177 (38), 149 (44), 148 (35), 110 (54), 95 (100), 82 (65), 43 (32); calcd for $C_{15}H_{24}O$ (M^+) *m/e* 220.1827, found *m/e* 220.1830. Anal. Calcd for $C_{15}H_{24}O$: C, 81.76; H, 10.97. Found: C, 81.58; H, 10.91.

(±)-Alloaromadendrane-4β,10α-diol (1). To a solution of 0.060 g (0.27 mmol) of olefin **5** in 5 mL of CH_2Cl_2 were added 5 mL of acetone, 5 mL of water, 0.005 g of 18-crown-6, and 0.100 g of $NaHCO_3$. The mixture was stirred vigorously and 1.36 mL of 0.29 M Oxone (0.79 mmol of $KHSO_5$) in water was added dropwise at 0 °C. Stirring was continued for an additional 80 min, after which time 5 mL of 10% aqueous $Na_2S_2O_3$ and 10 mL of saturated aqueous $NaHCO_3$ were added. The aqueous layer was extracted with seven 25-mL portions of CH_2Cl_2. The combined organic layers were dried and evaporated under reduced pressure. The remaining residue, according to GCMS and ^1H NMR analysis, a 4.3:1 mixture of the epoxides **19** [^1H NMR (main peaks, $CDCl_3$) δ 0.94 (s, 3 H), 1.02 (s, 3 H), 1.18 (s, 3 H), 2.50 (d, J = 4 Hz, 1 H), 2.95 (d, J = 4 Hz, 1 H); MS, *m/e* (rel intensity) 236 (M^+, 0.1), 221 (1), 218 (4), 203 (3), 187 (4), 175 (6), 163 (8), 145 (16), 133 (14), 121 (15), 105 (28), 81 (60), 55 (30), 43 (100)] and **20** [^1H NMR (main peaks, $CDCl_3$) δ 0.94 (s, 3 H), 1.04 (s, 3 H), 1.15 (s, 3 H), 2.40 (d, J = 4 Hz, 1 H), 2.88 (d, J = 4 Hz, 1 H); MS, *m/e* (rel intensity) 236 (M^+, 0.3), 221 (0.4), 218 (2), 203 (2), 187 (3), 175 (6), 160 (8), 145 (21), 134 (17), 105 (27), 81 (44), 55 (27), 43 (100)], respectively, was taken up in 5 mL of dry ether and an excess $LiAlH_4$ was added. The mixture was stirred at rt for 17 h, diluted with 75 mL of CH_2Cl_2, and then carefully quenched with a few drops of saturated aqueous Na_2SO_4. The mixture was dried and concentrated under reduced pressure. The remaining residue was flash chromatographed on silica gel (6:1 to 2:1 petroleum ether (bp 40–60 °C)/EtOAc) to give, in order of elution, 0.011 g (16%) of 4β,10β-diol **22**, 0.012 g (18%) of the cyclic hydroxy ether **21**, and 0.030 g (46%) of 4β,10α-diol **1**. Physical and spectroscopic data of **1**, **21**, and **22** follow.

1: mp 120–120.5 °C (from *n*-hexane); ^1H NMR ($CDCl_3$, 200 MHz) δ 0.48–0.68 (m, 2 H), 0.95 (s, 3 H), 1.00–1.95 (m, 11 H), 1.03 (s, 3 H), 1.24 (s, 3 H), 1.32 (s, 3 H), 2.23 (br q, J = 9.0 Hz, 1 H); ^{13}C NMR ($CDCl_3$, 50 MHz), see Table I; MS, *m/e* (rel intensity) 238 (M^+, 0.3), 220 (3), 205 (5), 202 (3), 187 (4), 177 (4), 162 (11), 149 (9), 147 (14), 139 (100), 121 (26), 81 (39), 43 (52); calcd for $C_{15}H_{26}O_2$ (M^+) *m/e* 238.1933, found *m/e* 238.1928. Anal. Calcd for $C_{15}H_{26}O_2$: C, 75.57; H, 10.99. Found: C, 75.30; H, 11.20.

21: mp 137–138 °C (from diisopropyl ether); ^1H NMR ($CDCl_3$, 200 MHz) δ 0.49 (d, J = 9.4 Hz, 1 H), 0.60–0.77 (m, 1 H), 0.90–1.89 (m, 10 H), 0.97 (s, 3 H), 1.01 (s, 3 H), 1.24 (s, 3 H), 2.19 (br s, 1 H), 3.31 (d, J = 9.5 Hz, 1 H), 3.37 (d, J = 9.5 Hz, 1 H); ^{13}C NMR ($CDCl_3$, 50 MHz) δ 15.41 (q), 17.48 (s), 18.15 (q), 20.67 (t), 22.08 (d), 23.26 (t), 25.38 (d), 29.35 (q), 35.57 (t), 36.17 (t), 44.65 (d), 50.94 (d), 68.96 (t), 83.81 (s), 85.76 (s); MS, *m/e* (rel intensity) 236 (M^+, 3), 218 (32), 205 (16), 160 (40), 147 (58), 145 (62), 134 (100), 105 (38), 91 (33), 43 (46); calcd for $C_{15}H_{24}O_2$ (M^+) *m/e* 236.1776, found *m/e* 236.1775. Anal. Calcd for $C_{15}H_{24}O_2$: C, 76.22; H, 10.23. Found: C, 76.51; H, 10.37.

