The mass spectra of both the heated and the unheated samples were essentially identical. The sample after heating was scanned to *m/e* 1600 and no peak corresponding to a dimer of 1 was observed. The C and H analyses for both the heated and unheated samples were satisfactory.

Registry No.—2, 479-33-4; 3, 16510-49-9; 4, 3432-73-3; 6, 16325-29-4; 7, 59907-77-6; 8, 13092-45-0.

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On the Photochemistry of Hexamethyl-2,4-cyclohexadienone 4,5-Epoxide and on Subsequent Rearrangements of Its Photoisomer, *endo*-5-Acetyl-1,3,3,4,5-pentamethylbicyclo[2.1.0]pentan-2-one

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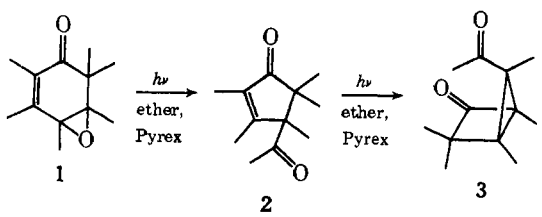
Irradiation (Pyrex) of hexamethyl-2,4-cyclohexadienone 4,5-epoxide (1) gives 2,3,4,5,5-pentamethyl-4-acetyl-2-cyclopentenone (2), which then photoisomerizes to *endo*-5-acetyl-1,3,3,4,5-pentamethylbicyclo[2.1.0]pentan-2-one (3). This bicyclic diketone is photochemically and thermally labile. On irradiation in ether through Corex, 3 is converted to lactones 4 and 5. The thermal rearrangements of 3, which probably proceed via ketene 7, show a remarkable solvent effect. In carbon tetrachloride the products are 2 and lactone 8, whereas in methanol the products are lactones 9 and 10. Mechanisms for all these transformations are proposed and supported by deuterium labeling experiments.

Although the photochemistry of α,β-epoxy ketones has been extensively studied,[1] only recently have the vinylogous α,β-unsaturated γ,δ-epoxy ketones received attention.[2-6] The few results reported thus far suggest that this class of epoxy ketones undergoes a wide range of fascinating photochemical rearrangements.

One class of easily accessible[7] α,β-unsaturated γ,δ-epoxy ketones whose photochemistry has not been studied are the 2,4-cyclohexadienone 4,5-epoxides. In this paper we describe the irradiation of hexamethyl-2,4-cyclohexadienone 4,5-epoxide (1).[8] The initial photoproduct undergoes further photoisomerization to a second product which itself is both photo- and thermolabile, resulting in an interesting array of molecular rearrangements.

Results and Discussion

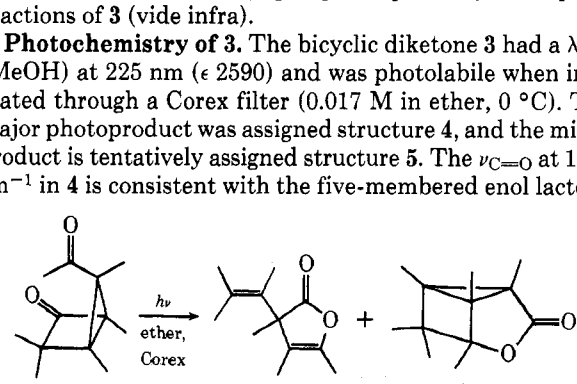
Photochemistry of 1. Irradiation of 1 (0.01 M in ether, 0 °C) through Pyrex was followed by NMR. As peaks due to 1 decreased in intensity, a new set of peaks which could be ascribed to the known 2[8] appeared. At 50% conversion both sets of peaks began to diminish in area in favor of a third set of peaks. After 16 h only the third set was present, and a crystalline product to which we assign structure 3 was isolated in



1 2 3

90% yield.[9] The structural assignment is based on spectra and on chemical transformations. Ir bands at 1760 and 1710 cm^{-1} are attributed to the cyclobutanone and acetyl absorptions, respectively. The absence of ir bands in the 1500–1680-cm^{-1} region together with the fact that all the methyl signals in the NMR spectrum (except the acetyl methyl, at δ 2.15) appeared as singlets above δ 1.3 indicated the absence of C=C bonds. The mass spectrum showed that 3 was an isomer of 1 and 2 (M^+ 194, 20%); the base peak at *m/e* 152 corresponded to loss of ketene (presumably from the acetyl group). The endo configuration for the acetyl group is required by subsequent reactions of 3 (vide infra).

