Chemistry of Singlet Oxygen. XXIV. Low Temperature Photooxygenation of 1,2-Dihydronaphthalenes[1]

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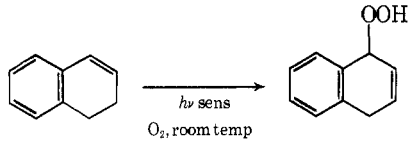
1,2-Dihydronaphthalenes react with singlet oxygen at −78 °C in acetone to yield products derived from both ene reaction and 1,4 cycloaddition; substitution of a phenyl group on the double bond strongly influences the course of the photooxygenation. The presumed initial 1,4 cycloadducts rearrange and react further to form two isomeric endoperoxide–bisepoxide compounds (**2** and **3**). The structures of these isomers have been determined; their formation suggests a benzene oxide–oxepin equilibrium at an intermediate stage of the photooxygenation. The dioxygenated products react smoothly with trimethyl phosphite to form triepoxides and with triethylamine to form γ-hydroxy-α,β-unsaturated ketones, and thermolyze to form dihydronaphthalene tetraepoxides.

In the accompanying paper,[1a] it was shown that substituted indenes can be photooxygenated at −78 °C in acetone to give dioxygenated products in good yields. This reaction proved to be so novel and preparatively interesting that its extension to other areas appeared worthwhile, and, for this purpose, a series of dihydronaphthalenes seemed to offer interesting possibilities.

Previously, only 1,2-dihydronaphthalene itself had been photooxygenated; at room temperature, the expected ene product was reported.[2] 1,2-dihydronaphthalene also gives Diels–Alder adducts with both dicyanoacetylene and dimethyl acetylenedicarboxylate, but these reactions require elevated temperatures, and the adducts lose ethylene to form the corresponding substituted naphthalenes under these conditions.[3] The results reported in this paper show a varied and interesting chemistry of photooxygenation which depends markedly on the substitution of the dihydronaphthalene.

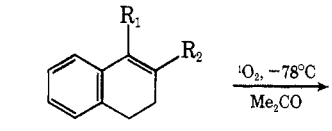


Results

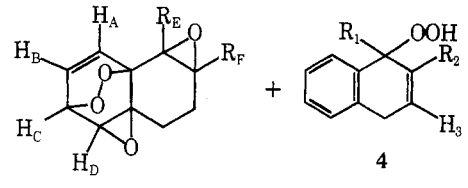
Low Temperature Photooxygenation. An acetone solution of 1-phenyl- 3,4-dihydronaphthalene (**1b**) was photooxygenated at −78 °C using rose bengal as sensitizer. As with the indenes,[1a] the solution took up 2.0 equiv of oxygen, and an NMR spectrum showed only dioxygenated products. However, two sets of olefinic protons appeared, indicating the formation of isomeric compounds (**2b** and **3b**) with very similar structures whose spectra were closely analogous to those of diepoxy endoperoxides formed in the indene series.[1a]

Under the same conditions, however, 2-phenyl-3,4-dihydronaphthalene (**1a**) reacted with only 1 equiv of singlet oxygen, and NMR showed the ene product (**4a**) to be the only product. Other dihydronaphthalenes (**1c–f**) gave mixtures of products **2** and **3** with **4** and/or **5**; Table I shows the product composition determined by NMR for all the compounds photooxygenated, along with yields of each compound as isolated.

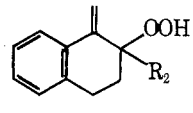
Isolation of the Products. When the reaction solutions were evaporated and redissolved in ether–petroleum ether, one of the two dioxygenated products crystallized preferentially.[4] This product is designated isomer **2**. The other isomer, **3**, would not crystallize in the presence of significant amounts of compound **4**, the ene product, unless the solution was seeded with crystals previously isolated by column chromatography. This was not possible for compounds **3e,f**,



1a, R_1 = H; R_2 = C_6H_5
b, R_1 = C_6H_5; R_2 = H
c, R_1 = R_2 = C_6H_5
d, R_1 = CH_3; R_2 = C_6H_5
e, R_1 = CH_3; R_2 = H
f, R_1 = R_2 = H



2,**3** **4**



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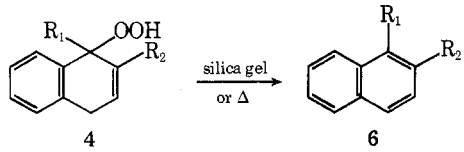
as both products had R_f values close to those of the ene products. In addition, the dioxygenated compounds slowly decompose on chromatography, further limiting their purity.

The products derived from ene reaction, **4**, could not be isolated pure enough for analysis. As might be expected, they tend to lose hydrogen peroxide readily; indeed, fractions of this product isolated by chromatography on silica gel were almost invariably contaminated by the corresponding naphthalene. Thus, identification of these compounds was based on their NMR and ir spectra and on their conversion to the naphthalenes.

Authentic samples of naphthalenes **6a**,[5] **6c**,[6,7] and **6d**[7] were prepared by the procedure of Campbell and Kidd[5] by



4 **6**

refluxing a xylene solution containing chloranil and the corresponding 3,4-dihydronaphthalene. These compounds, and purchased samples of **6e** and **6f**, had NMR and ir spectra identical with those of naphthalenes from compounds **4**.

Treating **4a** and **4e** with excess $NaBH_4$ led to the isolation of small amounts of the corresponding alcohols; how-

Table I. Products of Photooxygenation of 1,2-Dihydronaphthalenes[a]

Compd	R_1	R_2	Products of [2 + 4] attack 2, %	3, %	Products of "Ene" reaction 4, %[b]	5, %
1a	H	C_6H_5	0	0	100	c
1b	C_6H_5	H	40 (33)	60 (34)	0	c
1c	C_6H_5	C_6H_5	25 (20)	40 (32)	35	c
1d	CH_3	C_6H_5	4[d]	6[d]	85	5
1e	CH_3	H	25 (13)	35	40	e
1f	H	H	37.5 (17)	37.5	25	c

[a] Determined by NMR; numbers in parentheses are isolated yields. [b] Not isolated in pure form because of ready loss of H_2O_2. [c] Not applicable. [d] Compounds 2d and 3d were not isolated; the assignment is based on analogies to the chemical shifts of the products of the other reactions. [e] Presence uncertain; if present, the yield is included in the yield of compound 4e.

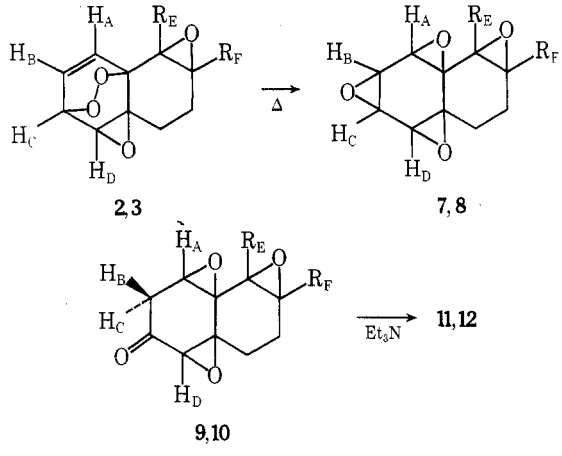
ever, on drying under high vacuum, the alcohols lost water to form the naphthalenes.

Characterization of the Dioxygenated Products. The analyses and mass spectra of the photooxygenation products were consistent with starting material plus two molecules of oxygen, although, unlike the analogous indene products,[1a] the peaks for P − 32 (loss of oxygen) were not significant. The ir spectra showed neither carbonyl nor hydroxyl absorptions, but there were many strong bands between 750 and 1280 cm^{-1}, the region containing substituted epoxide ring vibrations.[8] The compounds give a positive test for peroxide with acidified starch–iodide paper. The NMR spectra of these compounds are tabulated in Table II.

The NMR spectra all show two olefinic protons, an endoperoxy CH proton, and an epoxide proton that form an ABXY system (protons A–D). There are also one or two additional epoxide protons, depending on the substitution at positions E and F, and two methylene groups. The spectra are exactly analogous to the spectra of the dioxygenated indenes;[1a] the only difference is that, with the exception of **2b,** the ABXY system is degenerate (or simplified) because the difference in the chemical shift of the olefinic protons, A and B, is small (<~10 Hz) and the coupling pattern approaches that of an A_2XY system.[9]

The above data show that, for the same reasons advanced for the dioxygenated indenes,[1a] the general structure of these products must be diepoxy endoperoxides **2** and **3**. Discussion of the stereochemical assignments will be deferred until the Discussion.

