(1 mL) was added. After 15 min, triethylamine (0.943 g, 9.32 mmol) was added, and stirring was continued for 5 min. The mixture was warmed to room temperature and then partitioned between water and methylene chloride. Flash chromatography (ethyl acetate/hexanes, 1:1) afforded ketone 12 as a colorless oil (0.1 g, 82%): ^{1}H NMR (CDCl$_3$) δ 1.45–2.20 (m, 9 H), 2.56–2.75 (m, 2 H), 2.8–3.05 (m, 1 H), 3.35 (s, 3 H), 3.3–3.8 (m, 4 H), 4.20–4.35 (m, 1 H), 4.61 (s, 1 H); IR (CH$_2$Cl$_2$) 3420, 2930, 2860, 1710, 1620; CIMS, *m/z* (relative intensity) 256 (M$^+$ + 1, 100).

Anal. Calcd for $C_{13}H_{21}NO_4$: C, 61.16; H, 8.29. Found: C, 60.98; H, 8.31.

4-Carbomethoxy-4-hydroxy-3-methoxy-2,5-cyclohexadien-1-one (16). A mixture of 2 (100 mg, 0.54 mmol), pyridinium dichromate (0.89 g, 2.2 mmol), *tert*-butyl hydroperoxide (0.2 g, 2.2 mmol), and Celite (100 mg) in benzene (20 mL) was stirred at room temperature for 2 h. The reaction mixture was diluted with methylene chloride (50 mL), filtered through Celite, and concentrated at reduced pressure. Flash chromatography (silica gel, ethyl acetate/hexane, 1:1) and crystallization (ethyl acetate/hexane, 1:10) provided 16 as colorless crystals (83 mg, 77%): mp 124–125 °C; ^{1}H NMR (CDCl$_3$) δ 3.78 (s, 3 H), 3.82 (s, 3 H), 4.15 (s, exchangeable with D$_2$O, 1 H), 5.62 (d, $J = 1.4$ Hz, 1 H), 6.28 (dd, $J = 9.9$ Hz, $J = 1.5$ Hz, 1 H), 6.50 (d, $J = 9.9$ Hz, 1 H); $[\alpha]^{28}_{D}$ −18.2° (*c* 1.04, CHCl$_3$); IR (CHCl$_3$) 3200, 3050, 2950, 1760, 1665, 1625, 1600 cm^{-1}; UV (MeOH) λ_{max} (ϵ) 285 (3406), 234 (6744); CIMS *m/z* (relative intensity) 199 (M$^+$ + 1, 100).

Anal. Calcd for $C_9H_{10}O_5$: C, 54.55; H, 5.09. Found: C, 54.61; H, 5.22.

Acknowledgment. This work was supported by the National Institute of General Medical Science (Grant GM 33061). We thank Degussa AG for a generous gift of L-proline.

Oxidative Ring-Closure of Substituted Bisallenes: Example of an Unsymmetrical Nazarov-Type Ring Closure

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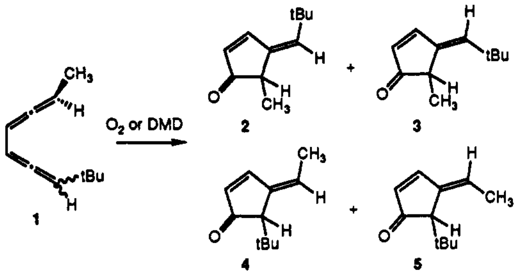
Introduction