Photochemistry of 3. The bicyclic diketone 3 had a λ_{max} (MeOH) at 225 nm (ϵ 2590) and was photolabile when irradiated through a Corex filter (0.017 M in ether, 0 °C). The major photoproduct was assigned structure 4, and the minor product is tentatively assigned structure 5. The $\nu_{C=O}$ at 1790 cm^{-1} in 4 is consistent with the five-membered enol lactone



3 4 (79.6%) 5 (20.4%)

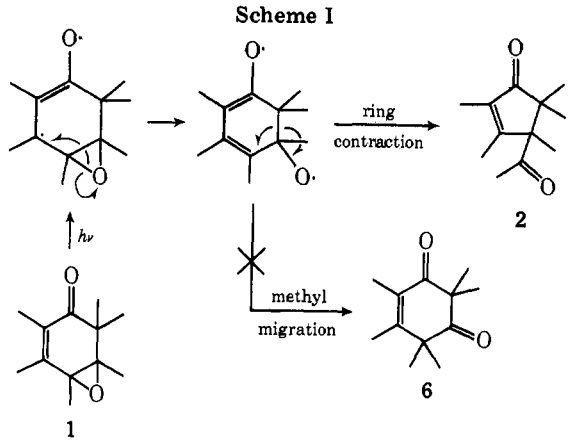
moiety. The NMR spectrum of 4 showed two homoallylically coupled methyl signals at δ 1.50 and 1.87 assigned (from labeling experiments; vide infra) to the allylic methyls of the lactone ring. Other allylic methyl signals appeared at δ 1.70 (6 H) and 1.37 (3 H),[10] and the aliphatic methyl was a sharp singlet at δ 1.30.

The minor product 5 had a $\nu_{C=O}$ at 1760 cm^{-1} consistent with a strained five-membered lactone. The absence of ir bands in the 1500–1680-cm^{-1} region and the location of all methyl singlets in the NMR spectrum at or above δ 1.20 showed the absence of C=C bonds. The mass spectrum of 5

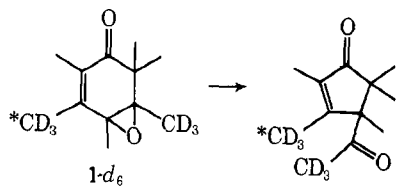
showed a small M^+ peak at m/e 194 (2%) and a base peak at m/e 135 corresponding to the loss of $CO_2 + CH_3$.[11]

Photochemical Mechanisms and Labeling Results. The photoisomerization of 1 to 2 proceeds according to Scheme I.[12]

Scheme I

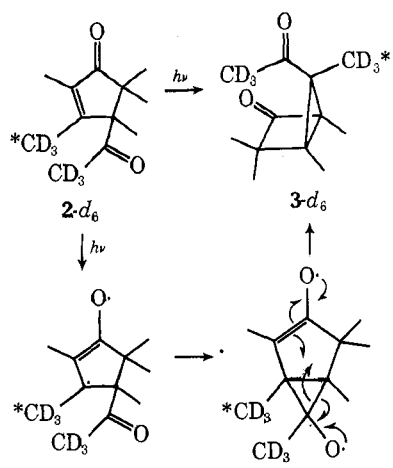


Following excitation and C_γ–O bond cleavage[2,3] a 1,2-alkyl shift occurs. Preferred ring contraction (to give 2) over methyl migration (to give 6) is consistent with the usual migratory aptitudes observed in the photorearrangement of α,β-epoxy ketones to β-diketones.[1,13] Consistent with this scheme, irradiation of labeled 1[8] (samples of 1-d_6, labeled in both the C-3 and C-5 methyl groups, and of 1*, labeled only in the C-3 or asterisked methyl group, were irradiated) gave labeled 2 as shown (the NMR spectrum of 2 is such that the location of the label was readily apparent).



The photoisomerization of 2 to 3 can be regarded as an oxa-di-π-methane rearrangement.[14] The reaction is stereoselective; only the endo-acetyl isomer is formed. Similar photoisomerizations of 4-acyl-2-cyclopentenones have been reported.[15,16] Consistent with this 1,2-acyl shift mechanism, we find the label results in Scheme II. The acetyl methyl label

