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(15) A. P. Sloan Fellow 1968–1972; J. S. Guggenheim Fellow 1972–1973.
(16) Western Fher Fellow 1972–1974. Abstracted in part from the doctoral dissertation.

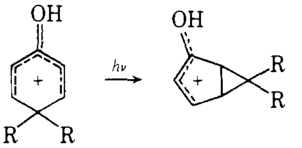
Waldemar Adam,*[15] Josefina Arce[16]
Department of Chemistry, University of Puerto Rico
Rio Piedras, Puerto Rico 00931

Received September 21, 1974

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.



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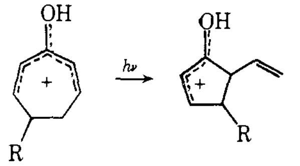
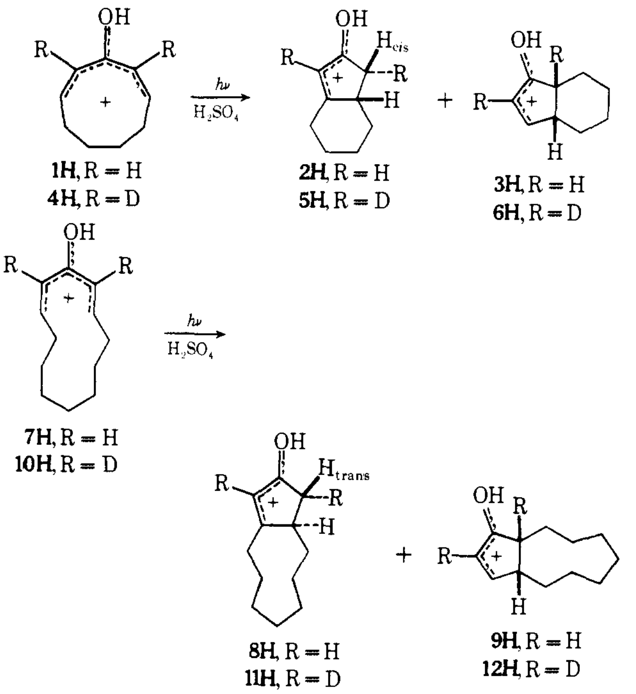


(2)

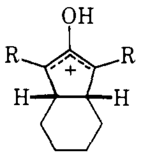
In the dark, 2,8-cyclononadienone (**1**) and 2,11-cyclododecadienone (**7**) in strong acids exist stable below room temperature. The oxygen-protonated cis,cis dienone **1H**[3] in 97% H_2SO_4 exhibits only one set of NMR signals due to the enone moiety at δ (TMS as external standard) 7.20 (d, J = 12 Hz, CH=C*H*C=O$^+$H) and 7.5–8.3 (m, C*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*H*C=O$^+$H), 7.30 (d, J = 15 Hz, *trans*-CH=C*H*C=O$^+$H), 7.1–7.5 (m, *cis*-C*H*=CHC=O$^+$H), and 8.1–8.8 (m, *trans*-C*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*H*C=O) and 7.52 (dd, J = 6 and 3 Hz, C*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*H*C=O) and 7.37 (dd, J = 6 and 3 Hz, C*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 mechanism consisting of an initial photochemical process to cause the β,β'-bonding and subsequent rapid thermal reaction of the reactive intermediates is in accord with the experimental findings. The first photochemical disrotatory cyclization of the nine-membered cis,cis dienone **1H** leads to the bicyclic cation **13** having a cis ring fusion, whereas the 12-membered cis,trans dienone **7H** gives rise to the trans-fused bicyclic intermediate **14.** These electrocyclizations are symmetry allowed, and an analogous mechanism has been advanced for the case of the six-membered dienones (eq 1).[1] Subsequent thermal suprafacial [1,4] hydride shifts **13** → **2H** and **14** → **8H**, regardless of the forbiddenness of the processes,[6] conclude the overall photoinduced rearrangements.[7] Cationic [1,4] sigmatropic rearrangements have been known to proceed only with inversion at the migrating center.[8] Although a [1_s,4_s] shift within a cationic species has been predicted to occur in certain cases,[9] no experimental evidence relevant to this prediction has been available. An explanation for the observed "symmetry-forbidden" pathway may be provided by the fact that the process involves migration of hydride. The symmetrical, low-lying (13.6 eV) 1s orbital can interact effectively with the second highest occupied molecular orbital of the 1,3-diene unit (butadiene ψ_1 11.34 eV), thereby strongly stabilizing the transition states of type **15.**[9] The smooth intramolecular change evading the possible intermolecular pathway (deprotonation from **13** or **14** followed by enol-keto tautomerization) would imply the transformation to be *energetically* concerted.[10] Furthermore, the present sigmatropic shifts would be facilitated by considerable thermodynamic driving force; an oxygen atom present in **13** or **14** does not stabilize, or even destabilizes, the cationic system because the heteroatom is located at the central carbon of the allylic moiety,[11] whereas the product **2H** or **8H** which can be represented by an oxonium ion-terminally hydroxylated allyl cation resonance hybrid is a very stable compound.



