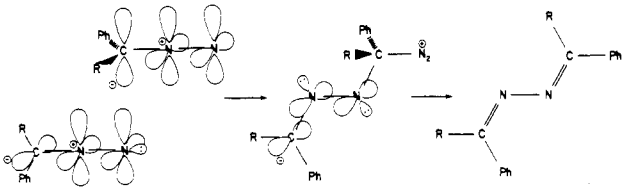
stereoselectivity, the solvent effects also support the initial step of the mechanism. The nucleophilic attack forms a charge-separated zwitterion. This process is expected to be facilitated by polar solvents that can stabilize charge separation. As expected, in acetonitrile the rate of loss of diazo compound is greater than in toluene. The lower stereoselectivity in toluene can be explained in part by the slower rate of reaction, so that the isomerization mechanism competes more effectively. This mechanism also predicts that **2** would suffer dimerization faster than would **1**. The methyl group increases the nucleophilicity of the carbon center, but it does not greatly affect the electrophilicity of the diazonium moiety.



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Ozonolysis of 1-Substituted 2,3-Diphenylindenes and *o*-(1-Substituted-2-phenyl-3-methoxy-2-propenyl)benzophenones. Remarkable Effects of the Method of Generation of the Carbonyl Oxide Intermediates on the Stereochemistries of Both the Ozonide and the Methanol-Derived Isochroman Products

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Abstract: Ozonolyses of 1-substituted 2,3-diphenylindenes **1a,b** and *o*-(1-substituted-2-phenyl-3-methoxy-2-propenyl)benzophenones **8a,b** in methanol–methylene chloride at −70 °C, which should proceed through common carbonyl oxide intermediates **11a,b**, afforded stereoisomeric methoxy hydroperoxides, **6a,b** and **9a,b**, respectively. The ozonide stereochemistry was also affected by the method of generation of the carbonyl oxide intermediate **11a**: ozonolyses of 1,2,3-triphenylindene (**1a**) in CCl_4, CH_3CN, CH_3CO_2H–CH_2Cl_2, and CF_3CH_2OH–CH_2Cl_2 gave predominantly the *exo*-ozonide **2a**, whereas the endo isomer **3a** was obtained exclusively from the ozonolysis of keto olefin **8a** in CH_3CO_2H–CH_2Cl_2 and CF_3CH_2OH–CH_2Cl_2. Moreover, in the ozonolysis of the keto olefin **8a**, protic solvents assisted ozonide formation; *endo*-ozonide **3a** was certainly obtained in the ozonolysis in the protic solvents (around 25% yield). No ozonides were isolated, however, from ozonolysis reactions carried out in aprotic solvents, CCl_4 and CH_3CN.

The chemistry of carbonyl oxides, key intermediates in ozonolysis, has attracted much attention.[2] To obtain further insight into the mechanism of ozonolysis of indene derivatives,[3] we have undertaken ozonolyses of 1-substituted 2,3-diphenylindene **1a,b** and *o*-(1-substituted-2-phenyl-3-methoxy-2-propenyl)benzophenone **8a,b**, each of which should give rise to a corresponding common ozonolysis intermediate **11a,b** (Scheme I).[4,5] Our results to date suggest that (a) the substrate, from which the carbonyl oxide **11a,b** is derived, exerts an unexpected influence on the stereochemistries of both the ozonide and the methanol-derived isochroman product and that (b) in the case of the carbonyl oxide intermediates **11a,b** generated from the keto olefins **8a,b**, protic solvents do not retard but instead accelerate the ozonide formation; such an assistance is not observed in the analogous indene-ozonolysis reactions.

Results

Ozonolysis of 1,2-Disubstituted 3-Phenylindenes. The ozonolysis of 1,2,3-triphenylindene (**1a**) in CCl_4, CH_3CN, CF_3CH_2OH–CH_2Cl_2, and CH_3CO_2H–CH_2Cl_2 gave, in each case, a mixture of *exo*-ozonide **2a** and the endo isomer **3a** in excellent yield, the

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(2) (a) Bailey, P. S. *Ozonation in Organic Chemistry*; Academic Press: New York, 1978, Vol. 1; 1982, Vol. 2. (b) Kuczkowski, R. L. In *1,3-Dipolar Cycloaddition Chemistry*; Padwa, A., Ed.; Wiley: New York, 1984; Vol. 2. (c) Kuczkowski, R. L. *Acc. Chem. Res.* **1983**, *16*, 42. (d) Kumar, S.; Murray, R. W. *J. Am. Chem. Soc.* **1984**, *106*, 1040. (e) Keul, H.; Kuczkowski, R. L. *Ibid.* **1984**, *106*, 5370. (f) Griesbaum, K.; Volpp, W.; Greinert, R. *Ibid.* **1985**, *107*, 5309. (g) Nakamura, N.; Nojima, M.; Kusabayashi, S. *Ibid.* **1986**, *108*, 4671. (h) Bunnelle, W. H.; Schlemper, E. O. *Ibid.* **1987**, *109*, 612. (i) Mori, M.; Nojima, M.; Kusabayashi, S. *Ibid.* **1987**, *109*, 4407. (j) LaBarge, M. S.; Keul, H.; Kuczkowski, R. L.; Wallasch, M.; Cremer, D. *Ibid.* **1988**, *110*, 2081.

(3) (a) Miura, M.; Ikegami, A.; Nojima, M.; Kusabayashi, S.; McCullough, K. J.; Nagase, S. *J. Am. Chem. Soc.* **1983**, *105*, 2414. (b) McCullough, K. J.; Nojima, M.; Miura, M.; Fujisaka, T.; Kusabayashi, S. *J. Chem. Soc., Chem. Commun.* **1984**, 35. (c) Miura, M.; Nojima, M.; Kusabayashi, S.; McCullough, K. J. *J. Am. Chem. Soc.* **1984**, *106*, 2932. (d) Miura, M.; Fujisaka, T.; Nojima, M.; Kusabayashi, S.; McCullough, K. J. *J. Org. Chem.* **1985**, *50*, 1504.