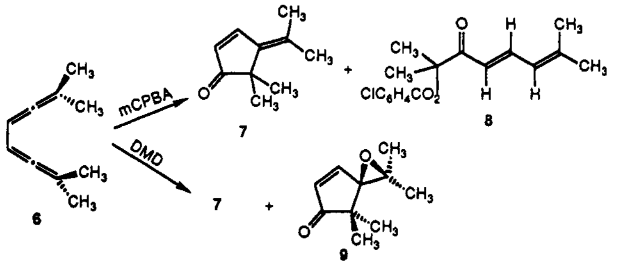
In an earlier study on the stereoselectivity of the (4 + 2) cycloaddition reactions of substituted bisallenes[1] it was observed that during the reaction of a 1:1 mixture of *erythro*- and *threo*-8,8-dimethyl-2,3,5,6-nonatetraene (1) with 0.5 molar equiv of *N*-phenylmaleimide exposed to the air a mixture of the 5-alkyl-4-alkylidenecyclopentenones 2–5 was formed. These observations have led to further studies on the oxidation and epoxidation of bisallenes. The recent article by Bartlett and Banavali on the "spontaneous oxygenation" of strained alkenes to produce epoxides[2] has helped to clarify the mechanism of the air oxidation of 1 and has prompted us to report our observations.

Results

Bisallene 1 on being stirred at room temperature in CDCl$_3$ solution exposed to the air for 24 h cleanly produces a mixture of 2–5 in a 24:25:32:19 ratio. Attempted chromatographic separation on silica gel resulted in the isolation of inseparable mixtures of 2 and 3 and 4 and 5. The infrared spectra of the two mixtures displayed an intense band in the carbonyl region at 1690 cm^{-1}. The ultraviolet spectra showed a λ_{max} at 280 nm versus a calculated value of 276 nm for the dienone chromophore in 2–5. The positions of the methyl groups in 2–5 were readily assigned on the basis of their chemical shifts in the NMR spectra, being at δ 1.33 and 1.21 in 2 and 3, and at much lower field at δ 1.83 and 1.92 in 4 and 5. The assignment of the stereochemistry about the exocyclic double bonds in 2–5 has been made on the basis of the relative magnitudes of the allylic coupling constants between the β and δ protons which are in general larger when syn compared to when anti.[3] In 3 and 5 the coupling constants are 1.58 and 1.63 Hz, while in 2 and 4 they are 0.48 and 0.62 Hz, respectively. The oxidation of 1 with dimethyldioxirane[4] (DMD) similarly produced a mixture of 2–5 in a 26:30:28:16 ratio which is considered to be within experimental error the same as that formed in the air oxidation of 1.



Interestingly, 2,7-dimethyl-2,3,5,6-octatetraene (6) does not undergo air oxidation. Treatment with *m*-chloroperbenzoic acid resulted in the formation of a 29:71 mixture of 7 and 8. The structure of 7 was readily apparent from its NMR spectrum which contained vinyl proton doublets and three singlets representing two different vinyl methyl and two identical saturated methyl groups. The structure of 8 was also readily apparent from its NMR spectrum which implicated the presence of a CH=CHCH= system, the presence of two vinyl methyl groups and two identical saturated methyl groups, and the presence of *m*-chlorophenyl group. The trans stereochemistry about the double bond is suggested by the magnitude of the vicinal coupling constant of 11.65 Hz. The reaction of 6 with 1 molar equiv of DMD produces a mixture of 7 and 9, along with some unreacted 6. Reaction of 6 with a excess of DMD cleanly produces only 9, which does not react further with the DMD.



Discussion

By analogy with the observations of epoxide formation in the spontaneous oxygenation of strained alkenes,[2] the air oxidation of the very reactive bisallene 1 would also appear to involve epoxide formation.[5] The similarity of the product ratios derived from the air oxidation and the reaction of 1 with DMD supports this view. The formation of the four products indicates that both allene chromo-

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(1) Pasto, D. J.; Yang, S.-H. *J. Org. Chem.* **1989**, *54*, 3978.

(2) Bartlett, P. D.; Banavali, R. *J. Org. Chem.* **1991**, *556*, 6043.

(3) Sternhall, S. *Rev. Pure Appl. Chem.* **1964**, *14*, 15.

(4) Murray, R. W.; Jeyaraman, R. *J. Org. Chem.* **1985**, *50*, 2847.

