Octalone 12c: IR 3020 (w, olefinic CH), 1718 (s, C=O), 1665 (w, C=C), 1399, 1368 (m, CMe_3) cm^{-1}; ^1H NMR δ 0.94 (s, 9, Me_3), 0.95 (d, 3, J = 6 Hz, 8-Me), 5.44 (br s, 2, H-6, H-7). Anal. Calcd for $C_{15}H_{24}O$: C, 81.76; H, 10.98. Found: C, 81.44; H, 10.93.

Decalone 15: IR 1714 (s, C=O) cm^{-1}; ^1H NMR δ 0.98 (d, 3, J = 5 Hz, Me). 2,4-Dinitrophenylhydrazone: mp 190–191 °C. Anal. Calcd for $C_{17}H_{22}O_4N_4$: C, 58.95; H, 6.40; N, 16.17. Found: C, 58.95; H, 6.14; N, 16.50.

Decalone 16: IR 1714 (s, C=O) cm^{-1}; ^1H NMR δ 0.91 (d, 3, J = 5 Hz, Me), 0.95 (d, 3, J = 6 Hz, Me). 2,4-Dinitrophenylhydrazone: mp 209–210 °C. Anal. Calcd for $C_{18}H_{24}O_4N_4$: C, 59.98; H, 6.71; N, 15.54. Found: C, 60.05; H, 6.62; N, 15.51.

Decalone 17: IR 1715 (s, C=O) cm^{-1}; ^1H NMR δ 1.02 (d, 3, J = 6 Hz, Me). Anal. Calcd for $C_{11}H_{18}O$: C, 79.46; H, 10.91. Found: C, 79.39; H, 10.82.

Decalone 18: IR 1717 (s, C=O) cm^{-1}; ^1H NMR δ 1.00 (d, 3, J = 6 Hz, Me), 1.10 (d, 3, J = 5 Hz, Me). Anal. Calcd for $C_{12}H_{20}O$: C, 79.94; H, 11.18. Found: C, 79.83; H, 11.28.

Decalone 19: IR 1722 (s, C=O), 1385, 1370 (m, $CHMe_2$) cm^{-1}; ^1H NMR δ 0.76, 0.99 (d, 3 each, J = 6 Hz, Me_2). 2,4-Dinitrophenylhydrazone: mp 207–208 °C. Anal. Calcd for $C_{19}H_{26}O_4N_4$: C, 60.93; H, 7.01; N, 14.96. Found: C, 61.21; H, 7.27; N, 14.70.

Decalone 20: IR 1710 (s, C=O), 1385, 1370 (m, $CHMe_2$) cm^{-1}; ^1H NMR δ 0.97, 1.00 (d, 3 each, J = 6 Hz, Me_2), 1.10 (d, 3, J = 7 Hz, 8-Me). Anal. Calcd for $C_{14}H_{24}O$: C, 80.71; H, 11.61. Found: C, 80.58; H, 11.60.

Decalone 21: IR 1713 (s, C=O), 1389, 1370 (m, $CHMe_2$) cm^{-1}; ^1H NMR δ 0.74, 0.97 (d, 3 each, J = 6 Hz, Me_2), 0.88 (d, 3, J = 7 Hz, 8-Me). 2,4-Dinitrophenylhydrazone: mp 157–158 °C. Anal. Calcd for $C_{20}H_{28}O_4N_4$: C, 61.84; H, 7.26; N, 14.42. Found: C, 61.50; H, 7.16; N, 14.11.

Decalone 22: IR 1713 (s, C=O), 1385, 1369 (m, $CHMe_2$) cm^{-1}; ^1H NMR δ 0.95 (d, 6, J = 5 Hz, Me_2), 1.07 (d, 3, J = 7 Hz, 8-Me). Anal. Calcd for $C_{14}H_{24}O$: C, 80.71, H, 11.61. Found: C, 80.95; H, 11.59.

Decalone 23: IR 1715 (s, C=O), 1395, 1369 (m, CMe_3) cm^{-1}; ^1H NMR δ 1.00 (s, 9, Me_3). Anal. Calcd for $C_{14}H_{24}O$: C, 80.71; H, 11.61. Found: C, 80.86; H, 11.63.

