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Ozonolysis of Vinyl Ethers. Evidence for Intramolecular Oxygen Transfer from a Carbonyl Oxide Moiety to a Methoxyvinyl Group

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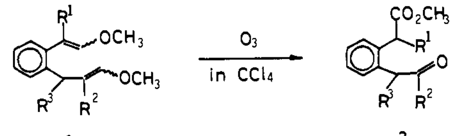
Abstract: Ozonolysis of diene **1** in carbon tetrachloride gave exclusively the keto ester **2**, while in methanol the keto olefin **17** was the major product. The behavior of model vinyl ethers **3a,b** has revealed that a mechanism involving intramolecular oxygen atom transfer from the carbonyl oxide moiety to a methoxyvinyl group is the most probable for the keto ester formation from diene **1**.

Several recent studies have investigated the transfer of an oxygen atom from carbonyl oxide intermediates as models for certain reactions catalyzed by monooxygenase enzymes.[1] Carbonyl oxides have, for example, been shown to function as the effective nucleophilic oxygen-transfer agents in the oxygenation of sulfoxides and electron-deficient olefins.[2] Although less effective, electrophilic transfer is also possible. The reaction of electron-rich alkenes with carbonyl oxides, produced via singlet oxygen oxidation of diazo compounds, yields the corresponding epoxides but generally in poor yield.[3] Oxygen transfer to aromatic rings also occurs, although the yield of the oxidation products is not satisfactory.[4] This is in marked contrast to the important finding by Murray that the isomeric dioxiranes oxidize these electron-rich substrates very efficiently.[5] We report herein that under certain conditions, however, electron-rich olefins can be effectively oxidized by carbonyl oxides.[6]

Results and Discussion

Ozonolysis of Dienes 1a–c in Carbon Tetrachloride. The reaction of diene **1a** with 1 equiv of ozone in carbon tetrachloride at 0 °C afforded the keto ester **2a** (61% yield) as the sole isolable product; unreacted starting material **1a** (35%) was also recovered. Treatment of **1a** with 2 mol equiv of ozone resulted in quantitative formation of the keto ester **2a** (eq i). The similar trends were observed for the reaction of dienes **1b,c** (Table I).



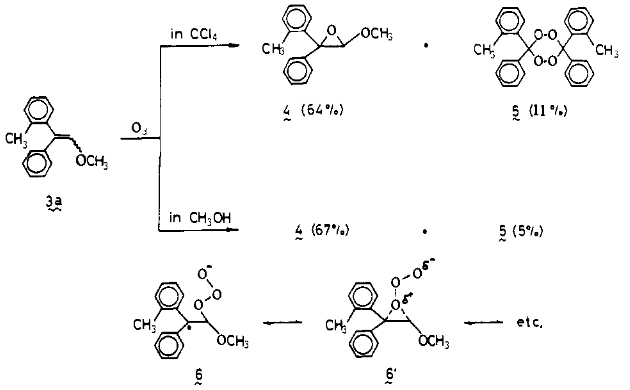
(i)

1 2

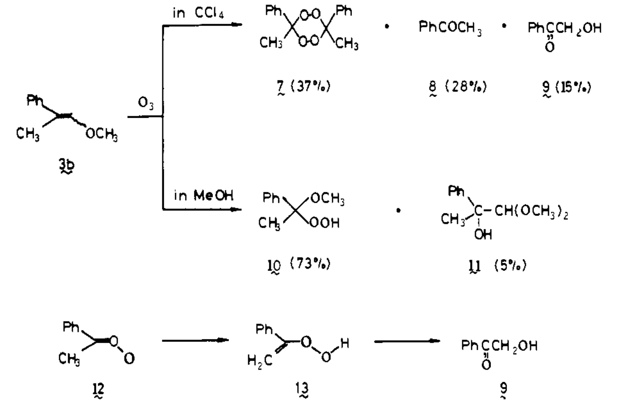
a; $R^1=R^2=Ph$, $R^3=H$ b; $R^1=CH_3$, $R^2=Ph$, $R^3=H$ c; $R^1=R^2=Ph$, $R^3=CH_3$

Ozonolysis of Model Vinyl Ethers 3a,b. To understand this novel oxidation of dienes **1a–c**, the ozonolysis of vinyl ethers **3a,b** was undertaken. When the structure of diene **1a** was compared with those of vinyl ethers **3a,b**, it was noted that vinyl ethers, **3a** and **3b**, would be the reasonable models of the more hindered double bond and the alternative site in the diene **1a**, respectively. Treatment of 1-(2-methylphenyl)-2-methoxystyrene (**3a**) with 1 equiv of ozone in carbon tetrachloride gave 64% yield of epoxide **4** together with tetroxane **5** (11% yield). The reaction in methanol also gave mainly the epoxide **4** (Scheme I).

Scheme I



Scheme II



For the formation of the epoxide **4**, two alternative paths would be postulated, i.e., partial cleavage of the double bond via a zwitterionic intermediate **6** (or its analogues) and oxygen transfer from 2-methylbenzophenone oxide to vinyl ether **3a**.[7] Of the two mechanistic alternatives, however, the latter process does not seem important, since the yield of epoxide **4** is more than 50% and the formation of the expected byproduct, 2-methylbenzophenone, is not observed.