(4) Since the ozonolysis of 1-methyl-2-methoxystyrene proceeds predominately by acetophenone oxide,[5] it is reasonable to expect that the related keto olefin **8** would yield primarily the carbonyl oxide intermediate **11**.

(5) Nakamura, N.; Nojima, M.; Kusabayashi, S. *J. Am. Chem. Soc.* **1987**, *109*, 4969.

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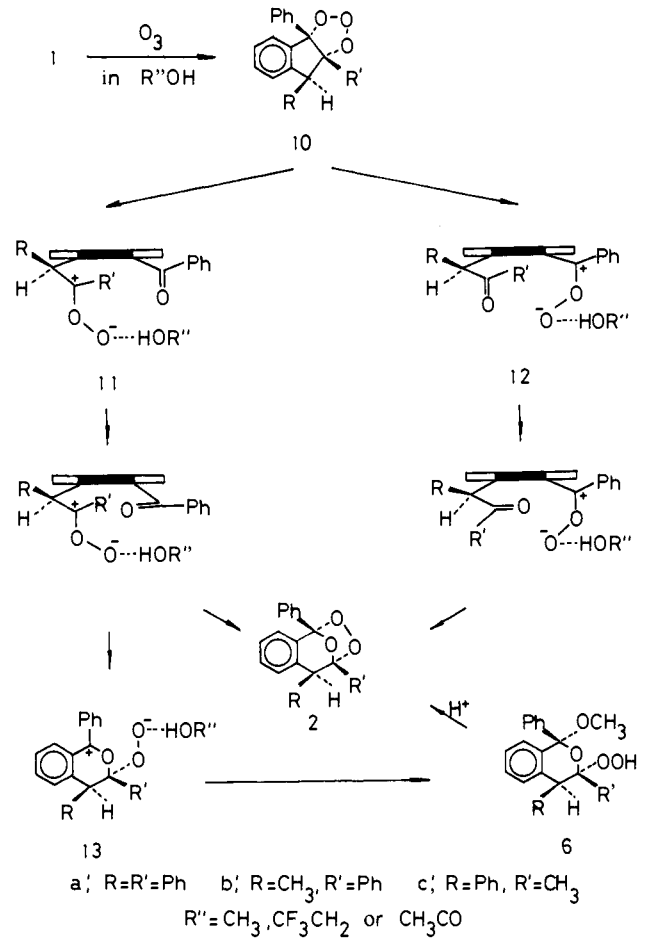
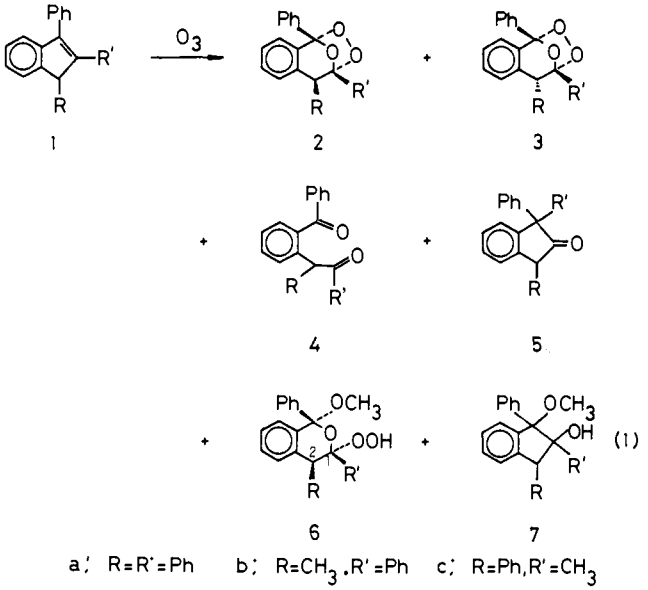
Scheme I



exo-ozonide **2a** being the predominant isomer. Similar trends were also observed for the ozonolysis of 1,3-diphenyl-2-methylindene (**1c**). In the ozonolysis of 1-methyl-2,3-diphenylindene (**1b**), however, the *endo*-ozonide **3b** was obtained predominantly in the aprotic solvents, whereas the *exo*-ozonide **2b** was the major isomer in the protic solvents (eq 1 and Table I).[3] These results lead us



(1)

to deduce that in the ozonolysis of the indenes **1a–c** (a) both the steric effects of the 1-substituent and the nature of the solvent play a significant role in determining the ozonide exo/endo ratio and (b) ozonide formation is the favored process even in the protic solvent.[6]

Table I. Ozonolysis of 1,2-Disubstituted 3-Phenylindenes **1a–c** and the Realted Keto Olefins **8a,b**

