(m, 12 H); GC-MS m/e 338 (M^+). Anal. Calcd for $C_{26}H_{26}$: C, 92.26; H, 7.74. Found: C, 92.46; H, 7.92.

1,4-Bis(1-naphthyl)benzene (7) was reduced according to general procedure under a variety of conditions as described in Table IV. After two crystallizations of the crude product (entry 3) from benzene, **1,4-bis(3,4-dihydronaphthyl)benzene (31)** was isolated as white needles (25%): mp 222-224 °C; NMR ($CDCl_3$) δ 2.45 (m, 4 H), 2.85 (t, 4 H), 6.15 (t, 2 H), 7.15 (m, 8 H), 7.38 (s, 4 H); GC-MS m/e 334 (M^+). Anal. Calcd for $C_{26}H_{22}$: C, 93.37; H, 6.63. Found: C, 92.73; H, 6.58.

Chromatography on silica gel followed by recrystallization from hexane of the crude product (entry 2) provided pure **1,4-bis(1,2,3,4-tetrahydro-1-naphthyl)benzene (33)** (60%) as white needles: mp 127-129 °C; NMR ($CDCl_3$) δ 1.7-1.95 (m, 8 H), 2.15 (m, 2 H), 2.85 (m, 4 H), 4.08 (t, 2 H), 6.85-7.15 (m, 12 H); GC-MS m/e 338 (M^+). Anal. Calcd for $C_{26}H_{26}$: C, 92.26; H, 7.74. Found: C, 92.28; H, 7.87.

Substantial separation of three additional compounds was achieved by column chromatography (80-90% by GLPC). However, further purification by attempted crystallization failed; they are probably oils. On the basis of NMR data and mass spectra, these compounds were assigned as **29**, **30**, **32** (they show similarity in nonaromatic area to **21**, **23**, and **24**, respectively.

Quinquephenyl (8) was treated with 5.5 mol of lithium at -33 °C according to the general procedure. Careful column chromatography of the crude mixture allowed isolation of tetrahydro isomer **34** as a major product (40%, 65% by GLPC): oil; NMR ($CDCl_3$) δ 3.06 (br s, 4 H), 4.06 (br s, 2 H), 5.73 (m, 2 H), 5.87 (m, 2 H), 6.07 (br s, 2 H), 7.10-7.26 (m, 14 H); λ_{max}^{MeOH} 205 (log ϵ = 4.99) 248 nm (log ϵ = 5.04); GC-MS m/e 386 (M^+). Anal. Calcd for $C_{30}H_{26}$: C, 93.22; H, 6.78. Found: C, 93.58; H, 6.61.

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Ozonolysis of Acenaphthylene and 1-Substituted Acenaphthylenes

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The ozonolysis of 1-methylacenaphthylene (**1b**) and acenaphthylene (**1c**) in carbon tetrachloride, acetonitrile, acetic acid, and trifluoroethanol revealed that the ozonide yield was much higher in reactions in protic solvents than in aprotic solvents. Such an assistance of the protic solvents on the ozonide formation was not observed in the case of the more bulky 1-phenylacenaphthylene (**1a**). In the ozonolysis of **1a-c** in methanol, capture of the ozonolysis intermediate by the solvent occurs significantly, affording in each case the corresponding naphthopyran derivative **3**. The structure of the methanol-derived product obtained from acenaphthylene (**1c**) is revised from the structure **14** reported by Callighan to the methoxynaphthopyran **3c**, based on NMR data and chemical transformations. The structure of the methanol-derived products **3a,b** demonstrates that fragmentation of the primary ozonide obtained from 1-methyl- and 1-phenylacenaphthylene occurs such that the hydroperoxide resides on the more substituted carbon. These data are compared with those of the ozonolysis of pyrene (**17**).

The ozonolysis of alkenes has attracted attention with regard to mechanism.[1] We were interested in the ozonlysis of 1-substituted acenaphthylenes **1a,b** for the following reasons. (a) The reaction of acenaphthylene (**1c**) in chloroform has been reported to afford exclusively the polymeric products, while in methanol a solvent-participated product is obtained in good yield.[2] Thus, it would be interesting to see if the phenyl and methyl substituent in **1a,b** could affect the course of the reaction, since these substituents are expected to exert a meaningful influence on the orientation of the carbonyl oxide and/or carbonyl moiety. (b) The structural assignment of the methanol-participated products from **1a,b** would provide information on the direction of cleavage of the corresponding primary ozonides.

Results and Discussion

Ozonolysis of 1-Phenylacenaphthylene (1a). Ozonolysis of **1a** in carbon tetrachloride or acetic acid gave the corresponding ozonide **2a** in around 55% yield (eq 1 and

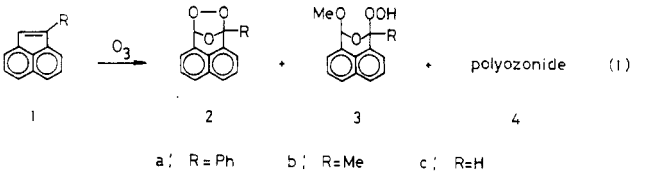
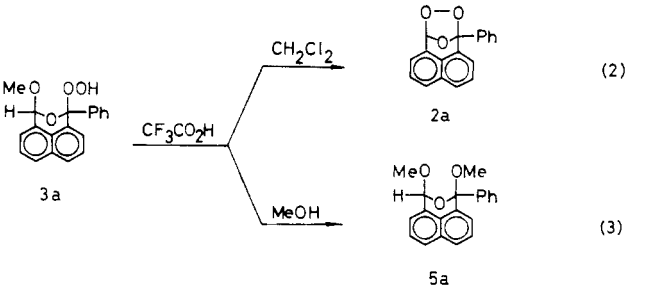


Table I). When the reaction was undertaken in methanol at -70 °C, however, the methanol-derived product **3a** was obtained in 30% yield, together with the ozonide **2a**. In accordance with the proposed structure, treatment of the methanol-derived product **3a** with trifluoroacetic acid in methylene chloride gave the ozonide **2a** quantitatively (eq 2) while the reaction in methanol resulted in exclusive



(1) (a) Bailey, P. S. *Ozonation in Organic Chemistry*; Academic Press: New York: Vol. 1, 1978; Vol. 2, 1982. (b) Kuczkowski, R. L. In *1,3-Dipolar Cycloaddition Chemistry*; Padwa, A., Ed.; Wiley: New York, 1984; Vol. 2.

