J. Am. Chem. Soc. 1986, 108, 6408-6409

Novel Formation of Bis-allylic Products by Autoxidation of Substituted Cyclohexa-1,4-dienes

A. L. J. Beckwith,* D. M. O'Shea, and D. H. Roberts[1]

Research School of Chemistry, Australian National University, Canberra, A.C.T. 2601, Australia

Received June 2, 1986

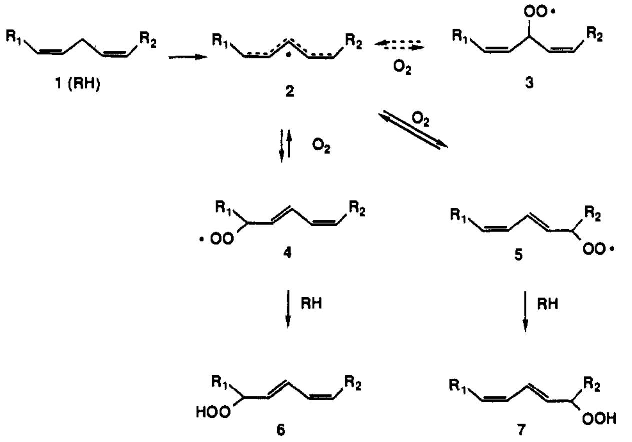
Coupling of pentadienylic radicals (**2**) with molecular oxygen is a key step in the generally accepted mechanism[2,3] of autoxidation of homoallylic dienes **1**. A curious and, as yet, unexplained feature of such autoxidations is that all of the products appear to arise from peroxy radicals **4** and **5** containing a conjugated diene system. No evidence has yet been adduced for the intermediacy of isomeric bis-allylic peroxy radicals **3**,[4] although the coupling of carbon centered radicals with oxygen, a process known to be rapid and insensitive to structural features,[6] would be expected to exhibit low regioselectivity. We now describe the formation of a bis-allylic oxygenated product by autoxidation of a cyclic diene and offer an explanation for this unprecedented behavior (Scheme I).

Birch reductive alkylation of methyl benzoate with butyl bromide afforded methyl 1-butylcyclohexa-2,5-diene-1-carboxylate (**8a**).[7] When stored under nitrogen **8a** was stable indefinitely, but on standing neat in air at ambient temperature, it rapidly underwent clean conversion into a mixture of the keto ester **12a** (65%)[8] and methyl benzoate (**13**, 35%). No other ketonic product could be detected by 200-MHz NMR.[9]

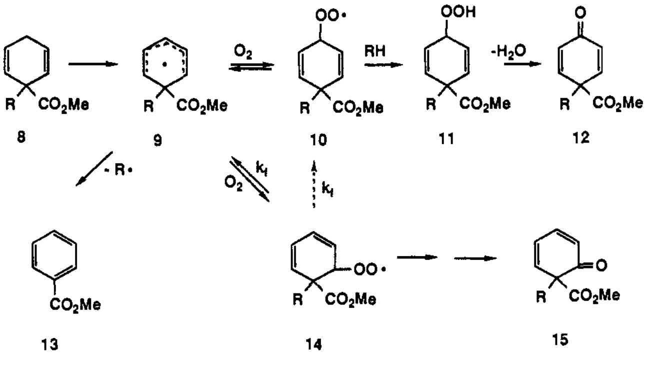
A plausible mechanism for the formation of **12a** and **13** involves the intermediacy of the dienylic radical **9a**, which can either undergo β-elimination to afford **13** or coupling with oxygen to given the peroxy radical **10a**, and hence the hydroperoxide **11a**. Since **11a** is a bis-allylic hydroperoxide its facile dehydration to give the ketone **12a** is not unexpected. What is unexpected by comparison with acyclic systems is the restriction of the site of oxygenation to the bis-allylic position.

It is not reasonable to attribute the difference in behavior between the cyclic and acyclic substrates to fundamental differences between the reactivities of the various sites in the two intermediate radicals, **2** and **9a**, toward coupling with oxygen. However, if each of the two sets of peroxy radicals, viz., **3**–**5** in the acyclic system and **10a** and **14a** in the cyclic system, were to come to rapid equilibrium, the outcome of the oxidations would then reflect, inter alia, the position of these equilibria. In the case of the acyclic system, the bis-allylic peroxy radical **3** should be about 4 kcal/mol less stable[10] than either of the conjugated isomers **4** or **5**. Provided that the rate of attainment of equilibrium is rapid by comparison with the rate of hydrogen atom transfer from RH to ROO•, this energy difference is sufficient to preclude the formation of products from **3** in detectable yield.