(5) The mechanistic details of the air oxidation of 1 to produce the epoxides have not been explored.

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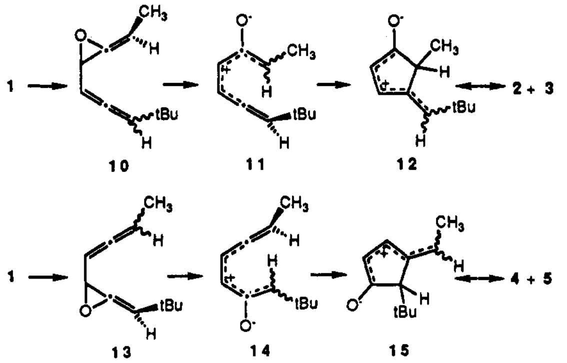
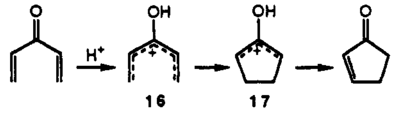
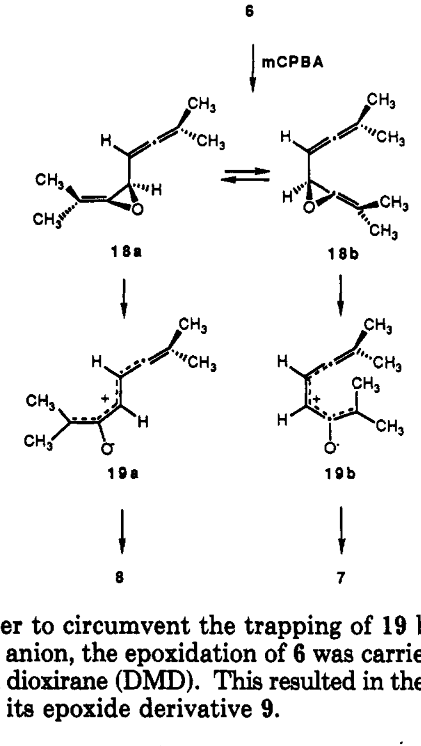
phores in 1 must undergo epoxidation with a slight preference for the epoxidation of the methyl-substituted allene chromophore of 1. Which double bond of the allene chromophore undergoes epoxidation is not known, although one would anticipate that the 3,4- and 5,6-double bonds of the central conjugated 1,3-diene system should be more reactive due to its possessing the higher-energy HOMO of 1. It is of little consequence, however, since the epoxide formed by epoxidation of either double bond of an allene chromophore will undergo ring opening to form the same oxyallyl cation intermediate, a well-known reaction of allene epoxides.[6,7] The ring opening of the epoxides 10 and 13 derived from 1 must produce the 2-oxypentadienyl zwitterions 11 and 14 which undergo electrocyclic ring closure to produce 12 and 15, which are simply resonance contributing structures of the product dienones 2 and 3 and 4 and 5.[8] This cyclization reaction is very similar to that observed with vinylallenes on epoxidation[9] and is very similar to the Nazarov cyclization of 3-hydroxypentadienyl cations,[10] derived by the protonation of divinyl ketones, which undergo electrocyclic ring closure to ultimately form cyclopentenones as illustrated in the following equation.



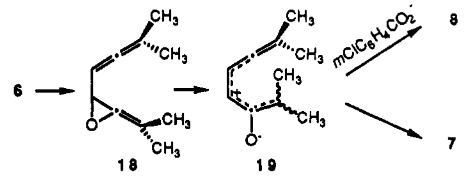


The electrocyclic ring closure of 16 produces a "cross-conjugated", 2-hydroxyallyl cation. The electrocyclic ring closure of 11 and 14, however, produces directly a "through-conjugated", 1-oxypentadienyl cation (a resonance contributing structure of an $\alpha,\beta,\gamma,\delta$-dienone) which should provide for a much greater driving force for this cyclization process compared to that in the Nazarov cyclization.

