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 CCl₄, CH₃CN, CH₃CO₂H-CH₂Cl₂, and CF₃CH₂OH-CH₂Cl₂ gave predominantly the exo-ozonide 2a, whereas the endo isomer 3a was obtained exclusively from the ozonolysis of keto olefin 8a in CH₃CO₂H-CH₂Cl₂ and CF₃CH₂OH-CH₂Cl₂. 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, CCl₄ and CH₃CN.

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 CCl₄, CH₃CN, CF₃CH₂OH-C- H_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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⁽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.

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



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

			ozonide	
sub		temn	ratio	other products
strate	solventa	°C	(% vield)	(% vield)
strate	Solvent		(10 91010)	
la	CCl ₄ ^o	20	78:22 (85)	4a (4)
la	CH ₃ CN	20	74:26 (72)	d
la	CF ₃ CH ₂ OH–CH ₂ Cl ₂	20	92:8 (84)	d
la	CH ₃ CO ₂ HCH ₂ Cl ₂	20	98:2 (64)	d
1a	MeOH-CCl ₄	20	89:11 (7)	6a (60), 7a (4)
1a	MeOH-CH ₂ Cl ₂	-70	100:0 (9)	4a (3), 6a (75), 7a (2)
1b	CCl ₄ ^b	20	29:71 (93)	5b (2)
1b	CH₃CN°	20	28:72 (92)	d
1b	CF ₃ CH ₂ OH-CH ₂ Cl ₂ ^c	20	55:45 (81)	d
1b	CH ₃ CO ₂ H–CH ₂ Cl ₂ ^c	20	76:24 (89)	d
1b	MeOH–CCl4 ^c	20	46:54 (72)	4b (6), 6b (7)
1b	MeOH-CH ₂ Cl ₂ ^c	-70	59:41 (30)	4b (5), 6b (58)
1c	CCl₄ ^b	20	96:4 (71)	d
1c	CH ₃ CO ₂ H-CH ₂ Cl ₂	20	73:27 (71)	4c (1)
1c	MeOH-CCl4	20	95:5 (71)	4c (2), 7c (7)
1c	MeOH-CH ₂ Cl ₂	-70	100:0 (21)	4c (4), 6c (47)
8a	CCl₄	0	. ,	e
8a	CH ₃ CN	0		е
8a	CF ₁ CH ₂ OH-CH ₂ Cl ₂	0	0:100 (23)	4a (37)
8a	CH,CO,H-CH,CI,	0	0:100(28)	4a (31)
8a	MeOH-CH ₂ Cl ₂	-70	0:100(3)	4a (41), 9a (44)
8b	CCL	0	33:67 (14)	4b (22)*
8b	CF ₂ CH ₂ OH-CH ₂ Cl ₂	Ō	0:100(32)	4b (31)
8b	CH ₂ CO ₂ H-CH ₂ Cl ₂	õ	0:100(37)	4b (41)
8b	MeOH-CH ₂ Cl ₂	Õ	0:100 (15)	4h (10), 9h (36)
8b	MeOH-CH ₂ Cl ₂	-70	0:100(4)	4b (7), 9b (61)
		. •		(,,, (,,,)

^aMeOH-CCl₄; 70:30 v/v. MeOH-CH₂Cl₂; 50:50 v/v. CH₃CO₂H-C-H₂Cl₂; 50:50 v/v. CF₃CH₂OH-CH₂Cl₂; 50:50 v/v. CF₃CH₂OH-CH₂Cl₂; 50:50 v/v. ^bTaken from the data in ref 3c. ^cTaken from the data in ref 3d. ^dOther byproducts were not determined. ^eUnidentified 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 fivemembered 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 L	engths (Å)	with Standard Devia	tions
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) Ang	les (deg) wit	th Standard Deviatio	ns
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

C(6) - C(7) - C(8)

C(3)-C(8)-C(7)

C(3)-C(8)-C(9)

C(7)-C(8)-C(9)