(2) Callighan, R. H.; Tarker, M. F.; Wilt, M. H. *J. Org. Chem.* **1961**, *26*, 1379. (b) Chen, P. N.; Junk, G. A.; Svec, H. *J. Environ. Sci. Technol.* **1979**, *13*, 451. (c) Lichtenthaler, F. W.; El-Scherbiny, A. *Chem. Ber.* **1968**, *101*, 1799.

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Table I. Ozonolysis of Acenaphthylene Derivatives 1a-c and the Keto Olefins 7a,b[a]

substr	solvent	reactn temp, °C	products (% yield)
1a	CCl_4	0	**2a** (54)
1a	CH_3CO_2H/CH_2Cl_2	0	**2a** (56)
1a	CH_3OH/CH_2Cl_2	0	**2a** (59), **3a** (16)
1a	CH_3OH/CH_2Cl_2	−70	**2a** (59), **3a** (30)
7a	CCl_4[b]	0	**13a** (~100)[c]
7a	CH_3CO_2H/CH_2Cl_2[b]	0	**2a** (36)
7a	CF_3CH_2OH/CH_2Cl_2[b]	0	**2a** (84)
7a	CH_3OH/CH_2Cl_2[b]	0	**2a** (16), **12a** (31)
7a	CH_3OH/CH_2Cl_2[b]	−70	**2a** (2), **12a** (47)
1b	CCl_4	0	**2b** (19), **4b** (60)
1b	CH_3CO_2H/CH_2Cl_2	0	**2b** (44)
1b	CF_3CH_2OH/CH_2Cl_2	0	**2b** (44)
1b	CH_3OH/CH_2Cl_2	0	**2b** (23), **3b** (28),[d] **5b** (19)
1b	CH_3OH/CH_2Cl_2	−70	**2b** (21), **3b** (59)[d]
7b	CCl_4[b]	0	**13b** (~100)[e]
7b	CH_3CO_2H/CH_2Cl_2[b]	0	**2b** (33)
7b	CF_3CH_2OH/CH_2Cl_2[b]	0	**2b** (40)
7b	CH_3OH/CH_2Cl_2[b]	−70	**2b** (10)
1c	CCl_4	0	**4c** (80)
1c	CH_3CO_2H/CH_2Cl_2	0	**2c** (9)[f]
1c	CF_3CH_2OH/CH_2Cl_2	0	**2c** (14), **15** (14)[f]
1c	CH_3OH/CH_2Cl_2	0	**2c** (13), **3c** (66)[g]
1c	CH_3OH/CH_2Cl_2	−70	**2c** (7), **3c** (69)[g]

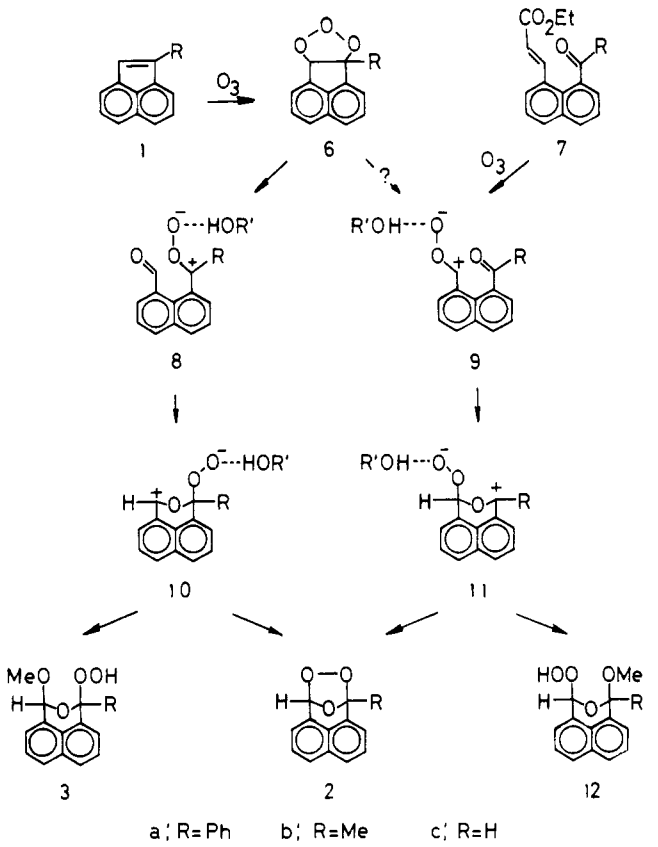
[a] The reaction with 1.2 equiv of ozone unless otherwise noted.[b] [b] The reaction with 4 equiv of ozone. [c] The ozonide **13a** was labile on silica gel, and, therefore, by column chromatography 1-benzoyl-8-formylnaphthalene was isolated in 80% yield. [d] A mixture of two stereoisomeric peroxides, the ratio being ca. 1:1. [e] The ozonide **13b** was labile on silica gel, and, therefore, by column chromatography 1-acetyl-8-formylnaphthalene was isolated in 75% yield. [f] Considerable amounts of unidentified products were also produced. [g] A mixture of two stereoisomeric peroxides, the ratio being around 4:1.

formation of the dimethoxy derivative **5a** (eq 3).

