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Chemistry of Singlet Oxygen. XXIII.[1,2] Low Temperature Photooxygenation of Indenes in Aprotic Solvent

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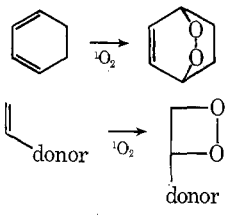
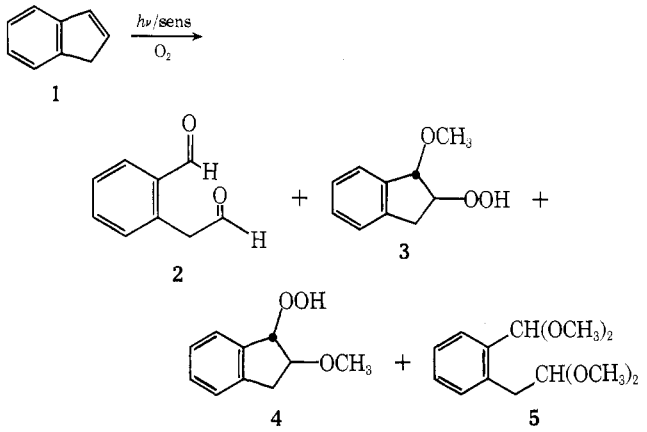
Indenes undergo dye-sensitized photooxygenation at −78 °C in acetone to yield unusual dioxygenated products **9** (2,3:7,9-diepoxy-6,9-peroxy-$\Delta^{4,5}$-hexahydroindenes). These compounds undergo thermal rearrangement to form indene tetraepoxides (benzene trioxides), react with trimethyl phosphite to form 2,3:4,9:7,8-triepoxy-$\Delta^{5,6}$-hexahydroindenes, and with triethylamine to form 2,3:7,8-diepoxy-6-keto-9-hydroxy-$\Delta^{4,5}$-hexahydroindenes. The probable mode of formation of the adducts **9** involves initial 1,4 addition of singlet oxygen to the indene, followed by rearrangement of the initial endoperoxide to a diepoxide and addition of a second mole of singlet oxygen.

The photosensitized 1,4 cycloaddition of oxygen to dienes is believed to involve singlet ($^1\Delta_g$) oxygen as an intermediate,[3] and 1,2 cycloadditions of singlet oxygen to electron-rich olefins have also been recognized.[4,5] The products of those 1,2 cycloadditions, dioxetanes, have been characterized from enamines,[6] vinyl ethers,[5] and a few less electron-rich olefins[7] such as adamantylideneadamantane.[7a] Dioxetanes have also been suggested as the reactive intermediates in certain other cases of oxidative double bond cleavage.[8]



Recent work has shown that the photooxygenation of certain substituted styrenes can lead to 1,4 cycloadducts in which the aromatic ring acts as part of the diene systems, in an unusual type of Diels–Alder reaction with singlet oxygen.[9] Although many examples of 1,4 cycloadditions of dienophiles to styrene derivatives are known,[10,11] these were the first examples involving singlet oxygen.

Consideration of the above results suggested that the photooxygenation of indene (1) should be reinvestigated. The original observations were that in methylene chloride, the product was homophthalaldehyde **2**,[12] while, in methanol, the products were (after reduction) **2**–**5**.[8c] These results were confirmed by Mazur,[9b] who found reaction to be extremely slow in aprotic solvents and accompanied by dye bleaching. In protic solvents, the reaction is much faster. The product proportions vary with the conditions, and other products are formed, such as indene oxide.



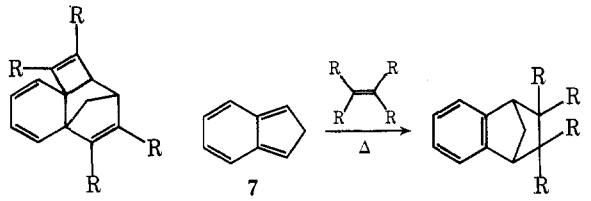
These products were suggested by Kearns et al.[8c] to derive from an initial 1,2 cycloaddition of singlet oxygen; no products were isolated that suggested a 1,4-cycloaddition reaction. (In fact, corresponding dioxetanes have subsequently been shown to be formed in good yield when the reaction of substituted indenes is carried out in methanol[13]). However, reactive dienophiles such as dicyanoacetylene and dimethyl acetylenedicarboxylate form Diels–Alder adducts with indene, although the yields are low.[11,14] These adducts were assigned the structure **6** (R = CO_2CH_3 or CN). At elevated temperatures (~200 °C) indene also forms cycloadducts such as **8** which are derived from an isoindene (2*H*-indene) intermediate (**7**).[15]

In an attempt to clarify the mechanism, Mazur photooxygenated indene at low temperature in an aprotic solvent (acetone, −78 °C); under these conditions the reaction proved to be much faster than at room temperature, and an unexpected product was formed in good yield.[9a,b] This paper describes in detail these results, and those obtained by pursuing this initial observation.

Table I. ^{1}H Chemical Shifts (δ, Me_4Si, $CDCl_3$, 60 MHz) of the Ring Protons of 9a–g[a]

	9a	9b[b]	9c[b]	9d	9e	9f	9g
H_A[c]	6.50	6.46	6.62	6.53	6.53	6.62	6.47
H_B[c]	6.27	6.29	6.27	6.31	6.27	6.19	6.24
H_C	5.15	5.06	5.03	5.07	5.04	4.97	4.63
H_D	3.7	3.81	3.65	3.73	3.72	3.73	
H_E	3.7				3.70		
H_F	3.62		3.60			3.38	3.56
H_G[d]	2.10	2.55	2.20	2.45	2.45	2.42	2.06
H_H	2.73	3.43	2.75	3.20	3.27		2.58

[a] Substituent resonances omitted for clarity. [b] 100-MHz spectra. [c] Chemical shifts determined by analysis of the ABX system of protons A–C.[18] [d] The lower field of G, H was assigned as H because phenyl substituents at E and F have larger effect on this resonance.

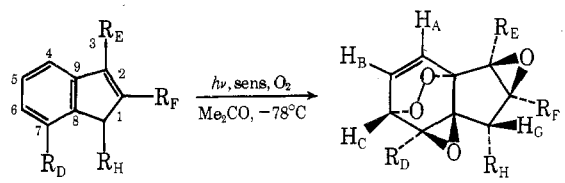


6 (R = CO_2CH_3, CN) 7 8

Results and Structure Assignments

Photooxygenation of the Indenes. Indene (**1a**) was photooxygenated at −78 °C in acetone containing rose bengal; the oxygen uptake was 1.5 equiv. Both the NMR spectrum and TLC showed mainly starting material and a single product (**9a**) which was isolated in 38% yield.[16]

Similarly, acetone solutions of **1b–g** were photooxygenated at −78 °C. These compounds took up oxygen at a faster rate than the parent indene and without dye bleaching (or with dye bleaching only at the end of the reaction). In all cases, 1.6–2.0 mol of O_2/mol of indene were taken up, and products **9b–g** were isolated in yields which varied from 40 to 93%.



1a–g **9a–g**

a, $R_D = R_E = R_F = R_H = H$
b, $R_D = R_H = H$; $R_E = R_F = C_6H_5$
c, $R_D = R_F = R_H = H$; $R_E = i\text{-}C_3H_7$
d, $R_D = R_H = H$; $R_E = CH_3$; $R_F = C_6H_5$
e, $R_D = R_E = R_H = H$; $R_F = C_6H_5$
f, $R_D = R_F = H$; $R_E = t\text{-}C_4H_9$; $R_H = CH_3$
g, $R_D = CH_3$; $R_E = i\text{-}C_3H_7$; $R_F = R_H = H$

All these compounds gave analyses and mass spectra consistent with formulation as starting material plus two molecules of oxygen. The mass spectra have significant peaks at P − 32 (loss of oxygen).

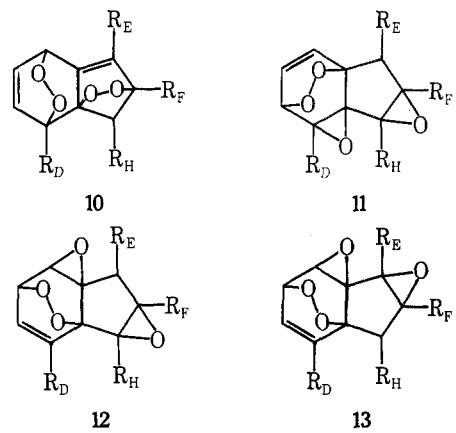
The compounds give a positive test for peroxide with acidified KI. The ir spectra show no carbonyl, hydroxyl, or hydroperoxyl bands, but there are many strong bands between 750 and 1280 cm^{-1}. This region contains the three substituted epoxide ring vibration bands.[17] The ^{1}H NMR chemical shifts of products **9a–g** are summarized in Table I; the couplings of these spectra (checked by double resonance) are summarized in Table II.

Since these compounds contain an O–O group but no OOH, they must contain an endoperoxide (also consistent with the loss of molecular oxygen in the mass spectra). The presence of only one proton with a resonance of δ ~5.0 in the NMR spectra, which is the region expected for an allylic proton α to an endoperoxide, eliminates structure **10** (or other structures containing more than one peroxide) as a possibility.