1,2-Dihydronaphthalene Tetraepoxides. As did the dioxygenated indenes,[1] the dioxygenated dihydronaphthalenes undergo thermal rearrangement. Refluxing benzene or xylene solutions of **2** or **3** gave tetraepoxides **7** or **8** in ~75% yield. In the two cases where the endoperoxides were not



isolated (**3e** and **3f**), the photooxygenated solutions, after crystallization of the other isomers (**2e** and **2f**), were evaporated and heated under vacuum at ~90 °C for several hours. In this manner, the ene products were converted to their corresponding naphthalenes, which did not interfere with the isolation of the tetraepoxides. The isomeric tetraepoxides (**7** and **8b,c,e,f**) were isolated and purified in 26–58% yield by repeated crystallization from benzene–heptane solution. The minor products of the thermolysis are β-epoxy ketones (**9** or **10**); an ir spectrum taken after each reaction showed a carbonyl band at ~1725 cm^{-1} and no hydroxyl band. These ketones are very sensitive to base, and readily isomerize to the corresponding γ-hydroxy-α,β-unsaturated ketones (**11** or **12**). However, it was possible to isolate and characterize **9e.**

The NMR spectra of the tetraepoxides are summarized in Tables III and IV. In contrast to the indene tetraepoxides,[1a] the relative chemical shifts o protons A–D show no general trends. In fact **8b, 7e,** and **7f** have almost equivalent chemical shifts for protons B–D. The assignment as A–D (and not the reverse, with A = D, etc.) was based on the following arguments. (1) As in the indenes, there is an upfield shift of δ 0.6–0.8 for proton A owing to the shielding of phenyl substituents; proton D shows only a small upfield shift. (2) This assignment gives the protons with the 0° dihedral angle the larger coupling constants (see Discussion). (3) This assignment then agrees with that of the indene tetraepoxides,[1a] which was confirmed by ^{13}C NMR;[10] the

Table II. ^1H Chemical Shifts (δ, Me_4Si, $CDCl_3$, 60 MHz) of the Ring Protons of the Dioxygenated Products

Proton	2b[a,b]	3b[a]	2c	3c	2e[a]	3e	2f	3f
H_A	5.90	6.13[c]	6.05[c]	6.09[c]	6.34[c]	6.33[c]	6.29[c]	6.30[c]
H_B	6.09							
H_C	4.96	4.92	4.97	4.96	5.02	4.98	5.03	4.98
H_D[d]	3.54	3.38	3.62	3.48	3.51	3.38	3.55[e]	3.45[e]
H_E[f]							3.24	3.21
H_F	3.72	3.25			3.21	3.24	3.44	3.45
$(CH_2)_2$	1.32 (1)		1.50 (1)		1.22 (1)		1.25 (1)	
	2.29 (2)	2.2 (4)		2.6 (4)	2.16 (2)	2.0 (4)		2.1 (4)
			2.6 (3)				2.4 (3)	
	2.71 (1)				2.57 (1)			

[a] 100-MHz spectra. [b] Protons A–C form an ABX system with J_{AB} = 8.9, J_{AC} = 2.9, and J_{BC} = 5.1 Hz. [c] Center of the AB portion of a degenerate ABX system. [d] J_{CD} = 4.2–4.5, J_{BD} < 1 Hz. [e] Proton D of D and E was assigned by decoupling proton C. [f] J_{EF} = 4.0 Hz.

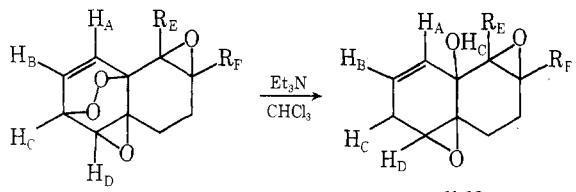
Table III. ^{1}H Chemical Shifts (δ, Me_4Si, $CDCl_3$, 100 MHz) of the Ring Protons of the Dihydronaphthalene Tetraepoxides

Proton	7b	8b	7c	8c	7e[a]	8e	7f	8f
H_A	3.02	2.92	2.83	2.80	3.65	3.66	3.60	3.56
H_B	3.19	3.19	3.13	3.14	3.36	3.40	3.37	3.37
H_C	3.35	3.19	3.36	3.30	3.36	3.31	3.37	3.32
H_D	3.43	3.19	3.49	3.27	3.36	3.17	3.37	3.18
H_E							3.02	2.74
H_F	3.28	3.19			3.23	3.21	3.47	3.33
$(CH_2)_2$	1.09 (1)	1.19 (1)	1.24 (1)	1.46 (1)	0.97 (1)	1.10 (1)	1.02 (1)	1.11 (1)
	2.30 (3)	2.30 (3)	2.50 (3)	2.60 (3)	2.20 (3)	2.20 (3)	2.20 (3)	2.20 (3)

[a] 60-MHz spectrum.

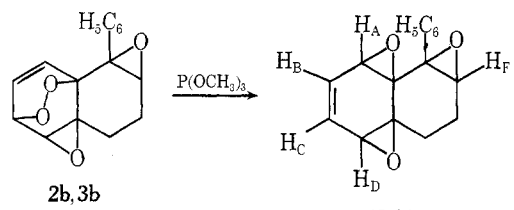
presence of an additional methylene group would not be expected to cause a complete reversal of the assignment.

Base-Catalyzed Rearrangement. Compounds **2** and **3** rearrange readily with triethylamine, as did the analogous indene compounds.[1a] The resulting α,β-unsaturated ketones (**11** and **12**) are formed in 83–97% yield. The ir spectra all show a strong hydroxyl band at ~3550 cm^{-1} and an α,β-unsaturated carbonyl band at 1680–1690 cm^{-1}.



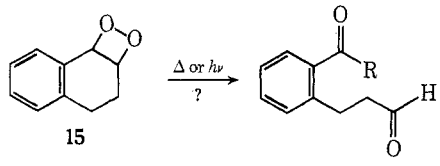
2,3 11,12

Reaction of 2 and 3 with Trimethyl Phosphite. As with the analogous indene products,[1a] compounds **2** and **3** also react with trimethyl phosphite. This was shown by the reaction of both isomers **2b** and **3b** to give the corresponding benzene dioxide compounds **13** and **14** in about 70% yield. The NMR spectra of **13** and **14** have an AA'XX' system, with the olefinic protons appearing as a complex multiplet.



2b,3b 13,14

Photooxygenations in Methanol. It was previously shown that, with indenes, carrying out the photooxygenations in methanol instead of acetone led to the isolation of dioxetanes in good yield.[11] This is not the case with the dihydronaphthalenes. The photooxygenation of **1b** and **1e** in methanol at −78 °C gave a product distribution almost identical with that of the reactions in acetone. There were very small triplet resonances at 9.64 ppm consistent with the aldehydes **16b** and **16e** (the expected thermolysis products of dioxetanes **15b** and **15e**), but integration showed them to be present in <1% of the total product. The solutions also did not show any fluorescence when heated in the presence of 9,10-diphenylanthracene. Thus, dioxetanes were formed in only trace amounts at most in these reactions.



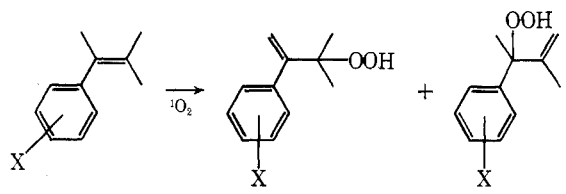
15 16

When the same reactions were carried out at room temperature, **1b** gave 23% **16b** (by NMR), and no fluorescence was observed on adding diphenylanthracene to reaction solutions and heating. The reaction of **1e** gave ~12% **16e** by NMR, and a very weak fluorescence was observed under the above conditions. Since potential routes which do not pass through **15** are conceivable for formation of **16**, the evidence is not conclusive for formation of any dioxetane.

Discussion

A directing effect of the phenyl group on the attack of singlet oxygen is clearly shown by Table I. The parent compound, 1,2-dihydronaphthalene (**1f**), gives 25% ene product. However, substitution of a phenyl group at the α position of the double bond (**1b**) eliminates the formation of this product, while substitution of a phenyl group at the β position (**1a**) causes the exclusive formation of ene product and no dioxygenated products (from [2 + 4] attack). With **1c** (phenyl substitution at both positions) the effect of the two phenyls are both felt, the β-phenyl perhaps more strongly since 35% of the ene product is formed compared to 25% in the unsubstituted compound. The phenyl group seems to direct the attack of singlet oxygen on the dihydronaphthalene ring, in one case to give an ene reaction, and in the other to give a 1,4 cycloaddition.

The reaction appears to form products with conjugated olefin preferentially; in **1b**, the ene product, which would have an unconjugated double bond, is not formed and the initial cycloadduct is further conjugated with the phenyl substituent; the ene product from **1a** is conjugated while the Diels–Alder product retains the same conjugation as the unsubstituted compound; both the ene product and the presumed initial Diels–Alder product from **1c** are conjugated.[12] This effect is reminiscent of the preferential formation of the conjugated ene product from the α,β,β-trimethylstyrenes,[13] and probably reflects productlike character in the transition state for the product-determining step.



2,7 1

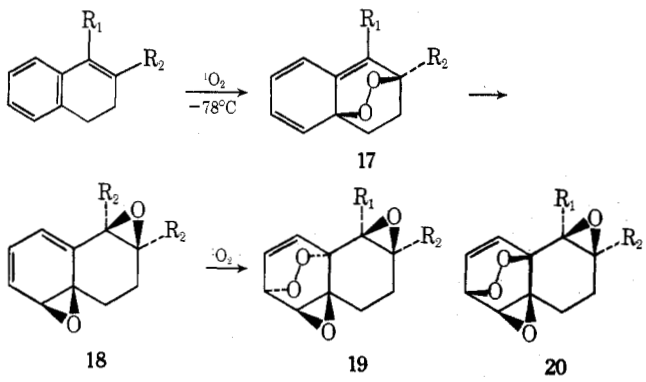
Stereochemistry of the Isomeric Dioxygenated Products. The physical and chemical properties of the two isomeric dioxygenated products formed in these photooxygenations show that they both must have the same general structure as those of the indene-derived products.[1a] That the less soluble isomers **2** all belong to the same stereochemical series is shown by the fact that their NMR spectra (Table II) all have one very high-field CH_2 proton (~1 ppm upfield from the other methylene protons), whereas all four CH_2 protons in the **3** series occur within a narrow

Table IV. Coupling Constants (Hz) for the Tetraepoxide Protons[a]

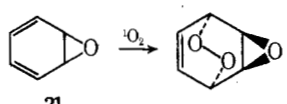
J	7b	8b[b]	7c	8c[c]	7e[c]	8e	7f[c]	8f
AB	3.3	3.3	3.3	3.3	3.3	3.3	3.0	3.2
BC	3.7		3.7	3.7	3.7	3.6		3.5
BD	1.1		1.2	1.4	1.0	1.1	1.3	1.1
CD	1.7		1.5	1.7	1.6	1.5	1.8	1.7
EF							3.7	3.5

[a] J_{AC} not resolved. [b] Protons B–D could not be separated with $Eu(fod)_3$. [c] $Eu(fod)_3$ was used to separate overlapping proton resonances; this technique was only partially successful with **7f**.