The fact that **3a** was the sole methanol-derived product from **1a**, suggests that of the two possible ozonolysis intermediates, **8a** and **9a**, only the former one, **8a**, participates (Scheme I). To confirm this, we then undertook the ozonolysis of the keto olefin **7a**, from which the carbonyl oxide **9a** is exclusively derived. The ozonolysis of the keto olefin **7a** in methanol gave certainly a methanol-derived product; structure **12a** was, however, different from that obtained from 1-phenylacenaphthylene (**1a**) (Scheme I and Table I).

Ozonolysis of 1-Methylacenaphthylene (1b). The ozonolysis of **1b** in carbon tetrachloride afforded mainly a polyozonide **4b**, along with small amounts of monoozonide **2b** (19% yield). On the basis of the molecular-weight measurement together with elemental analysis and IR/NMR spectra, the polyozonide **4b** was found to be a tetramer of the ozonolysis intermediate **8b**, although the detailed structure was not defined. Surprisingly, a relatively higher ozonide yield (around 40%) was observed in the ozonolysis in "participating" solvents, acetic acid or trifluoroethanol. Solvent polarity is not the reason, since the yield of ozonide **2b**, obtained from the reaction in acetonitrile having a higher polarity, was as low as 20%. Thus, in the case of 1-methylacenaphthylene (**1b**) the "participating" solvents, which can generally capture carbonyl oxides,[1a] seem to accelerate the formation of ozonide **2b**. In the reaction in methanol at −70 °C the expected methanol-derived product **3b** (a mixture of two stereoisomers) was obtained in a high yield of 59% (Table I).[3]

Scheme I



Probably the carbonyl and carbonyl oxide moieties in the intermediate **8b** are not held close together, and, hence, in aprotic solvents an intermolecular reaction would be forced to occur mainly. In protic solvents, however, solvation of the most polar carbonyl oxide moiety by the solvent would enhance the electrophilicity of the carbonyl oxide carbon, thereby facilitating partial capture of the carbonyl oxide moiety by the carbonyl group oxygen to yield the cyclic intermediate **10b**.[4b] In the intermediate **10b** both the peroxy group and methanol may subsequently compete for the incipient carbenium ion to give ozonide **2b** and the methanol-derived product **3b**, respectively. In a less nucleophilic solvent, acetic acid or trifluoroethanol, the formation of ozonide **2b** becomes a major process (Scheme I).

The ozonolysis of the keto olefin **7b** was also undertaken (Scheme I and Table I). In the ozonolysis in acetic acid or trifluoroethanol, the ozonide **2b** was isolated in around 35% yield. The reaction in methanol at −70 °C also yielded the ozonide in 10% yield, together with the unidentified polymeric products; regretfully, no evidence was obtained for the formation of the expected methanol-derived product **12b**.

Ozonolysis of Acenaphthylene (1c). Since novel assistance by protic solvents on the ozonide formation was observed in the reaction of **1b**, we undertook the ozonolysis

(3) On the basis of the fact that the ozonolysis of **1a** proceeds via **8a**, we considered that the similar intermediate **5b** is important in the ozonolysis is **1b** also. The structure of the methanol-derived product **3b** seems to be consistent with the hypothesis (reference the ^1H NMR spectra of **3a,b** and **12a**). For the formation of the tetramer **4b**, however, we cannot exclude the possibility of contribution of the alternative intermediate **9b**.

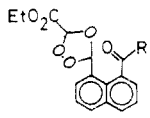
(4) (a) McCullough, K. J.; Nojima, M.; Miura, M.; Fujisaka, T.; Kusabayashi, S. *J. Chem. Soc., Chem. Commun.* **1984**, 35. (b) Nakamura, N.; Fujisaka, T.; Nojima, M.; Kusabayashi, S.; McCullough, K. J. *J. Am. Chem. Soc.* **1989**, *111*, 1799. (c) Griesbaum, K.; Meister, M. *Chem. Ber.* **1987**, *120*, 1573.

Table II. Ozonolysis of Pyrene (17) and the Keto Olefin 18[a]

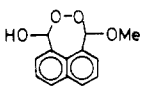
substr	solvent	reactn temp, °C	ozonide **20** (% yield)	peroxide **21** (% yield)	peroxide **21** ratio	recoved **17** (%)
17	CH_2Cl_2	−70	28			37
17	CH_3OH/CH_2Cl_2	0	9	35	34:66	34
17	CH_3OH/CH_2Cl_2	−70	3	26	75:25	41
18	CH_3OH/CH_2Cl_2	0	5	8	10:90	
18	CH_3OH/CH_2Cl_2	−70	5	17	70:30	

[a] The reaction of **17** with 2 equiv of ozone or the reaction of **18** with 4 equiv of ozone. [b] A mixture of two stereoisomeric peroxides. For details, see the Experimental Section.

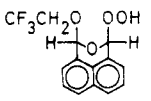
of parent acenaphthylene (**1c**) in various solvents (Table I). The reaction in carbon tetrachloride gave exclusively the polyozonide **4c**, as expected.[2] When the reaction was performed in trifluoroethanol or acetic acid, however, the corresponding ozonide **2c** was certainly obtained in a small but significant amount (14% yield). Thus, in this case also the protic solvents assisted the ozonide formation. The reaction in methanol gave, along with **2c** (7% yield), a methanol-derived product in a high yield of 69% (a mixture of two stereoisomers). The physical properties of the major product (mp 114–115 °C) were exactly the same as that reported by Callighan et al.[2] Although, they proposed the hemiperacetal structure **14**, we believe the methanol-derived product was 1-hydroperoxy-3-methoxy-1*H*,3*H*-naphtho[1,8-*cd*]pyran (**3c**), since in the ^1H NMR spectra the hydroperoxy proton appeared at δ 9.54.[4] In accordance with this, treatment of **3c** with trifluoroacetic acid in methanol gave exclusively the dimethoxy derivative **5c** (eq 4), while the reduction with triphenylphosphine yielded 1-hydroxy-3-methoxynaphthopyran **16** (eq 5).