substrate	solvent[a]	temp, °C	ozonide exo:endo ratio (% yield)	other products (% yield)
1a	CCl_4[b]	20	78:22 (85)	**4a** (4)
1a	CH_3CN	20	74:26 (72)	*d*
1a	CF_3CH_2OH–CH_2Cl_2	20	92:8 (84)	*d*
1a	CH_3CO_2H–CH_2Cl_2	20	98:2 (64)	*d*
1a	MeOH–CCl_4	20	89:11 (7)	**6a** (60), **7a** (4)
1a	MeOH–CH_2Cl_2	−70	100:0 (9)	**4a** (3), **6a** (75), **7a** (2)
1b	CCl_4[b]	20	29:71 (93)	**5b** (2)
1b	CH_3CN[c]	20	28:72 (92)	*d*
1b	CF_3CH_2OH–CH_2Cl_2[c]	20	55:45 (81)	*d*
1b	CH_3CO_2H–CH_2Cl_2[c]	20	76:24 (89)	*d*
1b	MeOH–CCl_4[c]	20	46:54 (72)	**4b** (6), **6b** (7)
1b	MeOH–CH_2Cl_2[c]	−70	59:41 (30)	**4b** (5), **6b** (58)
1c	CCl_4[b]	20	96:4 (71)	*d*
1c	CH_3CO_2H–CH_2Cl_2	20	73:27 (71)	**4c** (1)
1c	MeOH–CCl_4	20	95:5 (71)	**4c** (2), **7c** (7)
1c	MeOH–CH_2Cl_2	−70	100:0 (21)	**4c** (4), **6c** (47)
8a	CCl_4	0		*e*
8a	CH_3CN	0		*e*
8a	CF_3CH_2OH–CH_2Cl_2	0	0:100 (23)	**4a** (37)
8a	CH_3CO_2H–CH_2Cl_2	0	0:100 (28)	**4a** (31)
8a	MeOH–CH_2Cl_2	−70	0:100 (3)	**4a** (41), **9a** (44)
8b	CCl_4	0	33:67 (14)	**4b** (22)[e]
8b	CF_3CH_2OH–CH_2Cl_2	0	0:100 (32)	**4b** (31)
8b	CH_3CO_2H–CH_2Cl_2	0	0:100 (37)	**4b** (41)
8b	MeOH–CH_2Cl_2	0	0:100 (15)	**4b** (10), **9b** (36)
8b	MeOH–CH_2Cl_2	−70	0:100 (4)	**4b** (7), **9b** (61)

[a] MeOH–CCl_4; 70:30 v/v. MeOH–CH_2Cl_2; 50:50 v/v. CH_3CO_2H–CH_2Cl_2; 50:50 v/v. CF_3CH_2OH–CH_2Cl_2; 50:50 v/v. [b] Taken from the data in ref 3c. [c] Taken from the data in ref 3d. [d] Other byproducts were not determined. [e] Unidentified oligomeric products were also produced in considerable amounts (see the Experimental Section).

When the reaction of 1,2,3-triphenylindene (**1a**) was undertaken in methanol–methylene chloride at −70 °C, however, the novel solvent-derived product **6a** was isolated in a high yield of 75%, together with *exo*-ozonide **2a** (9% yield) (eq 1 and Table I). The solvent-derived product **6a** is not a solvolysis product from the *exo*-ozonide **2a** in methanol, since **2a** was stable even in refluxing methanol. The reaction of **1a** at 20 °C also gave mainly the methanol-derived product **6a** (60% yield). Subsequent treatment of **6a** with catalytic amounts of trifluoroacetic acid in methylene chloride gave exclusively the *exo*-ozonide **2a**, consistent with a trans relationship between the 2-phenyl group and the hydroperoxy group in **6a**. The preferential formation of the methoxy hydroperoxide **6a** from the indene **1a** indicates that of the two possible carbonyl oxide intermediates, **11a** and **12a**, the former one predominates, at least in the ozonolysis conducted in methanol (Scheme I).

From the ozonolysis of the 1,2,3-trisubstituted indenes **1b,c**, in methanol–methylene chloride at −70 °C also, the corresponding isochroman derivatives, **6b** and **6c**, were obtained in yields of 58% and 47%, respectively. The structure of **6b** has been unambiguously determined by X-ray analysis.[3b] In the case of these sterically less crowded indenes **1b,c**, however, the ozonolyses at 20 °C resulted in predominant formation of the mixtures of *exo*- and *endo*-ozonides **2b,c** and **3b,c** (Table I).

Ozonolyses of the Keto Olefins 8a,b. The keto olefins **8a,b** were ozonized in methanol–methylene chloride solution at −70 °C in order to generate specifically the corresponding carbonyl oxides **11a,b** and to examine their respective reactivities. From *o*-(1,2-diphenyl-3-methoxy-2-propenyl)benzophenone (**8a**), a solvent-

(6) Ozonide formation in protic solvents has been observed for the ozonolysis of 2,3-diphenylindene (a), certain tetra-, penta-, and hexasubstituted cyclobutenes (b), 2,3-disubstituted indenones (c), and certain other five-membered cyclic olefinic types (d). (a) Bailey, P. S. *Chem. Ber.* **1955**, *88*, 795. (b) Reinhardt, H. G.; Doorakian, G. A.; Freedman, H. H. *J. Am. Chem. Soc.* **1968**, *90*, 5934. Criegee, R.; Schröder, G.; Maier, G.; Fisher, H. G. *Chem. Ber.* **1960**, *93*, 1553. Criegee, R.; Askani, R.; Gruner, H. *Ibid.* **1967**, *100*, 3916. (c) Criegee, R.; De Bruyn, P.; Lohaus, G. *Justus Liebigs Ann. Chem.* **1953**, *583*, 19. (d) Criegee, R.; Lohaus, G. *Ibid.* **1953**, *583*, 12. Berner, E.; Kolsaker, P. *Acta Chem. Scand.* **1969**, *23*, 597.