Table II. Couplings (Hz) Derived from Peaks of Table I

J	9a	9b	9c	9d	9e	9f	9g
AB[a]	8.6	8.6	8.8	8.6	8.6	8.8	8.9
AC[a]	1.4	1.3	1.4	1.5	1.4	1.4	1.6
BC[a]	6.1	6.1	6.2	6.1	6.2	6.2	6.3
BD	~0.8	~0.6	~0.8	~0.6	~0.8	~0.9	
CD	4.0	4.0	4.0	4.2	4.2	4.4	
GH	16	16	16	16	16		16
FH[b]	1.3		1.1				1.3
FG	c		c			~0.8	~0.7
EF	c						
EG	c				~0.7		

[a] Couplings obtained from analysis of the ABX system of protons A–C.[18] [b] Proton F to lower field of G, H. [c] Coupling is either obscured by other resonances or not resolved.



10 **11**

12 **13**

Since there is only one peroxide, one O–O bond must be broken to give the observed products. Since neither carbonyl nor hydroxyl groups are present in the ir, the remaining oxygens must be ethers, and the NMR spectra show resonances between δ 3.6 and 3.8 which are assigned to protons α to epoxide groups in a system heavily substituted by electronegative groups. The NMR spectra also show two olefinic protons forming the AB part of an ABXY system with $J_{AD} \sim 0$ and the proton α to the endoperoxide and one epoxide proton forming the XY part. These four protons must be on the original six-membered ring of the indene, assuming no skeletal rearrangement. These spectra confirm the exclusion of **10** as a possibility. Possible structures with one endoperoxide and two epoxide groups are then limited to **9** and **11–13**. The latter three are ruled out by the spectra of the substituted compounds **9b–f**. The presence of a methylene group in **9b–d** excludes **11** and **12**, and the presence of both olefinic protons in **9g** rules out structure **13**, which has a methyl group at position D.

Strong further support has been obtained for these structures by the ^{13}C spectra, which were obtained using single-frequency and off-resonance proton decoupling, and have been published.[19] In addition, the chemistry of these substances, reported below, and an x-ray structure of a compound in the analogous dihydronaphthalene series[2] leave no doubt that structures **9a–f** are correct. The stereochemical assignments will be discussed in the Discussion.

Thermolysis of the Photooxygenation Products. On melting, **9d** and **9e** resolidified and then remelted at a higher temperature. Refluxing toluene or heptane solutions of

Table III. ^{1}H Chemical Shifts (δ, Me_4Si, $CDCl_3$, 100 MHz) of the Ring Protons of Thermolysis Products 14 and 15[a]

Proton	14a	14b	14c	14d	14f	14g	15d[b]	15f	15g
H_A	3.86	3.35	3.84	3.77	3.89	3.82	3.56	3.78	3.71
H_B	3.26	3.18	3.27	3.29	3.24	3.25[c]	2.74[e]	2.67[e]	2.75
H_C	3.43	3.44	3.42	3.43	3.41	3.25[c]	3.14	3.11	3.13
H_D	3.57	3.67	3.54	3.63	3.46		3.50	3.34	
H_E	3.31								
H_F	3.79		3.66		3.46	3.65		3.50	3.74
H_G[d]	1.92	2.19	1.83	2.05	2.00	1.86	2.19	2.00	1.98
H_H	2.52	3.31	2.51	3.05		2.40	3.24		2.40

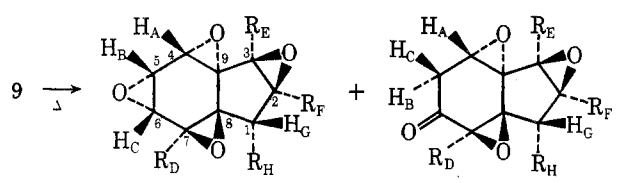
[a] Substituent resonances omitted for clarity; shifts are approximate multiplet centers. [b] 60-MHz spectrum. [c] Multiplet center of the AB portion of a degenerate ABX system. [d] Lower field of G, H assigned as H because of larger coupling to H and because the phenyl substituent has a larger effect on this resonance. [e] Lower field of B, C assigned to B owing to W coupling with D.

Table IV. Couplings (Hz) Derived from the Peaks of Table III

J	14a	14b	14c	14d	14f	14g	15d	15f	15g
AB	3.1	3.0	3.2	3.0	3.1	c	2.8	3.0	3.0
AC	b	b	b	b	b	c	1.4	1.2	1.1
BC	3.7	3.6	3.8	3.5	3.7	c	16.5	16.1	16.0
BD	1.0	1.0	1.0	1.0	1.0		0.8	1.0	
CD	1.7	1.7	1.7	1.7	1.7		b	b	
GH	15.1	14.8	14.8	14.8		14.9	16.0		16.0
FH[a]	1.2		1.1			1.1			1.0
FG	0.7		d		0.9	d		0.9	d
EF	2.6								
EG	d								

[a] Proton F to lower field of G, H; assignment as H consistent with observed coupling as shown by models. [b] No observed coupling. [c] Protons A, B, and C comprise a degenerate ABX system with the chemical shift of B and C nearly identical. [d] Coupling is not observed although peak broadening is present.

the photooxygenation products (9) led to the formation of two new compounds in the ratio of ~4:1. The major products (14) were isolated in 38–60% yield by chromatography on silica gel and/or crystallization. The analyses and mass



14 15

spectra of these compounds showed them to be isomeric with compounds 9. Their ir spectra showed neither carbonyl nor hydroxyl bands, and the NMR spectra (Tables III and IV) showed no resonances below 3.9 ppm (except phenyl when present as a substituent) and several resonances in the region associated with epoxides were present. These compounds were assigned the tetraepoxide (benzene trioxide) structure 14 on the basis of their NMR spectra (discussed below), their ^{13}C spectra,[19] and analogy with compounds in the dihydronaphthalene series[2] for which an x-ray structure is available. The minor products all showed a carbonyl band at 1720–1727 cm^{-1} (saturated ketone) and no hydroxyl absorption; these compounds could not be isolated in pure form, but the NMR spectra of several of them were determined (Tables III and IV) and are consistent with structure 15. They isomerized during chromatography to the unsaturated ketones (16) discussed below.

The coupling pattern of the ring protons A–D is identical in all the tetraepoxides; they form a system in which J_{AD} and J_{AC} are too small to resolve (≤0.5 Hz). The only difficulty in unequivocal assignment was the determination of which proton is A and which is D. The ^{1}H NMR of 14g did not solve the problem because the ring protons form a degenerate (deceptively simple) ABX system.[18] The marked upfield shift of 0.5 ppm for proton A in 14b (R_E = R_F = C_6H_5), due to shielding by the 3-phenyl substituent, supported this assignment, which was later conclusively confirmed by ^{13}C NMR spectroscopy.[19]

Models of the minor products, β-epoxy ketones (15), show that proton B, but not C, has the planar configuration with proton D required for W coupling.[20] This coupling is also lost in 15g, in which proton D is replaced by a methyl group. The larger value of J_{AB} compared to J_{AC} is also in agreement with this, since the dihedral angle between A and B is the smaller. The low-field proton in both 15d and 15f, therefore, must be A. This is unusual since proton D is α to a carbonyl group and would thus be expected to be at lowest field. The 7-methyl group of 15g also appears at higher field than the methyl of 14g; it appears that this shift is an effect similar to the inverted axial–equatorial chemical shift relationship experienced by the α protons of α-halocyclohexanones.[20]

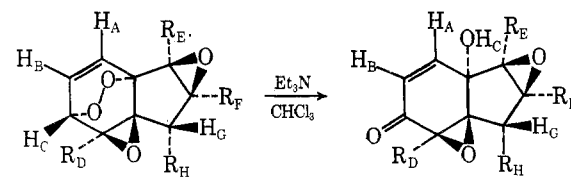
Table V. ^{1}H Chemical Shifts (δ, Me_4Si, $CDCl_3$, 60 MHz) of Ring Protons of Compounds 16a[a]

Proton	16a[b]	16b	16c	16d	16f	16g[c]
H_A[d]	6.95	6.66	7.02	6.90	7.18	6.93
H_B[e]	5.97	5.97	5.91	5.97	5.81	5.83
H_C[f]	g	2.77	3.00	3.42	2.74	4.82
H_D	3.54	3.68	3.46	3.60	3.42	
H_E	3.65[h]					
H_F	3.76[h]		3.62		3.40	3.60
H_G[i]	2.02	2.28	1.90	2.12	2.19	1.83
H_H[j]	2.83	3.66	2.80	3.36		2.68

[a] Substituent resonances omitted for clarity. [b] Impure compound obtained during chromatography of 15a. [c] In $CDCl_3$–$(CD_3)_2CO$. [d] J_{AB}: 10.5 (16a, 16c, and 16d), 10.6 (16f and 16g), and 10.0 Hz (16b). [e] J_{BD} = 2.0 Hz. [f] Chemical shift variable. [g] Obscured. [h] Relative assignment of E, F uncertain; J_{EF} = 3 Hz. [i] J_{GH} = 14 Hz. [j] J_{FH} = 1 Hz for 16c and 16g; obscured in 16a; proton H assigned as lower field of G, H owing to its absence in 16f and the large effect of phenyl substituent on this proton.

The rates of thermolysis of 9c (R_E = i-C_3H_7) and 9d (R_E = CH_3; R_F = C_6H_5) in $CDCl_3$ at 69.0 °C were determined by NMR spectroscopy by following the disappearance of the starting compounds. The thermolyses followed first-order kinetics; the rates were determined to be 8.2 × 10^{-5} s^{-1} for 9c and 8.0 × 10^{-5} s^{-1} for 9d.