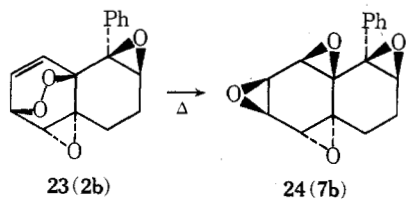
range. Similar regularities occur with protons C and D, all members of a series having resonances for a given proton either higher or lower field than in the other series. Also, the amount of **2** is always ≤3. Analogy with the indene case[1a] suggested that one isomer should be **19**. The rearrangement of an initial endoperoxide (**17**) would lead to a bisepoxide (**18**) in which the two epoxide groups must be cis. The second 1,4 cycloaddition of singlet oxygen would occur on the less hindered side, leading to **19**, in which the endoperoxide group is trans to the two epoxide groups.



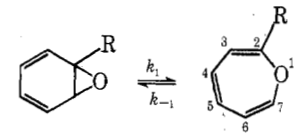
However, if the two epoxide groups in **18** must be cis, then the only possible structure for the second isomer would be **20**, in which the second addition of singlet oxygen occurs cis to the epoxide group. However, this conclusion did not seem reasonable since models showed that the diene system of both **18** and the analogous indene compounds should both favor the attack of singlet oxygen trans to the epoxide group. Furthermore, the analogous reaction of benzene oxide **21** with singlet oxygen leads to the formation of **22** with high stereospecificity.[14,15]



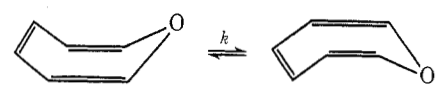
An x-ray crystal structure determination has been carried out on tetraepoxide **7b**;[16] this compound was chosen since it is more stable than the endoperoxide **2b**, and the two structures are directly related. The structure was unexpectedly found to be **24**; thus the structure of **2b** must be **23**, in which the two epoxide groups are trans!



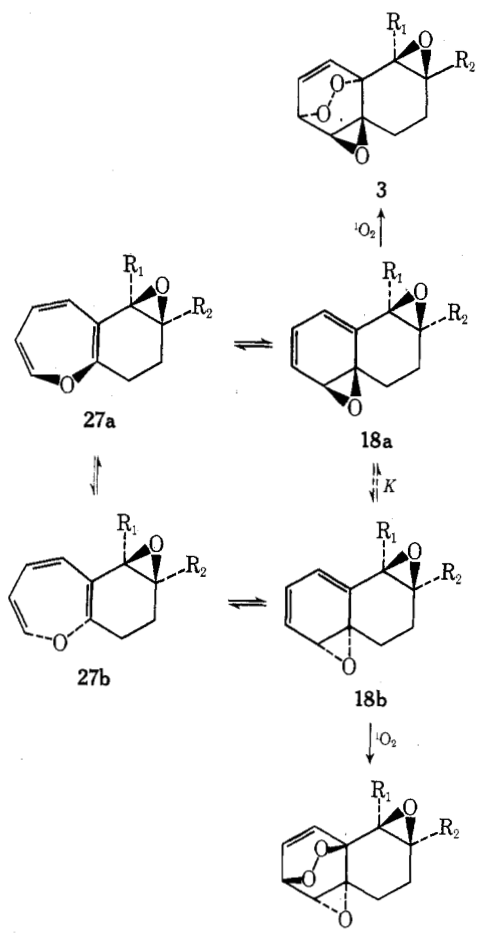
The formation of this isomer can be easily rationalized by the benzene oxide–oxepin chemistry observed by Vogel et al.[17] Benzene oxide was shown to equilibrate with its tautomer, oxepin (**25**, R = H).[17,18] Temperature-dependent



NMR studies of the equilibrium were carried out on both oxepin and 2-methyloxepin (**25**, R = CH_3).[19,20] At −78 °C, $k_1 = 2 \times 10^4$ s^{-1} and $K = 3.2$ for oxepin and $k_1 = 9.5 \times 10^3$ s^{-1} and $K = 4.0$ for 2-methyloxepin ($K = k_1/k_{-1}$). Thus, there are substantial amounts of both oxepins present. Substitution favors the oxepin form; however, even when the oxepin form is strongly favored, as in 2,7-dimethyloxepin (which shows no benzene oxide by spectroscopic methods),[17,20] a Diels–Alder reaction occurs readily with maleic anhydride[20] and proceeds via the benzene oxide form. Oxepin exists in a boat conformation with a very rapid interconversion between the two conformers (**26a** ⇄ **26b**).[20,21] One might expect the barrier to inversion to be comparable to that of cycloheptatriene, where Anet found $k = 180$ s^{-1} at −143 °C, $\Delta F^{\ddagger} = 6.1$ kcal mol^{-1}, and $\Delta S^{\ddagger} = 0$;[22] the calculated rate of inversion at −78 °C would be $k = 6.5 \times 10^5$ s^{-1}.

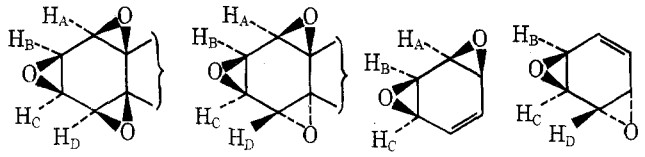


Thus, it seems likely that the benzene oxide intermediate **18a** can equilibrate readily with its isomer **18b** via the intermediate oxepin **27**. The stereospecific attack of singlet



oxygen on **18a** and **18b** would then give the two isomeric dioxygenated products, **2** and **3**.

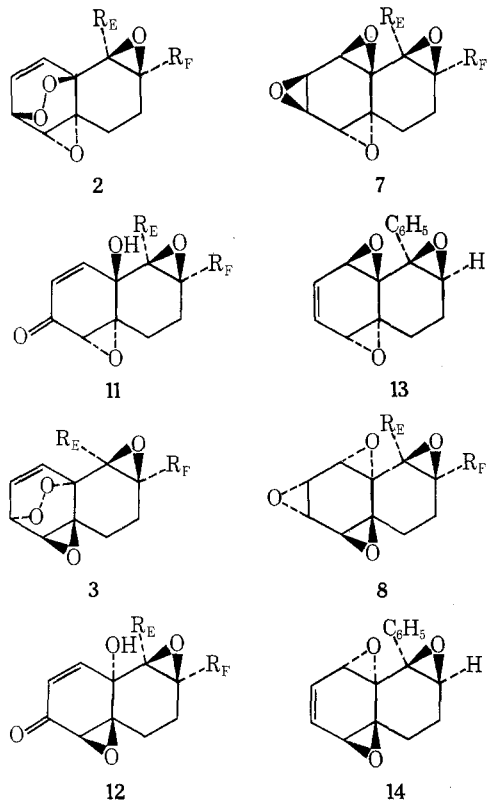
By this mode of formation, isomers **2** and **3** should have the same relative geometry for the ring containing the endoperoxide group (the A ring). That this is true can be shown by the NMR spectra of the corresponding tetraepoxide isomers (**7** and **8**). There are only two possible configurations, **28** and **29** for the A ring, and these can be compared with *syn*-benzene dioxide (**30**)[23] and *anti*-benzene dioxide (**31**),[23b,24] prepared by Vogel et al.[25] (see Table V).



28 **29** **30** **31**

Both **7** and **8** in the entire series of tetraepoxides have essentially the same coupling constants for the A ring. Moreover, Table V shows that J_{CD} for the tetraepoxides is only consistent with the *anti*-benzene oxide structure **29**, which has these protons on adjacent trans epoxide groups, with a dihedral angle of 50°.[27] Protons A and B must be on adjacent cis epoxide groups, with a dihedral angle of 0°, since the J_{AB} values are much larger than the J_{CD} value for **31**. The J_{BD} value for the tetraepoxides (J_{BD} ~1.0 Hz) is also closer to the value observed for **31** (J_{BD} = 0.8 Hz) for the long-range coupling of protons on trans epoxide groups. Since J_{AC} = 0.4 Hz for **30**, the corresponding AC coupling was probably not resolved in **7** and **8**. J_{BC} for **7** and **8** is approximately midway between the values of J_{BC} for the benzene dioxides.

We conclude from these data that both tetraepoxide isomers **7** and **8**, and, thus, the isomeric photooxygenation products **2** and **3**, have the same geometry for the A ring.[30] Therefore, the only possible structure for **3** is the one in which two cis epoxide groups are trans to the endoperoxide groups. The assignments of each series are then as shown below.



2 **7**

11 **13**

3 **8**

12 **14**

Table V. Coupling Constants (Hz) for the Tetraepoxide A Ring Protons and *syn*- and *anti*-Benzene Dioxide

J	Dihedral angle, deg	7, 8[a]	30	31
BC	0	3.7	3.5	4.2
AB	0	3.3	2.8	
CD	50	1.6		1.7
BD		1.1	0.4	0.8

[a] Average values of all compounds.