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(1) Hamilton, G. A. In *Molecular Mechanism of Oxygen Activation*; Hayaishi, O., Ed.; Academic: New York, 1974.

(2) (a) Pryor, W. A.; Govindan, C. K. *J. Am. Chem. Soc.* **1981**, *103*, 7681. (b) Sawaki, Y.; Kato, H.; Ogata, Y. *Ibid.* **1981**, *103*, 3832. (c) Adam, W.; Haas, W.; Sieker, G. *Ibid.* **1984**, *106*, 5020. (d) Griesbaum, K.; Hofmann, P. *Ibid.* **1976**, *98*, 2877.

(3) (a) Hinrichs, T. A.; Ramachandran, V.; Murray, R. W. *J. Am. Chem. Soc.* **1979**, *101*, 1282. (b) Agarwal, S. K.; Murray, R. W. *Photochem. Photobiol.* **1982**, *35*, 31. See also: (c) Keay, R. E.; Hamilton, G. A. *J. Am. Chem. Soc.* **1975**, *97*, 6876. (d) Gillies, C. W. *Ibid.* **1977**, *99*, 7239. (e) Cremer, D.; Bock, C. W. *Ibid.* **1986**, *108*, 3375.

(4) (a) Murray, R. W.; Banavali, R. *Tetrahedron Lett.* **1983**, *24*, 2327. (b) Jefford, C. W.; Boukouvalas, J.; Kohmoto, S. *Helv. Chim. Acta* **1986**, *69*, 941.

(5) (a) Murray, R. W.; Jeyaraman, R.; mohan, L. *J. Am. Chem. Soc.* **1986**, *108*, 2470. (b) Jeyaraman, R.; Murray, R. W. *Ibid.* **1984**, *106*, 2462. (c) Murray, R. W.; Jeyaraman, R. *J. Org. Chem.* **1985**, *50*, 2847. (d) Adam, W.; Rodoriguez, A. *Tetrahedron Lett.* **1981**, *22*, 3509.

(6) A part of this work was published in a preliminary form: Nakamura, N.; Nojima, M.; Kusabayashi, S. *J. Am. Chem. Soc.* **1986**, *108*, 4671.

(7) (a) Bailey, P. S. *Ozonation in Organic Chemistry*; Academic: New York; Vol. 1, 1978; Vol. 2, 1982. (b) Bailey, P. S.; Hwang, H. H.; Chiang, C. *J. Org. Chem.* **1985**, *50*, 231.

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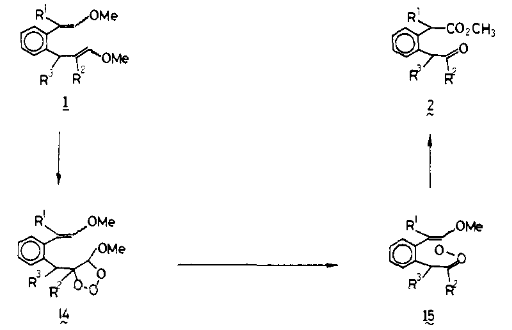
Table I. Ozonolysis of Diene **1a–c**

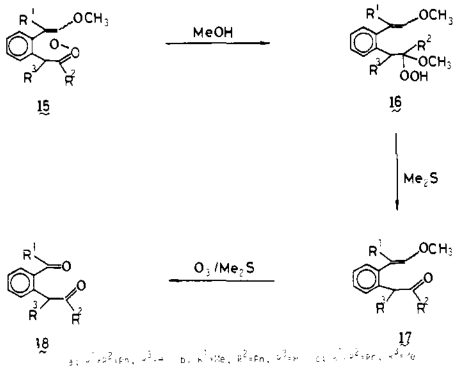
diene	ozone, equiv	solvent	additive (equiv)	temp (°C)	products (% yield)	recovered diene, %
1a	1	CCl_4		0	**2a** (62)	35
	2	CCl_4		0	**2a** (100)	
	1	CH_2Cl_2		−70	**2a** (68)	32
	3	CH_2Cl_2	Me_2S^a (3)	−70	**2a** (60)	
	3	CH_2Cl_2	Me_2SO^b (10)	−70	**2a** (64)	
	1	$MeOH/CH_2Cl_2{}^c$	Me_2S^a (10)	−70	**2a** (12), **17a** (26), **18a** (6)	36
1b	1	CCl_4		0	**2b** (70)	25
	2	CCl_4		0	**2b** (100)	
	1	$MeOH/CH_2Cl_2{}^c$	Me_2S^a (10)	−70	**2b** (20), **17b** (23)	26
	1	CCl_4		0	**2c** (16)^d	20
	1	$MeOH/CH_2Cl_2{}^c$	Me_2S (10)	−70	**2c** (8), **17c** (27)	12

[a] Dimethyl sulfide. [b] Dimethyl sulfoxide. [c] A mixed solvent; 1:1 (v/v). [d] A considerable amount of unidentified demethylated products was also produced.