Reaction with Base. Compounds 9b–g react exothermically with triethylamine in $CHCl_3$ to give γ-hydroxy-α,β-unsaturated ketones (16) in 37–96% yield. The reaction of



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9a (R_E = R_F = H) gave only a black, tarry residue, even with a milder base, N,N-dimethylaniline. The ir spectra (KBr) of these compounds had carbonyl bands at 1680–1700 cm^{-1} and a strong OH band at 3535–3580 cm^{-1} (16b showed a broad band at 3460 cm^{-1}). The NMR spectra are tabulated in Table V. Proton B is coupled with proton D

Table VI. ^{1}H Chemical Shifts (δ, Me_4Si, $CDCl_3$, 60 MHz) of the Ring Protons of 17[a]

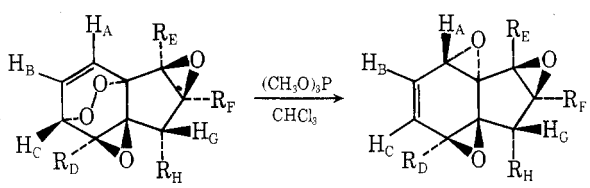
Proton	17a[b]	17b[b]	17c	17d	17f	17g[d]
H_A[c]	3.74[d]	3.42[e]	3.69[d]	3.60[d]	3.72[d]	3.67[f]
H_B	6.11	6.15[g]	6.12	6.12	6.07	6.02[h]
H_C	6.11	5.97	6.12	6.12	6.07	5.93
H_D	3.35	3.20	3.30	3.38	3.24	
H_E	3.36[i]					
H_F[j,k]	3.75		3.63		3.41	3.64
H_G[l]	2.02	2.29	1.95	2.14	2.10	1.95
H_H	2.64	3.42	2.64	3.21		2.55

[a] Substituent resonances omitted for clarity. [b] 100-MHz spectra. [c] Assignment based on presence of this proton in **17g**. [d] $J_{A(BC)} = J_{D(BC)}$: 2.7 (**17a**), 2.5 (**17c** and **17d**), and 2.8 Hz (**17f**). [e] $J_{AC} = J_{BD} = 2.0$ and $J_{AB} = J_{CD} = 3.4$ Hz. [f] An ABX system with $J_{AB} = 3.9$ and $J_{AC} = 1.7$ Hz. [g] $J_{BC} = 10.0$ Hz; relative assignment of protons B, C uncertain. [h] $J_{BC} = 10.0$ Hz. [i] $J_{EF} = 2.7$ Hz. [j] J_{FH}: 1.4 (**17a**), ~1 (**17c**), and 1.2 Hz (**17g**). [k] J_{FG}: 0.9 (**17f**) and <1 Hz (**17g**). [l] J_{GH} = 15 Hz; lower field of G, H assigned as H based on its absence in **17f** and the larger effect of the phenyl groups on this proton in **17b** and **17d**.

(J_{BD} = 2.0 Hz). This W coupling across the carbonyl group agrees with the value of 2.1 Hz found for 3,4-diphenyl-2,3-cyclopentenone oxide,[21] and it is absent in **16g**, in which proton D has been replaced by a methyl group.

These rearrangements are common with diene endoperoxides with a proton α to the peroxy group,[22,23] but, in those cases, the reactions require basic alumina or methanolic sodium hydroxide solution, indicating that endoperoxides **9** are more reactive.

Reaction with Trimethyl Phosphite. Compounds **9a–f** react exothermically with trimethyl phosphite in $CHCl_3$ solution to give benzene dioxides (**17**, 28–96% yield) with removal of one oxygen atom. Structure assignments are



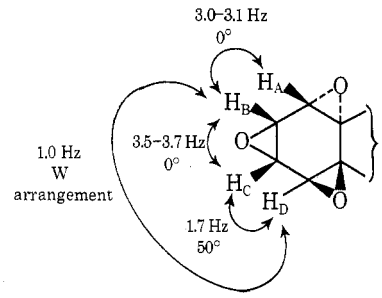
9 17

based on infrared (no carbonyl or OH) and NMR spectra (see Table VI) and analogy with simpler diene endoperoxides, for which the corresponding reaction is well known.[22c,d,24]

In **17a** and **17c–f** the olefinic protons have the same chemical shift, resulting in virtual coupling with protons A and D; thus, protons B and C together and protons A and B each appear as a triplet with splitting = $(J_{AB} + J_{AC})/2 = (J_{BD} + J_{CD})/2$ = 2.5–2.8 Hz. In **17b**, the olefinic protons have slightly different chemical shifts, and protons A–D form a four-spin system with $J_{AB} = J_{CD} = 3.4$, $J_{AC} = J_{BD} = 2.0$, $J_{BC} = 10$, and $J_{AD} \simeq 0$ Hz (not resolved). The substitution of a methyl group at the 7 position in **17g** reduces protons A–C to an ABX system, with $J_{AB} = 3.9$, $J_{AC} = 1.7$, and $J_{BC} = 10$ Hz.

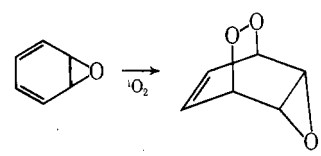
Discussion

Stereochemical Assignments. The magnitude of the couplings in Table IV allows stereochemical assignments in the six-membered ring of compounds **14**, and, by extension, to compounds **9**. Consider the four-spin system formed by protons ABCD. Proton D is assigned by the absence of this resonance in compound **14g**; proton C is coupled to it with a 1.7-Hz coupling, while proton B is coupled to D (four-bond coupling, presumably requiring the W arrangement) by 1.0 Hz. Proton B is coupled to C by 3.5–3.7 Hz, and to A by 3.0–3.1 Hz. Inspection of models shows that the *anti*-benzene trioxide geometry is the only one which permits appropriate dihedral angles (0° for the AB and BC pair, and 50° for the CD pair). These coupling constants compare well with those of other diepoxide compounds with similar stereochemistries.[2]

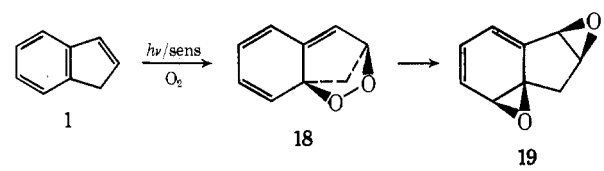


The proton assignments are confirmed by single frequency double resonance experiments in the ^{13}C spectrum.[19] In addition, the *anti*-benzene trioxide structure is the same one found by an x-ray structure of one of the corresponding tetraepoxides in the dihydronaphthalene series,[2] where the NMR coupling patterns are the same as with compound **14**.

The stereochemistry of the six-membered ring in endoperoxide compounds **9** is then that which would be expected on singlet oxygen addition to a benzene oxide from the less hindered anti side, which is the stereochemistry found in the parent system.[25,26]

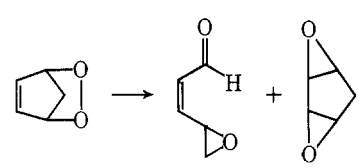


Mechanism of the Formation of 9. The mode of formation of compounds **9** can be readily understood if the first step is a Diels–Alder addition of singlet oxygen to the indene to give **18**. Rearrangement of this endoperoxide would give the bisepoxide **19**. Addition of another molecule of sin-



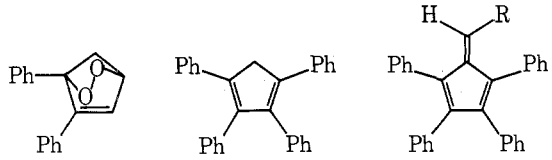
1 18 19

glet oxygen to **19** would give the observed products **9**, and should be more rapid than the initial addition to **1**. All attempts to detect either **18** or **19** as intermediates by running the photooxidation to partial conversion or in the presence of dienophiles have failed so far. The rearrangement of **18** to **19** at −78° is somewhat surprising, although cyclopentadiene endoperoxide undergoes a related reaction at higher temperatures; the product is mainly **20** along with some **21**.[27] The reaction proceeds explosively even in solution above 0 °C.