The epoxidation of 6 with *m*-chloroperbenzoic acid is expected to form epoxide 18 which can exist in the two conformations shown. Ring opening of 18a produces 19a which is trapped by the carboxylate anion to produce 8. Ring opening of 18b produces 19b which can directly undergo electrocyclic ring closure to produce 7.



In order to circumvent the trapping of 19 by the carboxylate anion, the epoxidation of 6 was carried out with dimethyl dioxirane (DMD). This resulted in the formation of 7 and its epoxide derivative 9.



In the presence of a large excess of DMD, 9 failed to undergo further reaction. The reactivity of 7 toward epoxidation to produce 9 can be attributed to a high-energy HOMO of the dienone chromophore which possesses the largest coefficients on the carbon atoms of the exocyclic double bond. The HOMO of the enone chromophore in 9 lies considerably lower in energy and is thus less reactive with the electrophilic DMD.[11] The lack of any significant reactivity of 2–5 toward further reaction with DMD would appear to be due to the slightly lower energy HOMO of the dienone chromophore due to lesser substitution on the exocyclic double bond.

Experimental Section

Air Oxidation of 8,8-Dimethyl-2,3,5,6-nonatetraene (1). A solution of 25 mg of 1 in 2 mL of $CDCl_3$ contained in a 10-mL round-bottomed flask equipped with a condenser was allowed to stir at rt for 24 h. Analysis by NMR indicated the absence of 1 and the presence of only a mixture of 2–5 in a ratio of 24:25:32:19. The solvent was removed, and the residue was subjected to chromatography on silica gel giving inseparable mixtures of 2 and 3 and 4 and 5.

2: 300-MHz ^{1}H NMR ($CDCl_3$) δ 1.19 (s, 9 H), 1.33 (d, J = 7.49 Hz, 3 H), 3.00 (dq, J = 1.27, 7.49 Hz, 1 H), 5.73 (dd, J = 1.27, 0.48 Hz, 1 H), 6.05 (dd, J = 5.44, 0.48 Hz, 1 H), 7.60 (d, J = 5.44 Hz, 1 H); UV (on mixture of 2 and 3) $\lambda_{max}^{C_2H_5OH}$ 276 nm; IR (on mixture of 2 and 3) $\nu_{C=O}$ 1690 cm^{-1}; HR-EIMS calcd for $C_{11}H_{16}O$ 164.1201, found 164.1200.

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(6) For a review describing the epoxidation of allenes see: Jacobs, T. L. In *The Chemistry of Allenes*; Landor, S. R., Ed.; Academic Press: New York, 1982; pp 493–491.

(7) Crandall, J. K.; Conover, W. W.; Komin, J. B.; Machleder, W. H. *J. Org. Chem.* **1974**, *39*, 1723. Crandall, J. K.; Machleder, W. H. *J. Heterocycl. Chem.* **1969**, *6*, 777. Crandall, J. K.; Machleder, W. H. *J. Am. Chem. Soc.* **1968**, *90*, 7347. Crandall, J. K. Machleder, W. H.; Thomas, M. J. *J. Am. Chem. Soc.* **1968**, *90*, 7346.

(8) The conformations shown in 10, 11, 13, and 14 are those necessary to undergo the electrocyclic ring closure to form 12 and 15 and are not implied to represent the lowest energy conformations of those intermediates.

(9) Bertrand, M.; Grimaldi, J. *Compt. Rend. C* **1967**, *265*, 196. Grimaldi, J.; Bertrand, M. *Tetrahedron Lett.* **1969**, 3269; *Bull. Soc. Chim. Fr.* **1971**, 957. Roumestant, M. L.; Malacria, M.; Gore, J.; Grimaldi, J.; Bertrand, M. *Synthesis* **1976**, 755.

(10) For a review of the Nazarov cyclization reaction see: Santelli-Rouvier, C.; Santelli, M. *Synthesis*, **1983**, 429.

