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Reactions of Hydroperoxy Radicals. Comparison of Reactivity with Organic Peroxy Radicals

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1,4-Cyclohexadiene, which oxidizes with the hydroperoxy radical as a chain carrier, has been cooxidized with butadiene, tetralin, and tetramethylethylene at 50 °C. The relative reactivities of 1,4-cyclohexadiene, butadiene, and tetralin toward the hydroperoxy radical are 1.0:0.23:0.18, while toward the butadiene and tetralin peroxy radicals they are 1.0:0.041:0.012 and 1.0:0.033:0.015, respectively. Thus the hydroperoxy radical is significantly less selective than the organic peroxy radicals generated from butadiene and tetralin. The cooxidation of 1,4-cyclohexadiene with tetramethylethylene indicates that the hydroperoxy radical has a greater tendency to form the tetramethylethylene epoxide than does the tetramethylethylene peroxy radical. This effect is due to a higher tendency of the hydroperoxy radical to add to the olefin to form the β-peroxyalkyl radical, although the rearrangement of this adduct to form the epoxide is somewhat slower than that of the β-alkylperoxyalkyl radical.

Earlier studies[1–3] have shown that cyclic olefins, conjugated olefins, and aralkanes generally have the same relative reactivity (±20%) toward the various corresponding peroxy radicals. For these peroxy radicals, the organic portions are sufficiently removed from the free valences so that they have little inductive or steric effect on reactivity. However, in one case where steric interference should be maximized,[2] the selectivities for the two peroxy radicals vary by a factor of 2 toward the same two hydrocarbons. This paper gives the reactivities of several hydrocarbons toward the hydroperoxy radical, the simplest of all peroxy radicals, and compares them with reactivities toward typical organic peroxy radicals.

We have shown that oxygen abstracts a hydrogen from the cyclohexadienyl radical in the main propagation step in the oxidation of 1,4-cyclohexadiene.[4] The propagation cycle is

$$HO_2\cdot + C_6H_8 \rightarrow H_2O_2 + C_6H_7\cdot \qquad (1)$$

$$C_6H_7\cdot + O_2 \rightarrow C_6H_6 + HO_2\cdot \qquad (2)$$

Thus cooxidation of 1,4-cyclohexadiene with a second hydrocarbon (RH) will involve the following propagation reactions:

$$HO_2\cdot + C_6H_8 \rightarrow H_2O_2 + C_6H_7\cdot \qquad (3)$$

$$HO_2\cdot + RH \rightarrow H_2O_2 + R\cdot \qquad (4)$$

$$RO_2\cdot + RH \rightarrow RO_2H + R\cdot \qquad (5)$$

$$RO_2\cdot + 1,4\text{-}C_6H_8 \rightarrow RO_2H + C_6H_7\cdot \qquad (6)$$

From the consumption of each reactant (measured by disappearance of reactant or formation of products), the two reactivity ratios, $r_{HO_2\cdot} = k_3/k_4$ and $r_{RO_2\cdot} = k_5/k_6$, are determined by using standard copolymerization and analysis techniques.[1] Thus if the two parent hydrocarbons have different relative reactivities toward each peroxy radical, then $r_{HO_2\cdot} \neq 1/r_{RO_2\cdot}$.

Experimental Section

Reactions were carried out using vacuum line procedures. All hydrocarbons were purchased through common commercial channels. 1,4-Cyclohexadiene (>99.8%), tetralin (>99.8%), tetramethylethylene (98.4%), and chlorobenzene (>99.9%) were passed through silica gel, stored over calcium hydride, and distilled into the reaction vessel as needed. Butadiene (99.88%) was stored as a gas in the vacuum line after distillation from −78 °C, and was measured as a gas in a standard bulb of the vacuum line. Other compounds that were liquids at room temperature were measured as liquids in calibrated tubes in the vacuum line. All reactions were carried out in a water bath at 50 (±0.1) °C. Gas–liquid mixing maintained by a Burell wrist-action shaker (330 cycles/min) and a Vibro Mixer (7500 cycles/min) gave identical results. The analyses of H_2O_2 and H_2O at the completion of the reaction were described previously.[4]

