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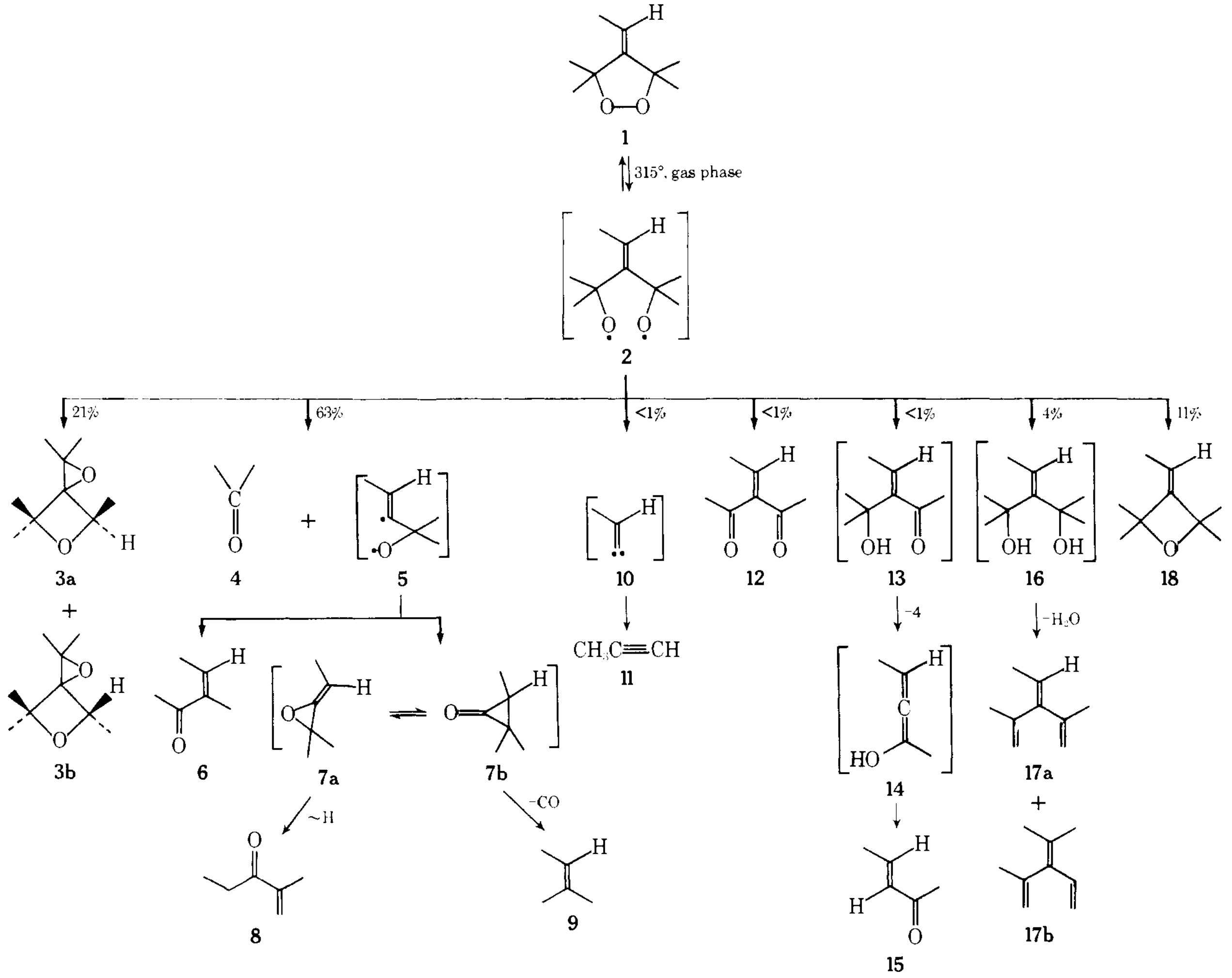
Thermolysis of the Cyclic Peroxide 4-Ethylidene-3,3,5,5-tetramethyl-1,2-dioxolane. Generation and Trapping of a 1,5-Diradical[1]