Scheme I



Scheme II



a, R = Bu; b, R = CH$_2$Ph; c, R = Me

The relative energies of the two peroxy radicals **10a** and **14a**, derived from the cyclic diene, are influenced by two opposing effects. On the one hand, conjugation between the two double bonds of **14a** should lower its energy relative to that of **10a** by an amount equal to or less than the resonance energy (3.6 kcal/mol) of buta-1,3-diene.[10] On the other, the energy of **14a** is raised relative to that of **10a** by steric interaction between the vicinal substituents.[11] Molecular mechanics calculations[13] give a difference in strain energy, E_{strain}(**14a**) − E_{strain}(**10a**), of 6.9 kcal/mol. We conclude that the nonconjugated bis-allylic peroxy radical **10a** is at least 3.3 kcal/mol more stable than its isomer, **14a**. Provided that the isomerization of **14a** into **10a** is more rapid than its conversion into a hydroperoxide, the difference in energy between the two is sufficient to direct product formation via the latter.

If one assumes that the rate constant for abstraction of a hydrogen atom from **8a** is similar to that ($k \approx 1.8 \times 10^{2}$ M^{-1} s^{-1})[3] for abstraction from 1,4-cyclohexadiene by the peroxy radical derived from linolenic acid, then the rate constant, k_i, for the isomerization, **14a** ⇌ **10a**, must be $\geq 1 \times 10^{4}$ M^{-1} s^{-1}. The generally accepted mechanism for this process involves β-fission of **14a** to afford **9a** and recombination of the latter with oxygen.[3,14] In this case $k_i = k_f$. Literature values for k_f are not available, but a recent theoretical study[15] indicates that the equilibrium between cyclohexadienyl radicals and derived peroxy radicals lies in favor of the former. This suggests that k_f is very large, and the kinetic requirements for the unique formation of **10a** are thus met. However, it is also possible that the isomerization **14a** → **10a** occurs in one step. Such a process involving a direct 2,3-pericyclic rearrangement analogous to that recently described for

---

[1] Present address: Battelle, Pacific Northwest Laboratories, Richland, WA 99352.

[2] For a general review, see: Howard, J. A. In *Free Radicals*, Kochi, J. K., Ed.; Wiley-Interscience: New York, 1973; Vol. 2, pp 3–62.

[3] Only a summary mechanism is presented here. For a more detailed analysis of current understanding, see: Porter, N. A.; Lehman, L. S.; Weber, D. A.; Smith, K. J. *J. Am. Chem. Soc.* **1981**, *103*, 6447.

[4] Two groups have reported trace amounts of bis-allylic oxidation products but in neither case were they isolated and fully characterised.[5]

[5] Roberts, D. H. Ph.D. Dissertation, Duke University, Durham, NC, 1982. Frankel, E. N.; Garwood, R. F.; Vihson, J. R.; Weedon, B. C. L. *J. Chem. Soc., Perkin Trans. 1* **1982**, 2707.

[6] Maillard, B.; Ingold, K. U.; Scaiano, J. C. *J. Am. Chem. Soc.* **1983**, *105*, 5095.

[7] Beckwith, A. L. J.; O'Shea, D.; Roberts, D. H. *J. Chem. Soc., Chem. Commun.* **1983**. Beckwith, A. L. J.; Roberts, D. H., manuscript in preparation.

[8] All products were identical with authentic materials.

[9] We estimate the detection limit to be 4%.

[10] Benson, S. W. *Chemical Kinetics*, 2nd ed.; Wiley: New York, 1976.

[11] Even the parent compound, cyclohexa-1,3-diene, is twisted out of the expected planar conformation in order to minimize nonbonded interactions between the vicinal methylene hydrogens.[12]

[12] Saebø, S.; Boggs, J. E. *J. Mol. Struct.* **1981**, *73*, 137.

[13] Allinger, N. A. *J. Am. Chem. Soc.* **1977**, *99*, 8127.

[14] Chan, H. W.-S.; Levett, G.; Matthew, J. A. *J. Chem. Soc., Chem. Commun.* **1978**, 756. Porter, N. A.; Weber, B. A.; Weenen, H.; Khan, J. A. *J. Am. Chem. Soc.* **1980**, *102*, 5597.