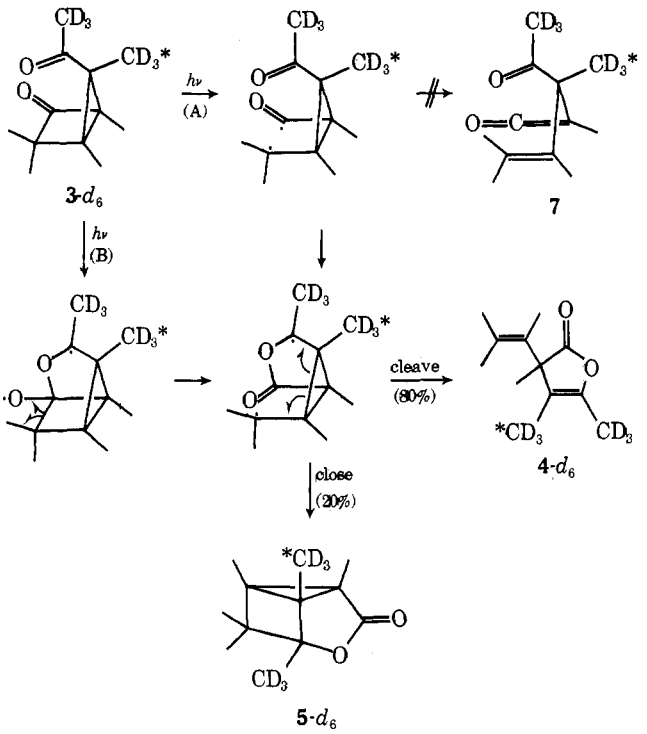
Scheme II



in 2-d_6 became the acetyl methyl in 3-d_6. On irradiation of 2*, the peak which disappeared from the spectrum of the resulting 3* was the peak at δ 1.23. Although there is no a priori way of assigning this signal from chemical shifts, we can confidently assign it (i.e., the CD_3* group in 3) to the C-5 methyl position as shown because of the label location in the products of subsequent photochemical and thermal rearrangements of 3 (vide infra).

Plausible mechanisms for the photoisomerization of 3 to 4 and 5 are shown in Scheme III. The formation of lactones

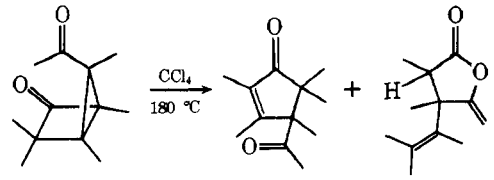
Scheme III



4 and 5 requires the endo geometry for the acetyl group in 3. Two paths (A and B) are possible. Path A begins with Norrish type I cleavage of the cyclobutanone ring, followed by lactonization to give a 1,4 diradical that can either cleave to give 4 or close to give 5. A possible flaw in this route is that the first formed diradical might be expected to cleave to give the ketene 7. Indeed the conversion of 3 → 7 does occur thermally (vide infra), but is not observed photochemically. Consequently we propose path B as perhaps a better alternative for the photoisomerization mechanism of 3. Both paths lead to the same diradical, but path B avoids an intermediate which could give ketene 7. The labeling consequences of both paths are identical; the paths differ only in the timing of events.

Irradiation of 3-d_6 gave 4-d_6 lacking methyl signals at δ 1.50 and 1.87. Irradiation of 3* gave 4* lacking the methyl signal at δ 1.50 and with the quartet at δ 1.87 (homoallylic coupling, J = 1 Hz) sharpened to a singlet. Consequently the two labeled methyl groups in 4-d_6 must be adjacent to one another, as shown in the structure and predicted from the mechanism in Scheme III. It is reasonable that of the two labeled methyl groups, the one at lower field (δ 1.87) is adjacent to the lactone oxygen atom.

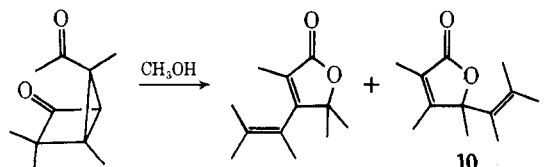
Thermal Rearrangements of 3. Diketone 3 was thermally labile. At room temperature the ir spectrum showed, in addition to the carbonyl bands at 1760 and 1710 cm^{-1}, a well-defined band at 2300 cm^{-1} attributable to a ketene. The relative intensities of these bands remained constant with time, suggesting an equilibrium between 3 and the ketene. Gradually, however, both sets of peaks decreased in intensity and were replaced with a new set of peaks characteristic of 2. Indeed, when 3 was stored for several weeks at −15 °C in the solid state it slowly reverted to 2. When 3 was heated in CCl_4 solution at 180 °C (sealed tube) it was converted mainly to 2, though a minor product to which we assign structure 8 was also



3 2 8

formed. The mass spectrum of 8 (M^+ *m/e* 194, 32%) showed it to be an isomer of **3**. The $\nu_{C=O}$ at 1795 cm^{-1} was characteristic of an enol lactone. The NMR spectrum showed two vinyl protons (δ 4.07, 4.53), and a mutually coupled methyl doublet at δ 1.02 and methine quartet at δ 2.38, the latter having a chemical shift consistent with location α to the carbonyl group. In addition there was a sharp methyl singlet at δ 1.50 and peaks due to the allylic methyls at δ 1.60 (6 H) and 1.70 (3 H).