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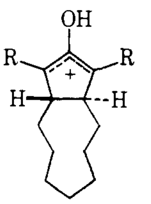

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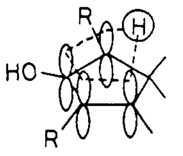

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The other type of photorearrangements **1H** → **3H** and **7H** → **9H** is considered to occur by a [$_\sigma 2_s$ + $_\pi 2_s$] mechanism; intramolecular addition of the γ-carbon-hydrogen bond (in the case of **7H,** that adjacent to the *cis*-CH=CH bond) across the diagonally situated carbon-carbon double bond leads to the bicyclic cyclopentenone products. The possible intermediacy of the hydroxyallyl cations in these reactions is highly unlikely in view of the fact that the species **13** (R = H) generated by reaction of H_2SO_4 and 2,8-*cis,trans*-cyclononadienone[12] (0°, in the dark) gave only **2H.**

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(3) The symbol **H** refers to an oxygen-protonated species throughout this paper. **1H** λ_{max} 285 (log ϵ 4.01) and 330 (3.58); **7H** λ_{max} 279 (4.03) and 317 nm (3.76).

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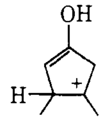
(7) A possibility that the conversion from the hydroxyallyl cations proceeds by a double [1,2] hydride shift might be conceivable. However, the possible concerted transformation which requires a trans ring fusion in the bicyclic intermediate is unlikely in view of the fact both cis- and trans-fused intermediates, **13** and **14**, equally afforded the cyclopentenone products. If hydrides were moving successively in a stepwise manner, substantial proton scrambling with solvent acids would be expected to take place at the stage of the initially formed enol intermediate of type i, in conflict with the experimental observation. The cationic species i could be deprotonated to give the hydroxycylopentadiene ii or iii which causes the proton scrambling.



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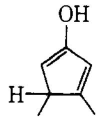

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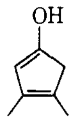

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R. Noyori,* Y. Ohnishi, M. Katô
Department of Chemistry, Nagoya University
Chikusa, Nagoya 464, Japan

Received October 3, 1974

An Electron Spin Resonance Study of Alkyl- and Aryl-Substituted Germyl Radicals[1]

Sir:

Although extensive studies of carbon-centered free radicals have been made by electron spin resonance, there have been relatively few reports on free radicals centered on group 4B elements other than carbon.[2] Particularly on germyl radicals, no report except $H_3Ge\cdot$,[3] $Cl_3Ge\cdot$,[4] and $Me_3Ge\cdot$[5] radicals has appeared. The present report describes information gained from electron spin resonance about several phenyl- and alkyl-substituted germyl radicals. So far as we are aware, this work also represents the first observation on the delocalization of an unpaired electron into a phenyl ring from the heavy group 4B atom-centered radicals. Because of the known stability of the triphenylmethyl radicals, examination of electron spin resonance spectra of such phenyl-substituted group 4B radicals is of great interest.[6]

The organogermyl radicals were generated by abstraction of hydrogen from the corresponding organogermanes with photochemically generated *tert*-butoxy radicals.[8,9] The

$$R_3GeH + (CH_3)_3CO\cdot \longrightarrow R_3Ge\cdot + (CH_3)_3COH$$

g factors and hyperfine coupling constants (hfcc) for a series of organogermyl radicals are given in Table I. As a typical example, Figure 1 shows the spectrum of the triphenyl-