[15] Finkel'shtein, E. I.; Gerasimov, G. N. *Russ. J. Phys. Chem. (Engl. Transl.)* **1984**, *58*, 570.

0002-7863/86/1508-6408$01.50/0

acyloxyalkyl radicals[16] is also compatible with the experimental data.

The proposed mechanism (Scheme II) shows that β-fission of **9a** to afford methyl benzoate competes directly with coupling with oxygen. Consequently, any structural change in R which increases the rate of β-fission should increase the yield of methyl benzoate. In fact, when the benzyl derivative **8b** was allowed to stand in air it was rapidly and quantitatively converted into a mixture of methyl benzoate and benzyl hydroperoxide. Apparently 9b, which is formally the structure of the intermediate in ipso attack of benzyl radicals on methyl benzoate, undergoes β-fission so rapidly that its coupling with oxygen cannot compete effectively.

The dependence of the rate of fission of **9** on the stability of the radical formed was also directly observed by ESR spectroscopy. UV irradiation of a mixture of **8c** and di-*tert*-butyl peroxide in the ESR cavity gave a good signal for **9c**, but similar treatment of **8b** gave only the signal for the benzyl radical.

Acknowledgment. We thank C. H. Schiesser for carrying out the MM2 molecular mechanics calculations.

---

[16] Saebø, S.; Beckwith, A. L. J.; Radom, L. *J. Am. Chem. Soc.* **1984**, *106*, 5119.

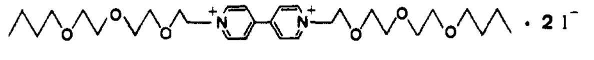
Electric Stimulus-Response Behavior of Liquid-Crystalline Viologen

Iwao Tabushi,* Kazuo Yamamura, and Kazuhiko Kominami

Department of Synthetic Chemistry, Kyoto University
Sakyo-ku Yoshida, Kyoto 606, Japan

Received March 10, 1986

Molecular electronics seems to be a very promising new field of chemistry, since a variety of novel approaches have been successfully attempted.[1-3] We wish to report a novel stimulus-response system, in which liquid-crystalline (semiconducting) viologen iodide $V_{O6}{}^{2+}\cdot 2I^-$ (**1**), inserted between two In_2O_3–SnO_2



1

electrodes, acquired ca 10^5-fold enhancement in electric conductivity, when an electric stimulus of 1–30 V was applied at 110 °C.

1 was prepared from bipyridyl and 3,6,9-trioxatridecyl iodide. Structure determination was performed by 400-MHz ^{1}H NMR ($CDCl_3$ δ from Me_4Si): 9.48 and 8.91 (AB quartet), 5.13 (triplet), 4.11 (α-CH_2), and others. Thermal analysis[5] and polarizing microscopic analysis showed a liquid-crystalline phase[6] at 63 °C(T_{C_1})–216 °C(T_{C_2}). **1** is a resistive material below T_{C_1} (L state, see Table I) ($\sigma = 10^{-11}$–(2×10^{-12}) Ω^{-1} cm^{-1} at 30 °C)[7] but becomes semiconducting ($\sigma = 4 \times 10^{-8}$ Ω^{-1} cm^{-1}) above T_{C_1} (M state).

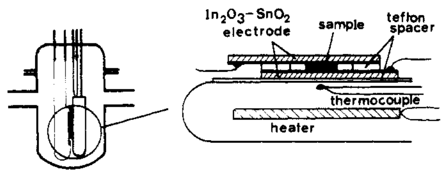


Figure 1. Apparatus and In_2O_3–SnO_2 sandwich cell. The thickness of the sample/spacer (0.1 mm) is grossly exaggerated.

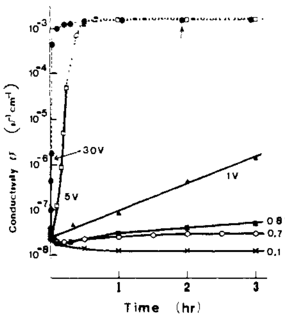


Figure 2. Dependence of conductivity (σ) vs. time plots on the applied voltage. Voltage was supplied through a variable resistor from a power source whose maximum output was set to 15 mA. Bald line represents the region where the indicated voltage initially applied was kept constant. In the broken line region, continuous voltage drop occurred to, e.g., 2.25 V, 15 mA at the arrow point.