Believing ketene **7** to be an intermediate in the conversion of **3** to **2** and **8**, and hoping to trap the ketene, we treated **3** with a few drops of methanol at room temperature. Under these conditions **3** rearranged to two new isomers **9** and **10** (in the



3 9 10

ratio 1:3). Each product had a $\nu_{C=O}$ at 1745 cm^{-1} consistent with a Δ^1-butenolide structure. Compound **9** had λ_{max} (MeOH) at 223 nm (ε 2600) and 255 (1070) consistent with the extended conjugated system, whereas **10** had a normal Δ^1-butenolide spectrum, λ_{max} (MeOH) 230 nm (ε 3100). The NMR spectrum of **9** showed a 6 H singlet at δ 1.40 for the *gem*-dimethyl group, and two 6 H multiplets at δ 1.60 and 1.77 for the four allylic methyl groups. Shift reagent showed that one of the peaks at δ 1.60 was due to the methyl α to the carbonyl group. The NMR spectrum of **10** showed only one aliphatic methyl singlet (δ 1.53) and five allylic methyls, as multiplets at δ 1.62 (6 H) and 1.72 (6 H) and a quartet at δ 1.82 due to the C-3 methyl (shown by deuterium labeling to be coupled to the C-2 methyl at δ 1.72).

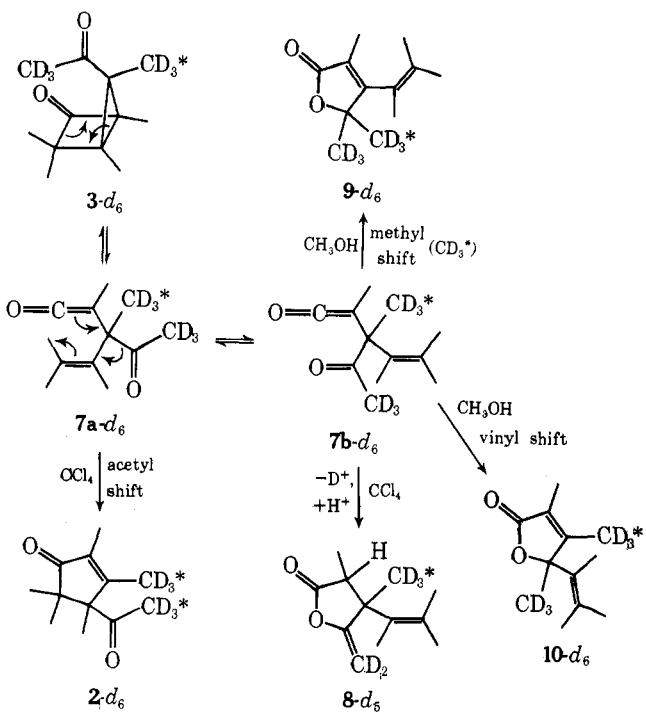
Mechanism of the Thermal Rearrangements of 3, and Supporting Labeling Experiments. We believe that all of the thermal rearrangement products of **3** (i.e., **2, 8, 9** and **10**) are derived from ketene **7** as shown in Scheme IV. Cyclization of the ketene in conformation **7a**, accompanied by a 1,2-acetyl shift as indicated by the arrows, can give **2**. Cyclization from conformation **7b** gives the three lactones. This can occur without any group migrations but with proton loss from the acetyl methyl group to give **8**, or with rearrangement of a methyl or vinyl group to give **9** and **10**, respectively.

We have no explanation for the dramatic solvent effects on these reactions. The inability of methanol to trap ketene **7** is not surprising, however, since hindered ketenes often are inert toward this relatively weak nucleophile.[17]

As indicated in Scheme IV, the proposed mechanisms imply certain labeling consequences, and these were verified experimentally. Rearrangement of **3*** in carbon tetrachloride gave **2*** in which the peak at δ 1.95 diminished in area from 6 H to 3 H, and that at δ 1.75 (due to the C-2 methyl) sharpened to a singlet. From **3**-d_6, the resulting **2**-d_6 lacked entirely the six-proton δ 1.95 peak due to the C-3 and acetyl methyls. In the same experiments, the resulting **8*** lost the sharp aliphatic methyl singlet at δ 1.50 and the **8**-d_5 lost the vinyl signals at δ 4.07 and 4.53 as well.

Rearrangement of **3*** in methanol gave **9*** in which the signal δ 1.40 due to the *gem*-dimethyl group decreased in area