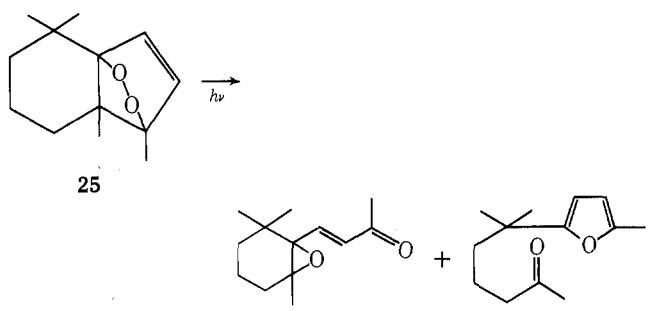
20 21

The endoperoxide **22**, derived from 1,2-diphenyl-1,3-cyclopentadiene, is also unstable above −20 °C.[28]



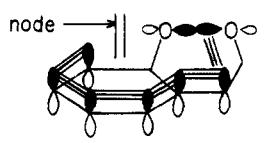
22 23 24 (R = H, Ph)

Diene endoperoxides can be rearranged photochemically as well as thermally, as they have tail absorptions which extend beyond 360 nm.[29] For example, the self-sensitized photooxygenation of **23** and **24** at −50 °C leads to the corresponding bisepoxides instead of the endoperoxide compounds (although dye-sensitized photooxygenation leads mainly to the endoperoxides owing to the greatly increased rate of photooxygenation relative to the rate of the subsequent rearrangement).[30] Direct photochemical rearrangement of **18**, however, does not account for the present results, since the photooxygenation of **1b** with light >525 nm led to exactly the same product. A rearrangement photosensitized by rose bengal is still possible, however. Ohloff et al. found that peroxide **25** rearranged in a reaction photosensitized by rose bengal, but not by methylene blue (which has a lower triplet energy).[31] The same products are

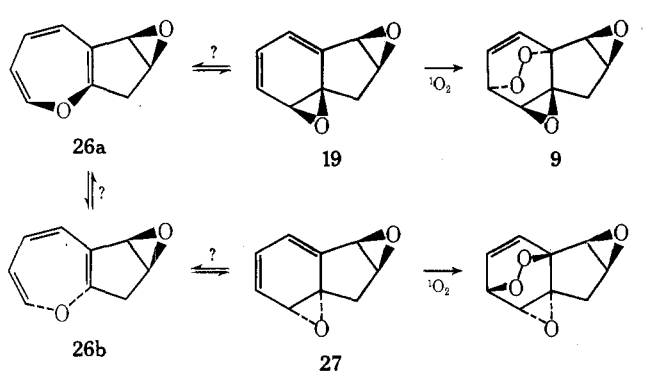


25

formed in this system by both rose bengal and methylene blue, however. The rearrangement in this case may be more facile than usual because the triene system in **18** is well set up to attack the ends of the peroxide bond in an eight-electron "Möbius" arrangement, which would be thermally allowed as a concerted process.[32] Whether concerted or not,



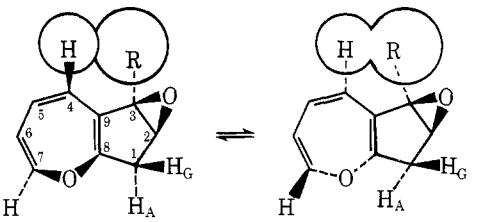
if the diepoxide is formed from the endoperoxide, the epoxide groups in **19** should be cis. However, the benzene oxide–oxepin equilibrium is facile and allows a mechanism for isomerization at this point; in fact, the tetraepoxide in the dihydronaphthalene series subjected to x-ray crystal structure determination actually has these two epoxide groups trans.[2]



26a 19 9

26b 27

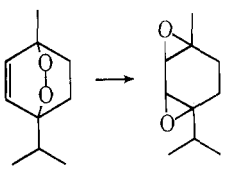
For this reason, and because the NMR is unhelpful, relative stereochemistry of the two epoxide groups in **9** or any of the transformation products cannot be assigned with confidence at present. It is significant that, in contrast to the situation in the dihydronaphthalenes, only a single isomer of **9** is actually formed. It is probably important that models of the two oxepins show **26b** to have a severe peri



26a 26b

interaction which is not present in the oxepins in the dihydronaphthalene series. If this interaction governs the equilibrium constant or rate of isomerization 19 ⇌ 27, then the cis isomer **19** should predominate in the indene series.

The rearrangement of peroxides **9** to the tetraepoxides **14** is a reaction exactly analogous to that of **18** to **19** and is well precedented in cyclohexane endoperoxide systems.[22] It is, however, much more facile than in simpler systems, for instance, for ascaridole (**28**). The data of Boche and Runquist[22a] allow calculation of the rate to be 6×10^{-8} s^{-1} at 69°, compared to 8×10^{-5} at this temperature for **9c** and **9d**. This surprising reactivity toward this rearrangement is also shown in the parent benzene oxide endoperoxide–benzene trioxide rearrangement.[25,26,33]



28

It is remarkable that in all of the indenes studied here, no "ene" product, or at most only traces, is formed, especially since Fenical, Kearns, and Radlick found that in 2,3-dimethylindene, photooxygenation at room temperature in CH_2Cl_2 gave 65% of the ene product;[8c] also, in the closely related dihydronaphthalene series, substantial amounts of ene product are formed in some cases under conditions very similar to the present ones. The balance of products seems very sensitive to structure and conditions.

The remarkable solvent and temperature effects on this reaction (slow reaction, complex product mixture at room temperature in aprotic solvents, fast reaction giving **9** at low temperature in aprotic solvents, and fast reaction giving dioxetanes at low temperature in methanol) are the subject of a current investigation.

Experimental Section

Boiling points and melting points are uncorrected. NMR spectra were taken on a Varian T-60 or HA-100 spectrometer; chemical shifts are relative to tetramethylsilane. Ir spectra were taken on a Perkin-Elmer Model 137 spectrophotometer calibrated with the 1603-cm^{-1} band of polystyrene. Mass spectra were obtained on an AEI MS-9 operated by Elizabeth Irwin. Elemental analyses were by Heather King. NMR spectral details listed in the tables are not repeated here.

Photooxygenations were carried out using a Sylvania DWY 650W tungsten–halogen lamp at 90 V. The reaction solutions were cooled with a dry ice–acetone bath contained in a half-silvered Dewar; oxygen was circulated through a capillary bubbler immersed in the solution using a Neptune diaphragm pump; the oxygen uptake was measured by a gas buret.

Starting Materials. 3-Isopropylindene (**1c**) was prepared by the method of Makosza:[34,35] bp 100–101 °C (12 mm) [lit.[36] bp 99–100 °C (9.5 mm)]; NMR (CCl_4) δ 1.23 (d, 6 H, J = 7 Hz), 2.85 (septet, 1 H), 3.15 (m, 2 H), 6.00 (m, 1 H) and 7.15 (broad m, 4 H); ir (KBr) 1389, 1377, 763, 717 cm^{-1}. 2,3-Diphenylindene [**1b,** mp 110–111 °C (lit.[37] 108.5–109.5 °C)] was prepared from 2-phenyl-1-indanone,[38] which was made from 2,3-diphenylpropionic acid.[38] 2-Phenyl-3-methylindene (**1d**), mp (ethanol) 76.7–77.4 °C (lit.[39] 75 °C), was prepared from 2-phenyl-1-indanone. 2-Phenylindene (**1e**), mp 167–169 ° (lit.[40] 167.5 °C), was made from 2-phenyl-1-indanone. 1-Methyl-3-*tert*-butylindene[41,42] (**1f**) was made from 3-methyl-1-indanone[41] (prepared in turn from β-phenylbutyric acid[43]) and had bp 70–71 °C (0.5 mm) [lit.[41] bp 70 °C (0.3 mm)] and was chromatographed on silica gel to remove unreacted starting material.

3-Isopropyl-7-methylindene (1g). 4-Methyl-1-indanone, mp 96–98 °C (lit.[44] 98–101 °C), was prepared by the method of Koo[45] from 3-(*o*-methylphenyl)propionic acid[46] prepared in turn from *trans*-*o*-methylcinnamic acid.[46,47] To a Grignard solution prepared from Mg (3.04 g) and isopropyl bromide (15.4 g, 0.125 mol) in 200 ml of anhydrous ether was added dropwise during 15 min 4-methyl-1-indanone (15.0 g, 0.103 mol) in 100 ml of anhydrous ether. After the solution was refluxed for 30 min, saturated NH_4Cl (25 °C) was added.[48] The solution was decanted and the residue washed with ether. The combined ether solutions were evaporated, and the residue was dissolved in 220 ml of benzene with 0.5 g of *p*-toluenesulfonic acid and refluxed (water trap) until the distillate was free of water. The solution was extracted with water and saturated NaCl solution, dried over $MgSO_4$, filtered, and evaporated. The residue was distilled to give 5.2 g of a partially solidified oil, bp 87–105 °C (3 mm), which was chromatographed on a 2.5 × 15 cm silica gel column with petroleum ether (bp 30–60 °C) to remove the starting material. Evaporation of the filtrate gave 3.0 g of **1g** (17%) as a colorless oil: NMR ($CDCl_3$) δ 1.25 [d, 6 H, $C(CH_3)_2$, J = 7 Hz], 2.28 (s, 3 H, CH_3), ca. 2.87 (symmetrical m, 1 H, CH), 3.10 (m, 2 H, CH_2), 6.12 (m, 1 H, C=CH), and 7.02 (m, 4 H, aromatic).

2,3:7,8-Diepoxy-6,9-peroxy-Δ^{4,5}-hexahydroindene (9a). Freshly distilled indene (**1a,**[16] 0.56 g, 4.8 mmol) in 5 ml of acetone containing 0.1 mg of rose bengal took up 165 ml of oxygen (1.5 equiv) during 80 min. The solution was warmed to room temperature and evaporated without heating to give a semicrystalline oil. Addition of methanol and filtration gave 311 mg (38%). The filtrate contained mostly indene (by NMR). Crystallization from methanol gave colorless crystals, mp 105.0–105.5 °C dec. **9a** gives a positive test for peroxide with acidified starch–iodide paper: mass spectrum (70 eV, source temperature 90 °C) *m/e* (rel intensity) 148 (M − 32, 26), 91 (15), 68 (15), 55 (13), 39 (15), 32 (17), 29 (14), 28 (100), 27 (15), 18 (87), and 17 (16); ir (KBr) 1370, 1281, 1260, 1219, 1028, 953, 919, 907, 860, 845, 811, 758, 734, and 708 cm^{-1}.

Anal. Calcd for $C_9H_8O_4$: C, 60.00; H, 4.48. Found: C, 60.19; H, 4.45.