Scheme III



Scheme IV



A remarkably different trend was observed for the ozonolysis of 1-methyl-2-methoxystyrene (**3b**). The reaction of **3b** with ozone in carbon tetrachloride gave a mixture of tetroxane **7**, acetophenone (**8**), and α-hydroxyacetophenone (**9**), while the reaction in methanol afforded the α-methoxy hydroperoxide **10** in 73% yield along with the acetal **11**[8] (5%) (Scheme II). These results are rationalized in terms of predominant formation of acetophenone oxide (**12**), followed by dimerization or capture by methanol to give the tetroxane **7** and the methoxy hydroperoxide **10**, respectively. α-Hydroxyacetophenone (**9**) is most likely to be formed by a hydrogen abstraction to yield vinyl hydroperoxide **13**, followed by a hydroxy migration (Scheme II).

Ozonolysis of Dienes 1a–c in Methanol. It is apparent that diene **1a–c** has two reaction sites toward the ozone molecule. Consequently, two alternative pathways leading to keto ester **2** would be postulated depending on the difference in the reaction site attacked first by ozone (Schemes III and IV).

Scheme V

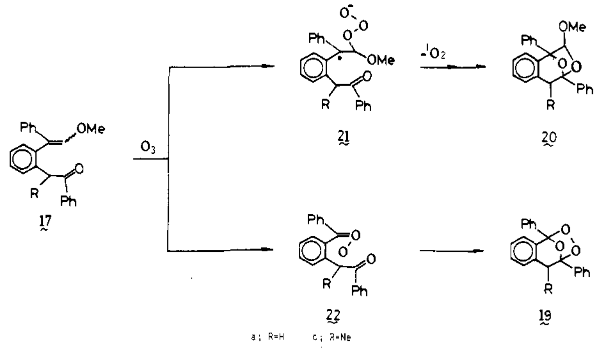


Table II. Ozonolysis of Keto Olefin **17**^{a}

keto olefin	solvent	temp, °C	products (% yield)
17a	CCl_4	0	**19a** (15), **20a** (40)
17a	$MeOH/CH_2Cl_2{}^b$	−70	**19a** (14), **20a** (41)
17c	CCl_4	0	**19c** (10),^{c} **20c** (12)
17c	$MeOH/CH_2Cl_2{}^b$	−70	**19c** (10),^{d} **20c** (63)

[a] The reaction of **17** with 1.5 equiv of ozone. [b] A mixed solvent, 1:1 (v/v). [c] An exo/endo mixture of 1-methyl-2,3-diphenylindene ozonide; the ratio being 71:29. [d] The ozonide exo/endo ratio 70:30.

We first consider a mechanism involving attack of ozone on the less-hindered double bond of **1a** in the first step (Scheme III). In analogy with the behavior of the model vinyl ether **3b**, this reaction would result in predominant formation of the carbonyl oxide **15a** via the primary ozonide **14a**. Subsequent intramolecular oxygen transfer, followed by a 1,2-hydride migration, would produce the keto ester **2a**. In this respect, the reaction of diene **1a** with 1 mol equiv of ozone in methanol in the presence of 10 mol equiv of dimethyl sulfide is suggestive. The reaction product consists of a mixture of keto ester **2a** (12%), keto olefin **17a** (24%), and diketone **18a** (6%); some starting material **1a** (26%) is also recovered. Exactly the same trend is observed in the reaction of dienes **1b,c** (Scheme IV and Table I). These results would be interpreted as that in methanol, trapping of carbonyl oxide **15a** competes strongly with the oxygen transfer process. Reduction of the hydroperoxide **16a**, thus formed, by dimethyl sulfide affords the keto olefin **17a**. Further reaction of the keto olefin **17a** ultimately leads to the formation of the diketone **18a** (Scheme IV).

The fact that the formation of the keto ester **2a** is not completely suppressed even in methanol would, however, imply that the intramolecular oxygen transfer must be extremely fast. Consistent with this, the ozonolysis of diene **1a** in carbon tetrachloride was not significantly perturbed by the presence of dimethyl sulfide or dimethyl sulfoxide which are well-known scavengers of carbonyl oxides (Table I).

The ozonolysis of keto olefin **17** was also undertaken to see if **17a** might be a probable precursor of keto ester **2a** (Scheme V

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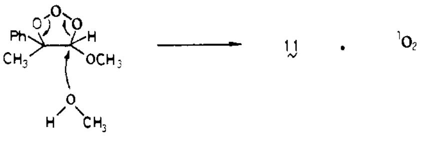
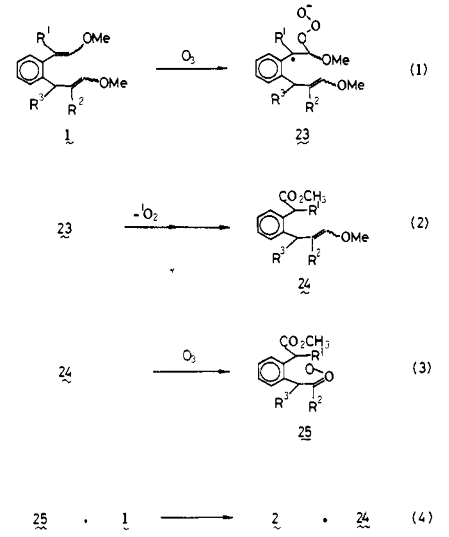
[8] For the formation of the acetal **11**, two alternative paths would be possible. (a) The first step involves epoxide formation (reference Scheme I), followed by methanolysis and (b) methanolysis of the 1,2,3-trioxolane (eq ii).