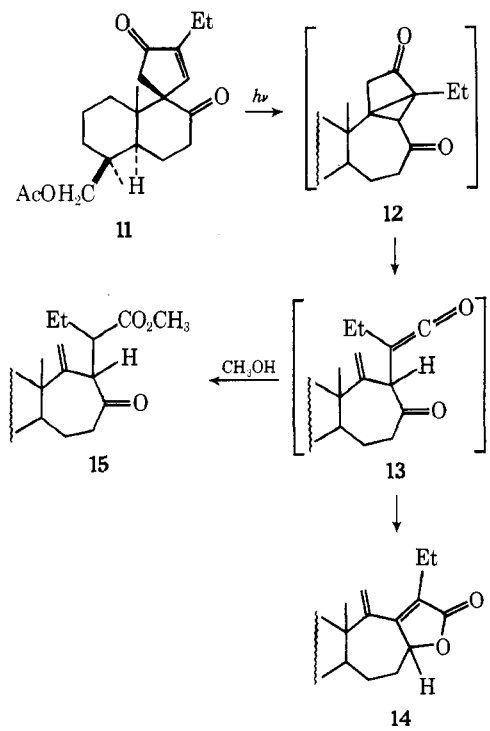
Scheme IV



from 6 H to 3 H; starting with **3**-d_6 this peak in **9**-d_6 disappeared entirely. In the same experiments, the resulting **10*** lacked the quartet at δ 1.82 and the peak at δ 1.72 sharpened to a singlet; in addition to these changes, the resulting **10**-d_6 also lacked the singlet at δ 1.53.

All the labeling results are consistent with the mechanism in Scheme IV.

Some thermal rearrangements similar to those of **15** have been reported,[15,16,18] and in some cases[18] the intermediate ketene can be trapped with methanol. For example, the irradiation of **11** gave the butenolide **14**,[18] presumably via dike-



tone **12** which then thermally rearranged to ketene **13**. When the irradiation of **11** was run in methanol, the product was **15**.

In summary, through photochemical or thermal rear-

rangements we have converted the epoxy ketone **1** to a rather wide array of structural isomers (**2, 3, 4, 5, 8, 9,** and **10**) and have established plausible mechanisms for these rearrangements. We are continuing to investigate structural effects on these rearrangements.

Experimental Section[19]

Irradiation of 4,5-Epoxy-2,3,4,5,6,6-hexamethyl-2,4-cyclohexadienone (1). A degassed solution of **1**[8] (50 mg, 0.26 mmol) in 25 ml of anhydrous ether was irradiated through Pyrex at 0 °C with a 450-W Hanovia Type L lamp. The reaction was followed by NMR. Signals due to **1** decreased in intensity as new peaks due to **2**[8] appeared. Gradually both sets of peaks were replaced by a new set due to **3**; the conversion of **1** to **3** required 16 h. Evaporation of the ether and recrystallization from petroleum ether (bp 30–60 °C) gave 5-acetyl-1,3,3,4,5-pentamethylbicyclo[2.1.0]pentan-2-one (**3**) as a white solid (45 mg, 90%, decomposed on heating): ir (CCl_4) 3000 (m), 1760 (s), 1710 (s), 1470 (w), 1400 (w), 1370 (w), 1230 cm^{-1} (w); uv (MeOH) λ_{max} 225 nm (ϵ 2590); NMR (CCl_4) δ 0.77 (s, 3 H, C-3 methyl), 1.07 (s, 3 H, C-3 methyl), 1.18 (s, 3 H), 1.23 (s, 3 H, C-5 methyl), 1.27 (s, 3 H), 2.15 (s, 3 H, acetyl methyl); mass spectrum (70 eV) *m/e* (rel intensity) 195 (3), 194 (20), 179 (9), 153 (13), 152 (100), 151 (31), 150 (9), 137 (56), 123 (48), 108 (54), 93 (28), 91 (18), 81 (34), 79 (13). Owing to the thermal instability of **3**, no attempt was made to obtain an elemental analysis.

Irradiation of Labeled 1. The irradiation and workup conditions were as described for the unlabeled epoxy ketone. From 4,5-epoxy-3-trideuteriomethyl-2,4,5,6,6-pentamethyl-2,4-cyclohexadienone (**1***) the resulting **2*** had an NMR spectrum identical with that of unlabeled **2**[8] except that the signal at δ 1.95 (C-3 and acetyl methyls) was reduced in area from 6 H to 3 H and the quartet at δ 1.75 (C-2 methyl) sharpened to a singlet. The **3*** obtained from further irradiation had an NMR spectrum identical with that of unlabeled **3** except that the singlet at δ 1.23 (C-5 methyl) was absent.

From 4,5-epoxy-3,5-bis(trideuteriomethyl)-2,4,6,6-tetramethyl-2,4-cyclohexadienone (**1-d_6**), the resulting **2-d_6** had an NMR spectrum identical with that of **2*** except that the signal at δ 1.95 (C-3 and acetyl methyls) was entirely absent. The **3-d_6** obtained from further irradiation had an NMR spectrum identical with that of **3*** except that the signal at δ 2.15 (acetyl methyl) was absent.