13

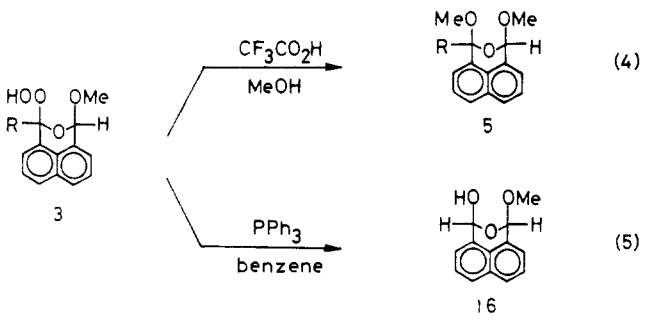


14



15

a; R=Ph b; R=Me



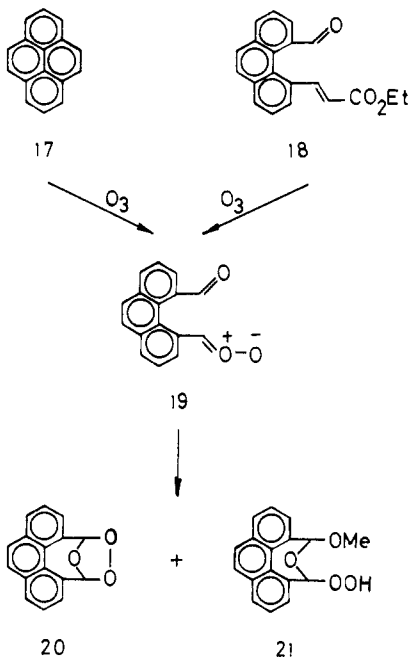
b; R = Me c; R = H

From the reaction in trifluoroethanol, the solvent-derived product **15** also was obtained in 14% yield along with the ozonide **2c** (14% yield), suggesting that in the case of less crowded cyclic intermediate **10c** this less nucleophilic solvent could also attack the carbocation center.

Ozonolysis of acenaphthylene (**1c**) on polyethylene also gave the corresponding ozonide **2c** in 10% yield, suggesting that this method developed by Griesbaum[5] is efficient in preparing an ozonide which is difficult to obtain by a conventional solution ozonolysis.

Ozonolysis of Pyrene (17). Since the ozonolysis of acenaphthylene (**1c**) in carbon tetrachloride gives exclusively the polyozonide **4c**, it is worth noting that the ozonolysis of pyrene (**17**) in methylene chloride or *tert*-butyl alcohol yields a significant amount of pyrene monoozonide (**20**) (around 30%) (Scheme II and Table II).[6]

Scheme II



In the more nucleophilic methanol, however, solvent participation certainly occurred to provide a mixture of two stereoisomer 4-hydroperoxy-6-methoxy-4,6-dihydrophenanthro[4,5-*cde*]oxepin (**21**) in good yields (Scheme II and Table II). Moreover, the ratio of the isomeric methanol-derived products was influenced by the reaction temperature. The ozonolysis of keto olefin **18**, from which the same carbonyl oxide intermediate **19** is derived, yielded also a mixture of two stereoisomeric methanol-derived products **21**. The following reactions of **21** were consistent with the proposed structure. (a) Treatment of the methanol-derived product **21** with trifluoroacetic acid in the methylene chloride gave the ozonide **20** (eq 6), (b) the reaction with trifluoroacetic acid in methanol led to the formation of the dimethoxy derivative **22** (eq 7), and (c) treatment with triphenylphosphine in benzene gave 4-hydroxy-6-methoxy-4,6-dihydrophenanthro[4,5-*cde*]oxepin (**23**) (eq 8).

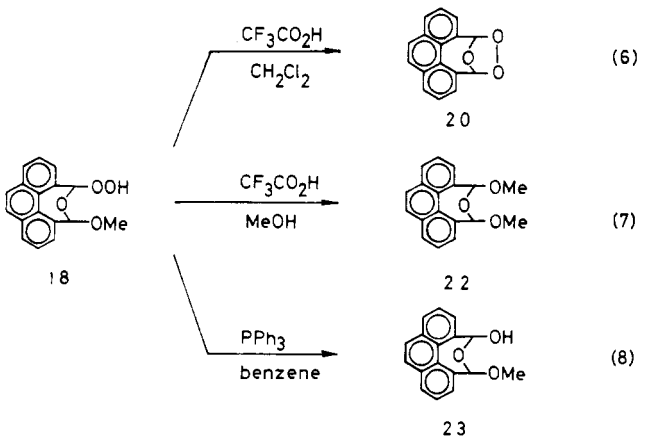
Experimental Section

^1H NMR spectra were obtained with a JNM-PS-100 spectrometer. Mass spectral data were obtained with a Hitachi RMU-6H spectrometer, and IR spectra with a Hitachi 215 spectrometer. 1-Phenylacenaphthylene (**1a**)[7] and 1-methylacenaphthylene (**1b**)[8] were prepared by the reported methods.

(5) Griesbaum, K.; Volpp, W.; Greinert, R.; Greunig, H.; Schmid, J.; Henke, H. *J. Org. Chem.* **1989**, *54*, 383.