(ii)

Scheme VI

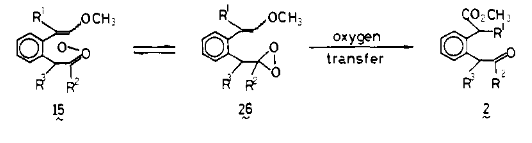


and Table II). The reaction in carbon tetrachloride gave a bicyclic ketal **20a** in 40% yield together with 2,3-diphenylindene ozonide (**19a**) (15% yield), as did the reaction in methanol. The same trend was observed for the ozonolysis of keto olefin **17c**. These results lead us to deduce that for the formation of keto ester **2a** from diene **1a** the process via keto olefin **17a** does not contribute to a significant extent. In analogy with the vinyl ether **3a** having a similar structure, the reaction of keto olefin **17a** seems to proceed mainly by a zwitterionic intermediate **21a**. In this intermediate **21a**, however, the interaction with the adjacent carbonyl group is important to yield the bicyclic ketal **20a** in good yield.

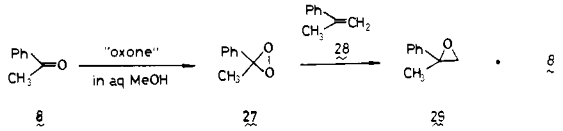
Thus, the mechanism involving initial attack of ozone on the less hindered double bond of diene **1** (Scheme III) seems to rationalize well the exclusive formation of keto ester **2** from the ozonolysis of diene **1** in carbon tetrachloride. One would suspect, however, that an alternative pathway involving initial attack of ozone on the more hindered double bond of **1** (Scheme VI) might contribute to some extent. In analogy with vinyl ether **3a**, this ozone attack would yield predominantly a zwitterionic intermediate **23** (reaction 1), followed by ejection of singlet oxygen and hydride migration to provide the ester **24** (reaction 2). Then, the remaining double bond would be attacked by ozone to yield the carbonyl oxide intermediate **25** (reaction 3). Subsequently, intermolecular oxygen transfer from **25** to diene **1** would occur to give keto ester **2** and regenerate ester **24** (reaction 4).[9,10] This sequence of events would ultimately result in exclusive formation of keto ester **2** from diene **1**.

The mechanism shown in Scheme VI might satisfactorily explain the following facts. (a) The reaction of **1a** with 1 equiv of ozone yields keto ester **2a** in more than 50% yield and (b) methanol as a solvent perturbs the reaction course remarkably. The predominant formation of keto olefin **17a** from the ozonolysis of **1a** in methanol in the presence of dimethyl sulfide, however, may suggest that ozone is more likely to attack first the less-hindered double bond of **1a** (Scheme III). Moreover, intermolecular oxygen transfer from the carbonyl oxide **25a** to diene **1a** (reaction 4 in Scheme VI) does not seem efficient, since no evidence is obtained for intermolecular oxygen transfer from acetophenone oxide (**12**) to vinyl ether **3b**. We therefore prefer to consider that the pathway illustrated in Scheme VI is not important for the formation of keto ester **2** from diene **1**.[11,12]

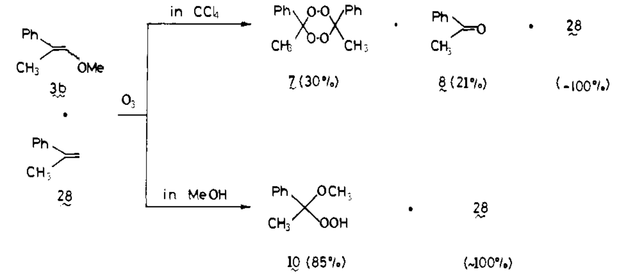
Scheme VII



Scheme VIII



Scheme IX



The Question for Carbonyl Oxide–Dioxirane Interconversion. All the evidence we obtained would suggest that the intramolecular oxygen transfer from the carbonyl oxide moiety to a methoxyvinyl group in the intermediate **15** is the key for the novel oxidation of diene **1a–c** with ozone. A question may, however, arise whether the oxygen transfer occurs from the carbonyl oxide moiety or alternatively the interconversion between the carbonyl oxide **15** and the isomeric dioxirane **26** occurs very easily, thereby the real oxygen transfer agent being the dioxirane **26** (Scheme VII).