Results

Cooxidations of 1,4-Cyclohexadiene and 1,3-Butadiene. Table I summarizes data for the cooxidation of 1,4-cyclohexadiene and 1,3-butadiene. The consumption of 1,4-cyclohexadiene was measured by formation of benzene, since reactions 3 and 6 are followed immediately by reaction 2. Less water (after reduction of H_2O_2) than benzene is formed because many of the hydroperoxy radicals add to butadiene. The amounts of hydrogen peroxide detected (not reported) are less than the water found after decomposition of hydrogen peroxide; therefore some decomposition

$$H_2O_2 \rightarrow H_2O + \tfrac{1}{2}O_2 \qquad (7)$$

occurs during the reaction as was observed previously.[4] The oxygen consumption is corrected for this decomposition by adding one-half the value of water present at the end of the reaction.

The consumption of butadiene is measured in four different ways. The first method is by measuring the difference in the butadiene before and after reaction; this entails separating butadiene from the reaction mixture, then measuring it as a gas in the standard bulb of the vacuum line. The efficiency of the separation was checked by GLC and correction made when necessary. The second procedure requires an assumption that 1 mol of oxygen is consumed for each mole of hydrocarbon consumed. Thus

$$\Delta 1,4\text{-}C_6H_8 + \Delta\text{hydrocarbon} = \Delta O_2\ (\text{corrected}) \qquad (8)$$

This equation is valid when chain lengths are long. Since we have measured the consumptions of oxygen (corrected) and 1,4-cyclohexadiene, the butadiene consumption is obtained

Table I. Cooxidations of Butadiene (B) and 1,4-Cyclohexadiene (C) At 50 °C with 0.01 M ABN and 3-4 Atm Oxygen

								ΔC,[b] mmol				
C_{av}, M	B_{av}, M	Liq vol, ml	Time, h	ΔC, mmol	ΔH_2O,[a] mmol	ΔO_2, mmol	ΔO_2 cor, mmol	Direct	ΔO_2,[c] C_6H_6	Residue, by NMR	Residue, titration	Weighted average
0.38	10.5	1.03	5.02	0.088	0.031	0.231	0.245	0.156	0.157	0.166	0.162	0.16
0.91	9.40	0.962	4.63	0.257	0.081	0.453	0.493	0.248	0.236		0.273	0.25
0.96	9.09	0.962	5.29	0.385	0.120	0.721	0.735	0.367	0.350	0.403	0.384	0.38
1.08	8.69	0.907	0.97	0.037		0.075		0.046			0.035	0.036
3.22	6.37	0.929	3.17	0.648	0.318	0.877	0.970	0.233	0.322	0.245	0.237	0.24

[a] Water present after decomposition of H_2O_2. [b] See text for different methods of determining ΔC_4H_6. [c] Correction equals ½ H_2O added to oxygen consumption.

Table II. Cooxidations of 1,4-Cyclohexadiene (C) with Tetralin (T) at 50 °C with 0.01 M ABN and 1-3 Atm Oxygen

Expt	C_{av}, M	T_{av}, M	Liq vol, ml	Time, h	ΔO_2, mmol	ΔC,[a] mmol	H_2O_2, mmol	H_2O,[b] mmol	$C_{10}H_{11}OH$, mmol	ΔT,[c] mmol
36	0.95	6.54	2.04	2.00	0.115	0.102	0.019	0.086	0.056	0.056
34	0.130	7.11	2.93	5.92	0.109	0.040	0.0105	0.029[d]	0.066	0.084
35	0.054	7.25	3.93	3.45	0.114	0.034	0.007	0.032	0.083	0.096

[a] Measured by benzene formed. [b] H_2O before H_2O_2 analysis. [c] $\Delta T = \Delta O_2$ (corrected) $- \Delta C$. [d] No direct measurement, estimated from $\Delta C - \Delta H_2O_2$.