22: mp 109 °C (from *n*-hexane); ^1H NMR ($CDCl_3$, 200 MHz) δ 0.60–0.75 (m, 1 H), 0.87 (br d, J = 7.4 Hz, 1 H), 0.93–1.47 (m, 3 H), 0.96 (s, 3 H), 1.05 (s, 3 H), 1.09 (s, 3 H), 1.20 (s, 3 H), 1.64–2.00 (m, 8 H), 2.20 (dt, J = 8.9, 11.0 Hz, 1 H); ^{13}C NMR ($CDCl_3$, 50 MHz), see Table I; MS, *m/e* (rel intensity) 238 (M^+, 0.3), 220 (7), 205 (4), 202 (4), 192 (5), 187 (4), 177 (5), 162 (7), 147 (10), 139 (100), 121 (60), 81 (34), 43 (46); calcd for $C_{15}H_{26}O_2$ (M^+) *m/e* 238.1933, found *m/e* 238.1930. Anal. Calcd for $C_{15}H_{26}O_2$: C, 75.57; H, 10.99. Found: C, 75.24; H, 11.22.

(±)-Alloaromadendrane-4α,10α-diol (23). To a solution of 0.100 g (0.45 mmol) of olefin **5** in 5 mL of dry pyridine was added 0.2 mL (1.0 mmol) of $SOCl_2$ at −15 °C. The mixture was stirred for 10 min and then poured into 100 mL of aqueous 20% H_2SO_4. The aqueous solution was extracted with five 50-mL portions of CH_2Cl_2. The combined organic layers were dried and the solvent was evaporated at atmospheric pressure. The remaining residue, a mixture of three products in a ratio of 6:3:1 according to GC analysis, was epoxidized and reduced as described above for olefin **5**. The workup and flash chromatography on silica gel (2:1 petroleum ether (bp 40–60 °C)/EtOAc) gave 0.025 g (23%) of pure **23**: mp 79–80 °C (from *n*-hexane); ^1H NMR ($CDCl_3$, 200 MHz) δ −0.03 (t, J = 9.6 Hz, 1 H), 0.60 (ddd, J = 5.2, 9.6, 11.3 Hz, 1 H), 0.99 (s, 3 H), 1.01 (s, 3 H), 1.10–2.11 (m, 11 H), 1.16 (s, 3 H), 1.30 (s, 3 H), 2.45 (m, 1 H); ^{13}C NMR ($CDCl_3$, 50 MHz), see Table I; MS, *m/e* (rel intensity) 238 (M^+, 1.7), 220 (18), 205 (18), 202 (21), 187 (19), 177 (11), 162 (100), 147 (52), 134 (24), 119 (51), 107 (48), 93 (49), 81 (33); calcd for $C_{15}H_{24}O$ ($M^+ - 18$) *m/e* 220.1827, found *m/e* 220.1825. Anal. Calcd for $C_{15}H_{26}O_2$: C, 75.57; H, 10.99. Found: C, 75.77; H, 11.30.

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Registry No. (±)-**1**, 136458-41-8; (±)-**2**, 136379-61-8; (±)-**3**, 136379-62-9; (±)-**4**, 136379-63-0; (±)-**5**, 136458-42-9; (±)-**6**, 87262-05-3; (±)-**7**, 136379-64-1; (±)-**8**, 136379-65-2; (±)-**9**, 136379-66-3; (±)-**10**, 136379-67-4; (±)-**11**, 136379-68-5; (±)-**12**, 136379-69-6; (±)-**13**, 136379-70-9; (±)-**14**, 136379-71-0; (±)-**15**, 136379-72-1; (±)-**16**, 136379-73-2; (±)-**17**, 136379-74-3; (±)-**18**, 136379-75-4; (±)-**19**, 136458-43-0; (±)-**20**, 136458-44-1; (±)-**21**, 136379-76-5; (±)-**22**, 136458-45-2; (±)-**23**, 136458-46-3.

Ozonolysis of Vinyl Ethers in the Presence of α-Diketones and α-Keto Esters

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Received May 20, 1991

Ozonolysis of vinyl ethers in the presence of α-diketones provided two types of products, i.e., a Baeyer–Villiger oxidation product and 3-acyl-1,2,4-trioxolane. The evidence suggests that the latter product is labile and, therefore, the former one might be produced by decomposition of the latter. In contrast, 1,2,4-trioxolane-3-carboxylates were stable. As a result, ozonolysis of vinyl ethers in the presence of α-keto esters yielded the expected ozonides in high yield.

The mechanism of the reaction of ozone with alkenes continues to attract considerable attention.[1] It is noted that in many cases ozonolyses of α,β-unsaturated ketones do not give the corresponding 1,2,4-trioxolanes but instead the "anomalous" products (carboxylic acid, ester, etc.).[2] In

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(1) (a) Bunnelle, W. H. *Chem. Rev.* **1991**, *91*, 335. (b) Kuczkowski, R. L. In *Advances in Oxygenated Processes*; Baumstark, A. L., Ed.; JAI Press: Greenwich, 1991; Vol. 3.

(2) Bailey, P. S. *Ozonation in Organic Chemistry*; Academic Press: New York, 1978; Vol. 1, 1982; Vol. 2.

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Table I. Ozonolysis of Vinyl Ether in the Presence of α-Diketone[a]

diketone	vinyl ether	solvent	products (% yield)	recovered diketone, %
4	**1a**	CH_2Cl_2	**5** (30)	70
4	**1b**	CH_2Cl_2	**5** (44), **6b** (50)	44
4	**1c**	CH_2Cl_2	**5** (30), **6c** (65)[b]	50
10	**1a**	ether	**12** (65)	28
10	**1b**	ether	**12** (79), **6b** (96)	
10	**1c**	ether	**12** (78), **6c** (88)	22
10	**1d**	ether	**12** (43), **6d** (30)	13
15[c]	**1b**	ether	**16** (62), **6b** (50)	
15[c]	**1d**	ether	**16** (74), **6d** (65)	
17	**1a**	ether		100
17	**1c**	ether	**6c** (58)[d]	100
18[e]	**1b**	CH_2Cl_2	**19** (33), **20** (14)	29
18[c]	**1a**	CH_2Cl_2	**24** (55)	
18[c]	**1b**	CH_2Cl_2	**20** (87)	
18[c]	**1c**	CH_2Cl_2	**21** (74)	
18[c]	**1d**	CH_2Cl_2	**22** (97)	

[a] Ozonolysis of a 1:1 mixture of vinyl ether and α-diketone at −70 °C unless otherwise noted. [b] 3,3,6,6-Tetraphenyl-1,2,4,5-tetroxane was also isolated in ca. 10% yield. [c] The ratio of diketone, vinyl ether, and ozone was 1:2:2; the reaction was undertaken at −70 °C for 15 and 0 °C for 18. [d] 3,3,6,6-Tetraphenyl-1,2,4,5-tetroxane was isolated in 26% yield. [e] Reaction at 0 °C.