Recent studies have revealed the interesting chemistry of dioxiranes. (a) The parent dioxirane, formed from gas-phase ozonolysis of ethylene, is detected spectroscopically,[13] (b) cyclopentadienone oxide, produced by photolysis of the corresponding diazoalkane in the presence of oxygen molecule, rearranges to the isomeric dioxirane under light,[14] and (c) dioxiranes, generated in situ from the reaction of carbonyl compounds with "oxone", can effectively oxidize alkenes and aromatic compounds.[5] Additional characteristics are that (d) cycloaddition to carbonyl compounds leading to 1,2,4-trioxolanes (final ozonides) does not occur and (e) the reaction with alcohols is very slow; the products are aldehydes or ketones.[15] These characteristics are quite different from those of carbonyl oxides.[7a]

The following facts would imply that the rearrangement of carbonyl oxide (generated by ozonolysis in solution) to the isomeric

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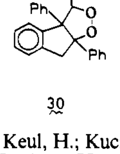
[9] As the alternative routes leading to keto ester **2**, (a) oxygen atom transfer from the carbonyl oxide intermediate **25** to unidentified reductants and (b) dimerization of carbonyl oxides **25** followed by ejection of oxygen molecule[10] would be also possible. It should be noted, however, that in these mechanistic alternatives 2 mol equiv of ozone is required to yield keto ester **2** from diene **1**.

[10] Sawaki, Y.; Ishiguro, K. *Tetrahedron Lett.* **1984**, *25*, 1487.

[11] A refree has suggested three alternative mechanisms for the formation of keto ester **2** from diene **1**. (a) The carbonyl oxide **15** cycloadds to the double bond to give a bicyclic dioxolane **30**,[12] which decomposes, perhaps during workup, to the keto ester **2**. (b) A periperoxide species **31** leads to simultaneous oxidation of both double bonds. (c) A mechanism involving multiple ozone attack would also contribute to a small but significant extent, since the reaction of, for example, diene **1b** with 1 equiv of ozone provides only 70% yield of keto ester **2b**. Although we prefer the mechanism illustrated in Scheme III, the possibility of participation of these mechanistic alternatives could not be excluded.



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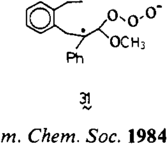

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[12] (a) Keul, H.; Kuczkowski, R. L. *J. Am. Chem. Soc.* **1984**, *106*, 5370. (b) Kuel, H.; Choi, H.; Kuczkowski, R. L. *J. Org. Chem.* **1985**, *50*, 3365.

[13] Suenram, R. D.; Lovas, F. J. *J. Am. Chem. Soc.* **1978**, *100*, 5117.

[14] (a) Bell, G. A.; Dunkin, I. R. *J. Chem. Soc., Chem. Commun.* **1983**, 1213. (b) Dunkin, I. R.; Shields, C. J. *Ibid.* **1986**, 154. (c) Werstiuk, N. H.; Casal, H. L.; Scaiano, J. *Can. J. Chem.* **1984**, *62*, 2391. (d) Chapman, O. L.; Hess, T. C. *J. Am. Chem. Soc.* **1984**, *106*, 1842.

[15] A private communication from Prof. R. W. Murray.

dioxirane, if it occurs, is very slow. 3-Phenyl-3-methyl-1,2-dioxirane (**27**), produced from the reaction of acetophenone (**8**) with "oxone" in aqueous methanol, was found to epoxidize α-methylstyrene (**28**) very efficiently (Scheme VIII). Therefore, if the rearrangment of acetophenone oxide (**12**) to the dioxirane **27** were fast, the reaction of vinyl ether **3b** in the presence of α-methylstyrene (**28**) might have resulted in the formation of significant amounts of α-methylstyrene oxide (**29**). Inconsistent with this, the ozonolysis in methanol gave exclusively the methanol-participated product **10**, while the ozonolysis in carbon tetrachloride resulted in the production of tetroxane **7** and acetophenone (**8**); in both cases α-methylstyrene (**28**) was recovered quantitatively (Scheme IX). These results clearly demonstrate that the dimerization of the carbonyl oxide **12** or the capture by methanol is much faster than the rearrangement to the dioxirane **27**. Although somewhat circumstantial, it would be therefore reasonable to consider that the rearrangement of the carbonyl oxide **15** (formed from the ozonolysis of diene **1**) to the isomeric dioxirane **26** is also not important. MO calculations of the model reactions support this conclusion.[16]

Experimental Section

Preparation of Diene 1a–c. In a 200-mL flask, equipped with a mechanical stirrer and maintained under nitrogen, was added (methoxymethyl)triphenylphosphonium chloride[17] (13 mmol) and then ether (100 mL). To this mixture was syringed an ether solution of phenyllithium (13 mmol) at −10 °C during 3 min. Subsequently an ether solution of (2-benzoylmethyl)benzophenone (**18a**; 6 mmol) was syringed in 1 min and the mixture was kept at 30 °C for 20 h. After workup, the crude products were triturated with ether–hexane to remove triphenylphosphine oxide. Then the organic layer was concentrated and the products were separated by column chromatography on silica gel (elution with benzene–hexane 1:2). From the first fraction was isolated the diene **1a** in around 10% yield: an oil, ^{1}H NMR δ 3.30 (s, 2 H), 3.47 (s, 3 H), 3.63 (s, 3 H), 5.73 (s, 1 H), 6.63–7.47 (m, 14 H); IR 1640 cm^{-1}. Anal. ($C_{25}H_{24}O_2$) C, H.