Decalone 24: mp 42–43 °C; IR 1716 (s, C=O), 1396, 1370 (m, CMe_3) cm^{-1}; ^1H NMR δ 1.00 (s, 9, Me_3), 1.13 (d, 3, J = 6 Hz, 8-Me). Anal. Calcd for $C_{15}H_{26}O$: C, 81.02; H, 11.78. Found: C, 81.13; H, 11.68.

Acknowledgment. F.F., F.P., A.T., and A.P.T. thank the Consiglio Nazionale delle Ricerche and F.F. and A.T. thank the Ministero Pubblica Istruzione for financial support of the work in Perugia. A.T. and E.W. are indebted to NATO for grant (No. 257.81) support. We are grateful to Professor F. Zanazzi (Istituto di Mineralogia, Università di Perugia) for his X-ray crystallographic analysis.

Diels-Alder Reactions of Cycloalkenones. 7. Reactions of Carvone[1]

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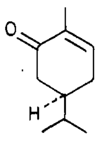
Received March 5, 1985

Diels–Alder reactions of (–)-carvone with 1,3-butadiene, isoprene, (*E*)-piperylene, and 1,3-dimethyl-1,3-butadiene under aluminum chloride catalysis are reported. Structure analysis of the products and some of their hydrogenated derivatives by ^{13}C NMR spectroscopy is described.

Recent, exhaustive studies of the acid-catalyzed Diels–Alder reaction of 4-[1] and 5-alkyl-2-cyclohexenones[3] with 1,3-butadiene and its 1- and 2-methyl derivatives have furnished a variety of octalones and decalones of potentially wide use. Thus, for example, the *tert*-butylated bicyclic ketones can be exploited in the area of conformational analysis and the methylated and isopropylated compounds in the field of terpene synthesis.[4] It now became of interest to investigate reactions of carvone (**1**) with dienes, not only for the rapid construction of sesquiterpenic ring skeleta containing an angular methyl group but also for gaining flexible entry into the realm of optically active substances in view of the ready availability of the monoterpene in (+) and (–) forms. As a consequence (–)-carvone (**1**) was submitted to Diels–Alder reactions with 1,3-butadiene (**2a**), isoprene (**2b**), (*E*)-piperylene (**2c**), and 1,3-dimethyl-1,3-butadiene (**2d**) under aluminum chloride catalysis.[5]



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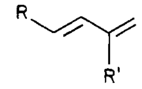

2a, R = R' = H
b, R = H; R' = Me
c, R = Me; R' = H
d, R = R' = Me

The reactions were carried out in toluene solution at 25–40 °C for 13–93 h and gave 80–88% yields of *cis*-octalones, as shown in Table I. The structures of the ketonic products were determined by ^{13}C NMR spectroscopy and the carbon shifts are listed in Table II.[7]

By comparison of the carbon shifts of angularly unmethylated *cis*-octalones and *cis*-decalones containing C(3)-isopropyl groups oriented cis to H(4a)[3] with ketones **3c,d** and **7**, respectively, it is possible to deduce the structures of the three new ketones as depicted by their

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[1] For part 6, see: Angell, E. C.; Fringuelli, F.; Halls, T. D. J.; Pizzo, F.; Porter, B.; Taticchi, A.; Tourris, A. P.; Wenkert, E. *J. Org. Chem.*, second in a series of three paper in this issue.

[2] (a) University of California. (b) Università di Perugia.

[3] Angell, E. C.; Fringuelli, F.; Minuti, L.; Pizzo, F.; Porter, B.; Taticchi, A.; Wenkert, E. *J. Org. Chem.*, first in a series of three papers in this issue.

[4] Fringuelli, F.; Pizzo, F.; Taticchi, A.; Ferreira, V. F.; Michelotti, E. L.; Porter B.; Wenkert, E. *J. Org. Chem.* **1985**, *50*, 890.

[5] For previous reactions of carvone with dienes, see (a) Nerdel, F.; Dahl, H. *Liebigs Ann. Chem.* **1967**, *710*, 90. (b) Harayama, T.; Cho, H.; Inubushi, Y. *Tetrahedron Lett.* **1975**, 2693; *Chem. Pharm. Bull. Jpn.* **1977**, *25*, 2273.

[6] Fringuelli, F.; Pizzo, F.; Taticchi, A.; Halls, T. D. J.; Wenkert, E. *J. Org. Chem.* **1982**, *47*, 5056.

