1 increases the efficiency of the sequence to 20%.

Radical Cation and Triplex Diels–Alder Reactions of 1,3-Cyclohexadiene

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Dimerization of 1,3-cyclohexadiene (CHD) can be accomplished under a wide range of reaction conditions. Thermolysis at 200 °C gives the [4 + 2] Diels–Alder dimers as a mixture of endo and exo isomers 1 and 2.[1,2] Triplet sensitization gives [2 + 2] dimers as a mixture of syn and anti configurations, 3 and 4, as well as some of the exo [4 + 2] adduct 2.[2] Schutte and
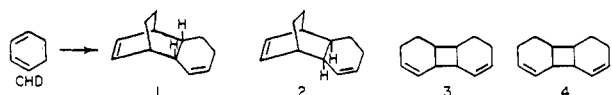
Freeman,[3] and later Hammond and co-workers,[4] studied the γ-radiation-induced dimerization and found that two processes were operating simultaneously. The first of these proceeds through triplet CHD (CHD*[3]). The second is a chain reaction that features the combination of cyclohexadiene radical cation (CHD⁺·) with neutral CHD. More recently, Bauld and his students[5] have reported that the oxidizing salt tris(p-bromophenyl)aminium hexachlorostibnate (E_{red} = +0.762 V)[6] initiates a radical cation chain dimerization of CHD, and some related dienes, that is in essence identical with the radiation-induced reaction. Jones[7] and later Bauld[8] found that these dimerizations can be initiated by singlet excited states of electron poor sensitizers.[9]

Herein we report the results of an investigation of the photochemical dimerization of CHD. The results implicate two distinct mechanisms. One of these operates in nonpolar solvent and appears to proceed through a triplex. The other sequence occurs in polar solvent and involves formation of CHD⁺·. Our findings provide a test for the role of CHD⁺· in the dimerizations initiated by the aminium salt.[5]

Oxidation of CHD to the radical cation is central to several routes suggested to lead to its dimerization. The cyclic voltammogram observed for this oxidation in acetonitrile is irreversible. The peak potential depends on the sweep rate and at 25 V/s occurs at 1.33 V.[6b]

Scheme I

In concert with expectation from the Weller equation,[10] CHD quenches the fluorescence of 1,4-dicyanonaphthalene (DCN) in either benzene or acetonitrile solution at approximately the diffusion-limited rate ($k_q\tau$ = 86 and 148 M⁻¹, respectively). CHD dimers are formed by this reaction in both solvents.

Irradiation of DCN (1.0 × 10⁻³ M) in a degassed acetonitrile solution containing 0.26 M CHD gives both [4 + 2] dimers 1 and 2 (ca. 6:1) and [2 + 2] dimers 3 and 4.[11] The [4 + 2] adducts comprise more than 80% of the dimer mixture at 5% conversion. The ratio of 1 to 2 and of [4 + 2] to [2 + 2] dimers does not change significantly when the concentration of CHD is increased to 2.1 M. However, the quantum yield for formation of the dimers is increased approximately threefold by this change. Even at the lowest diene concentration, greater than 97% of the singlet-excited DCN (DCN*[1]) is quenched by CHD.

Analysis of this reaction by laser flash photolysis clearly reveals the formation of radical ion intermediates.[12] Irradiation of an acetonitrile solution of DCN (1.0 × 10⁻³ M) and CHD (0.58 M) with the output of a nitrogen laser (337 nm, 15 ns, 7 mJ) generates dicyanonaphthalene radical anion (DCN⁻·).[13] The yield of DCN⁻· does not change significantly when the concentration of CHD is increased to 2.1 M.

The formation of endo [4 + 2] dimer 1 can be quenched selectively by addition of 1,3,5-trimethoxybenzene (TMB) (E_{ox} = 1.16 V[14,6b]). The Stern–Volmer slope depends on the CHD concentration and is 260 M⁻¹ when CHD is 0.21 M and 100 M⁻¹ when CHD is 0.42 M. In contrast, formation of the [2 + 2] dimer 4 is only slightly affected by TMB. When 4,4′-dimethoxybiphenyl (E_{ox} = 0.91 V[15,6b]) is the quencher analogous results are obtained, but indene (E_{ox} = 1.35 V[16,6b]) does not significantly inhibit dimer formation.