By the same procedure the dienes **1b,c** were prepared from the corresponding diketones. **1b**: an oil; ^{1}H NMR δ 1.86 (s, 3 H), 3.24 (d, J = 15.0 Hz, 1 H), 3.57 (s, 3 H), 3.57 (d, J = 15.0 Hz, 1 H), 3.69 (s, 3 H), 5.76 (s, 1 H), 6.45 (s, 1 H), 6.84–7.50 (m, 9 H); IR 1640 cm^{-1}. **1c**: mp 95 °C (from methanol); ^{1}H NMR δ 1.37 (d, J = 7.5 Hz, 3 H), 3.54 (s, 3 H), 3.63 (s, 3 H), 4.19 (q, J = 7.5 Hz, 1 H), 5.88 (s, 1 H), 5.91 (s, 1 H), 6.80–7.49 (m, 14 H); IR 1640 cm^{-1}; mass spectrum, 370 (M^+). Anal. ($C_{26}H_{26}O_2$) C, H.

Preparation of Vinyl Ethers 3a,b. Vinyl ether **3a** was prepared by treating 2-methylbenzophenone (20 mmol) with (methoxymethylene)triphenylphosphorane (30 mmol) in ether under reflux for 2 h. By distillation under reduced pressure, **3a** was isolated in a pure state (around 30% yield): bp 132 °C (2 mmHg); ^{1}H NMR δ 2.03 (s, 3 H), 3.73 (s, 3 H), 6.07 (s, 1 H), 6.70–7.30 (m, 9 H).[17] Treatment of acetophenone (30 mmol) with (methoxymethyl)triphenylphosphorane (30 mmol) in ether at room temperature for 5 h gave **3b** (a cis–trans mixture; ratio 2:1) in 20% yield: bp 115 °C (10 mmHg); ^{1}H NMR δ 1.93 (d, J = 2.0 Hz, 3 H), 3.60 (s, 3 H), 6.03 (q, J = 2.0 Hz, 1 H), 6.60–7.20 (m, 5 H), 1.87 (d, J = 2.0 Hz, 3 H), 3.53 (s, 3 H), 6.00 (q, J = 2.0 Hz, 1 H), 6.60–7.20 (m, 5 H).[18]

Ozonolysis of Diene 1a–c in Carbon Tetrachloride. The reaction of diene **1a** (1 mmol) with 1 equiv of ozone in carbon tetrachloride (30 mL) was undertaken at 0 °C. After evaporation of the solvent, the crude products were column chromatographed on silica gel. The first fraction (elution with benzene–hexane 1:2 (v/v)) contained diene **1a**. From the second fraction (elution with ether–benzene 1:100 (v/v)) was isolated keto ester **2a**: an oil; ^{1}H NMR δ 3.63 (s, 3 H), 4.17 (s, 2 H), 5.12 (s, 1 H), 6.67–8.10 (m, 14 H); IR 1735, 1690 cm^{-1}; mass spectrum, m/e 344 (M^+). Anal. ($C_{23}H_{20}O_3$) C, H.

The physical properties of the keto ester **2b,c** obtained from the ozonolysis of diene **1b,c** were as follows. **2b**: an oil, ^{1}H NMR δ 1.43 (d, J = 7.5 Hz, 3 H), 3.51 (s, 3 H), 3.72 (q, J = 7.5 Hz, 1 H), 4.11 (d, J = 16.5 Hz, 1 H), 4.28 (d, J = 16.5 Hz, 1 H), 6.78–7.95 (m, 9 H); IR 1730, 1690, 1600 cm^{-1}; mass spectrum, m/e 282 (M^+). **2c**: mp 143 °C (from benzene–hexane); ^{1}H NMR δ 1.49 (d, J = 6.0 Hz, 3 H), 3.68 (s, 3 H), 4.67 (q, J = 6.0 Hz, 1 H), 5.46 (s, 1 H), 6.59–7.94 (m, 14 H); IR 1740, 1690 cm^{-1}; mass spectrum, m/e 358 (M^+). Anal. ($C_{24}H_{22}O_3$) C, H.

Ozonolysis of Diene 1a–c in MeOH/CH$_2$Cl$_2$. To a methanol–methylene chloride solution (30 mL; 1:1 v/v) of diene **1a** (1 mmol) in the presence of dimethyl sulfide (10 mmol) was passed a slow stream of ozone (1 equiv) at −70 °C. After ether was added (50 mL), the organic layer was washed with aqueous potassium dihydrogen phosphate and then with saturated brine. The crude products were separated by column chromatography on silica gel. The first fraction contained diene **1a**. From the second fraction (elution with benzene) was obtained keto olefin **17a**: an oil; ^{1}H NMR δ 3.59 (s, 3 H), 3.95 (s, 2 H), 6.05 (s, 1 H), 6.81–7.83 (m, 14 H); IR 1690, 1640, 1240 cm^{-1}; mass spectrum, m/e 328 (M^+). Anal. ($C_{23}H_{20}O_2$) C, H. The third fraction (elution with ether-benzene 1:100 v/v) contained diketone **18a**: mp 67–68 °C (from ethanol); IR 1690, 1660 cm^{-1}.[22] From the final fraction (elution with ether–benzene 1:100 (v/v)) was obtained keto ester **2a**.