[7] On the basis of the present data the δ values of the two methyl groups in ketone **9f** as well as **25d** of ref 6 require reversal.

0022-3263/85/1950-4696$01.50/0

Table I. Aluminum Chloride Catalyzed Diels–Alder Reactions of (−)-Carvone (1) with Dienes 2[a]

diene	diene/ketone[b]	AlCl$_3$/ketone[b]	ketone (M)	reactn temp (°C)	reactn time (h)	product yield (%)[c]	products	product ratio	% anti addition
2a	15	0.2	0.2	40	93	86	**3a**, **5a**, **6**	20.5:1.3:1	>90
2b[d]	15	0.2	0.2	25	14	80	**3b**, **5b**	9.5:1	90
2c[e]	9	0.2	0.2	25	13	88	**3c**, **4c**	3:1	95
2d[d]	3	0.1	0.1	25	36	86	**3d**, **4d**	3.8:1	97

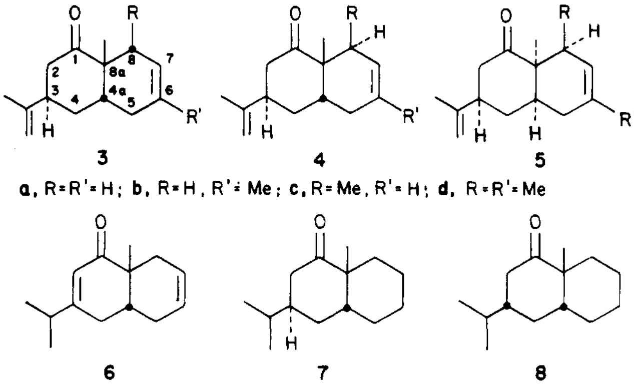
[a] Complexation time, 40 min; complexation temperature, 22 °C.[6] [b] Ratio of equivalents. [c] GC-based yields. [d] One isolated compound accounts for 0.5% and 3% of the mixtures of the reactions of **2b** and **2d**, respectively. [e] Two unisolated products account for 4% and 0.5% of the reaction mixture.

Table II. ^{13}C Chemical Shifts of Bicyclic Ketones 3–8[a]

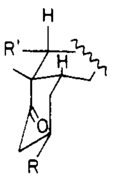
	3a	**3b**	**3c**	**3d**	**4c**	**4d**	**5a**	**5b**	**6**[b]	**7**[b]	**8**[b]
C(1)	214.4	214.6	213.5	213.6	214.3	214.9	214.5	215.2	204.1	216.0	216.8
C(2)	41.1	41.0	43.5	43.5	40.9	40.9	42.0	42.0	120.8	41.5	41.1
C(3)	40.9	40.8	42.3[c]	42.2	40.8	40.8	44.6	44.7	168.1	39.9	43.5
C(4)	30.0	30.0	30.3	30.3	29.6	29.7	33.6	33.7	31.2[c]	30.0[c]	30.5[c]
C(4a)	36.8	37.3	41.8[c]	42.2	36.1	36.7	39.6	40.4	37.5	44.5	41.0
C(5)	27.7	32.6	27.9	32.8	28.1	33.1	28.0	33.0	28.0	30.3[c]	27.1
C(6)	124.2	130.9	122.7	129.6	123.6	130.4	123.9	130.7	125.4	26.4	20.4
C(7)	123.7	117.6	131.7	126.0	129.5	123.7	122.4	116.3	124.0	23.2	21.3
C(8)	31.6	32.0	39.2	39.7	31.5	31.9	30.8	31.3	30.7[c]	34.6	30.4[c]
C(8a)	47.1	46.7	50.3	50.0	50.7	50.7	46.7	46.6	43.1	48.6	48.2
8a-Me	21.3	21.2	23.7	23.1	14.9[c]	15.2	19.4	19.4	20.4	27.4	19.5
6-Me		23.4		23.6		23.4		23.7			
8-Me			16.2	16.4	15.1[c]	15.2					
i-Pr Me	22.8	22.7	20.5	20.5	22.2	22.2	20.3	20.3			
i-Pr CH$_2$	110.9	110.9	109.7	109.7	112.1	112.1	109.4	109.4			
i-Pr C	147.1	147.1	147.4	147.5	147.0	147.0	147.5	147.6			

[a] The δ values are in parts per million downfield from Me$_4$Si; δ(Me$_4$Si) = δ(CDCl$_3$) + 76.9 ppm. [b] The δ values of the *i*-Pr methyl groups are for **6**, 20.7, 20.7; **7**, 19.7, 19.3; **8**, 19.5, 19.2 ppm. The δ values of the *i*-Pr methines are for **6**, 35.3; **7**, 32.9; **8**, 32.7 ppm. [c] Signals in any vertical column may be interchanged.