Irradiation of 5-Acetyl-1,3,3,4,5-pentamethylbicyclo[2.1.0]-pentan-2-one (3). A degassed solution of 100 mg (0.52 mmol) of **3** in 30 ml of anhydrous ether was irradiated through Corex with a 450-W Hanovia lamp at 0 °C. The photolysis was followed by NMR, and was complete in about 12 h. Analytical VPC (5 ft × 0.125 in. column, 10% FFAP on Chromosorb W, AW-DMCS 80/100, 165 °C) showed two components: **4** (79.6%, retention time 5 min) and **5** (20.4%, 7 min). Preparative VPC (5 ft × 0.25 in. column, 10% FFAP on Chromosorb W, 80/100, 145 °C) gave the pure lactones.

For **4**: ir (CCl_4) 2960 (w), 2910 (m), 2850 (w), 1790 (s), 1700 (w), 1450 (m), 1385 (m), 1370 (w), 1365 (w), 1290 (w), 1275 (w) 1225 (m), 1030 (s), 980 (m), 930 cm^{-1} (w); uv (EtOH) only end absorption; NMR (CCl_4), see footnote 20; the peaks at δ 1.50 and 1.87 were quartets, J = 1 Hz; mass spectrum (70 eV) *m/e* (rel intensity) 194 (13), 179 (6), 151 (100), 126 (21), 123 (35), 81 (26), 67 (14), 55 (15), 53 (19).

A microanalysis was done on a hexadeuterio sample of this lactone (**4-d_6**). Anal. Calcd for $C_{12}H_{12}D_6O_2$: C, 71.94. Found: C, 72.00.

For lactone **5**: mp 104–106 °C; ir (CCl_4) 2950 (m), 2920 (m), 2850 (m), 1760 (s), 1460 (w), 1380 (m), 1300 (m), 1050 (m), 950 cm^{-1} (m); uv (EtOH) λ_{max} 220 nm (ϵ 890); NMR (CCl_4) δ 0.70 (s, 3 H), 1.03 (s, 3 H), 1.12 (s, 6 H), 1.17 (s, 3 H), 1.20 (s, 3 H); mass spectrum (70 eV) *m/e* (rel intensity) 194 (2), 179 (2), 155 (55), 135 (100), 120 (16), 119 (42), 107 (19), 104 (22), 93 (21), 91 (27), 44 (60), 43 (25), 41 (24), 39 (20).

Anal. Calcd for $C_{12}H_{18}O_2$: C, 74.19; H, 9.34. Found: C, 74.22; H, 9.36.

Irradiation of Labeled 3. The conditions and workup procedure were as for the unlabeled material. From **3*** the resulting **4*** had an NMR spectrum identical with that of **4** except that the signal at δ 1.50 was absent and the peak at δ 1.87 sharpened to a singlet. The spectrum of the resulting **5*** was identical with that of **5** except that the singlet at δ 1.17 was absent.

From **3-d_6** the resulting **4-d_6** had an NMR spectrum identical with that of **4** except that the signals at δ 1.50 and 1.87 were absent. The NMR spectrum of the resulting **5-d_6** was identical with that of **5** except that the singlets at δ 1.17 and 1.20 were absent.

Thermal Rearrangement of 3 in CCl_4. When **3** (40 mg, 0.21 mmol) in 0.5 ml of CCl_4 was heated in a sealed tube at 180 °C for 3 h it was converted to a mixture of **2**[8] and **8** (ca. 9:1 by NMR). Preparative VPC (5 ft × 0.25 in. column, 10% FFAP on Chromosorb W, 80–100 mesh, 160 °C) gave diketone **2** (retention time 45 min) and lactone **8** (retention time 35 min). For lactone **8**: ir (CCl_4) 2950 (w), 1795 (s), 1695 (w), 1660 (m), 1460 (m), 1390 (w), 1250 (w), 1200 (w), 1130 (w), 1080 (w), 1050 (m), 990 (w), 860 cm^{-1} (w); uv (MeOH) λ_{max} 225 nm (ϵ 1310); NMR (CCl_4) see footnote 20; the peaks at δ 1.02 and 2.38 were a doublet and a quartet, respectively, J = 7 Hz, the peaks at δ 4.07 and 4.53 were doublets, J = 2 Hz, and the peak at δ 1.60 (6 H) was a multiplet; mass spectrum (70 eV) *m/e* (rel intensity) 194 (32), 179 (32), 152 (23), 151 (100), 137 (29), 136 (15), 133 (25), 123 (13), 121 (10), 109 (20), 107 (10), 91 (14), 81 (12), 79 (12), 77 (14).

Anal. Calcd for $C_{12}H_{18}O_2$: C, 74.19; H, 9.34. Found: C, 74.15; H, 9.34.