The reaction of diene **1a** in methanol at −70 °C followed by treatment of the reaction mixture with 10 mol equiv of dimethyl sulfide at −70 °C for 30 min also gave keto olefin **17a** in 27% yield, together with **2a** (9%) and **18a** (18%); some starting material **1a** (22%) was also recovered.

The physical properties of the keto olefin **17b,c** were as follows. **17b**: an oil; ^{1}H NMR δ 1.74 (br s, 3 H), 3.42 (s, 3 H), 4.14 (s, 2 H), 5.77 (br s, 1 H), 6.90–7.05 (m, 10 H); IR 1680 cm^{-1}. **17c**: an oil; ^{1}H NMR δ 1.19 (d, J = 6.0 Hz, 3 H), 3.63 (s, 3 H), 4.60 (q, J = 6.0 Hz, 1 H), 6.03 (s, 1 H), 6.65–7.78 (m, 14 H); IR 1690, 1640, 1240 cm^{-1}. Anal. ($C_{24}H_{22}O_2$) C, H. **Ozonolysis of Vinyl Ether 3a.** Vinyl ether **3a** (2 mmol) was treated with 1 equiv of ozone in carbon tetrachloride (30 mL) at 0 °C. The products were separated by column chromatography on silica gel. The first fraction contained tetroxane **5**: mp 198–200 °C (from ethanol); ^{1}H NMR δ 2.31 (s, 6 H), 6.90–8.37 (m, 18 H). Anal. ($C_{28}H_{24}O_4$) C, H. From the second fraction was isolated epoxide **4**: an oil; ^{1}H NMR δ 2.17 (s, 3 H), 3.40 (s, 3 H), 4.73 (s, 1 H), 6.70–7.83 (m, 9 H); mass spectrum, m/e 240 (M^+).

Ozonolysis of Vinyl Ether 3b in Carbon Tetrachloride. The ozonolysis of vinyl ether **3b** (2 mmol) in carbon tetrachloride was undertaken at 0 °C. The products were isolated by column chromatography on silica gel. The first fraction contained tetroxane **7**: mp 188–190 °C (from ethanol); ^{1}H NMR δ 1.32 (s, 6 H), 6.78–7.95 (m, 10 H).[19] From the second fraction acetophenone (**8**) was obtained. The final fraction contained α-hydroxyacetophenone (**9**): mp 88 °C (from ethanol); IR 3350, 1690, 1600 cm^{-1}; mass spectrum, m/e 136 (M^+); ^{1}H NMR δ 3.0 (br s, 1 H), 4.89 (s, 2 H), 7.05–8.10 (m, 5 H).

Ozonolysis of Vinyl Ether 3b in MeOH/CH$_2$Cl$_2$. The reaction of vinyl ether **3b** (2 mmol) with 1 equiv of ozone in MeOH/CH$_2$Cl$_2$ (30 mL; 1:1 (v/v)) was undertaken at −70 °C. The crude products were column chromatographed on silica gel. The first fraction contained alcohol **11**: an oil; ^{1}H NMR δ 1.43 (s, 3 H), 2.54 (br s, 1 H, H–D exchange in D$_2$O), 3.23 (s, 3 H) 3.38 (s, 3 H), 4.04 (s, 1 H), 6.89–7.41 (m, 5 H); IR 3380, 1450 cm^{-1}; mass spectrum, 165 (M^+ − 31).[20] From the second fraction was obtained methoxy hydroperoxide **10**: an oil; ^{1}H NMR δ 1.56 (s, 3 H), 3.24 (s, 3 H), 7.02–7.44 (m, 5 H), 8.75 (s, 1 H; H–D exchange in D$_2$O).[21] Treatment of **10** with triphenylphosphine in benzene yielded acetophenone quantitatively.

Ozonolysis of Keto Olefin 17a,c. The reaction of keto olefin **17a** with 1.5 equiv of ozone in carbon tetrachloride was undertaken at 0 °C. The products were separated by column chromatography on silica gel. The first fraction contained ozonide **19a**: mp 119 °C (from methanol); ^{1}H NMR δ 3.50 (d, J = 17 Hz, 1 H), 3.74 (d, J = 17 Hz, 1 H), 6.69–7.77 (m, 14 H).[22] From the second fraction was isolated a cyclic ketal **20a**: mp 121–123 °C (from methanol); ^{1}H NMR δ 3.26 (d, J = 18.0 Hz, 1 H), 3.51 (s, 3 H), 3.48 (d, J = 18.0 Hz, 1 H), 5.22 (s, 1 H), 6.60–7.68 (m, 14 H); mass spectrum, m/e 344 (M^+). Anal. ($C_{23}H_{20}O_3$) C, H.