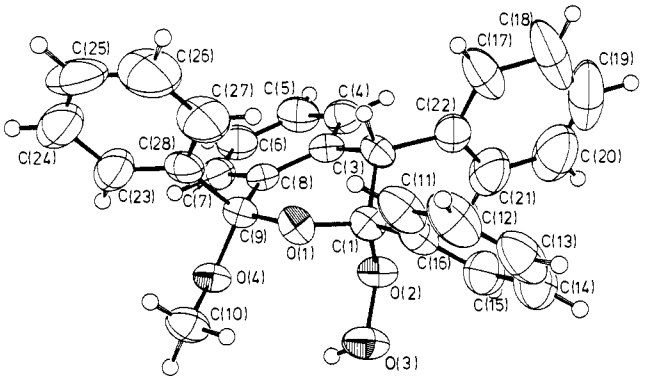


Figure 1. The crystal structure of the solvent-derived ozonolysis product (**9a**) (ORTEP, 50% probability elipsoids). The hydrogen atom labels have been omitted for clarity.

Table II. Derived Geometrical Parameters for Isochroman (**9a**)

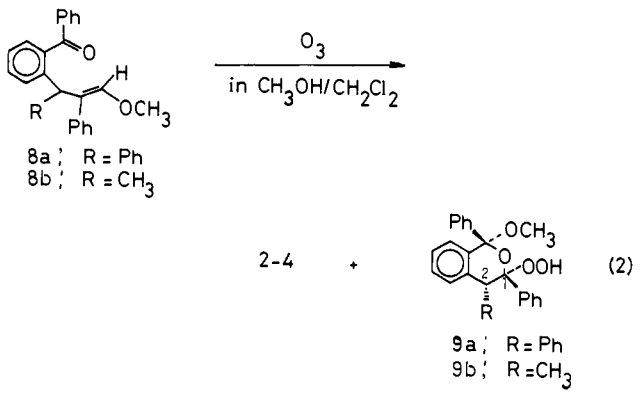
(a) Bond Lengths (Å) with Standard Deviations			
O(1)–C(1)	1.423 (6)	C(2)–C(22)	1.511 (7)
O(1)–C(9)	1.419 (6)	C(3)–C(4)	1.403 (7)
O(2)–O(3)	1.459 (5)	C(3)–C(8)	1.388 (7)
O(2)–C(1)	1.414 (6)	C(4)–C(5)	1.377 (8)
O(3)–H(3)	0.84 (6)	C(5)–C(6)	1.375 (8)
O(4)–C(9)	1.421 (6)	C(6)–C(7)	1.397 (8)
O(4)–C(10)	1.429 (6)	C(7)–C(8)	1.386 (7)
C(1)–C(2)	1.547 (7)	C(8)–C(9)	1.522 (7)
C(1)–C(16)	1.508 (6)	C(9)–C(28)	1.516 (6)
C(2)–C(3)	1.515 (7)		
(b) Angles (deg) with Standard Deviations			
C(1)–O(1)–C(9)	120.2 (4)	C(2)–C(3)–C(8)	118.7 (4)
O(3)–O(2)–C(1)	108.9 (3)	C(4)–C(3)–C(8)	118.8 (4)
O(2)–O(3)–H(3)	102.6 (42)	C(3)–C(4)–C(5)	121.1 (5)
C(9)–O(4)–C(10)	115.6 (3)	C(4)–C(5)–C(6)	119.8 (5)
O(1)–C(1)–O(2)	112.0 (4)	C(5)–C(6)–C(7)	120.1 (5)
O(1)–C(1)–C(2)	107.0 (4)	C(6)–C(7)–C(8)	120.1 (5)
O(1)–C(1)–C(16)	107.2 (4)	C(3)–C(8)–C(7)	120.2 (4)
O(2)–C(1)–C(2)	104.6 (4)	C(3)–C(8)–C(9)	120.6 (4)
O(2)–C(1)–C(16)	112.4 (4)	C(7)–C(8)–C(9)	119.2 (4)
C(2)–C(1)–C(16)	113.5 (4)	O(1)–C(9)–O(4)	108.5 (4)
C(1)–C(2)–H(2)	103.4 (30)	O(1)–C(9)–C(8)	113.9 (4)
C(1)–C(2)–C(3)	107.5 (4)	O(1)–C(9)–C(28)	107.5 (4)
C(1)–C(2)–C(22)	115.8 (4)	O(4)–C(9)–C(8)	105.8 (4)
C(3)–C(2)–C(22)	115.5 (4)	O(4)–C(9)–C(28)	111.3 (4)
C(2)–C(3)–C(4)	122.5 (4)	C(8)–C(9)–C(28)	109.9 (4)

derived product was isolated in 44% yield together with the *endo*-ozonide **3a** (3% yield) and the diketone **4a** (41% yield). Although this solvent-derived product was identified as an isochroman derivative, its chemical and physical properties were significantly different from those of the analogous compound **6a** derived from **1a**. Consequently, an X-ray crystallographic analysis of the solvent-derived product was undertaken.

The results of the X-ray analysis are illustrated in Figure 1 together with the numbering system adopted. A selection of the more pertinent bond distances and angles are listed in Table II. As depicted in Figure 1, this new product obtained from **8a** is the isochroman derivative **9a**, in which the phenyl group at C(2) and the adjacent hydroperoxy group at C(1) are cis related; in the indene derived products, **6a** and **6b**,[3b] the corresponding substituents are trans. Consistent with its molecular structure, treatment of **9a** with trifluoroacetic acid in methylene chloride results in exclusive formation of the *endo*-ozonide **3a**.

Under identical conditions, ozonolysis of the keto olefin **8b** afforded the corresponding isochroman derivative **9b** in 61% yield together with the *endo*-ozonide **3b** (4% yield) and the diketone **4b** (7% yield) (eq 2 and Table I). The *endo*-ozonides **3a,b** were found to be stable even in refluxing methanol, thereby ruling out the possibility that these ozonides could be solvolyzed under the ozonolysis conditions to yield the isochroman derivatives **9a,b**.