O(1)-C(9)-O(4)

O(1)-C(9)-C(8)

O(1)-C(9)-C(28)

120.1 (5)

120.2 (4)

120.6 (4)

119.2 (4)

108.5 (4)

113.9 (4)

107.5 (4)

107.0 (4)

107.2 (4)

104.6 (4)

112.4(4)

113.5 (4)

103.4 (30)

107.5 (4)

O(1) - C(1) - C(2)

O(1)-C(1)-C(16)

O(2)-C(1)-C(16)

C(2)-C(1)-C(16)

C(1)-C(2)-H(2)

C(1)-C(2)-C(3)

O(2)-C(1)-C(2)

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 we	a isolated i	n 11% wield togeth	ar with the
endo-ozonide 3a (3)	% vield) an	d the diketone 4 a ((41% vield)
Although this solver	nt-derived p	roduct was identifie	ed as an iso-
chroman derivative,	, its chemic	al and physical pro	perties were
significantly differer	nt from thos	e of the analogous c	ompound 6a
1. 1. 1. 1		Ŷ	•
derived from Ia. Con	nsequently, a	an X-ray crystallogra	phic 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 CH₃CO₂H-CH₂Cl₂ and CF₃CH₂OH-CH₂Cl₂ 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 CH₃CO₂H and CF₃CH₂OH, however, the keto olefin **8b** gave the endoozonide 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

$$\begin{array}{c} Ph \\ OCH_3 \\ CH_3 \\ Ph \end{array} \xrightarrow{O_3} 2b + 3b + OH_3 \\ CH_3 \\ 15 \end{array} \qquad (3)$$

(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

⁽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.

⁽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

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, CH₃CO₂H-CH₂Cl₂ and CF₃CH₂OH-CH₂Cl₂, are much higher than those obtained from the reactions in aprotic solvents CCl₄ and CH₃CN (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,



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) &}lt;sup>1</sup>H 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.

Ozonolysis of Substituted Diphenylindenes and Benzophenones

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 chloride¹³ (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); ¹H NMR & 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⁺); ¹H 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 C₂₄H₂₂O₂: 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-CH₂Cl₂ (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; ¹H 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 D₂O). Anal. Calcd for C₂₈H₂₄O₄: 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); ¹H NMR & 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); ¹H 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-CH₂Cl₂ (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); ¹H 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 C₂₃H₂₂O₄: 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; ¹H 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); ¹H 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 C₂₃H₂₂O₂: 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-CH₂Cl₂ (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).^{3e} 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); ¹H 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 D₂O). Anal. Calcd for C₂₈H₂₄O₄: C, 79.22; H, 5.70. Found: C, 79.15; H, 5.61. Treatment of **9a** with catalytic amounts of CF₃CO₂H in CH₂Cl₂ afforded exclusively the *endo*-ozonide **3a**.

The reaction in CCl₄, 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 CHCl₃). 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-CH₂Cl₂ (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); ¹H 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); ¹H 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 C₂₃H₂₂O₄: C, 76.24; H, 6.08. Found: C, 75.86; H, 6.20. Treatment of **9b** with catalytic amounts of CF₃CO₂H in CH₂Cl₂ afforded exclusively the *endo*-ozonide **3b**: mp 136-137 °C (from methanol).^{3a}

The reaction in CCl₄ 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; ¹H 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 CHCl₃). Anal. Calcd for $(C_{22}H_{18}O_3)_{ai}$: 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, $\alpha = 84.12^{\circ}$, $\beta = 71.13^{\circ}$, $\gamma = 76.90^{\circ}$, U = 1133.9 Å³, Z = 2, $D_c = 1.243$ g cm⁻³, space group $P\bar{I}$ (No. 2) from successful structure solution and refinement, $\lambda = 0.710693$ Å, μ (Mo K α) = 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 -2 θ scanning and graphite-monochromated Mo K α X-radiation over the region 1 < θ < 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 $\pm 0.15 \ e^{-3}$. 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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