Sir:

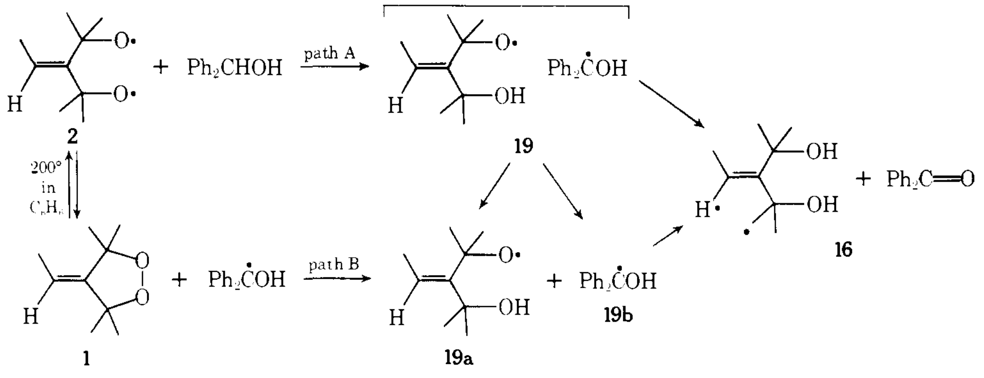
Due to the short lifetime ($\tau \leq 10^{-7}$ sec) of diradicals, it has been difficult to trap such reaction intermediates by external chemical means.[2] Factors that increase diradical lifetimes, e.g., electronic, conformational, and steric constraints, should enhance the chances of diradical trapping. Presently we report on such evidence in the thermolysis of the cyclic peroxide **1**. For example, static gas phase pyrolysis of **1** at 315° and 10 μ resulted in complete destruction of **1** within 5 hr, affording no less than 30 volatile products, of which **3a, b, 4, 6, 8, 9, 11, 12, 15, 17a, b,** and **18** (Scheme I) were isolated and characterized. Also ca. 19% involatile residue was formed in this thermolysis. However, heating of a benzene solution 1.3 *M* in **1** and 2.6 *M* in benzhydrol at 200° for 48 hr gave 1,3-diol **16** and benzophenone in stoichiometric amounts with no traces of rearrangement or cleavage products. In the absence of benzhydrol and under the same liquid phase thermolysis conditions, **1** did not decompose even after weeks of heating. Furthermore, in an effort of testing for surface catalysis and free radical chain processes, the gas phase pyrolysis was performed in an aged Pyrex vessel and in the presence of acetone, methanol, helium, nitrogen, and oxygen gases as diluents. The rate of decomposition and relative product composition of **1** were not affected, indicating that we were dealing with a clean unimolecular decompositon.

In Scheme I we offer a mechanistic rationalization for the formation of the gas phase thermolysis products of **1** in terms of the 1,5-diradical **2** as precursor, in analogy to our previous work on the thermolysis and photolysis of cyclic peroxides such as the 1,2-dixolanes,[3] β-peroxylactones,[4] γ-peroxylactones,[5] and 1,2-dioxanes,[6] which are efficient sources for diradicals. On thermal activation the oxygen-oxygen bond is cleaved in **1**, affording initially the 1,5-diradical **2**, which subsequently recyclizes into the isomeric epoxyoxetanes **3a** and **b**, fragments into acetone (**4**) and the 1,3-diradical **5**, or double hydrogen·abstracts to give the 1,3-diol **16** as major pathways. The latter dehydrates into the trienes **17a** and **b** under the thermolysis conditions, as confirmed by a control experiment for the authentic **16**. The 1,3-diradical **5** undergoes a 1,2-methyl shift to give the enone **6** or cyclizes to the allene oxide **7a**. The latter readily valence tautomerizes into the cyclopropanone **7b** and subse-