That two isomeric products should be formed here but only one in the indene series appears to be well accounted for by the absence of the severe peri interaction in the intermediate oxepins **27a,b**, which appears to inhibit the formation of one conformational isomer in the indene series.[1a] With a six-membered ring instead of a five-membered ring, the puckering of the ring decreases the interaction; the six-membered ring is also considerably less rigid than the cyclopentadiene epoxide ring in the intermediate, which should allow the ring to distort more to relieve peri interactions. (See ref 1a for further discussion of these points).

The ready rearrangement of the intermediate endoperoxide to the diepoxide is even more surprising than in the indene series, since ordinary cyclohexadiene endoperoxides are stable well above room temperature. The same arguments as in the case of the indene[1a,12] concerning the nature of this rearrangement must apply here, with even greater force.

Experimental Section

General conditions, including photooxygenation conditions, are as in the accompanying paper.[1a] Details of NMR spectra which occur in the tables are not repeated in this section.

Starting Materials. 2-Phenyl-3,4-dihydronaphthalene (**1a**) was prepared from 2-phenyl-1-tetralone[5] and had mp 61–62 °C (lit.[5] 64–66 °C). 1,2-Diphenyl-3,4-dihydronaphthalene (**1e**)[6] was prepared from 2-phenyl-1-tetralone and had mp 89.5–91 °C (hexane) (lit.[6] 76.5–77 °C, EtOH–EtOAc). 1-Methyl-2-phenyl-3,4-dihydronaphthalene (**1d**) was prepared from the 2-phenyl-1-tetralone with methyl Grignard and dehydration, and had mp 75–77 °C (lit.[31] 76 °C). 1-Methyl-3,4-dihydronaphthalene[31,32] (**1e**) was similarly prepared from α-tetralone and had bp 80–81 °C (5 mm) [lit.[32] bp 105 °C (14 mm)]. 1,2-Dihydronaphthalene (**1f**) was prepared by $LiAlH_4$ reduction of α-tetralone followed by dehydration and had bp 74–77 °C (7 mm) [lit.[33] bp 78 °C (6 mm)]. 1-Phenyl-3,4-dihydronaphthalene, purchased from Aldrich, was used as received.

Photooxygenation of 2-Phenyl-3,4-dihydronaphthalene (1a). A solution of 1.00 g (4.86 mmol) of **1a** in 175 ml of acetone containing ~2 mg of rose bengal took up 110 ml (0.92 equiv) of O_2 during 2.5 h. The solution was warmed to room temperature and evaporated; NMR showed **1a** (~10%), 2-phenylnaphthalene (**6a**, ~15%), and the ene product (**4a**, ~75%); NMR ($CDCl_3$) δ 3.37 (m, 2 H, CH_2), 5.65 (br t, 1 H, H_1, J = 2 Hz), 6.45 (d of d, 1 H, H_3, J = 4.6 and 3.4 Hz), 7.33 (m, 9 H, aromatic), and 7.75 (s, 1 H, OOH). The reaction mixture was dissolved in methanol and treated with excess $NaBH_4$; ether was added and the solution was extracted with water, dried over $MgSO_4$, and evaporated; NMR ($CDCl_3$) showed 1-hydroxy-2-phenyl-1,4-dihydronaphthalene (40%), **6a** (50%), and **1a** (10%). The material was chromatographed on a 2.5 × 20 cm silica gel column with $CHCl_3$. The forerun contained 500 mg of **1a** (25%) and **6a** (75%), colorless plates, (CH_3OH), mp 102–103 °C (lit.[5] 101–102 °C), not depressed by mixture with an authentic sample, and with NMR and ir spectra superimposable with those of an authentic sample. Other fractions gave 350 mg of crystalline 1-hydroxy-2-phenyl-1,4-dihydronaphthalene: NMR ($CDCl_3$) δ 2.0 (broad s, 1 H, OH, chemical shift variable, exchangeable with D_2O), 3.47 (m, 2 H, CH_2), 5.52 (broad t, 1 H, HOCH), 6.11 (t, 1 H, olefinic CH), and 7.35 (m, 9 H, aromatic); ir (KBr) 3490, 1487, 1436, 745, and 680 cm^{-1}. On drying under high vacuum, the alcohol dehydrated to form 2-phenylnaphthalene, identical with an authentic sample.

Photooxygenation of 1-Phenyl-3,4-dihydronaphthalene (1b). A solution of 3.00 g (14.5 mmol) of **1b** in 150 ml of acetone containing ~4 mg of rose bengal took up 666 ml (1.88 equiv) of

oxygen during 3.5 h. The solution was warmed to room temperature and evaporated; NMR ($CDCl_3$) showed two compounds, **2b** (40%) and **3b** (60%). Crystallization from ether gave 1.04 g of **2b**. The filtrate was evaporated, and the residue chromatographed on a 2.5 × 19 cm silica gel column with $CHCl_3$. The forerun contained ~75 mg (3%) of starting material (R_f 0.72). The fractions containing **3b** (R_f 0.42) were evaporated; crystallization from ether–pentane gave 1.32 g of **3b** (34%), mp 80–83 °C. The fraction containing **2b** (R_f 0.30) yielded a further 250 mg of **2b**; total recovered was 1.29 g (33%), mp 115.5–116.5 °C. The remaining material contained ~10% rearrangement products (**7b** and **8b**), ~10% **2** and **3b**, and other unidentified material. Both **2b** and **3b** free iodine from acidified KI. Recrystallization of **2b** from ether–petroleum ether gave colorless crystals: mp 115.5–116.5 °C dec; NMR ($CDCl_3$) δ 7.37 (s, 5 H, C_6H_5); ir (KBr) 1443, 1362, 1263, 1247, 962, 912, 887, 845, 758, 739, 700, and 694 cm^{-1}; mass spectrum (70 eV, source temperature 132 °C) *m/e* (rel intensity) 270 (4), 209 (5), 141 (6), 128 (6), 115 (4), 105 (28), 77 (10), 32 (15), 28 (100), and 18 (7).

Anal. Calcd for $C_{16}H_{14}O_4$: C, 71.10; H, 5.22. Found: C, 70.96; H, 5.15.

Recrystallization of **3b** from ether–petroleum ether gave colorless crystals: mp 80.0–80.5 °C dec; NMR ($CDCl_3$) δ 7.36 (m, 5 H, C_6H_5); ir (KBr) 1603, 1491, 1256, 1239, 968, 950, 916, 891, 838, 811, 798, 752, and 695 cm^{-1}; mass spectrum (70 eV, source temperature 140 °C) *m/e* (rel intensity) 270 (2), 241 (3), 209 (3), 128 (5), 115 (3), 105 (21), 77 (7), 32 (16), 28 (100), 18 (33), and 17 (6).

Anal. Calcd for $C_{16}H_{14}O_4$: C, 71.10; H, 5.22. Found: C, 70.90; H, 5.12.

Photooxygenation of 1,2-Diphenyl-3,4-dihydronaphthalene (1c). **1c** (1.00 g, 3.55 mmol) in 75 ml of acetone containing ~2 mg of rose bengal took up 151 ml (1.75 equiv) of oxygen during 5 h. The solution was warmed to room temperature and evaporated; NMR ($CDCl_3$) showed the diepoxy endoperoxides **2c** (25%) and **3c** (40%), and the ene product **4c** (35%). The addition of ether gave 280 mg of **2c** (containing 15% **3c**, by NMR). Seeding the concentrated filtrate with **3c** (from chromatography of a previous reaction mixture) gave 400 mg of **3c**. The filtrate was evaporated and chromatographed on a 2 × 25 cm silica gel column with $CHCl_3$. The first fractions contained 1,2-diphenylnaphthalene (**6c**) and **4c**: NMR ($CDCl_3$) δ 3.58 (d, 2 H, CH_2, $J_{H_3CH_2}$ = 2 Hz), 6.38 (t, 1 H, H_3), 7.14 (m, 14 H, aromatic), and 7.33 (s, 1 H, OOH). The residue from one fraction gave a further 35 mg of **3c**. The fractions containing **6c** and **4c** were combined and evaporated. The residue was treated with 10 ml of 4% ethanolic KOH solution; 50 ml of ether was added, and the solution was extracted with water and saturated NaCl solution, dried over $MgSO_4$, filtered, and evaporated to give 350 mg of **6c** (31%). Recrystallization gave 168 mg, mp 109 °C (ethanol), not depressed by mixture with an authentic sample, and with ir and NMR superimposable with those of an authentic sample.

Recrystallization of **2c** from methylene chloride–heptane gave 240 mg (20%): mp 130–131 °C dec; NMR ($CDCl_3$) δ 7.04 (s, 5 H, C_6H_5) and 7.10 (s, 5 H, C_6H_5); ir (KBr) 1603, 1241, 1232, 965, 923, 908, 900, 876, 868, 848, 763, 759, 703, and 697 cm^{-1}; mass spectrum (70 eV, source temperature 165 °C) *m/e* (rel intensity) 241 (8), 225 (4), 213 (4), 121 (5), 115 (5), 106 (9), 105 (100), 103 (5), 77 (25), 69 (6), 49 (5), 28 (7), and 18 (11).

Anal. Calcd for $C_{22}H_{18}O_4$: C, 76.28; H, 5.24. Found: C, 76.10; H, 5.42.