(11) The results of ab initio, nongeometry-optimized calculations at the 3-21G level on acrolein and (*Z*)-2,4-pentadienal (having the same C=O, C—C, C=C and C—H bond lengths) indicate energies for the HOMO of acrolein of 10.8 eV and for (*Z*)-2,4-pentadienal of 9.3 eV.

3: NMR ($CDCl_3$) δ 1.21 (d, J = 7.55 Hz, 3 H), 1.23 (s, 9 H), 2.70 (dq, J = 0.87, 7.55 Hz, 1 H), 5.64 (dd, J = 1.58, 0.87 Hz, 1 H), 6.21 (dd, J = 5.76, 1.58 Hz), 8.23 (d, J = 5.76 Hz, 1 H).

4: NMR ($CDCl_3$) δ 0.99 (s, 9 H), 1.83 (dd, J = 7.47, 0.58 Hz, 3 H), 2.67 (br d, J = 1.05 Hz, 1 H), 5.85 (qdd, J = 7.47, 1.05, 0.62 Hz, 1 H), 5.99 (ddq, J = 5.55, 0.62, 0.58 Hz, 1 H), 7.64 (d, J = 5.55 Hz, 1 H); UV (on a mixture of **4** and **5**) $\lambda_{max}{}^{C_2H_5OH}$ 282.1 nm; IR (on a mixture of **4** and **5**) $\nu_{C=O}$ 1690 cm^{-1}; HR-EIMS calcd for $C_{11}H_{16}O$ 164.1201, found 164.1201.

5: NMR ($CDCl_3$) δ 0.98 (s, 9 H), 1.92 (dd, J = 7.17, 0.65 Hz, 3 H), 2.43 (dq, J = 0.78, 0.65 Hz, 1 H), 5.70 (qddd, J = 7.17, 1.63, 0.92, 0.78 Hz, 1 H), 6.12 (ddd, J = 5.76, 1.63, 0.73, 1 H), 8.03 (dd, J = 5.76, 0.92 Hz, 1 H).

Reaction of 1 with Dimethyldioxirane (DMD). To a solution of 0.2 g of **1** in 10 mL of acetone was added 1 molar equiv of DMD.[4] The reaction mixture was allowed to stand at rt for 24 h. The solvent was removed under reduced pressure, and the NMR spectrum of the residue was recorded showing the presence of only **2**–**5** in a ratio of 26:30:28:16.

Reaction of 2,7-Dimethyl-2,3,5,6-octatetraene (6) with *m*-Chloroperbenzoic Acid. To a solution of 0.25 g (1.8 mmol) of **6** in 5 mL of CH_2Cl_2 was added a solution of 0.32 g of *m*-chloroperbenzoic acid in 10 mL of CH_2Cl_2. The reaction mixture was stirred at rt for 10 h. The reaction mixture was then washed with 5% aqueous $NaHCO_3$ until the evolution of CO_2 ceased. The solution was dried ($MgSO_4$), and the solvent was removed under reduced pressure. The NMR spectrum of the crude product mixture was recorded indicating the presence of only **7** and **8** in a 29:71 ratio. The residue was subjected to column chromatography on silica gel (3:2 hexanes–ether as eluent) giving pure fractions of **7** and **8**.

7: 300-MHz ^1H NMR ($CDCl_3$) δ 1.22 (s, 6 H), 1.96 (br s, 3 H), 1.97 (br s, 3 H), 6.08 (d, J = 5.74 Hz, 1 H), 8.01 (d, J = 5.74 Hz, 1 H); IR: $\nu_{C=O}$ 1710 cm^{-1}; HR-EIMS calcd for $C_{10}H_{14}O$ 150.0944, found 150.0944.