Chart I



formulas and their conformations as shown in part structure **9**. The introduction of the angular methyl group produces a γ-effect on C(2) and C(4), shielding these centers in the three compounds, with little variation of the shift pattern of the nonketonic ring. Since octalone **3a** was a ketone of known constitution[5b] and since compound **3b** exhibited carbon shifts different from those of ketone **3a** only by the variations expected for a butadiene- and an isoprene-based bicycle,[1,3,6] the structure of octalone **3b** was assured. Furthermore, the serious shift changes imposed on the bicyclic system by the introduction of an 8α-methyl group (**3a** and **3b** vs. **3c** and **3d**, respectively) suggested ketones **3a** and **3b** to exist predominantly in a conformation different from that of their 8α-methylated derivatives, i.e., part structure **10**. The latter conformation is preferred even more by ketones **4c** and **4d** in which the 8β-methyl group resides in an equatorial orientation. The angular methyl group of these compounds is shielded extraordinarily, presumably not only by the γ-effects imposed by C(5), C(7), and the 8β-methyl group but also by the carbonyl oxygen (due to the syn, periplanar relationship of the carbonyl and methyl groups in this conformation). The **5a–b** shift relationship is the same as that of the above **3a-b** octalone pair and ketone **5a** being of known structure[5b] settles the configuration of isoprene-derived ketone **5b**. Conformationally the latter two compounds are related to the **4c–d** octalone pair except for an axial isopropenyl group in compounds **4c** and **4d** and an equatorial C(3) side chain in substances **5a** and **5b**. This fact is substantiated by the shielding of C(4a) in the ketones with the axial substituent. The carbon shifts of bicycles **6** and **8** fit the structures determined earlier.[5b]



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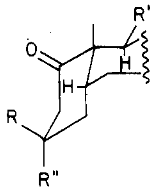

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By the use of the previously outlined procedure of the best reaction conditions for the acid-catalyzed Diels–Alder reactions of cycloalkenones[6,8] the four cycloadditions of (−)-carvone (**1**) could be performed in more than 80% yield (Table I). The reaction with butadiene (**2a**) gave products in twice the yield reported earlier[5b] and included the syn addition[3] product **5a** not observed heretofore.[5b] The conjugated ketone **6** is a product of acid-induced isomerization of the normal adducts **3a** and **5a** and its presence in the reaction mixture is a function of the reaction temperature and time (40 °C, 93 h → 5.5%; 25 °C, 50 h → trace). No side product of type **6** was obtained in the other Diels–Alder reactions in view of their lower reaction temperature (Table I). Whereas ketone **6** must have been optically impure in view of its derivation from the **3a–5a**

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[8] Fringuelli, F.; Pizzo, F.; Taticchi, A.; Wenkert, E. *J. Org. Chem.* 1983, *48*, 2802.

J. Org. Chem. **1985**, *50*, 4698–4702

ketone mixture, it could be obtained in pure state in high yield by the acid-promoted isomerization of octalone **3a**. Hydrogenation of ketones **3a**[5b] and **6** produced decalones **7** (88% yield) and **8** (accompanied by **7** in 3% yield of the mixture; 85% overall yield).[9] The easy two-step preparation of ketone **8** now replaces an earlier synthesis of the compound by a circuitous route from ketone **7**[5b] and makes available the two C(3) epimers **7** and **8** in high yield.