Scheme I



Scheme II

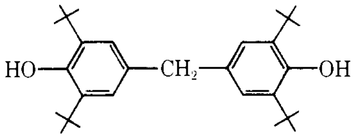


quent 1,4-hydrogen shift yields enone **8**, while decarbonylation affords olefin **9**. Similar chemistry of such 1,3-diradicals has been recently reported in the addition of triplet oxygen atoms to allenes.[7]

Minor, but mechanistically revealing, transformations of the 1,5-diradical **2** are double deketonation into vinylidene **10**, which subsequently rearranges to methylacetylene (**11**), double demethylation into enedione **12**, and the formation of the hydroxy ketone **13**, most likely via single demethylation and hydrogen abstraction. Control experiments show that **13** loses acetone (**4**) under the thermolysis conditions to give **15**, presumably via hydroxyallene **14**. The small amount of double deketonation is not surprising in view of our observation that malonyl peroxides resist double decarboxylation into methylenes. However, the lack of double demethylation of **2** to give **12** was unexpected since the related 1,3,5-trioxapentamethylenes, generated in the thermolysis[9a] and photolysis[9b] of ozonides, undergo such double fragmentations with great facility.

Our most convincing evidence for the 1,5-diradical **2** rests on the fact that in the presence of benzhydrol only diol **16** is formed, which under the liquid phase thermolysis conditions does not dehydrate into **17a** and **b** to any significant extent. Not even traces of rearrangement and fragmentation products are formed under these conditions, at which **1** is stable in the absence of benzyhydrol. Thus, the 1,5-diradical **2** is sufficiently long-lived that it is trapped by double hydrogen abstraction from benzhydrol via the caged radical pair **19** (path A, Scheme II). The alternative possibility of a very efficient radical chain process, carried by the hydroxymethyl radical **19b** (path B, Scheme II), in analogy to the mechanism of the reaction of *tert*-butyl peroxide with secondary alcohols,[10] could be ruled out by the following controls. The proposed chain carrying radical **19b** was generated by independent ways in the presence of the 1,2-dioxolane in order to test how susceptible **1** was toward free radical induced decomposition at the peroxide linkage. The radical **19b** was produced by thermolysis of *tert*-butyl peroxalate-Ph_2CHOH at 60°,[11] benzoyl peroxide-Ph_2CHOH at 90°, or *tert*-butyl peroxide-Ph_2CHOH at 135°,[10] and photolysis of Ph_2CHOH-$Ph_2C{=}O$ at 350 nm,[12] under conditions at which **1** was stable in the presence of benzhydrol alone. Although the *tert*-butyl peroxalate-Ph_2CHOH system did not promote consumption of **1**, the remaining three initiators did induce the decomposition of **1**, but without significant formation of the 1,3-diol **16**. Presumably with the latter initiators reaction at the double bond of **1** took place, diverting the reaction along alternative channels. Unfortunately, the experimental systems were too messy to permit product characterization and quantitation or kinetic scrutiny of these qualitative results.

Additional support for diradical trapping of **2** is provided by the observation that the 1,2-dioxolane **1** and bisphenol **20** afford 1,3-diol **16** and ketophenol **21** on heating. The latter is an efficient radical scavenger[13] and should have inhibited any radical chain process involving diradical **2**. Neither thermally nor photolytically could CIDNP[14] be generated from **1** in methanol.