From the keto ester **17c**, a mixture of 1-methyl-2,3-diphenylidene ozonide (**19c**; an exo/endo mixture)[23] and a cyclic ketal **20c** was obtained. **20c**: mp 122–124 °C (from methanol); ^{1}H NMR δ 1.28 (d, J = 7.5 Hz, 3 H), 3.53 (q, J = 7.5 Hz, 1 H), 3.57 (s, 3 H), 5.25 (s, 1 H), 6.60–7.68 (m, 14 H); mass spectrum, m/e 358 (M^+). Anal. ($C_{24}H_{22}O_3$) C, H.

Reaction of Acetophenone with Oxone (Aldrich) in the Presence of α-Methylstyrene. To a solution of acetophenone (4 mmol) in methanol (10 mL) was added à solution of 2KHSO$_4$–KHSO$_4$–K$_2$SO$_4$ (4 mmol) in H$_2$O (10 mL) at 0 °C and the mixture was kept at 0 °C for 1 h. Then

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a solution of α-methylstyrene (1.7 mmol) in methanol (10 mL) was added and the reaction was continued with stirring at 6–8 °C for 3 h. α-Methylstyrene oxide (**29**) and acetophenone (**8**) were isolated quantitatively by column chromatography on silica gel.

Treatment of α-methylstyrene with oxone in aqueous methanol in the absence of acetophenone, however, resulted in the recovery of α-methylstyrene.

Ozonolysis of 1-Methyl-2-methoxystyrene in the Presence of α-Methylstyrene. The reaction of a mixture of **3b** (2 mmol) and α-methylstyrene (**28**, 2 mmol) with an ozone molecule in carbon tetrachloride was undertaken at 0 °C. The products were separated by column chromatography on silica gel. From the first fraction **28** was recovered quantitatively. The second fraction contained tetroxane **7** (30% yield). From the final fraction acetophenone (**8**) was obtained in 21% yield.

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Volumes of Activation for the Cycloaddition Reactions of Phenylhalocarbenes to Alkenes

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Abstract: The absolute rate constants for the cycloaddition reactions of three arylhalocarbenes to two alkenes have been measured as a function of pressure in the range 0.1 to 203 MPa. In all cases the observed rate constants were found to increase with increasing pressure. The magnitude of the derived activation volumes falls in the range of −10 to −18 cm^3/mol and does not depend on solvent. The results rule out a late, two-bond transition state and a bipolar single-bond transition state but are consistent with the reversible formation of a carbene–alkene complex or an early one- or two-bond transition state.

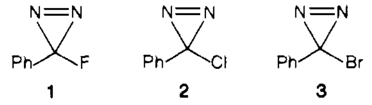
A considerable literature concerned with the effect of pressure on chemical reactions in solution has been developed over the past two decades.[1] Although the bulk of this literature is concerned with thermal reactions, an increasing number of reports concerned with the influence of pressure on photophysical processes in solution have recently begun to appear;[2,3] however, reports of the influence of high pressure on organic photoreactions in solution are scarce.[4] The few published examples include the effect of pressure on the product ratios in type II photoreactions,[5] on the product distributions in photocycloadditions to naphthalene,[6] and on the photoreduction of benzophenone.[7] To date, there have been no reports in the literature concerning the influence of pressure on the absolute rate constants of photoinduced cycloaddition reactions.[8]

We report here the results of an investigation of the influence of pressure in the range 0.1–203 MPa on the absolute rate constants for the additions of phenylhalocarbenes to alkenes. Many absolute rate constants for these reactions have been measured at 0.1 MPa (atmospheric pressure).[9a] The results of variable temperature experiments have demonstrated that negative temperature coefficients (faster rates at lower temperatures) are characteristic of the most rapid of these reactions.[9b] Arrhenius analysis of the data demonstrates that entropy factors are of critical importance in determining the absolute rate constants.[9] The factors that determine the effect of pressure on rate constants are often similar to those that determine entropy changes (i.e., the transition state has fewer degrees of freedom than the initial state),[1,10] so that it is of particular current interest to measure the influence of pressure on the magnitude of the absolute rate constants for the additions of phenylhalocarbenes to alkenes.

Experimental Section

Phenylfluorodiazirine (**1**), phenylchlorodiazirine (**2**), and phenylbromodiazirine (**3**) were synthesized and purified as described previously

Chart I



(Chart I).[11] Tetramethylethylene (TME; Aldrich) and *trans*-2-pentene (TP; Aldrich) were distilled immediately before use. Spectroscopic grade methylcyclohexane (MCH; Aldrich) was used without further purification. The samples were not degassed. The laser flash photolysis apparatus was similar to that described in the literature.[12a] The high-pressure cell and the associated techniques were described previously.[12b] Transient absorption experiments were performed by employing the third harmonic (355 nm) of a Quanta Ray Nd:YAG laser, pulse width ca. 10 ns. A 150-W xenon lamp, together with a PRA 301 power supply and a PRS

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