Recrystallization of **3c** from ether–chloroform solution gave 395 mg (32%): mp 112 °C dec (with resolidification and remelting at 205–215 °C dec); NMR ($CDCl_3$) δ 7.17 (m, 10 H, C_6H_5); ir (KBr) 1604, 1244, 1233, 937, 913, 902, 889, 876, 757, 748, 717, and 687 cm^{-1}; mass spectrum (70 eV, source temperature 180 °C) *m/e* (rel intensity) 105 (30), 77 (8), 32 (24), 28 (100), and 18 (11). Anal. Calcd for $C_{22}H_{18}O_4$: C, 76.28; H, 5.24. Found: C, 76.33; H, 5.33.

Photooxygenation of 1-Methyl-2-Phenyl-3,4-dihydronaphthalene (1d). A solution of 500 mg (2.77 mmol) of **1d** in 45 ml of acetone containing ~1 mg of rose bengal took up 61 ml (1.10 equiv) of oxygen during 70 min. The solution was warmed to room temperature and evaporated; NMR showed the diepoxy endoperoxides **2d** (4%, methyl singlet at δ 1.07) and **3d** (6%, methyl singlet at δ 1.00), the ene product **4d** (85%), NMR ($CDCl_3$) δ 1.42 (s, 3 H, CH_3), 3.44 (d, 2 H, CH_2, J_{3,CH_2} = 4 Hz), 6.08 (t, 1 H, H_3), 7.20 (s, 1 H, OOH), and 7.30 (m, 9 H, aromatic), and **5d** (~5%, olefinic protons as singlets at δ 5.13 and 5.67). The material was treated with 4% ethanolic KOH. After 10 min, 50 ml of ether was added, and the solution was extracted with water and saturated NaCl solution, dried over $MgSO_4$, filtered, and evaporated. Addition of ethanol gave 275 mg of **6d** (48%); recrystallization gave **6d**, mp 85–86 °C (lit.[7] 85 °C); the melting point was not depressed by mixture with an authentic sample (see below), and the ir and NMR spectra were superimposable.

Photooxygenation of 1-Methyl-3,4-dihydronaphthalene (1e). A solution of 3.00 g (20.8 mmol) of **1e** in 70 ml of acetone containing ~2 mg of rose bengal took up 752 ml (1.50 equiv) of oxygen during 3.3 h. The solution was evaporated at room temperature; NMR ($CDCl_3$) showed the diepoxy endoperoxides **2e** (25%) and **3e** (35%), and the ene product **4e** (40%). Trituration with ether–petroleum ether gave 555 mg (13%) of **2e**, mp 119–120 °C (hexane–CCl_4). **2e** freed iodine from acidified KI: NMR ($CDCl_3$) δ 1.49 (s, 3 H, CH_3); ir (KBr) 1366, 1260, 1206, 950, 914, 891, 855, 817, 799, 760, 745, and 704 cm^{-1}; mass spectrum (70 eV, source temperature 140 °C) *m/e* (rel intensity) 147 (2), 137 2), 79 (2), 55 (3), 44 (4), 43 (11), 41 (2), 39 (3), 32 (18), and 28 (100).

Anal. Calcd for $C_{11}H_{12}O_4$: C, 63.45; H, 5.81. Found: C, 63.35, H, 5.91.

The filtrate was evaporated and the residue chromatographed on a 2.5 × 25 cm silica gel column with CCl_4. The first fractions contained 1-methylnaphthalene (**6e**) and **4e**: NMR ($CDCl_3$) δ 1.41 (s, 3 H, CH_3), 3.28 (d of d, 2 H, CH_2, J_{2,CH_2} = 2, J_{3,CH_2} = 3 Hz), 5.82 (t of d, 1 H, H_2, $J_{2,3}$ = 11 Hz), 6.06 (t of d, 1 H, H_3), 7.30 (m, 4 H, C_6H_4), and 7.64 (s, 1 H, OOH). Rechromatography of this material gave only **6e** (800 mg, 27%), a colorless oil: NMR ($CDCl_3$) δ 2.44 (s, 3 H, CH_3); NMR and ir spectra were superimposable with those of a purchased sample (Aldrich); picrate, mp 240–241 °C (lit.[34] 241 °C). Trituration of the residue from another fraction with ether–petroleum gave 290 mg of impure **3e** (60% by NMR), which could not be purified for analysis, NMR δ 1.37 (s, 3 H, CH_3).

The photooxygenation was repeated with a solution of 300 mg (2.08 mmol) of **1e** in 10 ml of acetone. The solution was evaporated, redissolved in ethanol, and treated with excess $NaBH_4$. After 10 min, 50 ml of ether was added, and the solution was extracted with water, dried over $MgSO_4$, filtered, and evaporated. Crystallization from pentane gave 73 mg of 1-hydroxy-1-methyl-1,4-dihydronaphthalene: mp 87–90 °C; ir (KBr) 3350 cm^{-1}; NMR ($CDCl_3$) δ 1.48 (s, 3 H, CH_3), 2.14 (broad s, 1 H, OH), 3.33 (m, 2 H, CH_2), 5.90 (m, 2 H, olefinic protons), 7.18 (m, 3 H, aromatic), and 7.67 (m, 1 H, aromatic); on drying under high vacuum, the alcohol was dehydrated to 1-methylnaphthalene (**6e**).

Photooxygenation of 1,2-Dihydronaphthalene (1f). A solution of 2.00 g (15.4 mmol) of **1f** in 50 ml of acetone containing ~1 mg of rose bengal took up 610 ml (1.60 equiv) of oxygen during 8.5 h; the dye was replenished after 4.5 and 7 h. The solution was warmed to room temperature and evaporated; NMR ($CDCl_3$) showed the diepoxy endoperoxides **2f** (33.5%) and **3f** (33.5%), the ene product **4f** (23%), and unreacted **1f** (10%). The product was precipitated with ether and a small amount of methanol and recrystallized from heptane–methylene chloride to give 500 mg (17%) of **2f**: mp 118–120 °C dec; ir (KBr) 1257, 1229, 938, 923, 898, 875, 834, 815, 787, 746, and 701 cm^{-1}; mass spectrum (70 eV, source temperature 155 °C) *m/e* (rel intensity) 162 (7), 149 (10), 133 (11), 94 (10), 81 (13), 77 (11), 71 (10), 68 (28), 65 (11), 57 (16), 55 (19), 53 (11), 43 (13), 41 (25), 39 (27), 32 (16), 29 (16), 28 (100), 27 (20), 18 (86), and 17 (21).

Anal. Calcd for $C_{10}H_{10}O_4$: C, 61.85; H, 5.19. Found: C, 61.85, H, 5.35.

The filtrate was evaporated and the residue chromatographed on a 2.0 × 12 cm silica gel column with 1:1 $CHCl_3$–petroleum ether to remove unreacted **1f** and with $CHCl_3$ containing 1% methanol to collect **3f** and **4f**: NMR ($CDCl_3$) δ 3.40 (m, 2 H, CH_2), 5.35 (m, 1 H, H_1), 6.17 (m, 2 H, H_2 and H_3), 7.22 (s, 1 H, OOH), and 7.28 (m, 4 H, C_6H_5). Repeated attempts to isolate **3f** by chromatography and/or crystallization were unsuccessful.

Naphthalenes. 6a, 6c, and **6d** were prepared by the method of Campbell and Kidd[5] by refluxing 250–500 mg of the dihydronaphthalene with 1.0 equiv of chloranil in 20 ml of xylene for 2 days (for **1a**), 3 days (for **1c**), and 4 days (for **1d**). After work-up the products were crystallized from ethanol to give **6a** (85%), mp 101–103 ° (lit.[5] 101–102 °C), **6c** (67%), mp 108–109 °C (lit.[6] 109.5–110 °C), and **6d** (53%), mp 83–84 °C (lit.[7] 85 °C).

Thermolysis of the Dioxygenated Products. The dioxygenated dihydronaphthalene products (200–600 mg) were dissolved in 15 ml of toluene and the solutions refluxed for 2.5 h. On cooling, 1.5-ml aliquots were removed and treated with 0.25 ml of triethylamine; the solutions were warmed for several minutes and evaporated. NMR spectra ($CDCl_3$) of the residues showed 75% tetraepoxide and 25% γ-hydroxy-α,β-unsaturated ketone for each reaction. The remaining solutions were evaporated. Trituration with ether–petroleum ether gave crystals of the impure tetraepoxides;

they were purified by repeated crystallization from benzene–heptane, following the purity by TLC (silica gel–$CHCl_3$). Ir (KBr) spectra of further material collected from the first filtrates of each reaction showed a carbonyl band for the β-epoxy ketones: compound (carbonyl band) **9b** (1727 cm^{-1}), **10b** (1723 cm^{-1}), **9c** (1727 cm^{-1}), **10c** (1723 cm^{-1}), **9f** (1725 cm^{-1}). In one case (the reaction of **2e**), several recrystallizations of this further material gave 45 mg (8%) of the pure β-epoxy ketone **9e**: mp 111–113 °C; NMR ($CDCl_3$) δ 1.04 (m, 1 H, one methylene proton), 1.24 (s, 3 H, CH_3), 2.20 (m, 2 H, two methylene protons), 2.49 (m, 1 H, one methylene proton), 2.80 (one part of ABX, 1 H, H_B, J_{AB} = 2.7, J_{BC} = 16.5, J_{BD} = 0.8 Hz), 3.02 (ABX, 1 H, H_C, J_{AC} = 1.8 Hz), 3.16 (d, 1 H, H_D), 3.33 (m, 1 H, H_F), and 3.45 (ABX, 1 H, H_A); ir (KBr) 1727, 1244, 968, 947, 923, 888, 872, 844, 782, and 734 cm^{-1}; mass spectrum (70 eV, source temperature 180 °C) *m/e* (rel intensity) 137 (11), 123 (6), 110 (5), 109 (7), 79 (7), 55 (7), 43 (37), 41 (6), 39 (8), 28 (20), 27 (8), 18 (100), and 17 (19).