Thermal Rearrangement of Labeled 3 in CCl_4. The conditions and workup procedure were as described for unlabeled **3**. From **3*** the resulting **2*** had an NMR spectrum identical with that of unlabeled **2**[8] except that the peak at δ 1.95 (C-3 methyl and acetyl methyl) was reduced in area from 6 H to 3 H and the peak at δ 1.75 (C-2 methyl) sharpened to a singlet. The resulting **8*** had an NMR spectrum identical with that of unlabeled **8**[20] except that the singlet at δ 1.50 was absent. From **3-d_6** the resulting **2-d_6** had an NMR spectrum identical with that of **2*** except that the signal at δ 1.95 was absent. The resulting **8-d_5** had an NMR spectrum identical with that of **8*** except that the vinyl proton signals at δ 4.07 and 4.53 were almost entirely absent.

Thermal Rearrangement of 3 in Methanol. When compound **3** was treated with a few drops of methanol, it rearranged to a mixture of lactones **9** and **10** (ca. 1:3 as determined by NMR spectrum). Preparative VPC (5 ft × 0.25 in. column, 10% FFAP on Chromosorb W, 80–100 mesh, 170 °C) gave lactone **9** (retention time 25 min): ir (CCl_4) 2950 (w), 1745 (s), 1700 (m), 1460 (w), 1380 (w), 1280 (m), 1080 (m), 980 cm^{-1} (m); uv (MeOH) λ_{max} 223 nm (ϵ 2600), 255 (1070); NMR (CCl_4) see footnote 20; the peaks at δ 1.60 and 1.77 were multiplets; mass spectrum (70 eV) *m/e* (rel intensity) 195 (11), 194 (78), 179 (14), 151 (20), 136 (23), 123 (12), 109 (36), 108 (78), 107 (14), 93 (100), 91 (28), 77 (25), 65 (13), 53 (20).

Anal. Calcd for $C_{12}H_{18}O_2$: C, 74.19; H, 9.34. Found: C, 74.27; H, 9.50.

For lactone **10** (retention time 45 min): ir (CCl_4) 2950 (w), 1745 (s), 1450 (w), 1390 (w), 1330 (w), 1260 (w), 1130 (w), 1090 cm^{-1} (w); uv (MeOH) λ_{max} 230 nm (ϵ 3100); NMR (CCl_4) see footnote 20; the peak at δ 1.82 was a quartet, J = 1 Hz, and the peaks at δ 1.62 and 1.72 were multiplets; mass spectrum (70 eV) *m/e* (rel intensity) 194 (25), 179 (32), 151 (36), 150 (28), 149 (100), 137 (10), 136 (7), 135 (29), 134 (14), 133 (18), 126 (53), 125 (48), 123 (43), 119 (15), 109 (11), 107 (10), 97 (16), 93 (10), 91 (14), 81 (20).

Anal. Calcd for $C_{12}H_{18}O_2$: C, 74.19; H, 9.34. Found: C, 74.20; H, 9.47.

Thermal Rearrangement of Labeled 3 in Methanol. The conditions and workup procedure were as with unlabeled material. From **3*** the resulting **9*** had an NMR spectrum identical with that of **9**[20] except that the peak at δ 1.40 was reduced in area from 6 H to 3 H. The resulting **10*** had an NMR spectrum identical with that of **10**[20] except that the signal at δ 1.82 was absent and the multiplet at δ 1.72 sharpened to a singlet. From **3-d_6** the resulting **9-d_6** had a spectrum identical with that of **9**[20] except that the 6 H peak at δ 1.40 was absent. The resulting **10-d_6** had an NMR spectrum identical with that of **10*** except that the singlet at δ 1.53 was absent.

Acknowledgment. We are indebted to the National Institutes of Health (GM 15997) and the National Science Foundation (GP 43659X) for their support of this research.

Registry No.—**1**, 50506-42-8; **1***, 50506-43-9; **1-d_6**, 50506-44-0; **3**, 59873-39-1; **3***, 59873-40-4; **3-d_6**, 59873-41-5; **4**, 59873-42-6; **4-d_6**, 59873-43-7; **5**, 59873-44-8; **8**, 59873-45-9; **9**, 59873-46-0; **10**, 59873-47-1.

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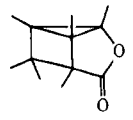
(8) The synthesis and acid-catalyzed rearrangement of **1** has been described: H. Hart, I. Huang, and P. Lavrik, *J. Org. Chem.*, **39**, 999 (1974).
(9) We are indebted to P. Lavrik for initial studies on this system.
(10) The chemical shift of this allylic methyl, which is at a remarkably high field, may be a consequence of shielding by the lactone carbonyl group.
(11) An alternative structure for **5** is