(6) (a) Sturrock, M. G.; Duncan, R. A. *J. Org. Chem.* **1968**, *33*, 2149. (b) Van Duuren, B. L.; Witz, G.; Agarwal, S. C. *Ibid.* **1974**, *39*, 1032.

(7) O'Brien, S.; Smith, D. C. *J. Chem. Soc.* **1963**, 2905.



Preparation of 1-Acyl-8-[(ethoxycarbonyl)vinyl]-naphthalene (7). A benzene solution of 1-benzoyl-8-formylnaphthalene (2.7 g) and [(ethoxycarbonyl)methylene]triphenylphosphorane (4.0 g) was refluxed for 3 h. Then the crude products were column chromatographed on silica gel. elution with ether–hexane (1:4 v/v) gave **7a** (1.7 g): mp 88–89 °C (from benzene–hexane); ^{1}H NMR δ 1.17 (t, J = 7 Hz, 3 H), 4.06 (q, J = 7 Hz, 2 H), 5.85 (d, J = 14 Hz, 1 H), 7.1–8.0 (m, 12 H); IR 1710, 1670, 1280, 1180 cm^{-1}. Anal. Calcd for $C_{22}H_{18}O_3$: C, 79.98; H, 5.49. Found: C, 80.10; H, 5.54. Under similar conditions 1-acetyl-8-[(ethoxycarbonyl)vinyl]naphthalene (**7b**) was obtained from 1-acetyl-8-formylnaphthalene. **7b**: an oil; ^{1}H NMR δ 1.34 (t, J = 7 Hz, 3 H), 2.40 (s, 3 H), 4.26 (q, J = 7 Hz, 2 H), 6.32 (d, J = 14 Hz, 1 H), 7.1–8.1 (m, 7 H).

Ozonolysis of 1-Phenylacenaphthylene (1a) in Methanol–Methylene Chloride. The ozonolysis of **1a** (2 mmol) was undertaken in methanol–methylene chloride (30 mL; 1:1 v/v) at −70 °C. After adding ether (50 mL), the organic layer was washed with ice-cold aqueous potassium dihydrogen phosphate and then with saturated brine. The crude products were column chromatographed on silica gel. The first fraction (elution with benzene) contained ozonide **2a**: mp 130–131 °C (from methanol); ^{1}H NMR δ 6.78 (s, 1 H), 7.1–7.9 (m, 11 H). Anal. Calcd for $C_{18}H_{12}O_3$: C, 78.25; H, 4.38. Found: C, 78.20; H, 4.41. From the second fraction (elution with ether–benzene 1:50) was obtained 1-phenyl-1-hydroperoxy-3-methoxy-1*H*,3*H*-naphtho[1,8-*cd*]pyran (**3a**): mp 154–155 °C (from ethyl acetate–hexane); ^{1} H NMR δ 3.84 (s, 3 H), 6.12 (s, 1 H), 7.1–7.9 (m, 11 H), 9.84 (s, 1 H); IR 3250, 1090, 1030, 980, 820, 760, 700 cm^{-1}. Anal. Calcd for $C_{19}H_{16}O_4$: C, 74.01; H, 5.23. Found: C, 74.02; H, 5.25.

Reaction of the Methanol-Derived Product 3a with Trifluoroacetic Acid. Treatment of **3a** with equimolar amounts of trifluoroacetic acid in methylene chloride at 20 °C for 1 h gave quantitatively the ozonide **2a**. The reaction of **3a** (0.5 mmol) with trifluoroacetic acid (5 mol equiv) in methanol–methylene chloride (15 mL, 1:1 v/v) was undertaken at 20 °C for 4 h. From the reaction mixture 1,3-dimethoxy-1-phenyl-1*H*,3*H*-naphtho[1,8-*cde*]pyran (**5a**) was obtained in 80% yield: mp 149–150 °C (from ether–hexane); ^{1}H NMR δ 3.35 (s, 3 H), 3.54 (s, 3 H), 6.05 (s, 1 H), 6.8–7.8 (m, 11 H). Anal. Calcd for $C_{20}H_{18}O_3$: C, 78.41; H, 5.92. Found: C, 78.34; H, 5.96.

Ozonolysis of Keto Olefin 7a. The keto olefin **7a** (1 mmol) was treated with ozone in methanol–methylene chloride (30 mL, 1:1 v/v) at −70 °C. Since the reaction was very slow, 4 mol equiv of ozone was passed into the solution. By column chromatography on silica gel, the ozonide **2a** was eluted first. From the second fraction was obtained 1-phenyl-1-methoxy-3-hydroxperoxy-1*H*,3*H*-naphtho[1,8-*cd*]pyran (**12a**): mp 132–134 °C (from ethyl acetate–hexane); ^{1}H NMR δ 3.36 (s, 3 H), 6.42 (s, 1 H), 7.1–8.0 (m, 11 H), 9.93 (s, 1 H). Anal. Calcd for $C_{19}H_{16}O_4$: C, 74.01; H, 5.23. Found: C, 73.78; H, 5.29. Treatment of **12a** with trifluoroacetic acid (1 equiv) in methylene chloride at 20 °C for 1 h gave the ozonide **2a** quantitatively.