Anal. Calcd for $C_{11}H_{12}O_4$: C, 63.45; H, 5.81. Found: C, 63.58; H, 6.09.

The following tetraepoxides were prepared.

7b (57%): mp 195.0–195.5 °C; NMR ($CDCl_3$) δ 7.29 (s, 5 H, C_6H_5); ir (KBr) 1252, 950, 923, 872, 842, 835, 800, 764, 743, 711, and 689 cm^{-1}; mass spectrum (70 eV, source temperature 220 °C) *m/e* (rel intensity) 270 (4), 241 (9), 183 (6), 169 (6), 142 (7), 141 (30), 129 (10), 128 (25), 127 (6), 115 (18), 106 (8), 105 (100), 91 (6), 85 (6), 77 (35), 55 (11), 51 (11), 39 (8), 29 (6), 28 (12), 27 (8), and 18 (20).

Anal. Calcd for $C_{16}H_{14}O_4$: C, 71.10; H, 5.22. Found: C, 71.03; H, 5.24.

8b (53%): mp 122–123 °C; NMR ($CDCl_3$) δ 7.31 (m, 5 H, C_6H_5); ir (KBr) 1279, 1254, 948, 919, 892, 866, 840, 819, 788, 755, 712, and 693 cm^{-1}; mass spectrum (70 eV, source temperature 210 °C) *m/e* (rel intensity) 270 (6), 241 (10), 197 (6), 183 (6), 169 (6), 142 (7), 141 (29), 129 (10), 128 (26), 127 (8), 115 (16), 106 (8), 105 (100), 91 (8), 85 (6), 77 (38), 55 (9), 51 (13), 39 (10), 32 (9), 29 (9), 28 (46), 27 (9), 18 (72), and 17 (16).

Anal. Calcd for $C_{16}H_{14}O_4$: C, 71.10; H, 5.22. Found: C, 71.09; H, 5.39.

7c (37%): mp 163.5–164.5 °C; NMR ($CDCl_3$) δ 7.06 (m, 10 H, aromatic); ir (KBr) 1268, 1250, 1230, 948, 926, 917, 903, 862, 855, 741, and 709 cm^{-1}; mass spectrum (70 eV, source temperature 200 °C) *m/e* (rel intensity) 241 (8), 213 (4), 115 (6), 105 (100), 103 (5), 78 (4), 77 (31), 51 (5), and 28 (8).

Anal. Calcd for $C_{22}H_{18}O_4$: C, 76.28; H, 5.24. Found: C, 76.27; H, 5.32.

8c (35%): mp 223–224 °C dec; NMR ($CDCl_3$) δ 7.07 (m, 10 H, aromatic); ir (KBr) 1272, 1251, 965, 957, 898, 859, 855, 840, 797, 769, 714, and 698 cm^{-1}; mass spectrum (70 eV, source temperature 205 °C) *m/e* (rel intensity) 241 (2), 213 (3), 144 (5), 129 (6), 105 (20), 97 (7), 85 (7), 83 (10), 81 (11), 73 (16), 71 (11), 70 (8), 69 (24), 60 (1)), 57 (23), 56 (8), 55 (22), 43 (28), 41 (25), 32 (21), 29 (10), 28 (100), and 18 (16).

Anal. Calcd for $C_{22}H_{18}O_4$: C, 76.28; H, 5.24. Found: C, 76.28; H, 5.23.

7e (58%): mp 150–152 °C NMR ($CDCl_3$) δ 1.25 (s, 3 H, CH_3); ir (KBr) 1271, 1246, 960, 934, 918, 886, 871, 845, 769, 747, and 717 cm^{-1}; mass spectrum (70 eV, source temperature 190 °C) *m/e* (rel intensity) 137 (6), 107 (6), 105 (5), 95 (7), 91 (5), 85 (7), 81 (6), 79 (12), 77 (10), 71 (5), 68 (7), 67 (6), 65 (6), 55 (11), 53 (8), 43 (48), 41 (9), 39 (11), 29 (6), 28 (22), 27 (9), 18 (100), and 17 (21).

Anal. Calcd for $C_{11}H_{12}O_4$: C, 63.45; H, 5.81. Found: C, 63.33; H, 5.90.

7f (46%): mp 157–158 °C; ir (KBr) 1278, 947, 907, 872, 850, 828, 784, 776, 759, and 741 cm^{-1}; mass spectrum (70 eV, source temperature 215 °C) *m/e* (rel intensity) 121 (17), 110 (14), 109 (16), 107 (15), 95 (15), 94 (18), 91 (16), 84 (15), 82 (13), 81 (42), 79 (20), 77 (22), 71 (35), 69 (16), 68 (100), 67 (17), 66 (12), 65 (30), 56 (13), 55 (45), 53 (34), 51 (23), 43 (21), 42 (20), 41 (56), 40 (17), 39 (69), 29 (46), 28 (23), 27 (54), and 26 (11).

Anal. Calcd for $C_{10}H_{10}O_4$: C, 61.85; H, 5.19. Found: C, 62.07; H, 5.32.

Preparation of Tetraepoxide 8e. A solution of 3.00 g (20.8 mmol) of **1e** in 100 ml of acetone containing ~2 mg of rose bengal as sensitizer was photooxygenated at −78 °C for 2 h (at 120 V); the solution took up 783 ml (1.54 equiv) of oxygen. The solution was warmed to room temperature and evaporated. The addition of ether–pentane gave 503 mg of the diepoxy endoperoxide **2e**. The filtrate was evaporated and the resulting oil, containing **3e** and the ene product (**4e**), was heated on a rotary evaporator under vacuum (0.1 Torr) at 85 °C for 4.5 h [1-methylnaphthalene (**6e**) was slowly given off]. Addition of ether to the resulting oil gave 867 mg of pale-yellow crystals (~90% **8e** by NMR). The crystals were dissolved in CH_2Cl_2 and filtered through silica gel. The filtrate was evaporated and the residue purified by repeated crystallizations from benzene–heptane to give 387 mg of **8e**: mp 156–158.5 °C; NMR ($CDCl_3$) δ 1.17 (s, 3 H, CH_3); ir (KBr) 1277, 1263, 1259, 955, 933, 911, 883, 842, 815, 776, 767, 750, and 705 cm^{-1}; mass spectrum (70 eV, source temperature 208 °C) *m/e* (rel intensity) 151 (6), 137 (12), 123 (10), 107 (10), 95 (12), 85 (13), 81 (10), 79 (24), 77 (19), 71 (10), 68 (11), 67 (11), 65 (11), 55 (19), 53 (16), 43 (100), 41 (21), 39 (25), 29 (14), 28 (17), 27 (22), and 18 (11).

Anal. Calcd for $C_{11}H_{12}O_4$: C, 63.45; H, 5.81. Found: C, 63.62; H, 5.69.

Preparation of Tetraepoxide 8f. A solution of 2.00 g (15.4 mmol) of **1f** in 50 ml of acetone containing ~1 mg of rose bengal was photooxygenated at −78 °C for 4.5 h (at 120 V); the solution took up 647 ml (1.72 equiv) of oxygen. The solution was warmed to room temperature and evaporated. The addition of ether to the resulting oil gave 622 mg of the diepoxy endoperoxide **2f**, mp 110–113 °C dec. The filtrate was evaporated, and the resulting oil, containing **3f** and the ene product (**4f**), was heated on a rotary evaporator under vacuum (0.1 Torr) at ~90 °C for 3.5 h. The resulting oil was chromatographed on a 2 × 24 cm silica gel column with $CHCl_3$. Evaporation of the forerun and addition of methanol gave 110 mg of naphthalene (**6f**); the NMR and ir spectra are superimposable with those of an authentic sample (Aldrich). Evaporation of the remaining fractions and addition of ether gave 537 mg of colorless crystals (20% **7f** and 80% **8f** by NMR). Repeated crystallizations from benzene–heptane finally gave 287 mg of **8f**: mp 151–152 °C; ir (KBr) 1268, 994, 944, 871, 835, 804, 779, 757, and 689 cm^{-1}; mass spectrum (70 eV, source temperature 205 °C) *m/e* (rel intensity) 121 (17), 110 (12), 109 (13), 107 (15), 95 (12), 94 (21), 91 (14), 84 (14), 82 (13), 81 (37), 79 (17), 77 (18), 71 (36), 69 (14), 68 (100), 67 (14), 66 (12), 65 (26), 56 (12), 55 (40), 53 (21), 51 (16), 43 (18), 42 (18), 41 (49), 40 (16), 39 (59), 29 (39), 28 (27), 27 (44), 26 (11), and 18 (14).

Anal. Calcd for $C_{10}H_{10}O_4$: C, 61.85; H, 5.19. Found: C, 62.04; H, 5.19.

General Procedure for the Preparation of the γ-Hydroxy-α,β-Unsaturated Ketones 11, 12. Triethylamine (0.25 ml) was added to solutions of 95–300 mg of **2** or **3** in 10 ml of $CHCl_3$, causing exothermic reactions. After cooling, the solutions were evaporated, and $CHCl_3$ solutions of the residues were filtered through silica gel. The filtrates were evaporated and crystallized by addition of ether; the products were then recrystallized from benzene–heptane. The following compounds were prepared.