In contrast to the above results, ozonolysis of keto olefin **8a** carried out in aprotic solvents, carbon tetrachloride or acetonitrile,



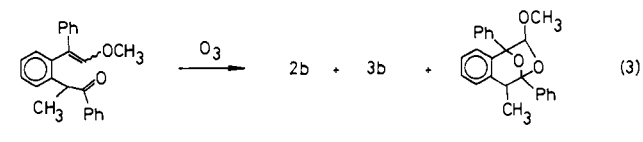
gave only oligomeric products, whereas in CH_3CO_2H–CH_2Cl_2 and CF_3CH_2OH–CH_2Cl_2 solvent mixtures the *endo*-ozonide **3a** and the diketone **4a** were each isolated in moderate yield (Table I). Similar solvent effects were noted for the ozonolyses of the keto olefin **8b**. Thus, a mixture of the isomeric ozonides **2b** and **3b** (14% yield) together with substantial quantities of oligomeric material were isolated from the ozonolysis reaction in carbon tetrachloride. In the presence of the protic solvents CH_3CO_2H and CF_3CH_2OH, however, the keto olefin **8b** gave the *endo*-ozonide **3b** and the diketone **4b** in yields of around 35% and 36%, respectively.

Discussion

The results described above can be broadly rationalized in terms of Criegee-type intermediates, which are widely regarded as important in liquid phase ozonolysis reactions.[2a–c] A mechanism, based on scission pathways of the primary ozonide **10a,b**, to account for the formation of the peroxidic products **2a,b** and **6a,b** from the ozonolysis of indene **1a,b** in methanol is outlined in Scheme I.[7] In order to produce an isochroman derivative such as **6a**, it is apparent that the corresponding primary ozonide **10a**, predominantly formed by a least hindered, anti approach of the ozone to the sterically congested indene **1a**, must undergo a selective cleavage in favor of the carbonyl/carbonyl oxide pair **11a** rather than **12a**;[8] **6a** is necessarily derived from the former. Since the carbonyl and carbonyl oxide groups are formed in close proximity to each other in **11a**, it seems likely that at low temperatures a kinetically controlled, intramolecular partial capture of the carbonyl oxide moiety by the terminal oxygen atom of the carbonyl group, prior to significant conformational reorganization by bond rotation, would give the pivotal carbocationic intermediate **13a**.[9] Subsequent nucleophilic attack on **13a** by methanol, with possible assistance from the neighboring peroxy group, would result

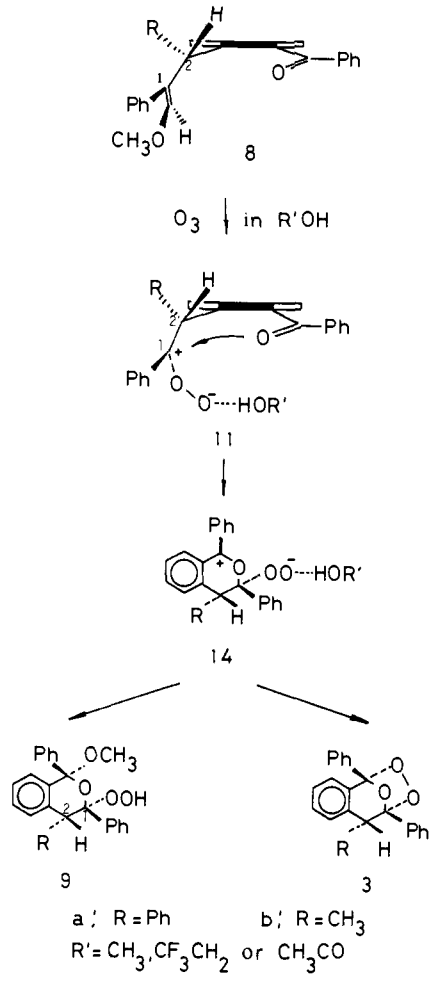
(7) The formation of products such as **5** and **7** suggests a comparatively minor competing ozonolysis route involving formation of a σ complex between ozone and the indene **1**. Among other things, this complex could give the epoxide of the indene, which would be solvolyzed to **7**. Carbonyl compounds such as **5** are known rearrangement products of such epoxides.[2a]

(8) Since no solvent-derived product uniquely attributable to the intermediacy of **12a,b** were observed, it is assumed to cyclize to give the respective ozonides **2** and/or **3**. Perhaps in accordance with this, the ozonolysis of keto olefin **15** in methanol–methylene chloride at −70 °C afforded a mixture of the isomeric ozonides, **2b** and **3b** (10% yield; the **2b**/**3b** ratio = 7:3), together with the partial-cleavage product **16** (63% yield) (eq 3): No evidence for methanol participation was observed.[5]



(9) The remarkable solvent effect on the ozonide exo/endo ratio observed in the ozonolysis of 1-methyl-2,3-diphenylindene (**1b**) could then be interpreted as that in the ozonolysis intermediate **11b** and/or **12b** the carbonyl and carbonyl oxide groups can competitively rotate, the rotation of the carbonyl group being increasingly preferred as the polar carbonyl oxide moiety is increasingly solvated. The solvation should increase the steric bulk of the carbonyl oxide group, and hence the rotation of this group should be substantially slowed down.

Scheme II



in the stereospecific formation of **6a**.

