necessary to have at least one other point along the curve. Such a system exists in the literature.[11] Compound **3** has bond lengths of 1.34 Å (av) and 1.49 Å (av)[11] which yields a difference in bond order of 77%[15] (i.e., ca. 15 kcal/mol barrier). A derivative of **3** with one ring substituted, **5**, is synthetically feasible, and we hope to gain information on the system, **5**Cr, in the near future.

This experiment corroborates the observation[11] that the central ring in *bent*-terphenylene is more cyclohexatriene-like than benzene-like. It also raises the question of whether one can use barriers to rotation around metal–arene bonds as a gauge for aromatic character in free arenes.

Presently we are probing this idea further by semiempirical calculational and crystallographic methods in order to present a more comprehensive picture of the cyclohexatriene fragment as a ligand.

Acknowledgment. We thank K.P.C. Vollhardt for helpful discussions. The VT-NMR work was done at UCLA thanks to F.A.L. Anet. Support for this work was provided by UCSD-Ac.Sen. Grant (RL208-G).

Registry No. 4, 65513-20-4; **4**-CR, 113779-29-6; $Cr(CO)_3(NH_3)_3$, 14974-11-9.

Evidence for a Chair Cyclohexane 1,4-Radical Cation Intermediate in the Single Electron Transfer Induced Cope Rearrangement of 2,5-Diaryl-1,5-hexadienes

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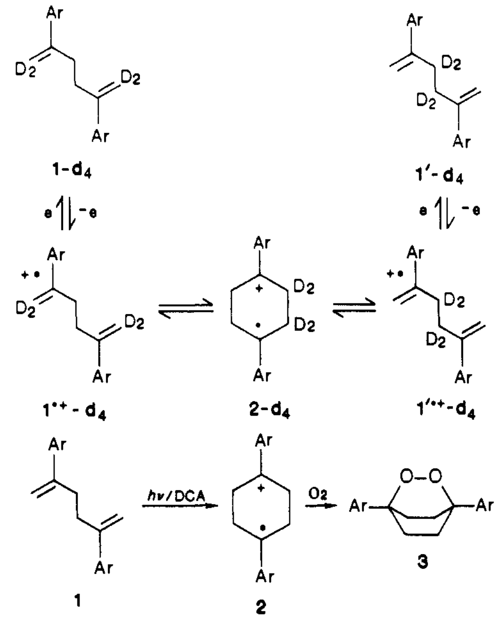
Received November 13, 1987

The possible intermediacy of cyclohexa-1,4-diyl in the Cope rearrangement, suggested by Grob[1] and Doering,[2] was supported by theoretical considerations.[3] However, kinetic experiments[4] rather suggest that cyclohexa-1,4-diyl is not a discrete intermediate in the thermal rearrangement pathway.[5]

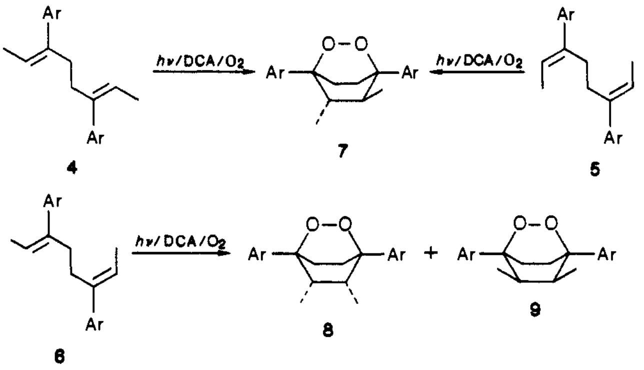
Our interest was an intermediacy of a radical cation counterpart on the radical cation energy surface.[7] If generated as a stable intermediate, it can be captured by molecular oxygen as trimethylenemethane radical cation is captured.[8] Although the photoassisted, zeolite-catalyzed Cope rearrangement of 1,3,4-triphenyl-1,5-hexadiene was reported and is proposed as the first example of a single electron acceptor (hole)-catalyzed Cope rearrangement,[9] no experimental information was available for an intermediacy in the radical cation rearrangement pathway.

Scheme I



a; Ar = C_6H_5. b; Ar = *p*-$MeOC_6H_4$

Scheme II



(Ar = *p*-$MeOC_6H_4$)

We thus investigated the photoinduced electron-transfer reactions of 2,5-diaryl-1,5-hexadienes (**1a**,**b**) and three isomers of 3,6-bis(*p*-methoxyphenyl)-2,6-octadienes (**4**–**6**), in which cyclohexane–1,4-radical cations would be most likely expected to be generated. Herein we, for the first time, demonstrate that the chair cyclohexane–1,4-radical cation serves as an intermediate in a single electron transfer induced Cope rearrangement of 2,5-diaryl-1,5-hexadienes.