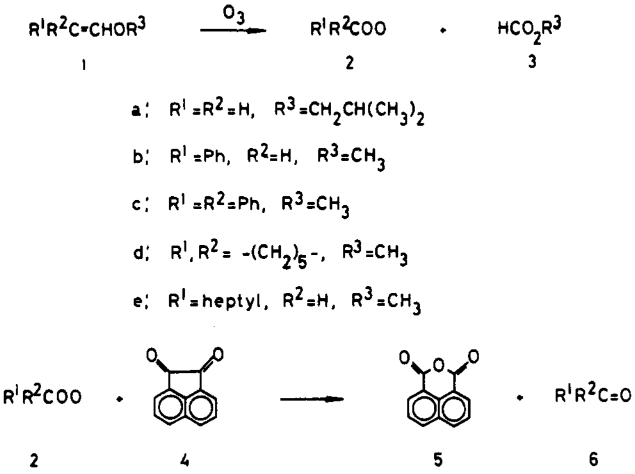
Table II. Ozonolysis of α,β-Unsaturated Ketone[a]

ketone	solvent	products (%, yield)	recovered ketone, %
7	CH_2Cl_2	**5** (~100), **6b** (~100)	
7	MeOH/CH_2Cl_2	**4** (60), **5** (15), **6b** (10), **9** (42)	
25	ether	**6b** (60), **26** (50)	13
25	MeOH/CH_2Cl_2	**6b** (38), **9** (29), **26** (20)	18
27	ether	**6d** (60), **26** (77)	
28	ether	**6b** (70), **30** (63)	22
29	ether	**6b** (43), **31** (68)	8

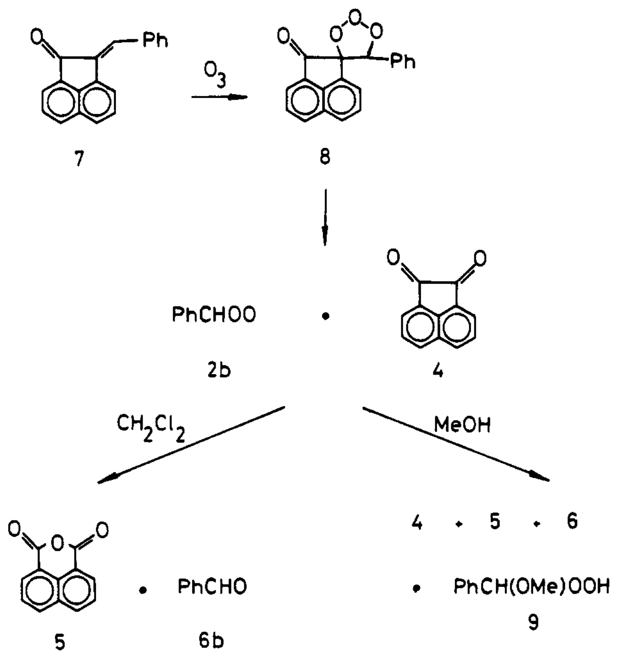
[a] Reaction of the ketone with 1 equiv of ozone at −70 °C.

this connection, Sawaki and associates[3] have found that benzophenone *O*-oxide, generated by photooxygenation of diphenyldiazomethane, transfers an oxygen atom to the coexisting acenaphthenequinone, yielding 1,8-naphthalic anhydride together with benzophenone. However, Griesbaum[4] and Bunnelle[5] have recently succeeded in isolating some labile α-oxo ozonides from ozonolysis of the corresponding α-oxoalkenes. In contrast to the dependence of products on the structure of α,β-unsaturated ketones, ozonolysis of a variety of α,β-unsaturated esters gives the corresponding ozonides in excellent yield.[5,6] To obtain further insight into these reactions, we have undertaken an investigation of the ozonolysis of vinyl ethers in the presence of α-diketones and α-keto esters; we expected that this approach would clarify the modes of reaction of carbonyl oxides toward the added substrates, since ozonolysis of vinyl ethers proceeds with virtually complete regioselectivity to the carbonyl oxide–ester pairs and, moreover, the esters show relatively low reactivity toward the carbonyl oxides.[1,7]

Scheme I



Scheme II



Results and Discussion

Reaction of Carbonyl Oxide with α-Diketone. Ozonolyses of vinyl ethers **1a–c** were conducted in the presence of acenaphthenequinone (**4**) in methylene chloride at −70 °C. 1,8-Naphthalic anhydride (**5**) was isolated in around 30% yield, together with the unreacted **4** (Scheme I and Table I). Under similar conditions quinone **4** did not react with ozone. These results imply that carbonyl oxides **2**, generated from **1**, apparently transfer an oxygen atom to **4**, yielding the Baeyer–Villiger type product **5**. Ozonolysis of benzylideneacenaphthenone (**7**)