These findings all point to a mechanism for dimerization of CHD in acetonitrile that is essentially identical with that suggested to occur on γ-irradiation.[3,4] The CHD*[3] formed from ion annihilation leads primarily to the [2 + 2] adducts, and a radical cation chain reaction, shown in Scheme I, yields mostly the endo [4 + 2] dimer. The selective quenchers (Q) intercept CHD⁺· and inhibit formation of 1 when their oxidation potential is below that of CHD. With the reasonable assumptions that the exothermic oxidations of CHD by the dimer radical cation (dimer⁺·) and of Q by CHD⁺· occur at the diffusion limit and are irreversible, then the application of eq 6 to the quenching data (constant [Q], vary

$$\frac{\phi}{\phi^\circ - \phi} = \frac{k_5[\text{DCN}^-\cdot]}{k_3[\text{Q}]} + \frac{k_2[\text{CHD}]}{k_3[\text{Q}]} \quad (6)$$

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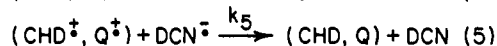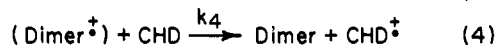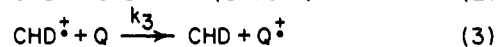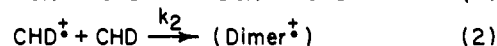(6) (a) Ledwith, A. *Acc. Chem. Res.* **1972**, *5*, 133. (b) All potentials given in this report are referenced or corrected to the Ag/Ag⁺ electrode.
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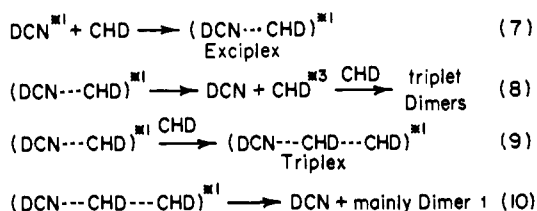(15) Ronlán, A.; Coleman, J.; Hammerich, O.; Parker, N. D. *J. Am. Chem. Soc.* **1974**, *96*, 845.
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Scheme II

$$DCN^{*I} + CHD \longrightarrow (DCN\cdots CHD)^{*I} \qquad (7)$$
$$\text{Exciplex}$$

$$(DCN\cdots CHD)^{*I} \longrightarrow DCN + CHD^{*3} \xrightarrow{CHD} \begin{array}{c}\text{triplet}\\\text{Dimers}\end{array} \qquad (8)$$

$$(DCN\cdots CHD)^{*I} \xrightarrow{CHD} (DCN\cdots CHD\cdots CHD)^{*I} \qquad (9)$$
$$\text{Triplex}$$

$$(DCN\cdots CHD\cdots CHD)^{*I} \longrightarrow DCN + \text{mainly Dimer 1} \qquad (10)$$

[CHD]) gives the bimolecular rate constant for reaction of CHD$^+$· with CHD (k_2, eq 2) equal to 3×10^8 M^{-1} s^{-1} from the slope of the linear plot.

The DCN-sensitized dimerization of CHD in benzene exhibits quite different properties. When the concentration of CHD is 0.11 M the major products (75%) are the triplet-derived [2 + 2] adducts and the ratio of endo to exo [4 + 2] dimers is 0.16. However, the yield of [4 + 2] adducts increases to 50% at 2.1 M CHD, and the endo to exo ratio becomes 1.30. The quenchers that inhibit formation of [4 + 2] dimer 1 in acetonitrile solution have no effect on the reaction in benzene. Finally, laser flash photolysis of DCN in benzene containing CHD shows quite clearly that no radical ion intermediates are formed.

The results suggest operation of the reaction sequence shown in abbreviated form in Scheme II. A key step in this sequence is the interception of an exciplex of CHD and DCN by CHD to form a triplex (eq 9). Triplexes have been observed before at high reagent concentrations,[19] and Jones[7] has suggested that one may participate in CHD dimerization.