2,3-Diphenyl-2,3:7,8-diepoxy-6,9-peroxy-Δ^{4,5}-hexahydroindene (9b). 2,3-Diphenylindene (**1b,** 0.573 g, 2.00 mmol) in 5 ml of acetone containing 0.1 mg of rose bengal took up 92 ml of oxygen (2.0 equiv) in 50 min. The solution was warmed to room temperature and evaporated to give a glass, which was passed through a 1 × 14 cm silica gel column with $CHCl_3$ to remove the rose bengal. Evaporation of the filtrate and trituration of the residue with ether gave 615 mg of **9b** (93%). Recrystallization by slow evaporation of a petroleum ether–CH_2Cl_2 solution gave colorless crystals, mp 107–108 °C dec. **9b** gives a positive test for peroxide with acidified starch–iodide paper: NMR (100 MHz) δ 7.18 (broad m, 10 H, aromatic); mass spectrum (70 eV, source temperature 105 °C) *m/e* (rel intensity) 300 (M − 32, 4), 105 (52), 86 (15), 84 (26), 77 (18), 72 (19), 57 (29), 49 (30), 43 (100), 42 (84), 41 (41), 39 (11), 29 (20), 28 (33), 27 (21), and 18 (87); ir (KBr) 1605, 1267, 1252, 957, 938, 903, 860, 834, 777, 762, 746, 733, 693, and 675 cm^{-1}.

Anal. Calcd for $C_{21}H_{16}O_4$: C, 75.89; H, 4.85. Found: C, 75.61; H, 4.71.

The reaction was repeated, irradiating the solution through a 0.11 M $K_2Cr_2O_7$ filter solution with a path length of 0.3 cm (cutoff 520 nm). The solution took up 2.0 equiv of oxygen, and an NMR ($CDCl_3$) of the reaction mixture showed only **9b.**

3-Isopropyl-2,3:7,8-diepoxy-6,9-peroxy-Δ^{4,5}-hexahydroindene (9c). 3-Isopropylindene (**1c,** 2.00 g, 12.7 mmol) in 45 ml of acetone containing ~1 mg of rose bengal took up 589 ml of oxygen (1.9 equiv) during 4.5 h with dye bleaching at the end of the reaction. The solution was warmed to room temperature and evaporated to give an oil, which crystallized on trituration with methanol to give 2.07 g of **9c** (74%). Recrystallization from methanol gave colorless needles, mp 95.3–96.5 °C dec. **9c** gives a positive test for peroxide with acidified starch–iodide paper: NMR ($CDCl_3$, 100 MHz) δ 0.97 and 1.07 [two d, 6 H, $C(CH_3)_2$, J = 7 Hz] and 2.26 (septet, 1 H, isopropyl CH); mass spectrum (70 eV, source temperature 98 °C) *m/e* (rel intensity) 190 (M − 32, 32), 173 (23), 147 (53), 119 (10), 71 (12), 55 (11), 43 (40), 41 (13), 39 (11), 32 (10), 28 (51), 27 (13), 18 (100), and 17 (18); ir (KBr) 1606, 1370, 1351, 1283, 1270, 1237, 1225, 1000, 978, 942, 932, 917, 899, 878, 850, 827, 813, 756, and 701 cm^{-1}.

Anal. Calcd for $C_{12}H_{14}O_4$: C, 64.85; H, 6.35. Found: C, 64.95; H, 6.27.

2-Phenyl-3-methyl-2,3:7,8-diepoxy-6,9-peroxy-Δ^{4,5}-hexahydroindene (9d). 2-Phenyl-3-methylindene (**1d,** 2.48 g, 12.0 mmol) in 200 ml of acetone containing 2 mg of rose bengal took up 585 ml (2.00 equiv) of O_2 in 5 h. The solution was warmed to room temperature and evaporated to give a yellow solid. Addition of methanol and filtration gave 2.52 g of **9d** (78%) which crystallized from methanol–$CHCl_3$ to give pale yellow needles, mp 135 °C dec, with resolidification and remelting at 183–189 °C. **9d** gives a positive test for peroxide with acidified starch–iodide paper: NMR ($CDCl_3$) δ 1.21 (s, 3H, CH_3) and 7.38 (s, 5 H, C_6H_5); mass spectrum (70 eV, source temperature 115 °C) *m/e* (rel intensity) 241 (21), 238 (M − 32, 44), 237 (10), 227 (16), 195 (11), 105 (100), 103 (31), 77 (49), 51 (12), 43 (59), 28 (18), and 18 (24); ir (KBr) 1603, 1278, 1255, 1001, 949, 937, 905, 877, 850, 833, 822, 760, 736, 707, 693, and 681 cm^{-1}.

Anal. Calcd for $C_{16}H_{14}O_4$: C, 71.10; H, 5.22. Found: C, 71.24; H, 5.29.

2-Phenyl-2,3:7,8-diepoxy-6,9-peroxy-Δ^{4,5}-hexahydroindene (9e). 2-Phenylindene (**1e,** 200 mg, 1.04 mmol) in 200 ml of 1:1 acetone–CH_2Cl_2 containing 3 mg of rose bengal took up 41 ml (1.6 equiv) of oxygen in 3 h. Most of the **1e** crystallized from the solution and slowly redissolved as the reaction proceeded. The solution was warmed to room temperature and evaporated to give a solid which was chromatographed on a 2.5 × 18 cm silica gel column with benzene to give 42 mg of **1e** (21%) and 125 mg of **9e** (49%). **9e** was recrystallized from methanol to give colorless needles, mp ~100 °C dec, with resolidification and remelting at 180–183 °C. **9e** gives a positive test for peroxide with acidified starch–iodide paper: NMR ($CDCl_3$) δ 7.33 (s, 5 H, C_6H_5); ir (KBr) 1603, 1263, 1245, 953, 939, 915, 891, 802, 753, 710, and 687 cm^{-1}.

Anal. Calcd for $C_{15}H_{12}O_4$: C, 70.30; H, 4.72. Found: C, 70.22; H, 4.86.

1-Methyl-3-*tert*-butyl-2,3:7,8-diepoxy-6,9-peroxy-Δ^{4,5}-hexahydroindene (9f). 1-Methyl-3-*tert*-butylindene (**1f,** 1.23 g, 6.59 mmol) in 25 ml of acetone containing ~1 ml of rose bengal took up 313 ml of oxygen (1.9 equiv) in 2.5 h. The solution was warmed to room temperature and filtered through charcoal. Evaporation of the filtrate and trituration with methanol gave 1.02 g of **9f** (62%). Recrystallization from ether–petroleum ether gave colorless crystals, mp 99–100 °C dec. **9f** gives a positive test for peroxide with acidified starch–iodide paper: NMR ($CDCl_3$) δ 1.07 [s, 9 H, $C(CH_3)_3$] and 1.26 (d, 3 H, CH_3, J_{HCCH_3} = 7 Hz); mass spectrum (70 eV, source temperature 150 °C) *m/e* (rel intensity) 218 (M − 32, 20), 161 (51), 69 (11), 57 (50), 43 (16), 41 (34), 39 (12), 29 (20), 28 (32), 27 (11), and 18 (100); ir (KBr) 1363, 1268, 1243, 1228, 983, 961, 935, 909, 902, 867, 841, 781, 737, 706, and 685 cm^{-1}.

Anal. Calcd for $C_{14}H_{18}O_4$: C, 67.18; H, 7.25. Found: C, 67.00: H, 7.22.

3-Isopropyl-7-methyl-2,3:7,8-diepoxy-6,9-peroxy-Δ^{4,5}-hexahydroindene (9g). 3-Isopropyl-7-methylindene (**1g,** 1.00 g, 5.82 mmol) in 50 ml of acetone containing ~2 mg of rose bengal took up 279 ml of oxygen (2.0 equiv) during 1.5 h. The solution was warmed to room temperature and evaporated without warming to give an oil. Trituration with methanol gave 560 mg of **9g** (40%), mp 88–89 °C dec. (A reaction carried out in an NMR tube with acetone-d_6 as solvent showed, by NMR, no starting material and >75% **9g.**) Recrystallization from methanol gave colorless crystals, mp 87–89 °C dec. **9g** gives a positive test for peroxide with acidified starch–iodide paper: NMR ($CDCl_3$) δ 0.97 and 1.08 [two d, 6 H, $C(CH_3)_2$, J_{CHCH_3} = 7 Hz], 1.53 (s, 3 H, CH_3), and 2.24 (septet, 1 H, isopropyl CH); mass spectrum (70 eV, source temperature 95 °C) *m/e* (rel intensity) 204 (M − 32, 63), 161 (33), 121 (11), 119 (13), 94 (22), 91 (13), 77 (13), 71 (22), 67 (11), 55 (29), 53 (12), 43 (100), 41 (25), 39 (23), 28 (55), 27 (30), and 18 (22); ir (KBr) 1475, 1289, 1270, 1250, 967, 955, 940, 926, 904, 891, 856, 829, 778, 714, and 701 cm^{-1}.

Anal. Calcd for $C_{13}H_{16}O_4$: C, 66.08; H, 6.83. Found: C, 65.83; H, 6.88.