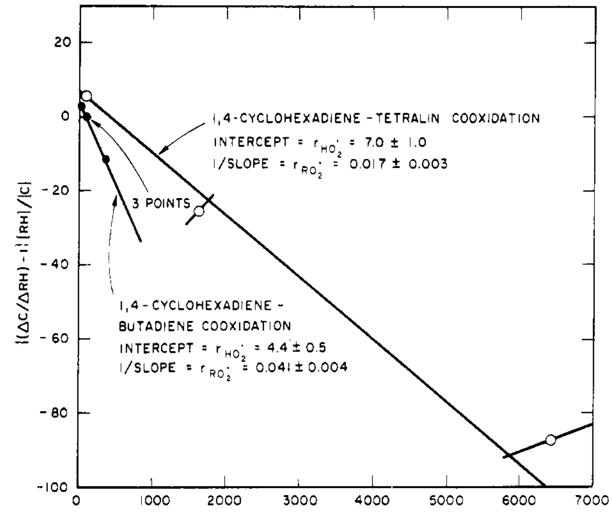


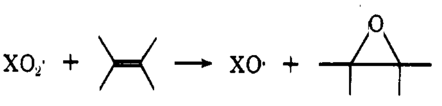
Figure 1.

by difference. The third method makes use of the weight of residue and the ratio of butadiene and hydroperoxy groups in residue as determined by NMR.[4] A fourth method entails subtracting the amount of peroxide oxygen by iodometric titration[4] from the total weight of the residue. A Fineman and Ross analysis (Figure 1) using the weighted average for butadiene consumption and other data in Table I gives $r_{HO_2\cdot} = 4.4 \pm 0.5$ and $r_{RO_2\cdot} = 0.041 \pm 0.004$, $(r_{HO_2\cdot})(r_{RO_2\cdot}) = 0.18 \pm 0.04$, significantly less than the unity expected if both radicals have the same selectivity.

Cooxidations with Tetralin. The amount of tetralin consumed in cooxidation with 1,4-cyclohexadiene was found by determining the tetralin product (generally 97% 1-tetralol and 3% 1-tetralone) by GLC analysis of a reaction mixture after reduction with triphenylphosphine and by use of eq 8. Initial experiments carried to higher conversions than those shown in Table II indicated that the consumed tetralin could not be accounted for as the corresponding alcohol or ketone after hydroperoxide reduction with triphenylphosphine. The average rates of oxidation were also larger than those observed in Table II. However, by carrying out the reactions to relatively low conversions, the two measures of tetralin consumption gave satisfactory agreement. These data are given in Table II. Under the conditions of these experiments (low conversions), the tetralol formation is a slightly better measurement of tetralin consumption and has been used in the Fineman and Ross analysis[1] of the data (Figure 1). The analysis gives the values of $r_{HO_2\cdot}$ and $r_{C_{10}H_{11}O_2\cdot}$ in this system as 7.0 ± 1.0 and 0.017 ± 0.001, respectively. Thus $(r_{HO_2\cdot})\cdot(r_{C_{10}H_{11}O_2\cdot}) = 0.12 \pm 0.02$, which is also significantly less than the unity expected if the two peroxy radicals had the same selectivity.

Cooxidations with Tetramethylethylene. Table III summarizes some oxidations of tetramethylethylene (TM) with and without 1,4-cyclohexadiene. Each reaction mixture was separated into volatile and nonvolatile fractions; the former was analyzed for H_2O_2 and H_2O, titrated for hyroperoxide,[6] and finally analyzed for epoxide and acetone by GLC. The residue was then analyzed for peroxide,[5] and the remainder was assumed to be tetramethylethylene. This procedure is similar to that used by Van Sickle et al.,[7] and our data for pure tetramethylethylene agree with those data; our yield of epoxide is 14%, while Van Sickle's data predict 18% under our conditions. The yields of tetramethylethylene oxide in the cooxidation are two to three times greater than for tetramethylene alone. In experiments 33, 34, and 24, where the ratios of reactants are about the same, the yields of epoxide vary from 44 to 26% as the oxygen pressure is increased from 0.8 to 3.0 atm. The corresponding yields from neat hydrocarbon are 25 to 16% over the same pressure range.[7]

For each molecule of epoxide in the products, one alkoxy or hydroxy radical is formed by the reaction



(9)

Because these radicals, as well as both peroxy radicals, are consuming both hydrocarbons, we are unable to evaluate accurately reactivity ratios. However, in the reactions where $HO_2\cdot$ is the major radical, tetramethylethylene is about one-fourth as reactive as 1,4-cyclohexadiene after correcting for concentration differences.

