (*t*, ^1J(C,H) = 125); 23.3 (*t*, ^1J(C,H) = 126). CI-MS (NH_3): 313 (100, $M^{+\bullet}$), 284 (73), 193 (20), 156 (64), 131 (94), 115 (45), 91 (25). Anal. calc. for $C_{24}H_{24}$ (313.45): H 7.69, C 92.31; found: H 7.79, C 92.34.

*(±)-1,4,5,6-Tetrahydronaphth[1,2-*d*][1,2]oxathiin 2-Oxide* (**23**). In a 5-mm NMR tube, a freshly prepared soln. of **11** (25 mg, 0.16 mmol), CD_2Cl_2 (0.15 ml), and $CFCl_3$ (100 mg) was degassed by several freeze-thaw cycles at 0.01 mbar on the vac. line. Degassed SO_2 (*ca.* 0.2 ml, 4–6 mmol) was transferred, and the NMR tube was sealed under vacuum at −196°, then warmed to −80° and left at this temp. for 15 h. The tube was then transferred to the probe of a *Bruker ARX-400* spectrometer cooled to −80° to be analyzed: complete conversion of **11** into **23**, **24**, and **14** in a 1:0.15:0.4 ratio was observed. ^{1}H-NMR (400 MHz, CD_2Cl_2/SO_2, 193 K): 8.00–6.90 (*m*, 4 arom. H); 4.56 (*dm*, ^2J = 17.3, H–C(4)); 4.39 (*dm*, ^2J = 17.3, H–C(4)); 3.73 (*dm*, ^2J = 16.6, H–C(1)); 3.23 (*dm*, ^2J = 16.6, H–C(1)); 3.00–2.00 (*m*, CH_2(6), CH_2(5)). ^{13}C-NMR (100.6 MHz, $CD_2Cl_2/CFCl_3/SO_2$, 193 K): detected signals: 127.9, 127.6, 127.5, 121.4 (4 arom. C); 59.8 (*t*, ^1J(C,H) = 153, C(4)); 45.9 (*t*, ^1J(C,H) = 138, C(1)); 26.2 (*t*, ^1J(C,H) = 127); 23.5 (*t*, ^1J(C,H) = 129).

*1,3,4,5-Tetrahydronaphtho[1,2-*c*]thiophene 2,2-Oxide* (**24**). A mixture of freshly prepared soln. of **11** (25 mg, 0.16 mmol) was mixed with pure SO_2 (0.2 ml) and placed in a *Pyrex* tube and degassed on the vac. line. After sealing the tube under vacuum, the mixture was left at 25° for 12 h. After cooling in liq. N_2, the tube was opened, and SO_2 was evaporated. The residue was purified by FC (CH_2Cl_2): 13 mg (37%) of **24** as a pale yellow oil. UV (MeCN): 262 (36000), 223 (53200), 216 (57200). IR (film): 2920, 1765, 1305, 1140, 1110, 800, 760, 605. ^{1}H-NMR (400 MHz, $CDCl_3$): 7.21 (*m*, 3 arom. H); 6.92 (*m*, arom. H); 4.15 (*dddd*, ^4J(1,3) = 1.5, 1.5, ^4J(3,4) = 1.5, H–C(3)); 4.01 (*ddddd*, ^4J(1,3) = 1.5, 1.5, ^5J(1,4) = 1.5, 1.5, H–C(1)); 2.97 (*dd*, ^3J(4,5) = 8.2, 8.2, CH_2(5)); 2.45 (*ddm*, ^3J(4,5) = 8.2, 8.2, H–C(4)). ^{13}C-NMR (100.6 MHz, $CDCl_3$): 134.5, 130.2, 129.7 (3*s*); 128.4, 128.1 (arom. C); 127.3 (*s*); 126.9, 123.4 (arom. C); 60.3 (C(1)); 56.1 (C(3)); 27.0 (CH_2); 24.3 (CH_2). CI-MS (NH_3): 220 (100, $M^{+\bullet}$), 156 (57), 141 (99), 128 (89), 115 (98), 105 (27), 84 (45).

X-Ray Crystal-Structure Determination of **14**. The colorless {010} platelet was mounted on a *Bruker CCD* system equipped with graphite-monochromatized Mo radiation, and a hemisphere of intensities was collected.

Table. *Crystal Data and Structure Refinement of Compound* **14**

Empirical formula	$C_{24}H_{24}$	F(000)	676
Formula weight	313.44	Crystal size [mm]	0.6 × 0.32 × 0.1
Temperature [K]	293(2)	Habitus Pinacoids	{010}, {10$\bar{1}$}, {12$\bar{1}$}
Wavelength [Å]	0.71073	Pedions	(01$\bar{1}$), (0$\bar{1}\bar{1}$), (1$\bar{3}$7), ($\bar{1}\bar{1}$5)
Crystal system	monoclinic	θ Range [°]	3.11 to 28.01
Space group	$P12_1/n1$	Index ranges	$-9 \le h \le 8$, $-29 \le k \le 27$, $-12 \le l \le 15$
Unit-cell dimensions a [Å]	7.1631(5)	Reflect. collected	10977
b [Å]	22.091(2)	Independent reflect.	4188 (R_{int} = 0.0442)
c [Å]	11.6215(8)	Refinement method	Full-matrix least-squares on F^2
α [°]	90	Data/restraints/parameters	4187/0/306
β [°]	106.5060(10)	Goodness-of-fit on F^2	2.789
γ [°]	90	Final R indices ($I > 2\sigma(I)$)	R_1 = 0.0596, wR_2 = 0.1032
V [Å^3]	1763.2(2)	R Indices (all data)	R_1 = 0.0840, wR_2 = 0.1056
Z	4	Weights	$[\sigma^2(F^2)]^{-1}$
Density calc. [Mgm^{-3}]	1.181	Extinction coeff.	0.0138(9)
Absorption coeff. [mm^{-1}]	0.066	Largest difference peak and hole [e · A^{-3}]	0.418 and −0.454
Absorption correction	Integration		
Max. and min. transmission	0.9934 and 0.9658		

The structure was solved by means of SIR97 [18], and refined with the help of SHEXTL [19]. All non-H-atoms were refined anisotropically, but the H-atoms isotropically. Crystallographic data (see *Table 1*), excluding structure factors, for compound **14** have been deposited with the *Cambridge Crystallographic Data Centre* as supplementary publication No. CCDC-165960. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK, fax: (++44)1223336033; e-mail: deposit@ccdc.cam.ac.uk).

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Received December 18, 2001