Thermolysis of 9a. 9a (400 mg) was refluxed in 15 ml of toluene

for 1 h and evaporated. TLC (silica gel–$CHCl_3$) showed only two compounds, with R_f 0.44 (**15a**) and 0.30 (**14a**). The material was chromatographed on a 2.5 × 93 cm nylon dry column containing silica gel with $CHCl_3$ as solvent. The first fraction (63 mg) contained **14a** and a new compound **16a** with R_f 0.07. One fraction contained 217 mg of **14a** and the last fraction (~5 mg) was mostly **16a,** which could not be isolated, but the NMR is satisfactory for 9-hydroxy-2,3:7,8-diepoxy-6-keto-$\Delta^{4,5}$-hexahydroindene: NMR (100 MHz), Table V. **14a** was recrystallized from toluene to give 203 mg of 2,3:4,9:5,6:7,8-tetraepoxyoctahydroindene (**14a,** 51%) as colorless needles: mp 178.5–180.5 °C; mass spectrum (70 eV, source temperature 200 °C) *m/e* (rel intensity) 125 (23), 95 (23), 81 (38), 71 (49), 68 (100), 67 (28), 55 (67), 53 (44), 52 (28), 51 (43), 50 (24), 43 (36), 42 (29), 41 (50), 40 (22), 39 (75), 29 (77). 28 (59), 27 (74), 26 (34), 18 (21) and 15 (23); ir (KBr) 1415, 1270, 1233, 933, 978, 964, 925, 891, 838, 805, 778, 765, 737, and 711 cm^{-1}.

Anal. Calcd for $C_9H_8O_4$: C, 60.00; H, 4.48. Found: C, 60.10; H, 4.53.

Thermolysis of 9b. 9b (500 mg) in 15 ml of toluene was refluxed for 1 h and the solution evaporated. TLC (silica gel–benzene) showed only two compounds, with R_f 0.32 (**15b**) and 0.12 (**14b**). The material was chromatographed on a 2.5 × 93 cm nylon dry column containing silica gel with benzene as solvent. The first fraction contained **15b** and a new compound (**16b**) with R_f 0.02. One fraction, containing 300 mg of almost pure **14b** (60%), was recrystallized three times by the slow evaporation of an ether–hexane solution to give 2,3-diphenyl-2,3:4,9:5,6:7,8-tetraepoxyoctahydroindene (**14b**): mp 149.0–150.5 °C; NMR ($CDCl_3$, 100 MHz) δ 7.16 (broad m, 10 H, aromatic); mass spectrum (70 eV, source temperature 195 °C) *m/e* (rel intensity) 331 (M − 1, 7), 303 (9), 227 (6), 212 (6], 105 (100), 103 (13), 77 (60), 51 (9), 28 (5), and 18 (6); ir (KBr) 1605, 1282, 1248, 997, 972, 930, 913, 883, 868, 843, 808, 757, 747, 737, 710, and 693 cm^{-1}.

Anal. Calcd for $C_{21}H_{16}O_4$: C, 75.89; H, 4.85. Found: C, 75.97; H, 4.85.

Thermolysis of 9c. 9c (500 mg) in 10 ml of heptane was refluxed for 1 h, and the solution evaporated. TLC (silica gel–$CHCl_3$) showed only two compounds, with R_f 0.42 (**15c**) and 0.24 (**14c**). The mixture was chromatographed on a 2.5 × 94 cm nylon dry column containing silica gel using $CHCl_3$ as solvent. The first fraction (25 mg) contained **15c** and a new compound, **16c,** with R_f 0.07. One fraction (260 mg) containing mostly **14c** was recrystallized from ether–hexane to give 220 mg of 3-isopropyl-2,3:4,9:5,6:7,8-tetraepoxyoctahydroindene (**14c,** 44%) as colorless needles: mp 123–124 °C; NMR ($CDCl_3$, 100 MHz) δ 0.88 and 0.98 [two d, 6 H, $C(CH_3)_2$, J_{CHCH_3} = 7 Hz] and 2.10 (septet, 1 H, isopropyl CH); mass spectrum (70 eV, source temperature 145 °C) *m/e* (rel intensity) 95 (23), 94 (53), 91 (38), 79 (37), 77 (50), 71 (29), 67 (30), 53 (23), 43 (100), 41 (62), 39 (43), 28 (51), and 27 (50); ir (KBr) 1373, 1359, 1263, 1218, 985, 929, 896, 872, 829, 790, 768, and 727 cm^{-1}.

Anal. Calcd for $C_{12}H_{14}O_4$: C, 64.85; H, 6.35. Found: C, 65.13: H, 6.44.

9c (400 mg) in 10 ml of heptane was refluxed for 5 min, and the solution evaporated. The residue was chromatographed as noted above. One fraction (220 mg) containing starting material and **15c** was rechromatographed; one fraction, an oil which crystallized on trituration with petroleum ether, was mainly **16c.** It was recrystallized three times from ether–hexane to give 3-isopropyl-9-hydroxy-2,3:7,8-diepoxy-6-keto-$\Delta^{4,5}$-hexahydroindene (**16c**): mp 122–124 °C; NMR ($CDCl_3$) δ 1.00 and 1.07 [two d, 6 H, $C(CH_3)_2$, J_{CHCH_3} = 7 Hz] and 2.58 (septet, 1 H, isopropyl CH); mass spectrum (70 eV, source temperature 210 °C) *m/e* (rel intensity) 151 (12), 123 (30), 95 (14), 77 (11), 71 (25), 67 (14), 55 (26), 51 (10), 43 (100), 41 (24), 39 (22), 28 (15), 27 (26), and 18 (10); ir (KBr) 3580, 1680, 1381, 1331, 1286, 1253, 1230, 1150, 1106, 1027, 963, 887, 826, 799, and 744 cm^{-1}.

Anal. Calcd for $C_{12}H_{14}O_4$: C, 64.85; H, 6.35. Found: C, 64.80; H, 6.23.

Thermolysis of 9d. 9d (2.00 g) in 20 ml of xylene was refluxed for 3 h, and the solution evaporated. TLC (silica gel–6% ethyl acetate in benzene) showed only two compounds, with R_f 0.52 (**15d**) and 0.31 (**14d**). NMR showed that the reaction mixture contained ~30% **15d** and ~70% **14d.** The reaction mixture was chromatographed on a 2.5 × 68 cm nylon dry column containing silica gel using 6% ethyl acetate in benzene as solvent. One fraction was recrystallized twice from ether–hexane to give 1.0 g of 2-phenyl-3-methyl-2,3:4,9:5,6:7,8-tetraepoxyoctahydroindene (**14d,** 50%) as colorless needles: mp 184.5–186 °C; NMR ($CDCl_3$ 100 MHz) δ 1.04 (s, 3 H, CH_3) and 7.33 (s, 5 H, C_6H_5); mass spectrum (70 eV, source temperature 200 °C) *m/e* (rel intensity) 269 (16), 241 (42), 139 (14), 105 (100), 103 (42), 77 (56), 51 (15), 43 (55), 39 (10), and 28 (37); ir (KBr) 1603, 1238, 1222, 1006, 974, 956, 930, 914, 903, 858, 827, 776, 753, 743, 718, and 693 cm^{-1}.

Anal. Calcd for $C_{16}H_{14}O_4$: C, 71.10; H, 5.22. Found: C, 70.94; H, 5.37.

Another fraction containing a new compound (**16d**) with R_f 0.12 was recrystallized from methanol–$CHCl_3$ to give 45 mg of 2-phenyl-3-methyl-9-hydroxy-2,3:7,8-diepoxy-6-keto-$\Delta^{4,5}$-hexahydroindene (**16d**) as colorless crystals: mp 183–184.5 °C dec; NMR ($CDCl_3$) δ 1.33 (s, 1 H, CH_3) and 7.38 (s, 5 H, C_6H_5); mass spectrum (70 eV, source temperature 220 °C) *m/e* (rel intensity) 225 (6), 165 (7), 137 (11), 105 (100), 103 (8), 77 (22), 55 (5), 51 (7), 43 (43), 39 (5), 28 (24), 18 (86), and 17 (18); ir (KBr) 3535, 1693, 1603, 1368, 1330, 1253, 1025, 982, 965, 908, 867, 832, 809, 768, 758, and 699 cm^{-1}.

Anal. Calcd for $C_{16}H_{14}O_4$: C, 71.10; H, 5.22. Found: C, 71.20; H, 5.24.

One fraction contained ~65% **16d** and ~35% 2-phenyl-3-methyl-2,3:4,9:7,8:triepoxy-6-ketooctahydroindene (**15d**), enabling an NMR of **15d** to be obtained: NMR ($CDCl_3$) δ 1.06 (s, 3 H, CH_3) and 7.38 (s, 5 H, C_6H_5); ir (KBr) 1724 cm^{-1}.

Thermolysis of 9f. 9f (836 mg) was refluxed in 25 ml of heptane for 2 h. While still hot, 1 ml of the solution was removed and evaporated, and the residue (~40 mg) was dissolved in 1 ml of $CHCl_3$ and treated with several drops of triethylamine. After 10 min the solution was evaporated; NMR ($CDCl_3$) showed ~80% **14f** and ~20% **15f.** On cooling, the remaining solution gave 640 mg of a mixture of **14f** and **15f.** Three recrystallizations from heptane gave 300 mg of 1-methyl-3-*tert*-butyl-2,3:4,9:5,6:7,8-tetraepoxyoctahydroindene (**14f,** 38%) as colorless crystals: mp 155.0–156.5 °C; NMR ($CDCl_3$, 100 MHz) δ 1.01 [s, 9 H, $C(CH_3)_3$] and 1.14 (d, 3 H, CH_3, J_{CHCH_3} = 7.2 Hz); mass spectrum (70 eV, source temperature 190 °C) *m/e* (rel intensity) 57 (6), 43 (4), 41 (6), 39 (4), 32 (8), 28 (100), 18 (85), and 17 (10); ir (KBr) 1375, 1357, 1242, 1227, 969, 948, 913, 887, 847, 831, 817, 806, 786, and 770 cm^{-1}.