Table III. Cooxidations of 1,4-Cyclohexadiene (C) with Tetramethylethylene (TM) at 50 °C with 0.1 M ABN

Expt	C_0, M	TM_0, M	Liq vol, ml	Av O_2, atm	Time, h	ΔO_2, mmol	ΔC, mmol	Epoxide, mmol (% ΔTM)[a]	Volatile ^-O_2H, mmol (% ΔTM)[a]	Residue, mg	TM in residue,[b] mmol (% ΔTM)[a]
25	2.63	6.11	1.08	1.8	3.76	0.862	0.532	0.175 (30)	0.085 (15)	38.4	0.310 (54)
33	0.98	7.39	1.06	3.0	3.72	0.262	0.109	0.042 (24)	0.005 (3)	16.0	0.125 (73)
34	0.97	7.39	1.07	0.8	3.76	0.253	0.135	0.078 (44)	0.018 (10)	10.6	0.078 (44)
24	0.93	7.42	1.00	2.4	2.94	0.186	0.084	0.046 (38)	0.000 (0)	10.1	0.072 (59)
23	0	8.12	1.924	2.6	5.55	0.192		0.027 (14)	0.084 (44)	7.8	0.067 (35)

[a] ΔTM determined from epoxide + RO_2H + residue plus 0.0014 to 0.005 mmol acetone for the cooxidations and 0.030 mmol for expt 23. [b] Assuming that all residue is TM except for titratable peroxide; if small amounts of nonperoxidic oxygen are present, these values may be slightly high.

Table IV. Relative and Absolute Reactivities of Some Hydrocarbons toward the Corresponding Peroxy Radicals at 50 °C [a]

		Relative reactivity[a]		
Registry no.	Hydrocarbon	$HO_2\cdot$	$\sim C_4H_6O_2\cdot$	$C_{10}H_{11}O_2\cdot$
628-41-1	1,4-Cyclohexadiene	1.0[b] (4200[c])	1.0[b] (~2900)	1.0[b] (1130)
106-99-0	1,3-Butadiene	0.23 (970)	0.041 (~120[c])	0.037 (42)
119-64-2	Tetralin	0.14 (590)	0.012 (~35)	0.017 (19.2[c])
563-79-1	Tetramethylethylene	0.25 (1050		

[a] Values in parentheses are propagation rate constants in (M s)$^{-1}$ units. [b] Assumed. [c] Reference 11. [d] The value for butadiene homopropagation is not known but is approximated by value for styrene (ref 3), since butadiene and styrene have similar relative reactivities toward peroxy radicals (1).

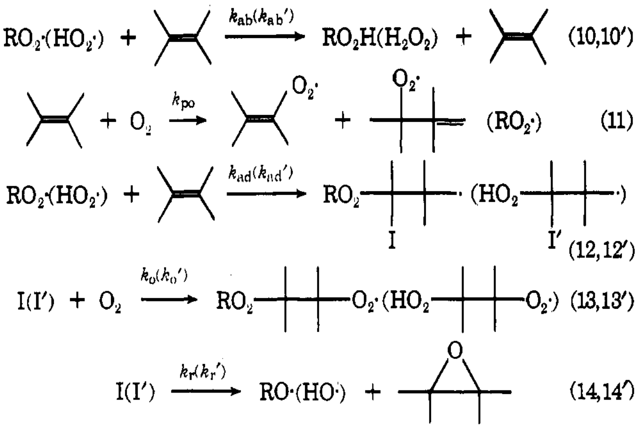
Discussion

Selectivity of Hydroperoxy Radicals in Cooxidation. Table IV summarizes the relative reactivities of butadiene, tetralin, and cyclohexadiene toward the corresponding peroxy radicals and shows that the hydroperoxy radical is less selective than peroxy radicals from tetralin or butadiene. Limited data for tetramethylethylene are included. The absolute propagation constants (calculated from appropriate relative reactivities and homopropagation constants) included in Table IV show that this reduction in selectivity corresponds with an increase in reactivity. The absolute rate constants decrease with increasing steric complexity of the peroxy radicals,[8]