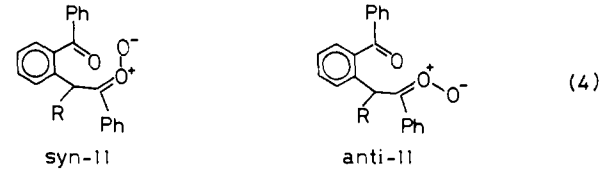
The selective formation of the isomeric methoxy hydroperoxide **9a** is consistent with the intermediacy of the cyclic intermediate **14a** (Scheme II), whose structure is most probably related to a preferred conformation of the substrate keto olefin **8a**. Inspection of molecular models suggests a conformation, as depicted in structural formula **8a**, which minimizes intramolecular steric interactions between the phenyl substituents at C(1) and C(2) and the benzoyl group.[10] According to the normal sequence of events, the ozonolysis of keto olefin **8a** provides the carbonyl oxide intermediate **11a**, having a conformation similar to that shown in Scheme II, which on intramolecular cyclization followed by nucleophilic attack by solvent affords the product **9a**. In addition, since there is little deviation of the geometrical parameters (Table II) around the highly substituted heterocyclic six-membered ring of **9a** from the expected values, it appears that the gauche relationship between the phenyl groups at C(1) and C(2) [torsion angle C(16)-C(1)-C(2)-C(22) 49.1 (6)°] does not introduce appreciable strain into the system.

Although indene **1a** and keto olefin **8a** are formally precursors of the same intermediate, **11a**, attack on each substrate directly results in the independent generation of two distinct conformers of **11a**, from which are derived the stereoisomeric methoxy hydroperoxides **6a** and **9a**, respectively. This implies that rotational interconversion of the conformers in the sterically crowded intermediate **11a** is significantly slower than the cyclization process.[11,12] As a consequence, the conformation of the carbonyl oxide **11a** plays a major role in determining the stereochemistry of the methanol-derived products, **6a** and **9a**. The stereoselective formation of *exo*-ozonide **2a** and the *endo*-isomer **3a** from the ozonolyses of the indene **1a** and the keto olefin **8a**, respectively, could be rationalized on a similar basis.[9] In addition, if **6a** and **9a** were the respective methanolysis products of ozonides **2a** and **3a**, it would seem likely that the configuration at C(9) (Figure 1) would be inverted in each case, resulting in an anti rather than the observed syn relationship between the hydroperoxy and the methoxy groups.

It is remarkable that the yields of the *endo*-ozonides **3a,b** obtained from the ozonolyses of keto olefins **8a,b** in protic solvents, CH_3CO_2H-CH_2Cl_2 and CF_3CH_2OH-CH_2Cl_2, are much higher than those obtained from the reactions in aprotic solvents CCl_4 and CH_3CN (Table I). As depicted in Scheme II, the ozonolysis intermediate **11a,b** generated from the keto olefin **8a,b** would be expected to adopt an extended conformation. This would be unlikely to produce the corresponding ozonide by a concerted pathway because, although the carbonyl group oxygen and carbonyl oxide group carbon would be relatively close in proximity, the carbonyl carbon and terminal oxygen of the carbonyl oxide would be spatially well separated. In the protic solvents, solvation of the more polar carbonyl oxide moiety would enhance the electrophilicity of the carbonyl oxide carbon hence facilitating intramolecular cyclization via the cyclic intermediate **14a,b** to yield the *endo*-ozonide **3a,b** in a stepwise fashion. Since no monomeric ozonides were isolated from the ozonolysis of the keto olefin **8a** in aprotic solvents, it is a priori assumed that the resulting intermediate **11a** must have sufficient lifetime to undergo intermolecular reactions leading to oligomeric products. It should be noted, however, that in the case of the sterically less crowded and hence more flexible intermediate **11b**, the intramolecular recombination leading to the *exo*- and *endo*-ozonides **2b** and **3b** could compete the intermolecular reactions.

The situation is quite different in the case of the carbonyl/carbonyl oxide pair **11a,b** generated from the corresponding indene **1a,b** because, following the cleavage of the primary ozonide, the respective carbonyl and carbonyl oxide groups would be formed in close proximity thereby facilitating intramolecular recombination, even in protic solvents, to give the ozonide via concerted and/or stepwise pathways (Scheme I).

The formation of the ozonolysis products from the indenes **1** and keto olefins **8** have been rationalized in terms of the conformational preferences of the substrates and/or the intermediates. In addition to having a conformational preference, the intermediate carbonyl oxide **11**, in appropriate circumstances, may exist as distinct syn and anti isomers, introducing an additional factor which could influence the product composition and stereochemistry. Although the concepts regarding ozonolysis product stereochemistry enunciated by Bauld and Bailey, and Kuczkowski (see ref 2a and references therein) are not so readily applicable to sterically congested cyclic olefins such as **1**, it follows, on the basis of the principles of least motion, that the primary ozonide **10** derived from indene **1** is likely to afford the isomer *syn*-**11**,



(4)

which is well set up to give the corresponding ozonide **2** and/or solvent-derived product **6** via the kinetically controlled processes described above. The isomeric intermediate *anti*-**11** should provide the solvent-derived product **6** as readily as the syn isomer, though formation of the ozonide **2** from *anti*-**11** via a concerted pathway would be disfavored.

(10) ^1H NMR spectra of keto olefin **8a** in CD_2Cl_2 were found to show no significant variation over the working temperature range −70 to 35 °C, which is not inconsistent with the notion that bond rotation in the side chain of **8a** is highly restricted, resulting in a high degree of conformational rigidity within the molecule.

(11) In less crowded carbonyl oxide intermediates, rotational interconversion of the conformers seems to be much faster than the cycloaddition yielding the corresponding ozonide.[12]

(12) Criegee, R.; Banciu, A.; Keul, H. *Chem. Ber.* **1975**, *108*, 1642.