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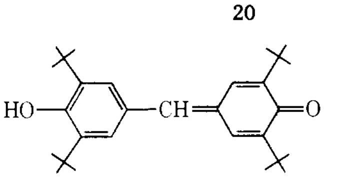

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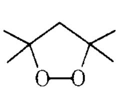

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The high thermal stability of the unsaturated 1,2-dioxolane **1** is unusual, especially if it is contrasted with the related 1,2-dioxolane **22**, the most stable dialkyl peroxide prior to this study,[3] which is destroyed in a few hours under conditions at which **1** shows insignificant decomposition after weeks of heating. The 4-alkylidene group in the 1,5-diradical **2** discourages deketonation due to electronic destabilization since a vinyl radical center would result, but it encourages reclosure to the cyclic peroxide **1** due to structural constraints since the two radical sites cannot wander apart sufficiently. Both factors enhance diradical lifetime. Thus, the high thermal stability of the cyclic peroxide **1** in part derives from fast but reversible rupture of the peroxide linkage to give the comparatively selective diradical **2**. The latter only occasionally climbs the extra energy hill to be converted into rearrangement and cleavage products, unless efficient hydrogen donors such as secondary alcohols intercept it, preventing reclosure to **1**.

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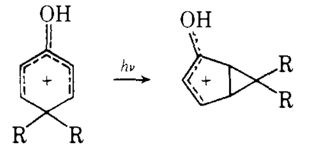
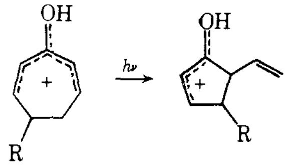
Novel Photorearrangements of Cyclic Cross-Conjugated Dienones in Sulfuric Acid. Transformations Involving a Stereospecific Symmetry-Forbidden Process

Sir:

The photochemistry of cyclic cross-conjugated dienones in strong acids is remarkably dependent on the ring size. The behavior of the six- and seven-membered dienones is illustrated in eq 1[1] and 2,[2] respectively. We report here two types of new rearrangements of protonated dienones and that one of them involves a stereospecific, orbital symmetry-forbidden process.

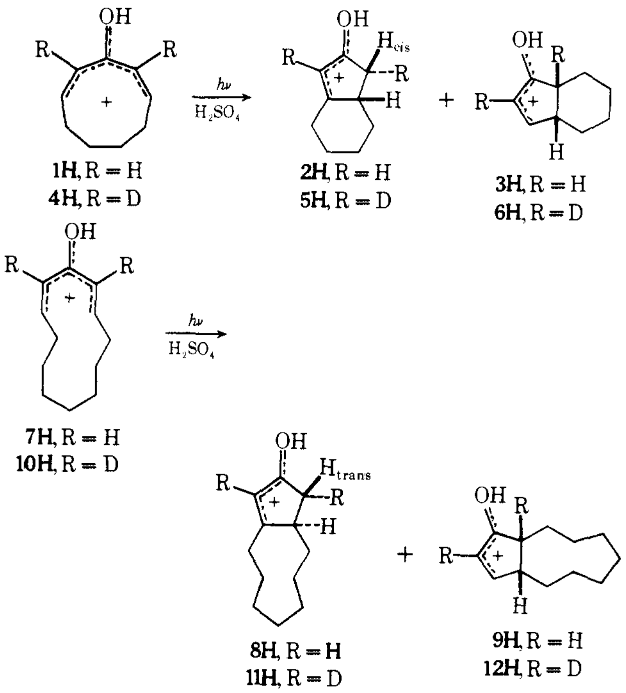


(1)



(2)