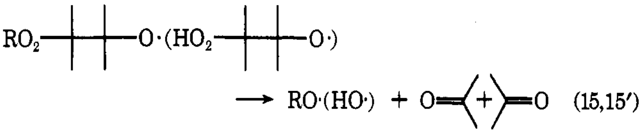
$$HO_2\cdot > \sim C_4H_6O_2\cdot > C_{10}H_{11}O_2\cdot$$

consistent with the trend observed by Howard and Ingold[9] that tertiary peroxy radicals abstract hydrogen and add to carbon–carbon double bonds more slowly than secondary or primary peroxy radicals. However, the large differences between the rate constants for hydroperoxy radicals and hydrocarbon peroxy radicals suggest that an inductive effect must be important. The reactivity increase parallels the increase in electron-withdrawing ability of the R group of RO_2.[10]

Selectivity in Addition and Abstraction. Table III shows that more addition products (epoxide and residue) are formed from tetramethylethylene in the presence of cyclohexadiene than in its absence. Thus the hydroperoxy radical has a greater tendency toward addition to the carbon–carbon double bond relative to hydrogen abstraction than do the peroxy radicals formed from tetramethylethylene. Product-producing reactions are



where reactions of $RO_2\cdot$ and $HO_2\cdot$ radicals are designated by unprimed and primed notations, respectively. The peroxy radical formed in reaction 13 or 13′ can react like $RO_2\cdot$. If it reacts by hydrogen abstraction, a stable material appears as residue. If it adds (reaction 12) and reaction 14 occurs, the resulting RO· radical is capable of decomposing to acetone and another RO· radical as in reaction 15.



In the oxidation of tetramethylethylene, the reacted olefin consumed by addition corresponds to the sum of epoxide, acetone, and one-half the residue, assuming that the residue is largely dimeric, $C_6H_{11}O_2C(CH_3)_2C(CH_3)_2O_2H$. Thus the data from experiment 23 in Table III give a value of 0.40 for the fraction of olefin consumed by addition (f_a), in agreement with the previously reported value of 0.42.[7] In the cooxidation experiments, the residue, from peroxide analyses, appears to be of the structure $HO_2C(CH_3)_2C(CH_3)_2O_2H$; thus the fraction of addition, the sum of epoxide, one-half the acetone, and all the residue, is approximately 0.9. Both hydroperoxy and tetramethylethylene peroxy radicals participate in the cooxidation experiments, so that the fraction of addition by hydroperoxy alone on tetramethylethylene (f_a') must be slightly larger than 0.9. Since for alkylperoxy radicals $f_a = k_{ad}/(k_{ad} + k_{ab}) = 0.40$ and for hydroperoxy radicals $f_a' = k_{ad}'/(k_{ad}' + k_{ab}')$

$\simeq 0.9$, the simpler ratios are $k_{ad}/k_{ab} \simeq 0.7$ and $k_{ad}'/k_{ab}' \simeq 9$; thus the hydroperoxy radical gives more addition with nonconjugated carbon–carbon double bonds (relative to hydrogen abstraction) than alkylperoxy radicals.

Epoxide Formation. In the oxidation of neat tetramethylethylene the kinetic expression for the mole ratio of olefin consumed to epoxide formed is given by the expression[6]

$$\frac{-d[TM]}{d[E]} = \frac{1 + f_a + [O_2]k_o/k_r}{f_a} \qquad (16)$$

If we assume that tetramethylethylene in the cooxidations is attacked only by hydroperoxy radicals, a similar expression is obtained:

$$\frac{-d[TM]}{d[E]} = \frac{f_a' + [O_2]k_o'/k_a'}{f_a'} \qquad (17)$$

Since $-d[TM]/d[E]$, f_a', and $[O_2]$ are known, the ratio k_o'/k_r' is evaluated as ~90 l./mol. The reported value of k_o/k_r is 32 l./mol, while from experiment 23 (Table III) and eq 26, a value of 50 l./mol is obtained. Since k_o' should be essentially the same as k_o, $k_r/k_r' = 1.5$–2.0. This difference is consistent with 5 kcal/mol weaker oxygen–oxygen bonds in dialkyl peroxides than in hydroperoxides.[12] Reaction 14 and 14′ are both exothermic and only a small portion of difference in heats is seen in the rate constants (about 0.5 kcal/mol) if all the difference is in the activation energy.

Registry No.—Hydroperoxy radical, 14691-59-9.