The fluorescence of 9,10-dicyanoanthracene (DCA) was quenched either by **1a** ($E^{\mathrm{ox}}_{1/2}$ = 1.70 V versus SCE) or **1b** ($E^{\mathrm{ox}}_{1/2}$ = 1.22 V versus SCE), giving Stern–Volmer slopes, $k_q\tau$ = 164 and 273 M^{-1} in acetonitrile, respectively, which indicate that **1a** and **1b** are effective quenchers of the DCA singlet. Upon irradiation (>390 nm) of a solution of DCA (0.5 mM) and 2,5-diphenyl-1,5-hexadiene-*1,1,6,6*-d_4 (**1a**-d_4) (0.1 M) in dichloromethane-d_2 or chloroform-*d* under argon, the degenerate Cope rearrangement to give a 1:1 photostationary mixture of **1a**-d_4 and 2,5-diphenyl-1,5-hexadiene-*3,3,4,4*-d^4 (**1a′**-d_4) was observed. Similar irradiation of **1b**-d_4 resulted in the formation of a 1:1 mixture of **1b**-d_4 and **1b′**-d_4.

The degenerate rearrangement can be most likely explained by a sequential cyclization–cleavage mechanism through **1**$^{\bullet+}$-d_4 and **2**-d_4.[10] In support of the key intermediacy of **2** was the photooxygenations of **1** leading to 1,4-diaryl-2,3-dioxabicyclo[2.2.2]octanes (**3**). Thus, upon irradiation in oxygen-saturated

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(5) A 1,4-cyclohexene-1,4-diyl as a metastable intermediate was also excluded in the Cope rearrangement of 1-hexen-5-yne.[6]

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(10) The initial cyclization of 1,5-hexadiene radical cation to cyclohexane-1,4-radical cation is supported by theoretical calculation[7] and is recently confirmed by Williams.[11] However, it cannot be ruled out that a direct precursor of the degenerate rearrangement of **1** is 1,4-diarylcyclohexane-1,4-diyl which can be generated by the back electron transfer of $DCA^{\bullet-}$ to **2**.

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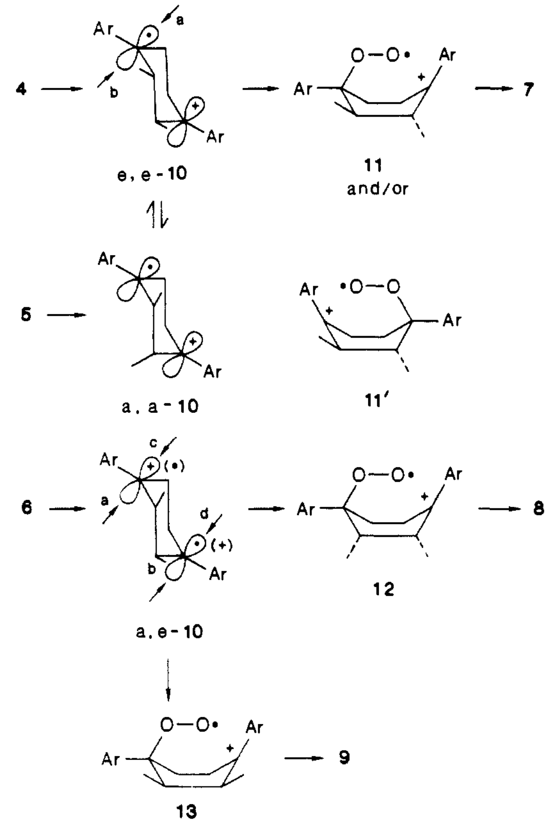
Scheme III



(Ar = *p*-MeOC$_6$H$_4$)

acetonitrile under the DCA-sensitized conditions **1a** and **1b** gave **3a**[12] and **3b**[12] in 6% and 72% yields, respectively. The yield of **3a** was increased to 48% by the addition of Mg(ClO$_4$)$_2$.[13]

If the initial cyclization occurs in a stereospecific manner, its stereochemical integrity should be conserved in the oxygenation product. In order to test this, the direct molecular oxygen trapping of intermediates was further applied for (*Z*,*Z*)-, (*E*,*E*)-, and (*E*,*Z*)-3,6-bis(*p*-methoxyphenyl)-2,6-octadienes (**4**), (**5**), and (**6**).[14] Observed stereochemical consequences were shown in Scheme II. Upon irradiation under similar oxygenation conditions, both the symmetrical **4** and **5** gave rise to the trans adduct **7**[12] in 72% and 80% yields, respectively, while a mixture of the *exo–cis*-**8** (58%)[12] and *endo–cis*-**9** (14%)[12] was obtained from **6**. The structure of **8** was determined by X-ray crystallographic analysis, and the unequivocal stereochemical assignments for **7** and **9** were obtained by comparisons of the ^{1}H NMR spectrum of **8** with those of **7** and **9** and by the observations of the NOE between the exo-C$_5$–CH$_3$ and exo-C$_8$–H for **7** and **8** but not for **9**. The stereospecific formations of those oxygenation products well rationalize the initial stereospecific formations of the chair cyclohexane-1,4-radical cations as shown in Scheme III.