The isomer distribution of the carbonyl oxides **11** derived from the acyclic keto olefins **8** is less readily predicted. Moreover, there are not straightforward experimental methods of determining either the ratio of the isomeric forms of the intermediate or their rate of interconversion. A preponderance of the more extended isomer *anti*-**11** might favor intermolecular reactions and consequently rationalize the apparent systematic decrease in the yields of monomeric peroxidic products, particularly the ozonides, from the keto olefins in comparison to the corresponding indenes. In methanol at −70 °c, however, formation of the solvent-derived products is affected to a lesser extent, suggesting that the solvent cage assists the intramolecular capture of the carbonyl oxide moiety by the neighboring carbonyl group.

Experimental Section

Preparation of Keto Olefin 8a,b. In a 200-mL flask, equipped with a mechanical stirrer and maintained under nitrogen, was added (methoxymethyl)triphenylphosphonium chloride[13] (6 mmol) and then ether (100 mL). Into this mixture was syringed a solution of phenyllithium (6 mmol) in ether (50 mL) at −10 °C over 3 min. Subsequently, a solution of diketone **4a** (6 mmol) in ether (50 mL) was syringed into the flask in 1 min and the mixture was kept at 20 °C for 20 h. After workup the crude products were triturated with ether–hexane to remove triphenylphosphine oxide. The organic layer was concentrated, and the products were separated by column chromatography with silica gel. From the first fraction was isolated 1-(1-phenyl-2-methoxyvinyl)-2-(1,2-diphenyl-3-methoxy-2-propenyl)benzene in around 10% yield. The second fraction (elution with benzene) gave the keto olefin **8a** (around 20% yield): mp 124–126 °C (from ether–hexane); ^{1}H NMR δ 3.39 (s, 3 H), 5.85 (s, 1 H), 6.09 (s, 1 H), 6.8–7.7 (m, 19 H); IR 1660, 1600 cm^{-1}. Anal. Calcd for $C_{29}H_{24}O_2$: C, 86.14; H, 5.94. Found: C, 85.88; H, 6.00.

From diketone **4b** was obtained the keto olefin **8b** in around 10% yield: an oil; MS, *m/e* 342 (M$^+$); ^{1}H NMR δ 1.45 (d, J = 7.5 Hz, 3 H), 3.39 (s, 3 H), 4.46 (q, J = 7.5 Hz, 1 H), 5.76 (s, 1 H), 6.7–7.7 (m, 14 H); IR 1660, 1600 cm^{-1}. Anal. Calcd for $C_{24}H_{22}O_2$: C, 84.11; H, 6.43. Found: C, 84.73; H, 6.38.

Ozonlysis of 1,2,3-Triphenylindene (1a). Through a solution of **1a** (2.9 mmol, 1.00 g) in MeOH–CH_2Cl_2 (40 mL, 1:1 v/v) was passed a slow stream of ozone (2 molar equiv) at −70 °C. Then the mixture was poured into ice-cold, aqueous potassium dihydrogen phosphate, and the products were extracted with ether. The organic layer was separated and dried over anhydrous magnesium sulfate, and the solvent was removed under vacuum. The crude products were triturated with ether–hexane to give a methanol-derived product, **6a** (924 mg): mp 161–162 °C (from ethyl acetate; ^{1}H NMR δ 3.41 (s, 3 H), 4.46 (s, 1 H), 6.4–7.8 (m, 19 H), 9.30 (s, 1 H; H–D exchange in D_2O). Anal. Calcd for $C_{28}H_{24}O_4$: C, 79.22; H, 5.70. Found: C, 79.24; H, 5.81. The column chromatography of the residue with silica gel gave first the *exo*-ozonide **2a** (102 mg): mp 171–173 °C (from methanol)[3c] and then the diketone **4a** (32 mg): mp 96–98 °C (from benzene–hexane); ^{1}H NMR δ 6.57 (s, 1 H), 6.8–8.1 (m, 19 H); IR 1690, 1660 cm^{-1}.[14] From the final fraction was isolated the partial-cleavage product **7a** (23 mg): mp 185–187 °C (from ethyl acetate); ^{1}H NMR δ 3.09 (s, 3 H), 4.56 (br s, 1 H), 5.09 (s, 1 H), 6.7–7.5 (m, 19 H). Anal. Calcd for $C_{28}H_{24}O_2$: C, 85.71; H, 6.12. Found: C, 85.50; H, 6.22.

Ozonolysis of 1,3-Diphenyl-2-methylindene (1c). The reaction of **1c** (3.54 mmol, 1.00 g) in MeOH–CH_2Cl_2 (30 mL, 1:1 v/v) with ozone (2 molar equiv) was undertaken at −70 °C. The trituration of the crude products with ether–hexane afforded the methoxy hydroperoxide **6c** (603 mg): mp 145–147 °C (from ethyl acetate–hexane); ^{1}H NMR δ 1.36 (s, 3 H), 3.44 (s, 3 H), 4.34 (s, 1 H), 7.0–7.8 (m, 14 H), 9.72 (br s, 1 H). Anal. Calcd for $C_{23}H_{22}O_4$: C, 76.23; H, 6.12. Found: C, 76.12; H, 6.13. The column chromatography of the residue with silica gel afforded, together with a mixture of exo and endo isomeric ozonides **2c** and **3c** (246 mg),[3c] the diketone **4c** (45 mg): an oil; ^{1}H NMR δ 2.06 (s, 3 H), 5.68 (s, 1 H), 7.1–7.8 (m, 14 H); IR 1720, 1660 cm^{-1}.

The reaction at 20 °C gave, together with ozonides **2c** and **3c** (865 mg) and diketone **4c** (22 mg), the partial-cleavage product **7c** (90 mg): mp 133–136 °C (from methanol); ^{1}H NMR δ 0.32 (s, 3 H), 3.03 (s, 3 H), 3.78 (s, 1 H), 4.64 (s, 1 H), 7.1–7.8 (m, 14 H); MS, *m/e* 330 (M$^+$). Anal. Calcd for $C_{23}H_{22}O_2$: C, 83.64; H, 6.67. Found: C, 83.55; H, 6.60.