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(9) From our data for the oxidations of butadiene (ref 5), the butadiene peroxy radical has the formula $Y(O_2C_4H_6)_xO_2$, where the end group Y is either a fragment from the initiator, a hydrogen atom, or a fragment corresponding to the cooxidant. In the oxidation of butadiene by itself, *x* averages about 30, but in the cooxidations it is generally of the order of 1–3 owing to extensive reaction of the other hydrocarbon by hydrogen abstraction. The C_4H_6 units in the final product are present as both 1,2 addition units and trans 1,4 addition units in approximately equal amounts. Thus butadiene peroxy radical comprises both primary and secondary allylperoxy radicals and is somewhat less sterically hindered than tetralin peroxy radical, which is a secondary benzylic peroxy radical.

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Multi-Bond Fragmentation of *tert*-Butyl 2-Methyl-2-*tert*-butylperoxyperpropanoate

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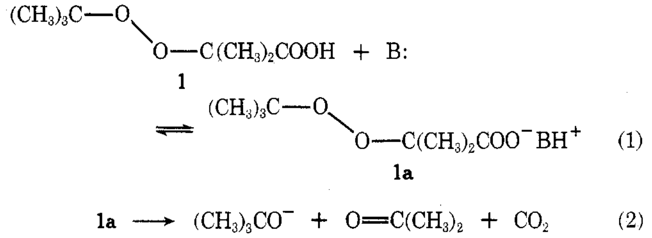
A kinetic study of the thermolysis of *tert*-butyl 2-methyl-2-*tert*-butylperoxyperpropanoate (**2**) and a model perester, *tert*-butyl 2-methoxy-2-methylperpropanoate (**5**), is presented. The decompositions follow first-order kinetics in the presence of styrene, where the activation parameters for **2** are $E_a = 18.8 \pm 0.4$ kcal/mol, $\Delta H^{\ddagger} = 18.2 \pm 0.4$ kcal/mol, log $A = 10.4$, and $\Delta S^{\ddagger} = -13.0 \pm 1.5$ eu. Activation parameters for **5** are $E_a = 20.6 \pm 0.2$ kcal/mol, $\Delta H^{\ddagger} = 20.1 \pm 0.2$ kcal/mol, log $A = 12.8$, and $\Delta S^{\ddagger} = 2.7 \pm 1.0$ eu. Products from the thermolysis of **2** in benzene are (in 100 mmol/mmol **2**) acetone (169), *tert*-butyl alcohol (102), and *tert*-butyl peroxide (9.5). Attempts to trap the radical $(CH_3)_3COO\dot{C}(CH_3)_2$, which could be generated by two-bond homolysis of **2**, were unsuccessful. CIDNP signals were not observed for the potential reaction of this radical with a *tert*-butoxy radical in or out of the solvent cage. However, CIDNP signals were not observed either in the thermolysis of **5**. Correlations of several peresters in $\Delta H^{\ddagger}$ vs. $\Delta S^{\ddagger}$ and $\Delta H^{\ddagger}$ vs. $\Delta H_r°$ plots were made in order to differentiate between two- and three-bond homolysis processes for **2**. Although the analysis is not unambiguous, the results tend to favor a three-bond homolysis for **2**. Excited state acetone is not produced by thermolysis of **2**, which is consistent with the maximum heat of reaction (−21.9 kcal/mol).

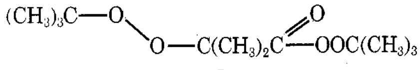
Previously we reported the base-catalyzed decomposition of 2-methyl-2-*tert*-butylperoxypropanoic acid (**1**). This reaction was most conveniently explained as a concerted fragmentation of the carboxylate anion (**1a**).[1]

Scheme I



$$\mathbf{1a} \longrightarrow (CH_3)_3CO^- + O{=}C(CH_3)_2 + CO_2 \qquad (2)$$

We now report an analogous free-radical decomposition in this peroxide system, namely, the thermolysis of *tert*-butyl 2-methyl-2-*tert*-butylperoxyperpropanoate (**2**). Three unimolecular homolytic reaction paths may be considered for perester **2** (Scheme II). As one proceeds from process 1 to 2 to 3, homolysis of one to two to three bonds occurs in the rate-determining step. A kinetic and product study, along with radical trapping experiments, are employed here in an attempt to differentiate between these three processes.



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