In the dark, 2,8-cyclononadienone (**1**) and 2,11-cyclododecadienone (**7**) in strong acids exist stable below room temperature. The oxygen-protonated cis,cis dienone **1H**[3] in 97% H_2SO_4 exhibits only one set of NMR signals due to the enone moiety at δ (TMS as external standard) 7.20 (d, J = 12 Hz, $CH{=}C\mathit{H}C{=}O^+H$) and 7.5–8.3 (m, $C\mathit{H}{=}CHC{=}O^+H$), whereas the cis,trans dienone **7H**[3] gives two sets of the vinylic proton signals at δ 6.76 (d, J = 12 Hz, *cis*-$CH{=}C\mathit{H}C{=}O^+H$), 7.30 (d, J = 15 Hz, *trans*-$CH{=}C\mathit{H}C{=}O^+H$), 7.1–7.5 (m, *cis*-$C\mathit{H}{=}CHC{=}O^+H$), and 8.1–8.8 (m, *trans*-$C\mathit{H}{=}CHC{=}O^+H$). When an H_2SO_4 solution of the dienone **1H** placed in a Pyrex tube in an ice-water bath was exposed to a 200-W high-pressure Hg arc, a 2:5 mixture of **2H** and **3H** was obtained. The photoreaction was very clean and proceeded quantitatively (uv analysis). The protonated cyclopentenone products were stable under the reaction conditions and no further skeletal changes were observed. Structures of **2H** and **3H** were established by isolation of the deprotonated ketones **2**[4] (ir (CCl_4) 1708 (C=O) and 1623 cm^{-1} (C=C); NMR (CCl_4) δ 5.66 (br s, =CH)) and **3** (ir 1710 cm^{-1} (C=O); NMR δ 6.03 (dd, J = 6 and 2 Hz, $CH{=}C\mathit{H}C{=}O$) and 7.52 (dd, J = 6 and 3 Hz, $C\mathit{H}{=}CHC{=}O$)) by careful quenching of the photolysate with solid $NaHCO_3$-ether at 0°. These ketones upon dissolving in H_2SO_4 regenerated **2H** and **3H** and by catalytic hydrogenation (Pd-C, C_2H_5OH gave the corresponding known cyclopentanones. In a similar manner, photolysis of **7H** gave a 7:3 mixture of **8H** and **9H** in quantitative yield. Spectral characteristics of the deprotonated enones were: **8** ir 1710, 1692, and 1609 cm^{-1}, NMR δ 5.95 (br s, =CH); **9** ir 1710 cm^{-1}, NMR δ 5.95 (dd, J = 6 and 2 Hz, $CH{=}C\mathit{H}C{=}O$) and 7.37 (dd, J = 6 and 3 Hz, $C\mathit{H}{=}CHC{=}O$). The cis-fused bicyclic enone **9** as well as the hydrogenated ketone was converted to the more stable trans isomer upon treatment with K_2CO_3-C_2H_5OH.



When the reaction course was monitored by uv-visible spectroscopy, absorptions of the starting protonated dienones decreased with simultaneous increase in absorptions due to the protonated cyclopentenone products. The observed occurrence of the isosbestic points in each case (222 and 273 nm for **1H** and 215 and 268 nm for **7H**) suggests that both rearrangements are void of intervention of any stable light-absorbing intermediates. The reaction in 96–98% D_2SO_4 (deuterium content >99%) did not result in deuterium incorporation in the products (except the oxygen-deuteration), indicating that the overall transformations are intramolecular in nature.

Further insights into the salient feature of the photorearrangements were afforded by the reaction with deuterium labeled substrates. The photolysis of the dideuterio derivative **4H** in H_2SO_4 gave a mixture of **5H** and **6H** and irradiation of **10H** yielded the corresponding cyclopentenones **11H** and **12H**. No appreciable loss of deuterium atom was caused during the reaction and work-up (H_2O quenching at 0°) conditions. Notably, the α methylene carbons of **5** and **11** have contrasting configurations, as revealed by examining their Eu(fod)$_3$-aided NMR spectra: the H_{cis} proton in **5** is coupled to the vicinal angular proton with J = 6 Hz, while the H_{trans} proton in **11** is coupled with J = 3 Hz.[5] Thus the double bond geometry of the starting dienones **4H** and **10H** (cis,cis vs. cis,trans) is clearly reflected in the stereochemistry of the photoproducts **5H** and **11H**.

The photo-induced transformations **1H** → **2H** and **7H** → **8H** have thus proved to proceed via a stereospecific intramolecular shift of β hydrogen of the dienones. Apparently a concerted transfer of the vinylic hydrogen to give the photoproducts directly is impossible, and only a two-step mecha-