The initial cyclizations of $\mathbf{4}^{\bullet+}$ and $\mathbf{5}^{\bullet+}$ give e,e-**10** and a,a-**10**, respectively. The oxygenation occurs at two sites, i.e., a and/or b in the more stable e,e-**10**. The subsequent recyclization through **11** and/or **11′**, thus, can afford the trans adduct **7**. On the other hand, oxygen can capture a,e-**10** from **6** at four different sites. Peroxyradical cation **12** captured at the less hindered site, i.e., a and/or b, recyclizes to afford **8** as a major product. The minor cis adduct **9** can be derived in a similar way from peroxyradical cation **13** captured at the more hindered site, i.e., c and/or d. Finally, it is of interest to note that the results of the Ce^{IV}-catalyzed reaction of 2,5-diphenyl-1,5-hecadiene[16] significantly differ from those of our photosensitized reactions.

Supplementary Material Available: X-ray experimental details for **8**, ^{1}H and ^{13}C NMR spectral data of 3,6-diaryl-2,6-octadienes and oxygenation products (**3a**, **3b**, and **4**–**9**), and listings of atomic positional parameters, anisotropic temperature factors, mean square displacement tensors, and bond lengths and bond angles (10 pages); listing of observed and calculated structure factors (18 pages). Ordering information is given on any current masthead page.

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(11) Guo, Q.-X.; Qin, X.-Z.; Wang, J. T.; Williams, F. *J. Am. Chem. Soc.*, in press. We thank Professor Williams for his generous offer of their EPR results before publication.

(12) Satisfactory elemental analyses and correct mass spectral data were obtained for all new compounds in this report, **3a** (mp 188–193 °C dec), **3b** (mp 198–204 °C dec), **4** (mp 55–56 °C), **5** (mp 86–87 °C), **6** (mp 52–54 °C), **7** (mp 197–199 °C), **8** (mp 195–196 °C), and **9** (mp 181–182 °C). **3a** was independently synthesized by the diimide reduction of 1,4-diphenyl-2,3-dioxabicyclo[2.2.2]oct-5-ene prepared by the dye-sensitized oxygenation of 1,4-diphenylcyclohexa-1,3-diene. The structures and stereochemical assignments of those compounds were unequivocally determined by the ^{1}H and ^{13}C NMR.

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(14) **4**, **5**, and **6** were prepared by the Wittig reaction of 1,4-bis(*p*-methoxyphenyl)butane-1,4-dione and ethyltriphenylphosphonium iodide by using *t*-BuOK in tetrahydrofuran in 42% 5%, and 17% yields, respectively. Stereochemical assignments are in agreement with those in previous reports.[15]

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Absence of a Common Ion Effect on the Hydrolysis of an α-Azido Ether of an Aliphatic Aldehyde[1]

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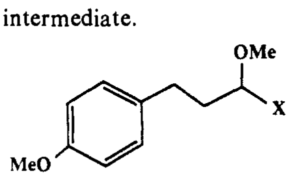
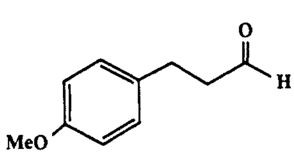
Hydrolysis of simple aliphatic acetals[2] and of the corresponding enol ethers[3] is widely believed to proceed via an oxocarbonium ion intermediate that reacts with water to give, ultimately, a common aldehyde product. Estimates of the stability of this intermediate have given rate constants for its reaction with water[4-6] ranging from $<5 \times 10^6$ to $\sim 10^{11}$ s^{-1}. We report here that there is no detectable trapping of an oxocarbonium ion intermediate, RCH=OMe$^+$, by 1 M azide ion, as determined by two different techniques. Added azide ion at constant ionic strength has little or no effect on the observed rate of solvolysis in aqueous solution of the α-azido ether **2**, and we use this fact to set an upper limit of 5×10^{-11} s for the lifetime of the putative oxocarbonium ion intermediate.



1 X = OAc
2 X = N$_3$



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A rate constant for the addition of water to protonated acetaldehyde of $<5 \times 10^6$ s^{-1} was estimated from the observed rate

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(1) Supported in part by grants from the National Institutes of Health (GM 20888) and the National Science Foundation (PCM 8117816).

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