11b (97%): mp 140–143 °C; NMR ($CDCl_3$, 100 MHz) δ 1.21 (m, 1 H, one methylene proton), 1.49 (m, 3 H, three methylene protons), 3.46 (d, 1 H, H_D, J_{BD} = 1.9 Hz), 3.47 (m, 1 H, H_F), 3.90 (s, 1 H, OH), 5.70 (half of AB q, 1 H, H_B, J_{AB} = 10.8 Hz), 5.95 (half of AB q, 1 H, H_A), and 7.31 (s, 5 H, C_6H_5); ir (KBr) 3530, 1683, 1266, 1241, 1229, 989, 927, 919, 902, 824, 813, 737, 711, 691 cm^{-1}; mass spectrum (70 eV, source temperature 190 °C) *m/e* (rel intensity) 165 (20), 146 (8), 145 (5), 138 (5), 133 (31), 115 (5), 110 (5), 106 (9), 105 (100), 77 (29), 51 (7), 39 (6), 28 (7), and 27 (6).

Anal. Calcd for $C_{16}H_{14}O_4$: C, 71.10; H, 5.22. Found: C, 71.01; H, 5.22.

12b (97%): mp 162.5–163.5 °C; NMR ($CDCl_3$, 100 MHz) δ 1.17 (m, 1 H, one methylene proton), 2.26 (m, 2 H, two methylene protons), 2.84 (m, 1 H, one methylene proton), 3.08 (d, 1 H, H_D, J_{BD} = 2.1 Hz), 3.20 (m, 1 H, H_F), 3.87 (s, 1 H, OH), 5.71 (half of AB q, 1 H, H_B, J_{AB} = 10.7 Hz), 6.48 (half of AB q, 1 H, H_A), 7.28 (m, 3 H, aromatic), and 7.58 (m, 2 H, aromatic); ir (KBr) 3580, 3410, 1680, 1276, 1250, 1239, 949, 898, 824, 814, 785, 751, and 691 cm^{-1}; mass spectrum (source temperature 200 °C) *m/e* (rel intensity) 165 (16), 146 (4), 133 (16), 115 (4), 105 (100), 77 (24), 55 (14), 51 (6), 39 (5), 28 (9), and 27 (5).

Anal. Calcd for $C_{16}H_{14}O_4$: C, 71.10; H, 5.22. Found: C, 70.88; H, 5.47.

11c (90%): mp 193–194.5 °C dec; NMR ($CDCl_3$) δ 1.36 (m, 1 H, one methylene proton), 2.67 (m, 3 H, three methylene protons), 3.54 (d, 1 H, H_D, J_{BD} = 1.7 Hz), 4.03 (s, 1 H, OH), 5.75 (half of AB q, 1 H, H_A, J_{AB} = 10.7 Hz), 5.84 (half of AB q, 1 H, H_B), and 7.07 (m, 10 H, aromatic); ir (KBr) 3510, 1693, 1270, 940, 856, 818, 741, and 685 cm^{-1}; mass spectrum (source temperature 225 °C) *m/e* (rel intensity) 214 (7), 105 (31), 77 (10), 69 (6), 57 (7), 55 (6), 43 (6), 41 (5), 32 (19), 28 (100), and 18 (15).

Anal. Calcd for $C_{22}H_{18}O_4$: C, 76.28; H, 5.24. Found: C, 76.16; H, 5.43.

12c (83%): mp 172–173.5 °C dec; NMR ($CDCl_3$) δ 1.39 (m, 1 H,

one methylene proton), 2.58 (m, 2 H, two methylene proton), 3.04 (m, 1 H, methylene proton), 3.21 (d, 1 H, H_D, J_{BD} = 2.0 Hz), 3.64 (s, 1 H, OH), 5.76 (half of AB q, 1 H, H_B, J_{AB} = 10.7 Hz), 6.43 (half of AB q, 1 H, H_A), and 7.20 (m, 10 H, aromatic); ir (KBr) 3540, 3470, 1681, 1275, 1229, 949, 886, 748, 733, and 682 cm^{-1}; mass spectrum (70 eV, source temperature 210 °C) *m/e* (rel intensity) 71 (5), 69 (9), 57 (12), 55 (10), 43 (10), 41 (8), 32 (23), 28 (100), and 18 (34).

Anal. Calcd for $C_{22}H_{18}O_4$: C, 76.28, H, 5.24. Found: C, 76.20; H, 5.47.

11e (88%): mp 102–103 °C; NMR ($CDCl_3$) δ 1.07 (m, 1 H, one methylene proton), 1.48 (s, 3 H, CH_3), 2.28 (m, 3 H, three methylene protons), 3.36 (m, 1 H, H_F), 3.37 (d, 1 H, H_D, J_{BD} = 2.0 Hz), 3.66 (s, 1 H, OH), 5.95 (half of AB q, 1 H, H_B, J_{AB} = 10.8 Hz), and 6.72 (half of AB q, 1 H, H_A); ir (KBr) 3550, 1687, 1271, 1237, 983, 968, 920, 878, 863, 829, 784, 743, and 709 cm^{-1}; mass spectrum (source temperature 180 °C) *m/e* (rel intensity) 165 (29), 137 (11), 123 (11), 109 (9), 91 (10), 84 (12), 77 (10), 71 (28), 69 (9), 65 (10), 55 (42), 53 (11), 51 (9), 43 (100), 41 (15), 39 (22), 32 (16), 28 (94), 18 (91), and 17 (18).

Anal. Calcd for $C_{11}H_{12}O_4$: C, 63.45; H, 5.81. Found: C, 63.45; H, 5.96.

11f (84%): mp 135.5–137°; NMR ($CDCl_3$) δ 1.21 (m, 1 H, one methylene proton), 2.31 (m, 3 H, three methylene protons), 3.35 (d, 1 H, H_E, J_{EF} = 3.9 Hz), 3.40 (s, 1 H, OH), 3.44 (d, 1 H, H_D, J_{BD} = 1.9 Hz), 3.59 (m, 1 H, H_F), 6.01 (half of AB q, 1 H, H_B, J_B = 10.4 Hz), and 6.56 (half of AB q, 1 H, H_A); ir (KBr) 3540, 1692, 1250, 1231, 980, 974, 944, 919, 860, 837, 820, and 788 cm^{-1}; mass spectrum (source temperature 195 °C) *m/e* (rel intensity) 165 (85), 149 (31), 138 (30), 137 (22), 123 (24), 122 (31), 121 (28), 120 (22), 119 (24), 110 (53), 109 (23), 97 (32), 96 (22), 91 (50), 82 (34), 81 (32), 79 (23), 77 (31), 70 (28), 69 (30), 68 (20), 67 (24), 57 (33), 55 (100), 53 (37), 51 (29), 43 (29), 41 (69), 39 (77), 29 (34), 28 (56), 27 (60), and 18 (26).

Anal. Calcd for $C_{10}H_{10}O_4$: C, 61.85; H, 5.19. Found: C, 62.01; H, 5.24.

Reaction of 2b and 3b with Trimethyl Phosphite. Trimethyl phosphite (100 mg, 0.80 mmol) was added to a solution of 200 mg (0.742 mmol) of **2b** in 2 ml of $CHCl_3$. An exothermic reaction occurred; after cooling, the solution was heated briefly and evaporated. The residue was passed through a 2.5 × 20 cm silica gel column with $CHCl_3$. Evaporation of the filtrate, crystallization from ether-pentane, and recrystallization gave 135 mg (68%) of triepoxide **13b:** mp 136–137.5 °C; NMR ($CDCl_3$, 100 MHz) δ 1.11 (m, 1 H, methylene proton), 2.45 (m, 3 H, three methylene protons), 2.83 (part of ABXY, 1 H, H_D[35], J_{CD} = 3.2, J_{BD} = 1.5 Hz), 3.10 (part of ABXY, 1 H, H_A, J_{AB} = 3.2, J_{AC} = 1.5 Hz), 3.22 (m, 1 H, H_F), 5.93 (part of ABXY, 1 H, H_C, J_{BC} = 9.8 Hz), 6.10 (part of ABXY, 1 H, H_B), and 7.29 (s, 5 H, C_6H_5); ir (KBr) 1608, 1276, 1234, 966, 939, 917, 875, 800, 769, 750, and 709 cm^{-1}; mass spectrum (70 eV, source temperature 250°C) *m/e* (rel intensity) 149 (9), 141 (10), 129 (5), 128 (6), 115 (10), 106 (8), 105 (100), 77 (28), 55 (5), 52 (6), 51 (7), 39 (8), 32 (6), 28 (53), 27 (5), and 18 (8).

Anal. Calcd for $C_{16}H_{14}O_3$: C, 75.57; H, 5.55. Found: C, 75.57; H, 5.74.

In the same manner, the addition of 87 mg (0.70 mmol) of trimethyl phosphite to a solution of 170 mg (0.630 mmol) of **3b** gave 116 mg of **14b** (73%), recrystallized to give pure **14b:** mp 132.5–134.5 °C; NMR ($CDCl_3$, 100 MHz) δ 1.24 (m, 1 H, one methylene proton), 2.45 (m 3 H, three methylene protons), 2.71 (part of ABXY, 1 H, H_D,[35] J_{CD} = 3.2, J_{BD} = 1.5 Hz), 2.88 (part of ABXY, 1 H, H_A, J_{AB} = 3.2, J_{AC} = 1.5 Hz), 3.28 (m, 1 H, H_F), 5.92 (part of ABXY, 1 H, H_C, J_{BC} = 9.8 Hz), 6.02 (part of ABXY, 1 H, H_B), 7.30 (m, 5 H, C_6H_5); ir (KBr) 1264, 1234, 944, 884, 867, 816, 788, 761, 729, and 700 cm^{-1}; mass spectrum (source temperature 200 °C) *m/e* (rel intensity) 197 (12), 170 (5), 149 (10), 141 (11), 129 (5), 128 (7), 115 (11), 106 (7), 105 (83), 77 (28), 55 (6), 52 (6), 51 (10), 41 (6), 39 (8), 32 (17), 28 (100), 27 (5), 18 (52), and 17 (10).