The reaction of **7a** with 4 equiv of ozone in carbon tetrachloride was undertaken at 0 °C. The ^{1}H NMR spectra of the crude products showed the formation of only the ozonide **13a** (an equimolar mixture of cis and trans isomers): an oil; ^{1}H NMR δ 1.07 (t, J = 7 Hz), 1.10 (t, J = 7 Hz), 3.94 (q, J = 7 Hz), 5.11 (s), 5.23 (s), 6.37 (s), 6.70 (s), 7.1–8.2 (m), the ratios of the peak areas being 3:3:4:1:1:1:1:22. However, this ozonide **13a** was very labile on silica gel and, consequently, by column chromatography only 1-benzoyl-8-formylnaphthalene was isolated in 80% yield: mp 89.5–90.5 °C (from ethyl acetate); ^{1}H NMR δ 7.1–8.2 (m, 11 H), 9.97 (s, 1 H); IR 1690, 1660, 1270, 1010, 770, 700, 670 cm^{-1}. Anal. Calcd for $C_{18}H_{12}O_2$: C, 83.06; H, 4.65. Found: C, 83.13; H, 4.63.

Ozonolysis of 1-Methylacenaphthylene (1b) in Methanol–Methylene Chloride. The reaction of **1b** (3 mmol) and 1.2 equiv of ozone was undertaken in methanol–methylene chloride (30 mL, 1:1 v/v) at −70 °C. The column chromatography of the crude products on silica gel gave first the ozonide **2b**: mp 119–120 °C (from methanol); ^{1}H NMR δ 2.13 (s, 3 H), 6.61 (s, 1 H), 7.1–7.8 (m, 6 H). Anal. Calcd for $C_{13}H_{10}O_3$: C, 72.89; H, 4.71. Found: C, 72.93; H, 4.78. From the second fraction was isolated 1-methyl-1-hydroperoxy-3-methoxy-1*H*,3*H*-naphtho[1,8-*cd*]pyran (**3b**): mp 104–105 °C (from ethyl acetate–hexane); ^{1}H NMR δ 1.98 (s, 3 H), 3.81 (s, 3 H), 5.91 (s, 1 H), 7.2–7.9 (m, 6 H), 9.87 (s, 1 H); IR 3270, 1020, 970, 960 cm^{-1}. Anal. Calcd for $C_{14}H_{14}O_4$: C, 68.28; H, 5.73. Found: C, 67.76; H, 5.61. The final fraction contained the stereoisomeric **3b**: mp 84–88 °C (from ether–hexane); ^{1}H NMR δ 1.89 (s, 3 H), 3.69 (s, 3 H), 5.97 (s, 1 H), 7.2–7.9 (m, 6 H), 8.64 (s, 1 H). Treatment of either of the isomeric hydroperoxides **3b** with trifluoroacetic acid (5 mol equiv) in methanol–methylene chloride at 20 °C for 4 h gave 1,3-dimethoxy-1-methyl-1*H*,3*H*-naphtho[1,8-*cd*]pyran (**5b**) in around 70% yield: mp 167–168 °C (from ethyl acetate–hexane); ^{1}H NMR δ 1.84 (s, 3 H), 3.25 (s, 3 H), 3.66 (s, 3 H), 5.90 (s, 1 H), 7.2–8.0 (m, 6 H); IR 1360, 1130, 1110, 1010, 800, 770 cm^{-1}; MS m/e 344 (M$^+$).

Ozonolysis of 1-Methylacenaphthylene (1b) in Carbon Tetrachloride. A carbon tetrachloride solution of **1b** (3 mmol) was treated with 1.2 equiv of ozone at 0 °C. The crude products were triturated with ether–hexane to afford a polyozonide **4b**: mp 158–160 °C dec; IR 3430, 1320, 1200, 1080, 820, 770 cm^{-1}; mol wt (vapor pressure osmometer) 813 (calcd for $(C_{13}H_{10}O_3)_4$, 856). Anal. Calcd for $(C_{13}H_{10}O_3)_4$: C, 72.89; H, 4.71. Found: C, 72.00; H, 4.77. The column chromatography of the residue on silica gel gave the ozonide **2b**.

Ozonolysis of Keto Olefin 7b. The keto olefin **7b** (1 mmol) was treated with 4 mmol of ozone in acetic acid–methylene chloride (30 mL, 1:1 v/v) at 0 °C. By column chromatography on silica gel, the ozonide **2b** was eluted first (33%). From the second fraction was obtained **7b** (5%). The final fraction contained 1-acetyl-8-formylnaphthalene (**20**%): mp 120–123 °C (from ethyl acetate); ^{1}H NMR δ 2.77 (s, 3 H), 7.2–8.2 (m, 6 H), 10.06 (s, 1 H); IR 1690, 1685 cm^{-1}. Anal. Calcd for $C_{13}H_{10}O_2$: C, 78.77; H, 5.08. Found: C, 78.85; H, 5.07.

The reaction of **7b** with 4 equiv of ozone in carbon tetrachloride was undertaken at 0 °C. The ^{1}H NMR spectra of the crude products showed the formation of only the ozonide **13b** (an equimolar mixture of cis and trans isomers): an oil; ^{1}H NMR δ 1.13 (t, J = 7 Hz), 1.32 (t, J = 7 Hz), 2.78 (s), 2.80 (s), 4.10 (q, J = 7 Hz), 4.28 (q, J = 7 Hz), 5.48 (s), 5.73 (s), 6.51 (s), 6.95 (s), 7.2–8.3 (m), the ratios of the peak areas being 3:3:3:3:2:2:1:1:1:1:12. However, this ozonide **13b** was very labile on silica gel and, consequently, by column chromatography 1-acetyl-8-formylnaphthalene was isolated in 75% yield.

Ozonolysis of Acenaphthylene (1c) in Methanol–Methylene Chloride. A methanol–methylene chloride solution (30 mL, 1:1 v/v) of **1c** (3 mmol) was treated with 1.2 equiv of ozone at −70 °C. Trituration of the crude products with ether–hexane afforded 1-hydroperoxy-3-methoxy-1*H*,3*H*-naphtho[1,8-*cd*]pyran (**3c**): mp 114–115 °C (from ethyl acetate–hexane); ^{1}H NMR δ 3.84 (s, 3 H), 5.97 (s, 1 H), 6.51 (s, 1 H), 7.1–7.9 (m, 6 H), 9.54 (s, 1 H); IR 3300, 1090, 1030, 990, 960, 810, 770 cm^{-1}. Anal. Calcd for $C_{13}H_{12}O_4$: C, 67.23; H, 5.21. Found: C, 67.19; H, 5.22.