Although this structure seems highly unlikely from a mechanistic viewpoint (see Scheme III), it cannot be conclusively eliminated from the structural data available.
(12) In a future paper we will show that this is not always the only path followed by 2,4-cyclohexadienone 4,5-epoxides and that it depends in part on the substituents attached to the ring.
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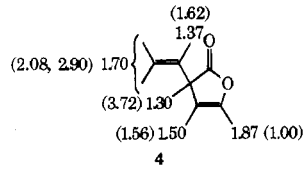
(19) NMR spectra were measured in $CDCl_3$ or CCl_4 solutions using Me_4Si as an internal standard, on a Varian T-60 or HA-100 spectrometer. Ir spectra were recorded on a Perkin-Elmer 237 grating spectrophotometer and were calibrated against a polystyrene film. Uv spectra were obtained on a Unicam SP-800 spectrometer. Mass spectra were obtained with a Hitachi Perkin-Elmer RMU-6 operated at 70 MeV; we are indebted to Mrs. Ralph Guile for this service. Melting points were determined with a Thomas-Hoover melting point apparatus and are uncorrected. Analyses were performed by Spang Microanalytical Laboratories, Ann Arbor, Mich.
(20) The NMR assignments for **4, 8, 9,** and **10,** are shown below in δ units, with relative downfield shifts in the presence of Eu(fod)$_3$ given in parentheses.



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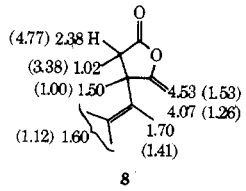

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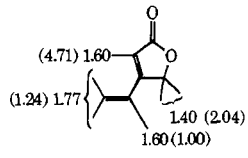

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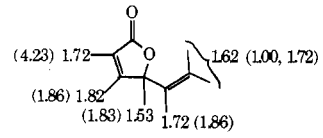

10

Thermal α-Deoxysilylation of *N,O*-Bis(Trimethylsilyl)-*N*-phenylhydroxylamine

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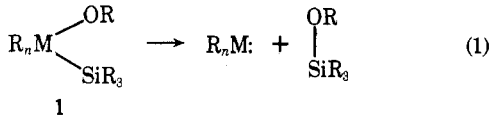
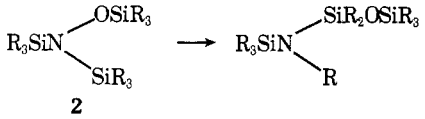
Heating *N,O*-bis(trimethylsilyl)-*N*-phenylhydroxylamine (**4**) at 100 °C in cyclohexene leads to expulsion of hexamethyldisiloxane and formation of mainly aniline (53%), together with a small amount (2%) of 7-phenyl-7-azabicyclo[4.1.0]heptane, and other minor products consistent with the intermediacy of phenylnitrene (PhN̈:). Attempts to trap PhN̈: with stilbenes met with only very limited success; however, thermolysis of **4** in the presence of diethylamine, dibutylamine, and cyclohexylamine gave 85–95% yields of ring-expanded azepine trapping products. The yield of aniline varied (~20–80%) with solvent and was found to generally parallel the H-donating ability of a solvent. Kinetic experiments demonstrated that the thermal fragmentation of **4** is unimolecular and is characterized by $\Delta H^{\ddagger}$ = 27.7 kcal/mol and $\Delta S^{\ddagger}$ = −3.8 eu. The effect of inert solvent variation on the thermolysis rate of **4** is small; a maximal rate acceleration factor of ~6.5 obtains for benzonitrile vs. hexafluorobenzene. A limited amount of comparative thermolysis data was obtained for *O*-methyl-*N*-trimethylsilyl- (**9**) and *O*-methyl-*N*-triethylsilyl-*N*-phenylhydroxylamine (**10**). Various mechanistic aspects relating to the intermediacy of PhN̈: are briefly discussed.

Thermally induced fragmentations of compounds represented by general structure **1** to afford an electron-deficient species and a silyl ether (eq 1) have been reported for cases



(1)

1



(2)

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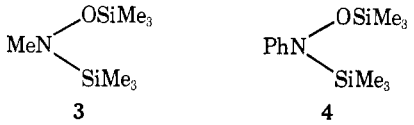

3 **4**

wherein M = C[1] and Si,[2] thus providing a method for carbene (R_2C:) and silylene (R_2Si:) generation, respectively. While such α-deoxysilylation reactions do not apparently obtain for tris(organosilyl)hydroxylamines (**2**), which instead undergo rearrangement according to eq 2,[3] Boudjouk and West[3] were the first to note that hexamethyldisiloxane ($Me_3SiOSiMe_3$) was formed upon heating *N,O*-bis(trimethylsilyl)-*N*-methylhydroxylamine (**3**), and thereby obtained prima facie evidence for the operation of eq 1 in a system having reaction center M = N. We have subsequently reported[4] preliminary observations regarding the thermolytic behavior of analogous silylated hydroxylamine derivatives, and now present details of solvent trapping and kinetic experiments with *N,O*-bis(trimethylsilyl)-*N*-phenylhydroxylamine (**4**), together with ancillary studies of two of its *O*-methyl relatives. Our findings are consistent with unimolecular fragmentation of **4** to afford phenylnitrene (PhN̈:).