Anal. Calcd for $C_{16}H_{14}O_3$: C, 75.57; H, 5.55. Found: C, 75.47; H, 5.82.

Photooxygenation of 1b and 1e in Methanol at −78 °C. A solution of 100 mg (0.486 mmol) of **1b** in 10 ml of 9.1 methanol–acetone solution containing 0.1 mg of rose bengal took up 22 ml (2.0 equiv) of oxygen during 3 h. The solution was warmed to room temperature and evaporated; the NMR ($CDCl_3$) spectrum was almost identical with that taken after the photooxygenation in acetone. A small resonance at 9.64 ppm (presumably due to **16b**) was observed (<1%). No fluorescence was observed in the dark on heating the solution in the presence of 9,10-diphenylanthracene.

A similar photooxygenation of 100 mg (0.695 mmol) of **1e** in 10 ml of methanol took up 25.5 ml (1.50 equiv) of oxygen during 2 h. The NMR ($CDCl_3$) spectrum of the evaporated solution gave similar results.

Photooxygenation of 1b and 1e in Methanol at Room Temperature. The above photooxygenations were repeated at room temperature. **1e** took up 16.8 ml (1.0 equiv) of oxygen during 30 min; the NMR ($CDCl_3$) spectrum showed a resonance near 9.6 ppm attributable to ~12% **16e.** When the NMR solution was saturated with 9,10-diphenylanthracene and heated to ~80°C, only a very weak fluorescence was observed in the dark. **1b** took up 16.4 ml (1.38 equiv) of oxygen during 35 min; the NMR ($CDCl_3$) spectrum showed a resonance near 9.6 ppm (~23% **16e**), and no fluorescence was observed on the addition of 9,10-diphenylanthracene. The NMR spectra did show the presence of the endoperoxides **2b** and **3b.**

Registry No.—**1a,** 20669-52-7; **1b,** 7469-40-1; **1c,** 57652-90-1; **1d,** 1022-15-7; **1e,** 4373-13-1; **1f,** 447-53-0; **2b,** 57652-91-2; **2c,** 57652-92-3; **2e,** 57652-93-4; **2f,** 57652-94-5; **3b,** 57694-05-0; **3c,** 57694-06-1; **3e,** 57694-07-2; **3f,** 57694-08-3; **4a,** 57652-95-6; **4c,** 57652-96-7; **4d,** 57652-97-8; **4e,** 57652-98-9; **4f,** 57652-99-0; **5d,** 57653-00-6; **6a,** 612-94-2; **6c,** 30877-08-8; **6e,** 90-12-0; **7b,** 57653-01-7; **7c,** 57653-02-8; **7e,** 57653-03-9; **7f,** 57653-04-0; **8b,** 57694-09-4; **8c,** 57694-10-7; **8e,** 57694-11-8; **8f,** 57694-12-9; **9e,** 57653-05-1; **11b,** 57653-06-2; **11c,** 57653-07-3; **11e,** 57653-08-4; **11f,** 57653-09-5; **12b,** 57694-13-0; **12c,** 57694-14-1; **13b,** 57653-10-8; **14b,** 57694-15-2; **30,** 39078-08-5; **31,** 51153-58-3; 2-phenyl-1-tetralone, 7498-87-5; α-tetralone, 529-34-0; oxygen, 7782-44-7; 1-hydroxy-2-phenyl-1,4-dihydronaphthalene, 57653-11-9; 1-hydroxy-1-methyl-1,4-dihydronaphthalene, 2042-22-0; trimethyl phosphite, 121-45-9.

References and Notes

(1) (a) Part XXIII: P. A. Burns, C. S. Foote, and S. Mazur, *J. Org. Chem.*, preceding paper in this issue. (b) Supported by National Science Foundation Grants GP 37165X and GP 25790 and Public Health Service Grants AP-00681 and GM 20080. (c) Taken in part from P. A. Burns, Dissertation, University of California, Los Angeles, 1975.

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Thermal and Photochemical Decomposition of Silver Carboxylates

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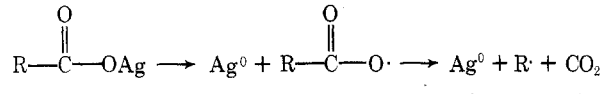
Silver salts of carboxylic acids decompose at 200–350 °C to silver, carbon dioxide, and radicals. Silver benzoate at 276 °C gives polyphenyls containing two to five benzene rings, as well as benzene, benzoic acid, and 3,4-benzocoumarin. Arylation of benzophenone was effected by silver benzoate at 300 °C, along with formation of biphenyl and benzophenone dimer. An intimate mixture of silver isonicotinate and silver benzoate at 275 °C gave coupling products of phenyl and pyridyl radicals with themselves and with each other. Silver trifluoroacetate decomposes thermally above 260 °C or irradiated with ultraviolet light in solution at 25 °C, to silver, carbon dioxide, and trifluoromethyl radicals. As silver trifluoroacetate, unlike most silver salts, is relatively soluble in organic solvents, it may be used as a convenient source of trifluoromethyl radicals. With benzene at 325 °C it gave 38 mol % of benzotrifluoride; 57 mol % of benzotrifluoride resulted from the photochemical reaction. Benzonitrile gave a good yield of the three isomeric trifluoromethyl benzonitriles, mainly ortho. With 4-benzoylpyridine at 300 °C silver trifluoroacetate gave derivatives formed predominantly by addition of trifluoromethyl radicals to the benzene ring. Silver salts of polycarboxylic acids decompose at 200–425 °C to silver, carbon dioxide, and products apparently formed from polyradicals. Silver isophthalate, pyrolyzed under nitrogen at 375 °C and cooled under hydrogen, gives silver imbedded in a black, carbonlike polymer that ignites at 25 °C when exposed to air. Different silver salts give a wide variety of different shapes upon being pyrolyzed. Heteroatoms are retained; silver pyridine-3,5-dicarboxylate at 310 °C yielded carbon dioxide, silver, and black polymer with the theoretical amount of nitrogen. Considerable control of pore-size distribution and surface area for silver imbedded in carbonlike polymers has been achieved by pyrolyzing the appropriate silver polycarboxylate. Silver carboxylates represent a new class of stable radical precursors of great variety, ready availability, and easy preparation.

As organic chemistry developed in the middle and late 19th century, silver salts of carboxylic acids were among the first derivatives prepared, primarily because they were easy to make and to purify. Surprisingly, except for a few scattered references in the literature dealing with explosives,[1] the behavior of silver carboxylates at elevated temperatures has been wholly ignored.

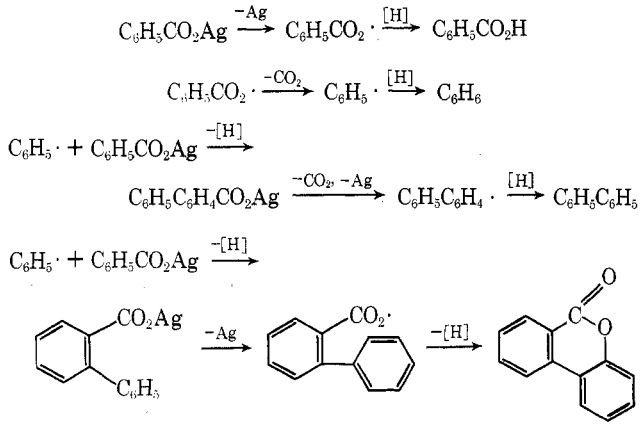
We have discovered that silver carboxylates decompose, when heated, according to the scheme



As an example, 45.8 g (200 mmol) of silver benzoate (276 °C dec), heated in a Pyrex tube under a stream of nitrogen to 280 °C for 1 min, gave the products shown in Table I. The gas evolved, together with benzoic acid and benzocoumarin, accounted for 196 mmol (98%) of CO_2; the products listed in Table I accounted for 197.4 mmol (98.7%) of phenyl radicals.

Silver benzoate was pyrolyzed under a variety of conditions: diluted with twice its weight of silica; in a bomb under 300 psi autogenous pressure; and in a pellet formed under 10 000 psi. In all cases the identical products were formed and in about the same proportions.

Benzene and benzoic acid are the products of hydrogen abstraction by phenyl and benzoyloxy radicals, respectively.[2] Biphenyl and higher polyphenyls may form by phenylation of silver benzoate and subsequent decomposition; ortho phenylation gives 3,4-benzocoumarin. Some biphenyl may result from dimerization of phenyl radicals trapped in a solid matrix, although dimerization is not favored in liquid or gas phase reactions of phenyl radicals.[3]



Silver salts of substituted benzoic acids behave similarly to silver benzoate. Silver *p*-fluorobenzoate and silver pentafluorobenzoate, each decomposed at 300 °C under nitrogen, gave the products shown in Tables II and III, respectively.

Among the heterocyclic compounds, silver thiophene-2-carboxylate at 275 °C gave thiophene and bithiophene in a weight ratio of 3:1. Silver salts of pyridinecarboxylic acids at 280–320 °C gave bipyridyls and terpyridyls with varying amounts of pyridine, as shown in Table IV. Hydrogen ab-