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(3) Ishiguro, K.; Hirano, Y.; Sawaki, Y. *J. Org. Chem.* **1988**, *53*, 5397. For representative examples of oxygen atom transfer from carbonyl oxide to various substrates, see the following literature. (a) Hamilton, G. A.; Giacin, J. R. *J. Am. Chem. Soc.* **1966**, *88*, 1584. (b) Hinrichs, T. A.; Ramachandran, V.; Murray, R. W. *J. Am. Chem. Soc.* **1979**, *101*, 1282. (c) Pryor, W. A.; Govindan, C. K. *J. Am. Chem. Soc.* **1981**, *103*, 7681. (d) Nakamura, N.; Nojima, M.; Kusabayashi, S. *J. Am. Chem. Soc.* **1987**, *109*, 4969. (e) Murray, R. W.; Banavali, R. *Tetrahedron Lett.* **1983**, *24*, 2327. (f) Jefford, C. W.; Boukouvalas, J.; Jaggi, D.; Kohmoto, S.; Bernardinelli, G. *Helv. Chim. Acta* **1986**, *69*, 941. (g) Ando, W.; Kabe, Y.; Miyazaki, H. *Photochem. Photobiol.* **1980**, *31*, 191. (h) Sawaki, Y.; Kato, H.; Ogata, Y. *J. Am. Chem. Soc.* **1981**, *103*, 3832. (i) Adam, W.; Durr, H.; Haas, W.; Lohray, B. *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 101.

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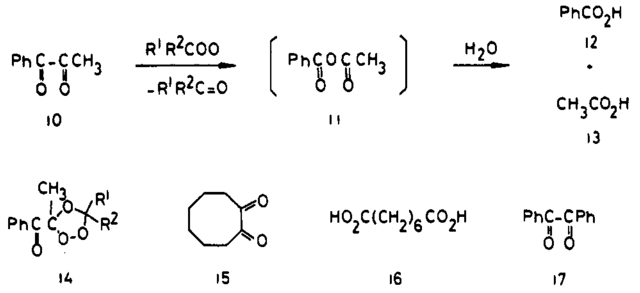
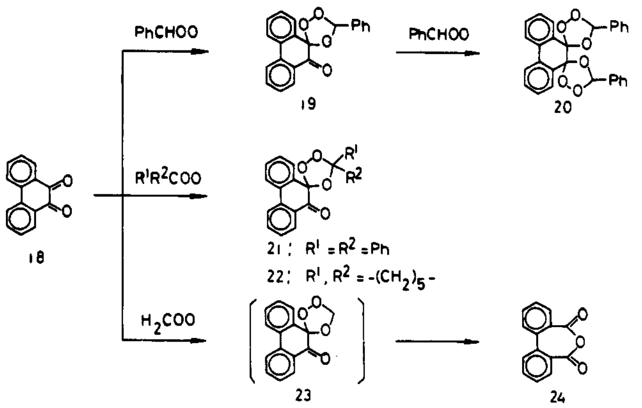
Scheme III



Scheme IV

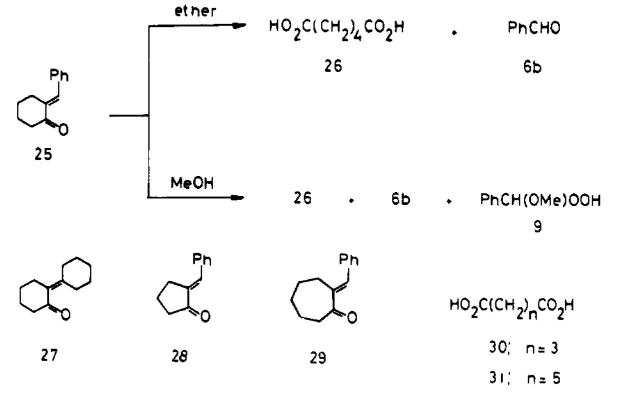


was also undertaken (Table II). The reaction in methylene chloride gave anhydride **5** and benzaldehyde (**6b**) quantitatively. When the reaction was performed in methanol/methylene chloride, α-methoxybenzyl hydroperoxide (**9**) and quinone **4** were obtained in yields of 42% and 60%, respectively, with a concomitant decrease in yield of anhydride **5** (15%). A probable mechanism for the reaction of **7** is illustrated in Scheme II.

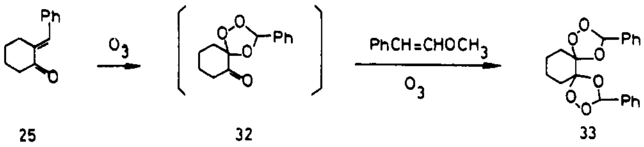
Similar behavior was observed for 1-phenyl-1,2-propanedione (**10**). Ozonolysis of vinyl ether **1** in the presence of **10** in ether, followed by column chromatography on silica gel, resulted in the isolation of benzoic acid (**12**) in excellent yield (Table I). From the reaction with 1,2-cyclooctanedione (**15**) was isolated suberic acid (**16**) in good yield. A possible mechanism involves an oxygen atom transfer from a carbonyl oxide **2** to **10**, giving first anhydride **11**, which in turn decomposes on silica gel to yield **12** (Scheme III). However, an alternative pathway may be considered which involves [3 + 2] cycloaddition of carbonyl oxide **2** with diketone **10** to yield the 3-benzoyl-3-methyl-1,2,4-trioxolane **14**; subsequent decomposition of **14** would lead to the formation of acid **12**. Perhaps consistent with the latter, Griesbaum et al. have found that ozonolysis of 2-methoxypropene in the presence of 2,3-butanedione in pentane gives a mixture of acetic anhydride (39%), methylene diacetate (22%), and 3,3′-dimethyl-3,3′-bi-1,2,4-trioxolane (12%). These products are most likely produced via 3-acetyl-3-methyl-1,2,4-trioxolane, the [3 + 2] cycloaddition product between formaldehyde *O*-oxide and 2,3-butanedione.[4] Ozonolysis of vinyl ether in the presence of the more bulky benzil (**17**), however, resulted in the quantitative recovery of **17** (Table I).