The reaction of (−)-carvone (**1**) and isoprene (**2b**) led, by predominant anti addition,[3] to diastereomers **3b** and **5b**.[10] An even higher stereochemical preference is shown by the reactions of (−)-carvone (**1**) with (*E*)-piperylene (**2c**) and 1,3-dimethyl-1,3-butadiene (**2d**). In analogy with the behavior of 2-methyl-2-cyclohexenone[6] the last two cycloadditions produce both endo (**3c**, **3d**) and exo (**4c**, **4d**) products, the former predominating. The close similarity of the endo/exo product ratio of the two reactions and that of 2-methyl-2-cyclohexenone with (*E*)-piperylene (**2c**)[6] indicates the low influence of the isoprene methyl group on the diene–dienophile interaction complex even in cases of monosubstituted 2-cyclohexenones[1] and 2-methyl-2-cyclohexenones.

Experimental Section

The experimental conditions of the Diels–Alder reactions and the hydrogenations as well as the specifics on the spectral analyses of all ketones and on the instruments used are delineated in the Experimental Section of the adjoining publication.[3,6] The details of the reaction conditions are listed in Table I. The 2,4-dinitrophenylhydrazones were crystallized in 95% ethanol. The spectral data of octalones **3a** and **5a** and decalones **7** and **8** as well as the melting points of their 2,4-dinitrophenylhydrazones (**7**: mp 112–113 °C) were the same as those reported earlier.[5b]

Octalone 3b: IR 3095 (w, olefinic CH), 1710 (s, C=O), 1646 (w, C=C), 900 (m, C=CH_2) cm^{-1}; ^{1}H NMR δ 1.10 (s, 3, Me), 1.64 (s, 3, 6-Me), 1.75 (s, 3, Pr Me), 4.67, 4.78 (br s, 1 each, olefinic CH_2), 5.24 (br s, 1, H-7). 2,4-Dinitrophenylhydrazone: mp 109–110 °C. Anal. Calcd for $C_{21}H_{26}O_4N_4$: C, 63.30; H, 6.57; N, 14.06. Found: C, 63.41; H, 6.77; N, 13.90.

Octalone 3c: IR 3080, 3023 (w, olefinic CH), 1715 (s, C=O), 1646 (w, C=C), 890 (m, C=CH_2) cm^{-1}; ^{1}H NMR δ 1.20 (d, 3, *J* = 7 Hz, 8-Me), 1.37 (s, 3, Me), 1.78 (s, 3, Pr Me), 4.75 (br s, 2, olefinic CH_2), 5.45 (br s, 2, H-6, H-7). 2,4-Dinitrophenylhydrazone: mp 142–143 °C. Anal. Calcd for $C_{21}H_{26}O_4N_4$: C, 63.30; H, 6.57; N, 14.06. Found: C, 63.41; H, 6.77; N, 13.90.

Octalone 3d: IR 3080 (w, olefinic CH), 1715 (s, C=O), 1645 (w, C=C), 890 (m, C=CH_2) cm^{-1}; ^{1}H NMR δ 1.14 (d, 3, *J* = 7 Hz, 8-Me), 1.35 (s, 3, Me), 1.62 (s, 3, 6-Me), 1.77 (s, 3, Pr Me), 4.73 (s, 2, olefinic CH_2), 5.15 (br s, 1, H-7). 2,4-Dinitrophenylhydrazone: mp 170–171 °C. Anal. Calcd for $C_{22}H_{28}O_4N_4$: C, 64.06; H, 6.84; N, 13.58. Found: C, 64.12; H, 6.81; N, 13.78.

Octalone 4c: IR 3080, 3020 (w, olefinic CH), 1705 (s, C=O), 1646 (w, C=C), 900 (m, C=CH_2) cm^{-1}; ^{1}H NMR δ 0.80 (d, 3, *J* = 7 Hz, 8-Me), 0.91 (s, 3, Me), 1.74 (s, 3, Pr Me), 4.69, 4.74 (br s, 1 each, olefinic CH_2), 5.52 (m, 2, H-6, H-7). Anal. Calcd for $C_{15}H_{22}O$: C, 82.52; H, 10.15. Found: C, 82.42; H, 10.16.

Octalone 4d: IR 3080 (w, olefinic CH), 1705 (s, C=O), 1647 (w, C=C), 905 (m, C=CH_2) cm^{-1}; ^{1}H NMR δ 0.76 (d, 3, *J* = 7 Hz, 8-Me), 0.86 (s, 3, Me), 1.66 (s, 3, 6-Me), 1.76 (s, 3, Pr Me), 4.68, 4.83 (s, 1 each, olefinic CH_2), 5.05 (br. s, 1, H-7). 2,4-Dinitrophenylhydrazone: mp 119–120 °C. Anal. Calcd for $C_{22}H_{28}O_4N_4$: C, 64.06; H, 6.84; N, 13.58. Found: C, 64.15; H, 6.78; N, 13.46.