These findings can be applied to the analysis of the aminium salt initiated dimerization of CHD in acetonitrile solution. The yield of Diels–Alder dimers is decreased more than fivefold when 2.8×10^{-2} M TMB is included with 0.21 M CHD and the reaction is initiated by addition of tris(*p*-bromophenyl)aminium hexachlorostibnate (1×10^{-2} M). This finding supports operation of the radical cation chain mechanism for the dimerization of CHD in acetonitrile. However, the maximum equilibrium concentration of CHD$^+$· (at 1 M CHD) under these conditions is only ca. 10^{-11} M. The large value we obtain for k_2 provides an explanation for how this low concentration of ions can give a good yield of dimers. However, in general this reaction will be sensitive to steric and electronic retardation and thus may often require much higher steady-state concentrations of active ions to give useful yields of dimer products by this mechanism.

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Stereospecific, Regioselective, and Catalytic Monoepoxidation of Polyolefins by the Use of a P-450 Model, H$_2$–O$_2$–TPP·Mn–Colloidal Platinum
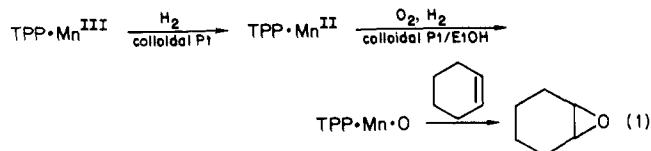
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Although a variety of successful attempts have been made for the structure elucidation of the probable intermediates involved in the reductive activation of dioxygen by cyt P-450,[1] real activation of dioxygen by artificial porphyrin–metal complexes in the presence of reducing reagents had not been achieved until the recent finding of an efficient catalytic system consisting of dihydrogen–TPP·Mn (manganese complex of tetraphenylporphyrin)–methylimidazole–colloidal platinum.[2] Simple olefins were monooxygenated with the P-450 model system, giving the corresponding epoxides as the major products with excellent turnover (64.7 recycling number, i.e., 64.7 mol of cyclohexene oxide per 1 mol of TPP·Mn used), and with some loss of the catalyst (60% of the catalyst remained unchanged,[2] or 162 mol of the epoxide formed per 1 mol of TPP·Mn consumed).

$$TPP\cdot Mn^{III} \xrightarrow[\text{colloidal Pt}]{H_2} TPP\cdot Mn^{II} \xrightarrow[\text{colloidal Pt/EtOH}]{O_2,\ H_2}$$

$$TPP\cdot Mn\cdot O \longrightarrow \quad + \quad \bigcirc\!\!\!-\!\!O \qquad (1)$$

Now the authors wish to report the stereospecific, regioselective, and efficiently catalytic (with large turnover) monoepoxidation of polyolefins by the use of the artificial P-450-type O$_2$ activating system (colloidal Pt, H$_2$, and TPP·Mn^{III}). Aqueous T$_{SO_3Na}$PP·Mn^{III} was preferred to TPP·Mn^{III} in organic solvents, because colloidal platinum is much more stable in water than in organic solvents.

Colloidal platinum supported on poly(vinyl alcohol) (PVA) or poly(vinylpyrrolidone) (PVP) was prepared according to the literature[3] (with slight modifications[2]). Experimental results and reaction conditions employed are listed in Table I.

The most important finding is the large size of the recycling numbers obtained for the present catalyst systems, especially in aqueous ethanol. After 48 h, 30–150 mol of the epoxide were formed per unit mol of TPP·Mn^{III} used, where loss of TPP·Mn^{III} was less than 27% (the theoretical recycling number is 280–533 mol product/mol of TPP·Mn consumed). The electron-transfer activity of colloidal Pt was also preserved. Under appropriate conditions, colloidal Pt was still active after 264 recyclings (products mol/Pt atom equiv used). Therefore, preservation of the activities of both catalysts, TPP·Mn and colloidal Pt, were quite satisfactory in the protic solvents. In an aprotic solvent like benzene, preservation of catalytic activity of colloidal Pt was somewhat lower than in a protic solvent.

The second advantage of the present H$_2$–O$_2$ epoxidation is the almost exclusive monoepoxidation of the polyolefins. In aqueous ethanol, formation of diepoxides from nerol and geraniol was negligible or very small (almost none and less than 3%, respectively), when 85% of the diolefin was converted to the epoxides, based on the GLC analyses.

In addition to these remarkable characteristics, the present P-450-type monoepoxidation preserves two important characteristics which were observed in appropriate noncatalytic epoxidizing reagents,[4] regioselectivity and stereospecificity.[5] The regioselectivity in the present monoepoxidation of geraniol and related compounds was high, as determined by 400-MHz ^{1}H

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