The [3 + 2] cycloaddition products were obtained from the reaction with phenanthrenequinone (**18**) (Scheme IV and Table I). Ozonolysis of a 1:1 mixture of 1-methoxy-2-phenylethene (**1b**) and **18** in methylene chloride at 0 °C gave the corresponding α-oxo ozonide **19**; although the ^{1}H NMR spectra of the crude products showed the formation of **19** as a mixture of two isomers (ca. 1:1; 60% yield), only one isomer of **19** could be isolated in 33% yield by column chromatography on silica gel. When the reaction of **1b** and ozone (2 mmol in each) was undertaken in the presence of 1 mmol of **18**, the corresponding diozonide **20** was obtained in 87% yield. Thus, the α-oxo ozonide **19** is able to sustain additional attack by **2b**. Under the same conditions, however, the bulkier carbonyl oxides, benzophenone *O*-oxide (**2c**) and cyclohexanone *O*-oxide (**2d**), attacked only one of the carbonyl groups of **18**, to provide the α-oxo ozonides **21** and **22** in high yield. In contrast, the reaction of formaldehyde *O*-oxide (**2a**) and **18** led to exclusive formation of diphenic anhydride (**24**). Probably the instability of the cycloadduct **23** was the reason. A brief comment is made here for the qualitative stability of the α-oxo ozonides, **19**, **21**, and **22**. These ozonides seem to be much more stable than those reported by Griesbaum[4] and Bunnelle.[5] At 7–10 °C the ozonides, **19**, **21**, and **22**, did not decompose for 2 weeks. Even in $CdCl_3$ at room temperature they were stable at least for 1 day.

Scheme V



Scheme VI



Thus, the products from the reaction of carbonyl oxides and α-diketones are remarkably influenced by structure, especially that of the α-diketones. The question is whether the apparent Baeyer–Villiger type products, e.g., **5**, **12**, and **16**, are produced by a direct oxygen atom transfer from carbonyl oxide to α-diketone or, alternatively, by decomposition of α-oxo ozonide formed first by [3 + 2] cycloaddition of carbonyl oxide to α-diketone. In this respect, the following observation is suggestive. Ozonolysis of benzylidenecyclohexanone (**25**) in ether, followed by column chromatography on silica gel, resulted in the isolation of a mixture of adipic acid (**26**; 50%) and benzaldehyde (**6b**; 60%) (Scheme V and Table II). Similarly, ozonolyses of α,β-unsaturated ketones **27**–**29** gave **26**, glutaric acid (**30**), and pimelic acid (**31**), respectively. When the reaction of **25** was undertaken in methanol, α-methoxy hydroperoxide **9** was obtained in 29% yield, together with **26** (20%) and **6b** (38%) (Scheme V and Table II). These results are very similar to those observed for the ozonolysis of benzylidenenaphthenone (**7**).

However, the following result suggests that adipic acid (**26**) was the decomposition product from α-oxo ozonide **32**. A solution of **25** in ether was treated with 1 equiv of ozone at −70 °C. Immediate addition of 2 equiv of vinyl ether **1b** into the reaction mixture, followed by treatment with ozone, gave diozonide **33** in 58% yield (Scheme VI). This result implies that (a) benzaldehyde *O*-oxide can

Scheme VII

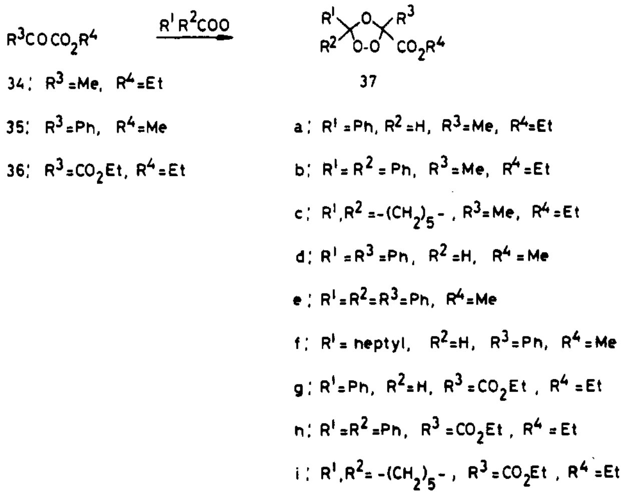


Table III. Ozonolysis of Vinyl Ether in the Presence of α-Keto Ester[a]

keto ester	vinyl ether	products (%, yield)	recovered keto ester, %
34	**1b**	**37a** (90)	
34	**1c**	**37b** (86)	
34	**1d**	**37c** (84)	
35	**1b**	**37d** (77)	20
35	**1c**	**37e** (80), **6c** (18)	13
35	**1e**	**37f** (46)	52
36	**1b**	**37g** (66), **6b** (9)	33
36	**1c**	**37h** (89)	10
36	**1d**	**37i** (83)	11

[a] Ozonolysis of a 1:1 mixture of vinyl ether and α-keto ester was undertaken in ether at −70 °C.

cycloadd to cyclohexane-1,2-dione to yield α-oxo ozonide **32** and (b) α-oxo ozonide **32** has a finite lifetime at least at −70 °C.[8]

Reaction of Carbonyl Oxides with α-Keto Esters. In contrast to the reactions with the α-diketones, cycloaddition of carbonyl oxide to α-keto esters proceeded very smoothly. Thus, the ozonolysis of vinyl ethers **1** in the presence of ethyl pyruvate (**34**) or methyl benzoylformate (**35**) in ether gave the ozonides **37a–f** in high yield. Similar behavior was observed for diethyl oxomalonate (**36**) (Scheme VII and Table III). Of particular interest is the finding that these ozonides are stable enough to be isolated by conventional column chromatography on silica gel without significant decomposition.