Anal. Calcd for $C_{14}H_{18}O_4$: C, 67.16; H, 7.25. Found: C, 67.27; H, 7.33.

Concentration of the first filtrate, followed by filtration and evaporation of the filtrate, gave 68 mg of material containing ~30% **14f** and ~70% 1-methyl-3-*tert*-butyl-2,3:4,9:7,8-triepoxy-6-ketooctahydroindene (**15f**): NMR ($CDCl_3$, 100 MHz) δ 1.02 [s, 9 H, $C(CH_3)_3$] and 1.17 (d, 3 H, CH_3, J_{CHCH_3} = 7.1 Hz); ir (KBr) 1727 cm^{-1}.

Thermolysis of 9g. 9g (580 mg) was refluxed for 6 h in a benzene–heptane solution. Crystallization of the reaction solution gave 538 mg of a mixture of **14g** and **15g.** (A reaction carried out in a sealed NMR tube using $CDCl_3$ as solvent showed, by NMR, ~85% **14g** and ~15% **15g.**) Seven recrystallizations from heptane–benzene gave 300 mg of 3-isopropyl-7-methyl-2,3:4,9:5,6:7,8-tetraepoxyoctahydroindene (**14g,** 52%) as colorless crystals: mp 161–162 °C; NMR ($CDCl_3$, 100 MHz) δ 0.87 and 0.96 [two d, 6 H, $C(CH_3)_2$, J_{CHCH_3} = 7.0 Hz), 1.47 (s, 3 H, CH_3), and 2.08 (septet, 1 H, isopropyl CH); mass spectrum (70 eV, source temperature 225 °C) *m/e* (rel intensity) 149 (5), 95 (6), 94 (21), 93 (6), 91 (7), 79 (7), 77 (9), 67 (5), 55 (8), 43 (38), 41 (14), 39 (8), 28 (26), 27 (10), 18 (100), and 17 (21); ir (KBr) 1372, 1356, 1281, 1272, 1246, 985, 980, 931, 877, 863, 852, 837, 767, 749, and 696 cm^{-1}.

Anal. Calcd for $C_{13}H_{16}O_4$: C, 66.08; H, 6.83. Found: C, 66.07; H, 6.73.

Concentration of the mother liquor from the first two crystallizations gave 50 mg of material containing ~55% **14g** and ~45% 3-isopropyl-7-methyl-2,3:4,9:7,8-triepoxy-6-ketooctahydroindene (**15g**): NMR ($CDCl_3$, 100 MHz) δ 0.92 and 0.95 [two d, 6 H, $C(CH_3)_2$, J_{CHCH_3} = 7.0 Hz], 1.33 (s, 3 H, CH_3), and 2.08 (septet, 1 H, isopropyl CH); ir (KBr) 1720 cm^{-1}.

9-Hydroxy-2,3:7,8-diepoxy-6-keto-$\Delta^{4,5}$-hexahydroindene (16a). All attempts to isolate **16a** from the base-catalyzed rearrangement of **9a** using triethylamine or *N,N*-dimethylaniline were unsuccessful, giving only black tars.

2,3-Diphenyl-9-hydroxy-2,3:7,8-diepoxy-6-keto-$\Delta^{4,5}$-hexahydroindene (16b). Triethylamine (0.5 ml) was added to a solution of **9b** (200 mg, 0.603 mmol) in 4 ml of $CHCl_3$. An exothermic reaction took place. After cooling, the solution was evaporated to give an oil which crystallized on trituration with ether–petroleum ether. Recrystallization by slow evaporation of an ether–hexane solution (the product tends to oil out of solution) gave 100 mg of **16b** (50%) as colorless needles: mp 156–158 °C dec; NMR ($CDCl_3$) δ 7.22 (s, 5 H, C_6H_5) and 7.35 (m, 5 H, C_6H_5); mass spectrum (70 eV, source temperature 200 °C) *m/e* (rel intensity) 227 (8), 199 (17), 116 (9), 115 (8), 105 (100), 77 (28), 57 (6), 56 (7), 43

(6), 41 (5), 28 (8), 18 (25), and 17 (5); ir (KBr) 3460, 1675, 1603, 1268, 1245, 1023, 1006, 895, 834, 814, 782, 757, 741, and 692 cm^{-1}.

Anal. Calcd for $C_{21}H_{16}O_4$: C, 75.89; H, 4.85. Found: C, 76.07; H, 5.08.

3-Isopropyl-9-hydroxy-2,3:7,8-diepoxy-6-keto-$\Delta^{4,5}$-hexahydroindene (16c). Triethylamine (0.5 ml) was added to a solution of **9c** (250 mg, 1.13 mmol) in 3 ml of $CHCl_3$. An exothermic reaction took place. After cooling, the solution was evaporated, and trituration of the residue with ether gave a yellow-brown precipitate. The material was passed through a 1 × 19 cm silica gel column with $CHCl_3$ to remove the colored impurities. Evaporation of the filtrate gave 224 mg of **16c** (96%). Recrystallization from hexane–CH_2Cl_2 gave colorless crystals, mp 122.5–124.0 °C, with properties identical with those of material obtained on chromatography of the product of thermolysis of **9c**.

2-Phenyl-3-methyl-9-hydroxy-2,3:7,8-diepoxy-6-keto-$\Delta^{4,5}$-hexahydroindene (16d). Triethylamine (0.25 ml) was added to a solution of **9d** (200 mg, 0.742 mmol) in 3 ml of $CHCl_3$. An exothermic reaction took place. After cooling, the solution was evaporated, and the crystalline residue was washed with hexane to give 192 mg of **16d** (96%), with properties identical with those of material obtained in chromatography of the product of thermolysis of **9d**.

1-Methyl-3-*tert*-butyl-2,3:7,8-diepoxy-6-keto-9-hydroxy-$\Delta^{4,5}$-hexahydroindene (16f). Triethylamine (0.25 ml) was added to a solution of **9f** (64 mg, 0.25 mmol) in 3 ml of $CHCl_3$. After 10 min, the solution was evaporated, and the residue passed through a 1 × 18 cm silica gel column with $CHCl_3$. Evaporation of the filtrate gave a semicrystalline oil which gave 53 mg of **16f** (83%) from ether–petroleum ether. Crystallization from heptane gave colorless needles: mp 162–163 °C; NMR ($CDCl_3$) δ 1.18 [s, 9 H, $C(CH_3)_3$] and 1.34 (d, 3 H, CH_3, J_{CHCH_3} = 7 Hz); mass spectrum (70 eV, source temperature 200°) *m/e* (rel intensity) 193 (5), 166 (5), 165 (10), 147 (5), 137 (14), 123 (8), 109 (5), 105 (24), 91 (7), 77 (9), 69 (8), 57 (66), 55 (8), 43 (19), 41 (23), 39 (11), 32 (16), 29 (13), 28 (100), 27 (7), 18 (55), and 17 (13); ir (KBr) 3577, 1700, 1381, 1359, 1281, 1245, 1171, 1060, 1028, 1020, 919, 901, 844, 830, 815, 802, and 775 cm^{-1}.

Anal. Calcd for $C_{14}H_{18}O_4$: C, 67.16; H, 7.25. Found: C, 67.04; H, 7.22.

3-Isopropyl-7-methyl-2,3:7,8-diepoxy-6-keto-9-hydroxy-$\Delta^{4,5}$-hexahydroindene (16g). 3-Isopropyl-7-methylindene (**1g**, 400 mg, 2.32 mmol) in 25 ml of acetone with ~1 mg of rose bengal took up 115 ml of oxygen (2.0 equiv). To the cold solution was added 0.5 ml of triethylamine, and the solution was warmed to room temperature for 1 hr. The solution was heated briefly to boiling and evaporated. The residue was passed through a 2.5 × 20 cm silica gel column with $CHCl_3$. Evaporation of the filtrate gave 205 mg of **16g** (37%). Recrystallization from benzene–heptane gave colorless crystals: mp 185–186.5 °C; NMR ($CDCl_3$, Me_2CO-d_6) δ 0.94 and 1.06 [two d, 6 H, $C(CH_3)_2$, J_{CHCH_3} = 7 Hz], 1.36 (s, 3 H, CH_3), and 2.60 (septet, 1 H, isopropyl CH); mass spectrum (70 eV, source temperature 225 °C) *m/e* (rel intensity) 193 (12), 166 (10), 165 (29), 137 (21), 123 (23), 105 (30), 77 (14), 71 (36), 55 (28), 43 (100), 41 (22), 39 (17), 28 (27), 27 (24), and 18 (27); ir (KBr) 3350, 1675, 1605, 1370, 1356, 1335, 1285, 1260, 1232, 1017, 982, 951, 921, 902, 873, 857, 811, 777, 763, and 702 cm^{-1}.

Anal. Calcd for $C_{13}H_{16}O_4$: C, 66.08; H, 6.83. Found: C. 66.27; H, 6.68.