Octalone 5b: IR 3090 (w, olefinic CH), 1710 (s, C=O), 1648 (w, C=C), 890 (m, C=CH_2) cm^{-1}; ^{1}H NMR δ 1.03 (s, 3, Me), 1.65 (s, 3, 6-Me), 1.72 (s, 3, Pr Me), 4.67 (br s, 2, olefinic CH_2), 5.25 (m, 1, H-7). Anal. Calcd for $C_{15}H_{22}O$: C, 82.52; H, 10.15. Found: C, 82.58; H, 10.15.

Hexalone 6. A solution of 800 mg of octalone **3a** and 160 mg of *p*-toluenesulfonic acid in 40 mL of toluene was heated at 80 °C for 24 h. Upon dilution with water the cooled mixture was extracted with ether. The extract was washed with 10% sodium bicarbonate solution, dried (Na_2SO_4), and evaporated under vacuum. Chromatography of the residue on silica gel and elution with 20:1 hexane-ether gave 700 mg (87%) of colorless, liquid ketone **6**: IR 3030 (w, olefinic CH), 1670 (s, C=O), 16.35 (w, C=C), 1386, 1372 (m, $CHMe_2$) cm^{-1}; ^{1}H NMR δ 1.12 (s, 3, Me), 1.12 (d, 6, *J* = 7 Hz, Pr Me_2), 5.60 (m, 3, H-2, H-6, H-7). 2,4-Dinitrophenylhydrazone: mp 135–136 °C. Anal. Calcd for $C_{20}H_{24}O_4N_4$: C, 62.48; H, 6.29; N, 14.57. Found: C, 62.59, H, 6.33; N, 14.50.

Acknowledgment. F.F., F.P., and A.T. thank the Consiglio Nazionale delle Ricerche and F.F. and A.T. the Ministero Pubblica Istruzione for financial support of the work in Perugia. A.T. and E.W. are indebted to NATO for grant (No. 257.81) support.

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[9] In view of the >90% anti addition[3] experienced in the **1**–**2a** cycloaddition (Table I) the claim of the exclusive formation of a syn adduct in the aluminum chloride catalyzed Diels–Alder reaction of 5-isopropyl-2-methyl-2-cyclohexenone with 1,3-butadiene (**2a**) [Yamamoto, K.; Kawasaki, I.; Kaneko, T. *Tetrahedron Lett.* **1970**, 4859] is suspect.

[10] In contrast to the report of the isolation of regioisomers (albeit with undefined stereochemistry) in 7% yield from an uncatalyzed reaction.[5a]

Ozonolysis of Some Tetrasubstituted Ethylenes

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Received March 14, 1985

The olefins 1,4-dibromo-2,3-dimethyl-2-butene, 1-bromo-2,3-dimethyl-2-butene, and 2,3-dimethyl-2-butene were ozonized under a variety of conditions. Ozonolysis of 1,4-dibromo-2,3-dimethyl-2-butene in acetone solvent leads to the unexpected products acetone diperoxide and triperoxide. The results are discussed with respect to questions of concertedness in ozonide formation, the need for activating groups in ozonide formation, and the possible intermediacy of dioxiranes.

As a result of extensive investigation the reaction between ozone and alkenes is now reasonably well understood.[1] It seems certain, for example, that the reaction is a complex one which occurs in three distinct steps (eq 1–3). Within the general framework of this three-step scheme lie a number of vexsome questions pertaining to the details of the mechanism. Much of the recent effort relative to this process has been aimed at understanding the apparent influence of olefin stereochemistry on ozonide stereochemistry. The work of Bailey and co-workers[1a] and Kuczkowski and co-workers,[1b] as well as some of our own

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[1] For an excellent survey of the current situation regarding the mechanism of ozonolysis, see: (a) Bailey, P. S. "Ozonation in Organic Chemistry"; Academic Press: new York; 1978; Vol. I. (b) Kuczkowski, R. L. *Acc. Chem. Res.* **1983**, *16*, 42.

0022-3263/85/1950-4698$01.50/0