Experimental Section

^{1}H NMR and ^{13}C NMR spectra were obtained in $CDCl_3$ with JNM-PS-100 and JEOL-GSX-400 spectrometers, respectively. Vinyl ethers **1b–e**,[7d] 1,2-cyclooctanedione,[9] α,β-unsaturated ketones **7**,[10] **25**,[11] **27**,[12] **28**,[11] and **29**[11] were prepared by the reported methods. The starting materials **1a**, **10**, **17**, **18**, 1,2-cyclohexanedione, and **34–36** and the authentic samples of products **5**, **16**, **24**, **26**, **30**, and **31** were purchased from Aldrich Chemical Co. The ozonolysis procedure has been described previously;[7e] the concentration of ozone in oxygen was determined by passing a stream of ozone through an aqueous acetic acid solution of KI, followed by back-titration with aqueous $Na_2S_2O_3$.

CAUTION. During this study, we did not experience any problems during handling the α-oxo ozonides and the diozonides. They are, however, potentially explosive compounds, and therefore, appropriate precautions should be taken.

Ozonolysis of Vinyl Ether in the Presence of Acenaphthenequinone (4). Through a solution of **4** (50 mg, 0.27 mmol) and a vinyl ether (0.27 mmol) in CH_2Cl_2 (15 mL) was passed a slow stream of O_3 (0.27 mmol) at −70 °C. After warming to rt and evaporation of the solvent in vacuo, the composition of the benzene-insoluble products (1,8-naphthalic anhydride (**5**) and the unreacted quinone **4**) was determined by comparing the intensity of the characteristic absorptions of **5** (1760 cm^{-1}) and **4** (1720 cm^{-1}). These products were separated by column chromatography on silica gel (elution with benzene/CH_2Cl_2, 10:1). The physical properties of **5** (mp 267–269 °C) were identical with those of the authentic sample. The benzene-soluble products were also separated by column chromatography on silica gel (elution with benzene).

Ozonolysis of Benzylideneacenaphthenone (7) in MeOH/CH_2Cl_2. The ozonolysis of **7** (200 mg, 0.71 mmol) was conducted in methanol/CH_2Cl_2 (20 mL; 1:1) at −70 °C. After addition of ether (100 mL), the organic layer was washed with ice-cold aqueous KH_2PO_4 and then with saturated brine. After evaporation of the solvent, the products were triturated with benzene/hexane to give a mixture of **4** and **5**, the composition being determined by IR spectroscopy. The products soluble in benzene/hexane were separated by column chromatography on silica gel. The first fraction (elution with benzene/hexane, 1:1) contained benzaldehyde (**6b**). α-Methoxybenzyl hydroperoxide (**9**)[7d] was obtained by the subsequent elution with ether/benzene (1:50).

Ozonolysis of a 1:1 Mixture of 1-Methoxy-2-phenylethene (1b) and Phenanthrenequinone (18). Through a CH_2Cl_2 solution of **1b** and **18** (1 mmol in each) was passed a slow stream of O_3 at 0 °C. The ^{1}H NMR spectra of the crude products showed the production of two isomers of the α-oxo ozonide **19** (δ 6.45 (s) and 6.72 (s); ca. 1:1) in around 60% yield. However, column chromatography on silica gel resulted in the isolation of only one isomeric α-oxo ozonide **19** (110 mg, 33%), together with the diozonide **20** (18 mg, 4%) and **18** (50 mg, 29%).

Spiro[(3-phenyl-1,2,4-trioxolane)-5,9′-(10′-oxo-9′,10′-dihydrophenanthrene)] (19): mp 95 °C; ^{1}H NMR δ 6.45 (s, 1 H), 7.2–8.2 (m, 13 H); ^{13}C NMR δ 102.25, 107.43, 123.38–135.99 (18 C), 191.64; IR 1710, 1600, 1458, 1270, 1210, 1158, 1105, 1010, 915, 750, 680 cm^{-1}. Anal. Calcd for $C_{21}H_{14}O_4$: C, 76.37; H, 4.24. Found: C, 75.62; H, 4.30.

Ozonolysis of a Vinyl Ether in the Presence of 0.5 equiv of Phenanthrenequinone (18). The ozonolysis of a mixture of **1b** and **18** is representative. Through a solution of **18** (208 mg, 1 mmol) and **1b** (268 mg, 2 mmol) in CH_2Cl_2 (15 mL) was passed a stream of O_3 (2 mmol) at 0 °C. After evaporation of the solvent, the products were separated by column chromatography on silica gel. Elution with benzene/hexane (1:1) afforded dispiro[(3-phenyl-1,2,4-trioxolane)-5,9′-(9′,10′-dihydrophenanthrene)-10′,5″-(3″-phenyl-1″,2″,4″-trioxolane)] (**20**) as a mixture of two isomers (2:1; 403 mg, 87% yield). Repeated column chromatography gave first the major isomer of **20**: viscous oil; ^{1}H NMR δ 6.57 (s, 2 H), 7.1–8.1 (m, 18 H); ^{13}C NMR δ 106.16 (2 C), 106.66 (2 C), 124.34–133.78 (24 C). Anal. Calcd for $C_{28}H_{20}O_6$: C, 74.34; H, 4.42. Found: C, 75.50; H, 4.61. The subsequent elution gave the minor isomer in an admixture with 40% of the major one: viscous oil; ^{1}H NMR δ 6.36 (s, 1 H), 6.45 (s, 1 H), 7.1–8.1 (18 H); ^{13}C NMR δ 106.11 (2 C), 106.34 (2 C), 124.28–134.76 (24 C); IR 1460, 1395, 1220, 1050, 990, 745, 700 cm^{-1}. Anal. Calcd for $C_{28}H_{20}O_6$: C, 74.34; H, 4.42. Found: C, 74.51; H, 4.50. Either of the isomeric diozonides **20** reacted immediately with 2 equiv of triphenylphosphine in $CDCl_3$, giving phenanthrenequinone and benzaldehyde quantitatively.