Reaction of the Photooxygenation Products with Trimethyl Phosphite. To solutions of 0.250–1.00 g of the photooxygenation products **9a–d** and **9f** in 5 ml of $CHCl_3$ was slowly added ~1.25 equiv of trimethyl phosphite. Exothermic reactions took place, causing the solutions to boil. After cooling, the solutions were evaporated, and the residues filtered through 1 × 20 cm silica gel columns with $CHCl_3$. Evaporation of the filtrates and trituration of the residues with ether–petroleum ether gave crystalline products. Recrystallizations gave the following compounds.

2,3:4,9:7,8-Triepoxy-$\Delta^{5,6}$-hexahydroindene (**17a**, 79%): mp 94–95 °C (methanol); mass spectrum (70 eV, source temperature 160 °C) *m/e* (rel intensity) 135 (6), 109 (5), 107 (7), 77 (6), 52 (8), 51 (5), 39 (6), 32 (18), 28 (100), 27 (5), 18 (80), and 17 (17); ir (KBr) 1387, 1357, 1267, 1234, 1014, 968, 936, 915, 864, 838, 826, 812, 803, 765, 713, and 706 cm^{-1}.

Anal. Calcd for $C_9H_8O_3$: C, 65.83; H, 4.91. Found: C, 65.91; H, 4.96.

2,3-Diphenyl-2,3:4,9:7,8-triepoxy-$\Delta^{5,6}$-hexahydroindene (**17b**): mp 150–153 °C after three crystallizations from benzene–cyclohexane (tends to oil out); NMR ($CDCl_3$, 100 MHz) δ 7.14 (m, 10 H, aromatic); ir (KBr) 1603, 1224, 983, 929, 908, 866, 843, 776, 758, 729, 699, and 685 cm^{-1}.

Anal. Calcd for $C_{21}H_{16}O_3$: C, 79.73; H, 5.10. Found: C, 79.41; H, 5.11.

3-Isopropyl-2,3:4,9:7,8-triepoxy-$\Delta^{5,6}$-hexahydroindene (**17c**, 96%): mp 92–93 °C after three crystallizations from hexane–CH_2Cl_2; NMR ($CDCl_3$) δ 0.90 and 0.99 [two d, 6 H, $C(CH_3)_2$, J_{CHCH_3} = 7 Hz] and 2.17 (septet, 1 H, isopropyl CH); mass spectrum (70 eV, source temperature 200 °C) *m/e* (rel intensity) 191 (11), 177 (43), 163 (35), 135 (52), 107 (35), 91 (20), 79 (26), 77 (33), 55 (34), 52 (22), 43 (89), 41 (28), 39 (24), 28 (68), 27 (28), 18 (100), and 17 (20); ir (KBr) 1383, 1357, 1270, 1248, 1221, 985, 911, 876, 857, 833, 794, 767, 723, and 708 cm^{-1}.

Anal. Calcd for $C_{12}H_{14}O_3$: C, 69.88; H, 6.84. Found: C, 69.97; H, 7.09.

2-Phenyl-3-methyl-2,3:4,9:7,8-triepoxy-$\Delta^{5,6}$-hexahydroindene (**17d**, 77%): mp 161.5–163 °C (hexane–CH_2Cl_2); NMR ($CDCl_3$) δ 1.05 (s, 3 H, CH_3) and 7.50 (s, 5 H, C_6H_5); mass spectrum (70 eV, source temperature 200 °C) *m/e* (rel intensity) 253 (10), 225 (62), 105 (69), 103 (45), 85 (34), 77 (36), 51 (12), 43 (30), 41 (5), 39 (6), 28 (26), 18 (100), and 17 (22); ir (KBr) 1609, 1390, 1238, 1165, 1077, 1029, 1007, 921, 897, 867, 848, 802, 778, 769, 737, 722, and 706 cm^{-1}.

Anal. Calcd for $C_{16}H_{14}O_3$: C, 75.57; H, 5.55. Found: C. 75.43; H, 5.36.

1-Methyl-3-*tert*-butyl-2,3:4,9:7,8-triepoxy-$\Delta^{5,6}$-hexahydroindene (**17f**, 55%): mp 148–150 °C (hexane); NMR ($CDCl_3$) δ 1.02 [s, 9 H, $C(CH_3)_3$] and 1.16 (d, 3 H, CH_3, J_{HC,CH_3} = 7 Hz); mass spectrum (70 eV, source temperature 200 °C) *m/e* (rel intensity) 219 (14), 205 (28), 177 (48), 149 (56), 121 (28), 91 (24), 77 (21), 69 (32), 57 (86), 52 (19), 43 (19), 41 (62), 32 (11), 29 (33), 28 (100), and 18 30); ir (KBr) 1380, 1355, 1282, 1240, 1224, 1106, 991, 948, 902, 880, 834, 822, 804, 788, 743, and 721 cm^{-1}.

Anal. Calcd for $C_{14}H_{18}O_3$: C, 71.75; H, 7.75. Found: C, 71.84; H, 7.68.

3-Isopropyl-7-methyl-2,3:4,9:7,8-triepoxy-$\Delta^{5,6}$-hexahydroindene (17g). 3-Isopropyl-7-methylindene (**1g**, 800 mg, 4.65 mmol) in 30 ml of acetone with ~1 mg of rose bengal took up 230 ml of oxygen (2.0 equiv) during 90 min. To the cold solution was added 1.25 ml of trimethyl phosphite, and the solution was warmed to room temperature for 1 h. The solution was briefly heated to boiling and evaporated to give a red oil. The oil was chromatographed on a 2.5 × 15 cm silica gel column with $CHCl_3$ to remove the trimethyl phosphate. Evaporation of the filtrate gave a mixture of product and trimethyl phosphite, which was removed under high vacuum at 60 °C. The residue was rechromatographed on a 2.5 × 19 cm silica gel column with $CHCl_3$. Evaporation of the filtrate and trituration of the residue with ether gave 289 mg of **17g** (28%). Recrystallization from heptane gave colorless crystals: mp 109.5–110.5 °C; NMR ($CDCl_3$) δ 0.90 and 0.98 [two d, 6 H, $C(CH_3)_2$, J_{CHCH_3} = 7 Hz], 1.38 (s, 3 H, CH_3), and 2.16 (septet, 1 H, isopropyl CH); mass spectrum (70 eV, source temperature 190 °C) *m/e* (rel intensity) 205 (32), 191 (51), 177 (57), 149 (55), 135 (20), 121 (26), 95 (24), 91 (22), 79 (20), 77 (28), 71 (22), 66 (26), 43 (100), 41 (31), 39 (36), 28 (79), 27 (32), and 18 (77); ir (KBr) 1381, 1357, 1276, 1239, 1075, 980, 962, 913, 867, 856, 842, 827, and 743 cm^{-1}.

Anal. Calcd for $C_{13}H_{16}O_3$: C, 70.89; H, 7.32. Found: C, 70.81; H, 7.10.

Rate of Thermolysis of 9c. A solution of **9c** and $CHCl_3$ in $CDCl_3$ was sealed in an NMR tube. The solution was heated at 69.0 °C by placing the NMR tube in a silicone oil filled finger well protruding into a flask containing refluxing hexane. NMR spectra were taken at 1-h intervals, and the amount of **9c** was measured by the ratio of the average of the area of protons A, B, and C of **9c** to that of $CHCl_3$. After completion of the reaction, the NMR showed 85% **14c** and 15% **15c**. The following data were obtained [h (% **9c** remaining)]: 0 (100), 1 (79), 2 (56), 3 (43), 4 (32), and 5 (23). Fitting the equation for ln [**9c**] vs. time by least squares gave a straight line with slope −0.295, intercept 4.631, and a correlation coefficient 0.9990.

Rate of Thermolysis of 9d. The rate study was done as described for **9c**, but without the $CHCl_3$ as an internal standard. The loss of **9d** was determined by the ratio of the area of the CH_3 group of **9d** to the total CH_3 group areas. The following data were obtained [h (% **9d** remaining)]: 0 (96), 1 (74), 2 (54), 3 (41), and 5 (23). The NMR after completion of the reaction showed 80% **14d** and 20% **15d**. Least-squares treatment gave a straight line with slope −0.287, intercept 4.573, and correlation coefficient 0.9998.

Registry No.—**1a**, 95-13-6; **1b**, 5324,00-5; **1c**, 57653-14-2; **1d**, 10425-96-4; **1e**, 4505-48-0; **1f**, 944-98-9; **1g**, 57653-15-3; **9a**, 40237-80-7; **9b**, 40237-81-8; **9c**, 40237-82-9; **9d**, 40237-83-0; **9e**, 57694-16-

3; **9f,** 57694-17-4; **9g,** 57653-16-4; **14a,** 57694-18-5; **14b,** 57694-19-6; **14c,** 57694-20-9; **14d,** 40237-84-1; **14f,** 57694-21-0; **14g,** 57694-22-1; **15d,** 57653-17-5; **15f,** 57653-18-6; **15g,** 57653-19-7; **16a,** 57653-20-0; **16b,** 57653-21-1; **16c,** 57653-22-2; **16d,** 57653-23-3; **16f,** 57653-24-4; **16g,** 57653-25-5; **17a,** 57694-23-2; **17b,** 57760-11-9; **17c,** 57694-24-3; **17d,** 57760-12-0; **17f,** 57694-25-4; **17g,** 57694-26-5; 2-phenyl-1-indanone, 16619-12-8; 3-methyl-1-indanone, 6072-57-7; 4-methyl-1-indanone, 24644-78-8; isopropyl bromide, 75-26-3; oxygen, 7782-44-7; trimethyl phosphite, 121-45-9.

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