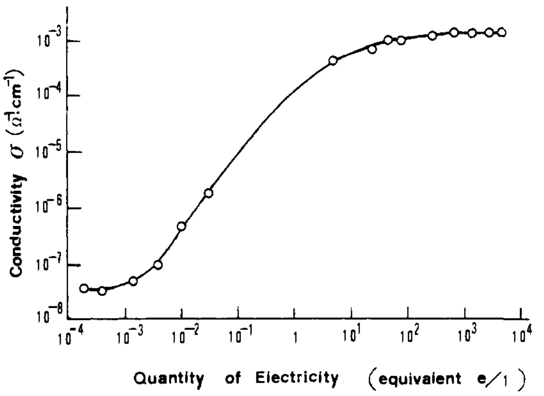
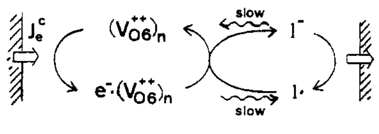


Figure 3. Conductivity change of **1** with the quantity of electricity passed through **1** at the liquid-crystalline state. At 110 °C initial voltage, 30 V, maximum current output was set to 15 mA.

Chart I



A remarkable further DC conductivity increase progressed autocatalytically, when a certain voltage, from 1 to 30 V, was applied to liquid-crystalline **1** of 0.1-mm thickness (Figure 1). The voltage–conductivity profile was very sensitive to the magnitude of the applied voltage (Figure 2). Except for the short induction period initially observed, the DC conductivity increment due to the electric stimulus was roughly proportional to the quantity of electricity passed through the liquid crystal (from $\sigma = 10^{-7}$ to 4.3×10^{-4} Ω^{-1} cm^{-1}) (see Figure 3), suggesting that a higher conductivity state, H, was produced by the electric current until saturation was attained at $\sigma = (1.2 \pm 0.2) \times 10^{-3}$ Ω^{-1} cm^{-1}. The σ value was ca. 2×10^{-3} Ω^{-1} cm^{-1}, when determined by the four-probe method. The H state, once formed, was kept for 3 days under Ar at room temperature without application of any "stimulating" voltage. The H state showed an electric response current of 23 μA, for example, on application of a "monitoring" voltage of 0.2 V. The state H was also stable toward further application of "monitoring" voltage (below 1 V) for 4 h at least, allowing 2900 electrons/1 viologen molecule to pass through.

---

* To whom correspondence should be addressed.

[1] (a) Baker, G. L.; Bates, F. S. *Mol. Cryst. Liq. Cryst.* **1985**, *117*, 15. (b) Chang, C. K.; Druy, M. A.; Gau, S. C.; Heeger, A. J.; Louis, E. J.; MacDiarmid, A. G.; Park, Y. W.; Shirakawa, H., *J. Am. Chem. Soc.* **1978**, *100*, 1013.

[2] (a) Ferraris, J.; Cowan, D. O.; Walatka, V., Jr.; Perlstein, J. H. *J. Am. Chem. Soc.* **1973**, *95*, 948. (b) Coleman, L. B.; Cohen, M. J.; Sandman, D. J.; Yamagishi, F. G.; Garito, A. F.; Heeger, A. J. *Solid State Commun.* **1973**, *12*, 1125.

[3] (a) White, H. S.; Kittlesen, G. P.; Wrighton, M. S. *J. Am. Chem. Soc.* **1984**, *106*, 5375. (b) Kittlesen, G. P.; White, H. S.; Wrighton, M. S., *J. Am. Chem. Soc.* **1985**, *107*, 7373. (c) Reference 8d,e.

[4] (a) Subbarao, E. C., Ed. *Solid Electrolytes and Their Applications*; Plenum Press: New York, 1980. (b) Fujimoto, M.; Nogami, T.; Mikawa, H. *Chem. Lett.* **1982**, 547. (c) Shimidzu, J.; Nogami, T.; Mikawa, H. The 50th Annual Meeting of the Chemical Society of Japan, 1985, 2A08.

[5] McAdie, H. G. In Thermal Analysis; Schwenker, Fr., R. F., Garn, P. D., Eds.; Academic Press: New York, 1969; Vol. I, p 639.

[6] Tabushi, I.; et al., unpublished results.

[7] Observed conductivity was varied depending on the solid layer preparation.