Spiro[(3,3-diphenyl-1,2,4-trioxolane)-5,9′-(10′-oxo-9′,10′-dihydrophenanthrene)] (21): mp 125–130 °C (from methanol); ^{13}C NMR δ 104.06, 113.22, 123.35–141.23 (24 C), 191.61; IR 1705,

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(8) The ozonolysis of a 2:1 mixture of **1b** and 1,2-cyclohexanedione in ether at −70 °C resulted in the formation of a complex mixture of unidentified products, probably because 1,2-cyclohexanedione existed as a mixture with the enol form. The formation of the α-oxo ozonide **32** from the ozonolysis of **25** would then imply that cycloaddition of benzaldehyde *O*-oxide (**2b**) to the 1,2-cyclohexanedione produced in situ during the ozonolysis was significantly faster than the enolization.

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1600, 1448, 1275, 1210, 1150, 1100, 1040, 1010, 958, 910, 740, 685 cm^{-1}. Anal. Calcd for $C_{27}H_{18}O_4$: C, 79.80; H, 4.43. Found: C, 79.77; H, 4.70.

Dispiro[cyclohexane-1,3′-(1′,2′,4′-trioxolane)-5′,9″-(10″-oxo-9″,10″-dihydrophenanthrene)] (22): mp 95–96 °C dec (from methanol); ^{13}C NMR δ 23.67–41.98 (5 C), 102.39, 113.00, 123.33–136.07 (12 C), 192.11; IR 2935, 2860, 1715, 1605, 1455, 1278, 1175, 1095, 1020, 982, 920, 760 cm^{-1}. Anal. Calcd for $C_{20}H_{18}O_4$: C, 74.53; H, 5.59. Found: C, 74.22; H, 5.66.

Preparation of Dispiro[(3-phenyl-1,2,4-trioxolane)-5,1′-cyclohexane-2′,5″-(3″-phenyl-1″,2″,4″-trioxolane)] (33). A solution of benzylidenecyclohexanone (**25**; 186 mg, 1 mmol) in ether (15 mL) was treated with 1 mmol of O_3 at −70 °C. Then, vinyl ether **1b** (268 mg, 2 mmol) dissolved in ether (5 mL) was added, and the mixture was treated with 2 mmol of O_3 at the same temperature. After evaporation of the solvent, the products were triturated with ether/hexane to give the diozonide **33** (206 mg, 58%) as a ca. 1:1 mixture of two isomers. Recrystallization from ethyl acetate yielded a ca. 3:2 mixture, but further separation of each isomer failed. This mixture showed the following physical properties: mp 95–100 °C; ^{1}H NMR δ 1.4–3.0 (m, 8 H), 6.14 (s, CH, minor), 6.35 (s, CH, major), 7.3–8.4 (m, 10 H); ^{13}C NMR (major) δ 21.94, 22.58, 32.82, 34.18, 104.25, 104.94, 108.29, 109.01, 128.01–130.98 (12 C); ^{13}C NMR (minor) δ 22.07 (2 C), 34.53 (2 C), 105.10 (2 C), 108.52 (2 C), 127.94–131.13 (12 C); IR 2950, 2920, 1460, 1390, 1320, 1180, 1110, 1040, 1010, 760, 700 cm^{-1}. Anal. Calcd. for $C_{20}H_{20}O_6$: C, 67.41; H, 5.62. Found: C, 67.42; H, 5.63.

Ozonolysis of Vinyl Ether in the Presence of α-Keto Ester. The ozonolysis of a mixture of vinyl ether **1b** and ethyl pyruvate (**34**) is representative. A solution of **1b** (134 mg, 1 mmol) and **34** (116 mg, 1 mmol) in ether (15 mL) was treated with 1 mmol of O_3 at −70 °C. Subsequent column chromatography on silica gel (elution with benzene) gave ethyl 3-methyl-5-phenyl-1,2,4-trioxolane-3-carboxylate (**37a**) (214 mg, 90%) as a mixture of two isomers (2:3): oil; ^{1}H NMR δ 1.32 (t, J = 7 Hz, 3 H), 1.73 (s, 3 H), 4.28 (q, J = 7 Hz, 2 H), 6.02 (s, CH, major), 6.24 (s, CH, minor), 7.3–7.7 (m, 5 H); ^{13}C NMR δ 13.93 (minor), 13.96 (major), 18.95 (major), 19.36 (minor), 62.06 (major), 62.26 (minor), 104.28 (major), 105.07 (minor), 105.13 (major), 105.16 (minor), 126.95–134.04 (6 C), 167.65 (minor), 168.60 (major). Anal. Calcd for $C_{12}H_{14}O_5$: C, 60.51; H, 5.88. Found: C, 60.56; H, 5.99.

Ethyl 3,3-diphenyl-5-methyl-1,2,4-trioxolane-5-carboxylate (37b): mp 35–36 °C (from hexane); ^{1}H NMR δ 1.26 (t, J = 7 Hz, 3 H), 1.55 (s, 3 H), 4.23 (q, J = 7 Hz, 2 H), 7.2–7.7 (m, 10 H); ^{13}C NMR δ 13.99, 19.38, 62.10, 105.91, 111.50, 126.39–140.41 (12 C), 168.61. Anal. Calcd for $C_{18}H_{18}O_5$: C, 68.79; H, 5.73. Found: C, 69.33; H, 5.77.

Ethyl 9-methyl-7,8,10-trioxaspiro[5.4]decane-9-carboxylate (37c): oil; ^{1}H NMR δ 1.32 (t, J = 7 Hz, 3 H), 1.56 (s, 3 H), 1.2–1.9 (m, 10 H), 4.23 (q, J = Hz, 2 H); ^{13}C NMR δ 13.93, 19.25, 23.31, 23.80, 24.62, 32.35, 35.05, 103.87, 111.26, 168.99. Anal. Calcd for $C_{11}H_{18}O_5$: C, 57.39; H, 7.83. Found: C, 57.12; H, 7.95.