Ozonolysis of Keto Olefin 8a. Treatment of keto olefin **8a** (1 mmol, 404 mg) with 1.5 molar equiv of ozone in MeOH–CH_2Cl_2 (30 mL, 1:1 v/v) at −70 °C, followed by column chromatography on silica gel, afforded first the *endo*-ozonide **3a** (29 mg): mp 180–182 °C (from methanol).[3c] From the second fraction diketone **4a** (154 mg) was obtained. The third fraction contained the methoxy hydroperoxide **9a** (199 mg): mp 154–155 °C (from ethyl acetate–hexane); ^{1}H NMR δ 3.57 (s, 3 H), 4.50 (s, 1 H), 6.9–8.1 (m, 19 H), 8.85 (s, 1 H; H–D exchange in D_2O). Anal. Calcd for $C_{28}H_{24}O_4$: C, 79.22; H, 5.70. Found: C, 79.15; H, 5.61. Treatment of **9a** with catalytic amounts of CF_3CO_2H in CH_2Cl_2 afforded exclusively the *endo*-ozonide **3a**.

The reaction in CCl_4, followed by column chromatography on silica gel, afforded only an unidentified oligomeric product (300 mg): a glassy material: IR 1660, 1600, 1440, 1300, 1280, 1180, 1140 cm^{-1}; mol wt 805 (vapor pressure osmometer; solvent $CHCl_3$). Anal. Calcd for $(C_{27}H_{20}O_3)_n$: C, 82.63; H, 5.14. Found: C, 81.05; H, 6.06.

Ozonolysis of Keto Olefin 8b. The reaction of keto olefin **8b** (1 mmol, 342 mg) with 1.5 equiv of ozone in MeOH–CH_2Cl_2 (30 mL, 1:1 v/v) at −70 °C, followed by column chromatography on silica gel, afforded first the *endo*-ozonide **3b** (12 mg). From the second fraction was obtained the diketone **4b** (22 mg): mp 108–109 °C (from benzene–hexane); ^{1}H NMR δ 1.45 (d, J = 6.0 Hz, 3 H), 5.12 (q, J = 6.0 Hz, 1 H), 7.3–8.1 (m, 14 H); IR 1680, 1660 cm^{-1}. The third fraction contained the methoxy hydroperoxide **9b** (220 mg): mp 153–155 °C (from ethyl acetate–hexane); ^{1}H NMR δ 1.31 (d, J = 7.5 Hz, 3 H), 3.50 (s, 3 H), 3.41 (q, J = 7.5 Hz, 1 H), 7.1–8.0 (m, 14 H), 8.94 (s, 1 H). Anal. Calcd for $C_{23}H_{22}O_4$: C, 76.24; H, 6.08. Found: C, 75.86; H, 6.20. Treatment of **9b** with catalytic amounts of CF_3CO_2H in CH_2Cl_2 afforded exclusively the *endo*-ozonide **3b**: mp 136–137 °C (from methanol).[3a]

The reaction in CCl_4 gave, together with the *exo*- and *endo*-ozonides **2b** and **3b** (46 mg) and the diketone **4b** (69 mg), an unidentified oligomeric product (180 mg): a glassy material; ^{1}H NMR δ 0.94 (br d, J = 7.5 Hz), 1.39 (br d, J = 7.5 Hz), 3.52 (br q, J = 7.5 Hz), 6.60–8.10 (m), the ratio of the peak areas being around 3:3:2:28; IR 1660, 1600 cm^{-1}; mol wt 650 (vapor pressure osmometer; solvent $CHCl_3$). Anal. Calcd for $(C_{22}H_{18}O_3)_n$: C, 79.98; H, 5.40. Found: C, 76.73; H, 5.12.

Crystal data for solvent-derived product 9a: colorless needles; M = 424.48, triclinic, a = 8.984 (2) Å, b = 10.854 (3) Å, c = 12.622 (4) Å, α = 84.12°, β = 71.13°, γ = 76.90°, U = 1133.9 Å^3, Z = 2, D_c = 1.243 g cm^{-3}, space group $P\bar{1}$ (No. 2) from successful structure solution and refinement, λ = 0.710693 Å, μ (Mo Kα) = 0.77 cm^{-1}, $F(000)$ = 448, data crystal ca. 0.6 × 0.2 × 0.15 mm.

Structure Solution and Refinement. The intensity data were collected on a Enraf-Nonius CAD-4 diffractometer using ω–2θ scanning and graphite-monochromated Mo Kα X-radiation over the region $1 < \Theta < 23°$. The 1580 observed intensities with $I > 3\sigma(I)$ were corrected for Lorentz and polarization but not for absorption or crystal decay. The structure was solved by direct methods (SHELXS86) and refined by using full-matrix least-squares techniques (SHELX76) with anisotropic temperature factors for the non-hydrogen atoms. All the hydrogen atoms were located on a difference Fourier map and included in the refinement process on idealized positions (C–H 0.95 Å). At convergence, the conventional and weighted R factors ($w^{-1} = [\sigma^2(F) + 0.000451(F^2)]$) were 0.051 and 0.059, respectively. The final difference Fourier map contained no features greater than ±0.15 e Å^{-3}. Tables of the atomic fractional coordinates, the anisotropic vibration factors, and the observed and calculated structure factor amplitudes have been deposited as supplementary material.[15]

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Supplementary Material Available: Tables of atomic fractional coordinates and anisotropic vibration parameters (3 pages); listing of observed and calculated structure factors (10 pages). Ordering information is given on any current masthead page.

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