The residue was column chromatographed on silica gel. The first fraction contained the ozonide **2c**: mp 102–103 °C (from methanol); ^{1}H NMR δ 6.63 (s, 2 H), 7.3–7.9 (m, 6 H); IR 1340, 1040, 890, 820, 780 cm^{-1}. Anal. Calcd for $C_{12}H_8O_3$: C, 72.00; H, 4.03. Found: C, 71.55; H, 4.01. From the second fraction was obtained **3c** (major isomer): mp 114–115 °C. The final fraction contained the stereoisomeric **3c** (minor one): an oil; ^{1}H NMR δ 3.69 (s, 3 H), 6.09 (s, 1 H), 6.49 (s, 1 H), 7.2–7.9 (m, 6 H), 9.45

(8) Lazach, N.; Mollier, Y. *Bull. Soc. Chem. Fr.* **1950**, 1243.

(s, 1 H). The ratio of the two stereoisomeric methanol-derived products was 86:14.

The reaction at 0 °C gave also a mixture of two isomeric hydroperoxides **3c** (66% yield), together with the ozonide **2c** (13% yield). The ratio of the isomeric hydroperoxides **3c** was 78:22. Treatment of either of the methanol-derived products **3c** with trifluoroacetic acid (5 mol equiv) in methanol–methylene chloride at 20 °C for 12 h gave 1,3-dimethoxy-1*H*,3*H*-naphtho[1,8-*cd*]pyran (**5c**): mp 56 °C; ^{1}H NMR δ 3.73 (s, 6 H), 6.00 (s, 2 H), 7.2–7.9 (m, 6 H); MS *m/e* 230 (M^+).[2c] The reaction of methanol-derived product **3c** with triphenylphosphine in benzene at 20 °C for 10 min gave 1-hydroxy-3-methoxy-1*H*,3*H*-naphtho[1,8-*cd*]pyran (**16**) in 90% yield: mp 90–95 °C (from ether–hexane) (a mixture of two stereoisomers, ratio 18:82); ^{1}H NMR δ 3.5 (br s, OH), 3.75 (s, OMe, minor), 3.77 (s, OMe, major), 5.92 (s, minor), 5.98 (s, major), 6.3 (br s), 7.2–7.8 (m); IR 3320, 1360, 1325, 1005, 785 cm^{-1}. Anal. Calcd for $C_{13}H_{12}O_3$: C, 79.21; H, 5.59. Found: C, 78.92; H, 5.57.

Ozonolysis of Acenaphthylene (1c) in Carbon Tetrachloride. The reaction of acenaphthylene (**1c**) (3 mmol) with ozone (1.2 equiv) in carbon tetrachloride (30 mL) was undertaken at 0 °C. Trituration of the crude products with ether gave a polyozonide **4c**: mp 131–133 °C dec; IR 3430, 1320, 1050, 810, 760 cm^{-1}. Anal. Calcd for $(C_{12}H_8O_3)_n$: C, 72.00; H, 4.03. Found: C, 70.63; H, 4.13.

Ozonolysis of Acenaphthylene (1c) in Trifluoroethanol–Methylene Chloride. The reaction of **1c** (3 mmol) with 1.2 equiv of ozone was undertaken in trifluoroethanol–methylene chloride (30 mL, 1:1 v/v) at 0 °C. After conventional workup the products were column chromatographed on silica gel. The first fraction (elution with benzene) contained a complex mixture of unidentified products. From the second fraction (elution with ether–benzene, 5:95) was obtained 1-hydroperoxy-3-(trifluoroethoxy)-1*H*,3*H*-naphtho[1,8-*cd*]pyran (**15**): mp 257–260 °C (from ethyl acetate–hexane); ^{1}H NMR δ 4.28 (q, 2 H), 6.09 (s, 1 H), 6.33 (s, 1 H), 7.2–7.8 (m, 6 H), 9.02 (s, 1 H); IR 3430, 2930, 1320, 1080, 1010, 830, 790, 770 cm^{-1}. Treatment of **15** with 1 equiv of trifluoroacetic acid in methylene chloride at 20 °C for 1 h yielded quantitatively the ozonide **2c**.

Ozonolysis of Pyrene (17) in Methanol–Methylene Chloride. The reaction of pyrene (500 mg) with 2 equiv of ozone was undertaken in methanol–methylene chloride (30 mL, 1:1 v/v) at −70 °C. Column chromatography of the crude products on silica gel gave first pyrene (204 mg). From the second fraction was obtained the ozonide **20** (20 mg): mp 163–165 °C.[6] The third fraction contained 4-hydroperoxy-6-methoxy-4,6-dihydrophenanthro[4,5-*cde*]oxepin (**21**): mp 146–148 °C (from ethyl acetate–hexane); ^{1}H NMR δ 3.53 (s, 3 H), 5.77 (s, 1 H), 6.28 (s, 1 H), 7.5–8.0 (m, 8 H), 9.18 (s, 1 H). Anal. Calcd for $C_{17}H_{14}O_4$: C, 72.33; H, 5.00. Found: C, 71.96; H, 4.99. From the final fraction was obtained the stereoisomeric **21** (a minor isomer): mp 71–73 °C; ^{1}H NMR δ 3.65 (s, 3 H), 5.70 (s, 1 H), 6.40 (s, 1 H), 7.5–8.0 (m, 8 H), 9.53 (s, 1 H). The ratio of the two isomeric hydroperoxides was ca. 3:1.