Methyl 3,5-diphenyl-1,2,4-trioxolane-3-carboxylate (37d): a mixture of two isomers (2:3); oil; ^{1}H NMR δ 3.81 (s, CH_3, minor), 3.86 (s, CH_3, major), 6.15 (s, CH, major), 6.36 (s, CH, minor), 7.2–7.9 (m, 10 H). By repeated column chromatography the major isomer could be isolated in a pure state: oil; ^{13}C NMR δ 53.15, 106.08, 106.18, 126.22–131.81 (12 C), 168.68. Anal. Calcd for $C_{16}H_{14}O_5$: C, 67.13; H, 4.90. Found: C, 67.70; H, 4.96.

Methyl 3,3,5-triphenyl-1,2,4-trioxolane-5-carboxylate (37e): mp 106–108 °C (from benzene/hexane); ^{1}H NMR δ 3.83 (s, 3 H), 7.3–7.7 (15 H). Anal. Calcd for $C_{22}H_{18}O_5$: C, 72.93; H, 4.97. Found: C, 72.95; H, 4.99.

Methyl 3-phenyl-5-heptyl-1,2,4-trioxolane-3-carboxylate (37f): a mixture of two isomers (2:3); oil; ^{1}H NMR δ 0.8–2.0 (m, 15 H), 3.71 (s, 3 H), 5.24 (t, J = 4.5 Hz, CH, major), 5.45 (t, J = 4.5 Hz, CH, minor), 7.2–7.6 (m, 5 H).

Diethyl 5-phenyl-1,2,4-trioxolane-3-malonate (37g): oil; ^{1}H NMR δ 1.35 (t, J = 7 Hz, 6 H), 4.32 (q, J = 7 Hz, 4 H), 6.13 (s, 1 H), 7.2–7.8 (m, 5 H). Anal. Calcd for $C_{14}H_{16}O_7$: C, 56.75; H, 5.41. Found: C, 56.80; H, 5.43.

Diethyl 5,5-diphenyl-1,2,4-trioxolane-3-malonate (37h): mp 38–43 °C; ^{1}H NMR δ 1.18 (t, J = 7 Hz, 6 H), 4.17 (q, J = 7 Hz, 4 H), 7.2–7.8 (m, 10 H); ^{13}C NMR δ 13.84 (2 C), 63.05 (2 C), 101.18, 113.41, 127.71–136.13 (12 C), 163.62 (2 C). Anal. Calcd for $C_{20}H_{20}O_7$: C, 64.51; H, 5.38. Found: C, 64.75; H, 5.30.

Diethyl 7,8,10-trioxaspiro[5.4]decane-9,9-dicarboxylate (37i): oil; ^{1}H NMR δ 1.32 (t, J = 7 Hz, 6 H), 1.2–2.1 (m, 10 H), 4.25 (q, J = 7 Hz, 4 H).

Registry No. **1a**, 109-53-5; **1b**, 4747-15-3; **1c**, 40237-72-7; **1d**, 19096-89-0; **1e**, 120872-41-5; **4**, 82-86-0; **5**, 81-84-5; **6b**, 100-52-7; **6c**, 119-61-9; **6d**, 108-94-1; **7**, 963-63-3; **9**, 10027-71-1; **12**, 65-85-0; **16**, 505-48-6; **18**, 84-11-7; *trans*-**19**, 136460-07-6; *cis*-**19**, 136460-08-7; **20**, 136460-09-8; **21**, 136460-10-1; **22**, 136460-11-2; **24**, 6050-13-1; **25**, 5682-83-7; **27**, 1011-12-7; **28**, 5679-13-0; **29**, 42063-01-4; **30**, 110-94-1; **31**, 111-16-0; **33**, 136460-21-4; **34**, 617-35-6; **35**, 15206-55-0; **36**, 609-09-6; *trans*-**37a**, 136460-12-3; *cis*-**37a**, 136460-13-4; **37b**, 136460-14-5; **37c**, 136460-15-6; *trans*-**37d**, 136460-16-7; *cis*-**37d**, 136460-17-8; **37e**, 136460-06-5; *trans*-**37f**, 136460-18-9; *cis*-**37f**, 136460-19-0; **37g**, 136460-20-3; **37h**, 136460-22-5; **37i**, 136460-23-6; 3,3,6,6-tetraphenyl-1,2,4,5-tetroxane, 16204-36-7.

Transformation of Neoclerodane Diterpenoids into 19-Norneoclerodane Derivatives

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The neoclerodane diterpenoid eriocephalin (**1**) was transformed into its 19-nor derivatives **3** and **4** by reaction with potassium *tert*-butoxide in THF, whereas with the same treatment compound **6** yielded only the transacetylation derivative **7**. These results indicated that 19-acetoxy-4α,18-epoxy-7α-hydroxy-6-oxoneoclerodane derivatives are transformed into the corresponding 19-nor compounds in a retroaldol reaction by loss of the C-19 carbon as formaldehyde followed by opening of the oxirane ring and intramolecular attack by a C-18 alkoxide on the carbonyl C-6 carbon atom, giving the allylic hemiacetal **3**, which is easily dehydrated to the furanic derivative **4**. Compound **4** was transformed into the α,β-unsaturated γ,δ-enol γ-lactone **8** by an oxidation reaction with atmospheric oxygen in chloroform solution. Alternatively, it gave the α,β-unsaturated γ-lactone **11** under acid catalysis. These reactions allowed the partial syntheses of the naturally occurring diterpenoids teuscorolide (**9**) and teucvin (**12**) and are of interest for chemical transformations of substances of this kind.

A large number of neoclerodane and 19-norneoclerodane diterpenoids[2] have been isolated from plants in the last few years.[3] These compounds have attracted interest owing to their biological activities, especially as insect