8: NMR ($CDCl_3$) δ 1.64 (s, 6 H), 1.85 (br d, J = 0.98 Hz, 3 H), 1.92 (br d, J = 1.08 Hz, 3 H), 6.09 (br d, J = 11.65 Hz, 1 H), 6.81 (dd, J = 11.65, 11.65 Hz, 1 H), 7.36 (dqq, J = 11.65, 1.08, 0.98 Hz, 1 H), 7.4–8.0 (m, 4 H); IR $\nu_{C=O}$ 1710 and 1679 cm^{-1}; EIMS no parent ion could be observed; CIMS m/z 307 for M + 1.

Reaction of 6 with DMD. The reaction of **6** with 1 molar equiv of DMD in acetone solution at rt produced mixtures of **7** and **9** and unreacted **6**. The reaction of **6** with 2 or more molar equiv of DMD in acetone solution at rt for 24 h produces only **9**. The solvent was removed under reduced pressure giving a colorless, viscous oil: 300-MHz ^1H NMR ($CDCl_3$) δ 1.18 (s, 3 H), 1.22 (s, 3 H), 1.32 (s, 3 H), 1.48 (s, 3 H), 6.07 (d, J = 10.48 Hz, 1 H), 6.82 (d, J = 10.48 Hz, 1 H); HR-EIMS calcd for $C_{10}H_{14}O_2$ 166.0893; found 166.0891.

Acknowledgment. Acknowledgement is made to the Donors of The Petroleum Research Fund, administered by the American Chemical Society, for the partial support of this research.

Supplementary Material Available: ^1H NMR spectra of **7** and **9** (2 pages). Ordering information is given on any current masthead page.

Additions and Corrections

Vol. 56, 1991

James A. Marshall* and Xiao-jun Wang. Highly Diastereoselective S_E' Additions of Enantioenriched Allenylstannanes to (*S*)-2-(Benzyloxy)propanal.

Page 3213. In footnote 14, acetonide vii was prepared from alcohol **20**, not iv. We thank Professor Wolfgang Oppolzer for calling our attention to this discrepancy.

Philip G. Hultin, Franz-Josef Mueseler, and J. Bryan Jones*. Enzymes in Organic Synthesis. 48. Pig Liver Esterase and Porcine Pancreatic Lipase Catalyzed Hydrolyses of 3,4-(Isopropylidenedioxy)-2,5-tetrahydrofuranyl Diesters.

Page 5377. In the Discussion on the reduction of **1** to **2**, for which ref 11 was cited, the correct citation is the work of Kelly, James E. "Polyesters Based on 2,5-Disubstituted Furans in Various States of Reduction". Ph.D. Thesis, Rennselaer Polytechnic Institute, 1975.

Page 5380. The Acknowledgment inadvertently omitted "We thank Professor J. A. Moore for his help in providing information on the **1** → **2** reduction prior to publication".

Vol. 57, 1992

J. T. Arnold, T. O. Bayraktaroglu, R. G. Brown, C. R. Heiermann, W. W. Magnus, A. B. Ohman, and R. G. Landolt*. Hypochlorite-Induced Substitution of Chlorine for Bromine in Aromatic Compounds.

Page 391. We failed to cite the following paper: O'Connor, K. J.; Burrows, C. J. *J. Org. Chem.* **1991**, *56*, 1344. This described efficient, nickel(II) complex catalyzed aryl–halogen exchange (including quantitative conversion of PhBr to PhCl in 30 min) using NaOCl with a phase-transfer catalyst. In contrast, only 1–2% production of PhCl from PhBr was observed in the absence of Ni^{II} catalyst. In addition to describing a breadth of synthetic utility for the Ni^{II}-catalyzed system, the O'Conner/Burrows paper includes pertinent mechanistic discussion. We are grateful to Dr. Burrows for bringing her work to our attention.

Patrick Dussault* and Ayman Sahli. 2-Methoxyprop-2-yl Hydroperoxide: A Convenient Reagent for the Synthesis of Hydroperoxides and Peracids.

Page 1009. A reference to a related strategy in the synthesis of α-(silyloxy) peresters (Nagata, R.; Saito, S. *Synlett* **1990**, 291) was unfortunately omitted. We apologize for this oversight.