Treatment of either of the isomeric methanol-derived products **21** with 1 equiv of trifluoroacetic acid in methanol–methylene chloride (20 mL, 1:1 v/v) at 20 °C for 5 h gave 4,6-dimethoxy-4,6-dihydrophenanthro[4,5-*cde*]oxepin (**22**) quantitatively: an oil; ^{1}H NMR δ 3.62 (s, 6 H), 5.57 (s, 2 H), 7.4–7.8 (m, 8 H); IR 2930, 1340, 1080, 1040, 820 cm^{-1}; MS *m/e* 280 (M^+). Anal. Calcd for $C_{18}H_{16}O_3$: C, 77.12; H, 5.75. Found: C, 77.17; H, 5.69.

The reaction of **21** (major isomer) with 1 equiv of triphenylphosphine in benzene at 20 °C for 10 min afforded 4-hydroxy-6-methoxy-4,6-dihydrophenanthro[4,5-*cde*]oxepin (**23**) in 75% yield: mp 125–130 °C; IR 3400, 1080, 1045, 1020, 815 cm^{-1}; ^{1}H NMR δ 3.42 (d, *J* = 6 Hz, 1 H), 3.69 (s, 3 H), 5.85 (s, 1 H), 6.33 (d, *J* = 6 Hz, 1 H), 7.5–8.0 (m, 8 H). Anal. Calcd for $C_{17}H_{14}O_3$: C, 76.68; H, 5.30. Found: C, 76.49; H, 5.27.

Ozonolysis of Pyrene in Methylene Chloride. The ozonolysis of pyrene (500 mg) with 2 equiv of ozone in methylene chloride (30 mL) was undertaken at −70 °C. Trituration of the reaction mixture with ether afforded the polyozonide: mp 108–113 °C dec; IR 3400, 1170, 830 cm^{-1}.[6a] This compound was labile and, therefore, the exact physical properties and the elemental analysis data were not obtained. Column chromatography of the residue on silica gel (elution with benzene–hexane, 1:1 v/v) gave the monoozonide **20**: mp 163–165 °C.[6a]

Preparation of 4-[(Ethoxycarbonyl)vinyl]-5-formylphenanthrene (18). A benzene solution of 4,5-diformylphenanthrene (2.6 g) and [(ethoxycarbonyl)methylene]triphenylphosphorane (4.9 g) was refluxed for 3 h. Elution with ether–benzene (1:9 v/v) gave **18** (1.0 g): mp 123–124 °C (from ethyl acetate–hexane); ^{1}H NMR δ 1.34 (t, *J* = 7 Hz, 3 H), 4.29 (q, *J* = 7 Hz, 2 H), 6.69 (d, *J* = 15 Hz, 1 H), 7.6–8.1 (m, 9 H), 9.86 (s, 1 H); IR 1700, 1680, 1310, 1190, 840 cm^{-1}. Anal. Calcd for $C_{20}H_{16}O_3$: C, 78.93; H, 5.30. Found: C, 78.60; H, 5.37.

Ozonolysis of Keto Olefin 18 in Methanol–Methylene Chloride. A methanol–methylene chloride solution (20 mL, 1:1 v/v) of **18** (200 mg) was treated with 4 mol equiv of ozone at −70 °C. After workup, the products were column chromatographed on silica gel. Elution with benzene–hexane (1:1 v/v) gave the ozonide **20** (9 mg, 5%). Subsequent elution with ether–benzene (1:25) gave a mixture of two stereoisomeric methanol-derived products **21** (15 mg, 8%), the isomer ratio being 1:9.

Ozonolysis of Acenaphthylene (1c) on Polyethylene. Acenaphthylene (200 mg) was loaded on 20 g of polyethylene from an ether solution and ozonized for 19 min (8 equiv of ozone) at −70 °C. After extraction with ether, the products were column chromatographed on silica gel. Elution with benzene–hexane (1:1 v/v) gave first the unreacted **1c** (24 mg) and then the ozonide **2c** (24 mg).

Hazards. During this study, we did not experience trouble on treatment of the ozonides **2a–c**, **13**, and **20** and the hydroperoxides **3a–c**, **12**, **15**, and **21**. They are, however, potentially explosive compounds and, therefore, careful treatment is required.

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Registry No. **1a**, 4044-56-8; **1b**, 19345-99-4; **1c**, 208-96-8; **2a**, 127064-91-9; **2b**, 127064-92-0; **2c**, 196-15-6; **3a**, 127064-93-1; *cis*-**3b**, 127064-94-2; *trans*-**3b**, 127064-95-3; *cis*-**3c**, 127064-96-4; *trans*-**3c**, 127064-97-5; **5a**, 127064-98-6; **5b**, 127064-99-7; **5c**, 17216-18-1; **7a**, 127065-00-3; **7b**, 127065-01-4; **12a**, 127065-02-5; *cis*-**13a**, 127065-03-6; *trans*-**13a**, 127065-04-7; *cis*-**13b**, 127065-05-8; *trans*-**13b**, 127065-06-9; **15**, 127065-07-0; *cis*-**16**, 127065-08-1; *trans*-**16**, 127065-09-2; **17**, 129-00-0; **18**, 127065-10-5; **20**, 16203-57-9; *cis*-**21**, 127065-11-6; *trans*-**21**, 127065-12-7; **22**, 127065-13-8; **23**, 127065-14-9; 1-benzoyl-8-formylnaphthalene, 126614-37-7; 1-acetyl-8-formylnaphthalene, 127065-15-0; 4,5-diformylphenanthrene, 16162-34-8.