

## REMOTE FUNCTIONALISATION BY FERROUS ION-CUPRIC ION INDUCED DECOMPOSITION OF ALKYL HYDROPEROXIDES

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**Abstract**—By decomposition of alkyl hydroperoxides 1–8 with ferrous sulfate–cupric acetate reagent, intramolecular functionalisation of remote non-activated C atom takes place and unsaturated alcohols with double bond mainly at  $\delta$ -position are obtained. The reaction proceeds involving the corresponding alkoxy radical 9 and  $\delta$ -carbon radical 10 as intermediates. One-electron oxidative interception of  $\delta$ -carbon radical by cupric acetate does not involve the corresponding carbonium ion; instead, the alkyl-copper intermediate 11 is formed and by elimination affords olefinic alcohols. The isotope effect for this elimination process was found to be  $k_H/k_D = 6.1$ .

Intramolecular functionalisation of remote non-activated C atoms was achieved by hydrogen transfer from conformationally close  $\delta$ -C atom to the electron-deficient alkoxy or amino radicals, as a key step in this type of reaction.<sup>1–4</sup> Alkoxy radicals can be generated from different types of precursors. However, in all cases where intramolecular hydrogen abstraction takes place, alkoxy radicals are part of a radical pair system.<sup>1–7</sup> The participation of the radical X $\cdot$  (eq. 1) in the 1,5-hydrogen transfer process and functionalisation of  $\delta$ -C atom was widely investigated.<sup>1–7</sup>

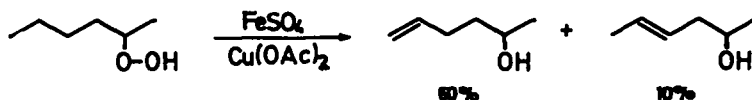


Alkyl hydroperoxides are convenient substrates which, by metal-ion-promoted decomposition, can generate the alkoxy radicals that cannot be in the radical pair system with metallic ions.<sup>8,9</sup> Tertiary alkyl hydroperoxides can be converted into the corresponding  $\delta$ - or  $\gamma$ -unsaturated alcohols by ferrous and cupric ion promoted decomposition.<sup>9</sup>

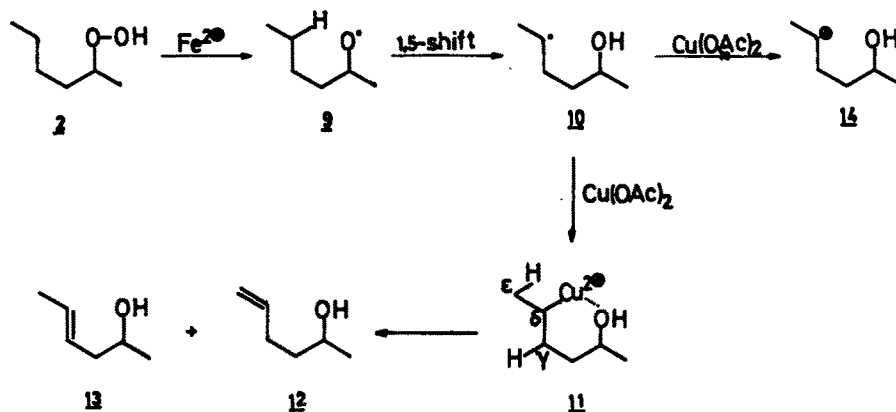
This reaction has been extended to the primary and secondary alkyl hydroperoxides containing a side chain of at least four C atoms.<sup>8</sup> The reaction is more successful with primary and secondary alkyl hydroperoxides than with tertiary systems, presumably because the competing  $\beta$ -fragmentation reaction is suppressed (Scheme 1). Although disproportionation of alkoxy radicals to corresponding saturated alcohols and carbonyl compounds takes place to some extent it is still less than  $\beta$ -cleavage pro-

cess in the decomposition of tertiary alkyl hydroperoxides.<sup>8,9</sup>

The ferrous sulfate–cupric acetate promoted decomposition of primary and secondary alkyl hydroperoxides 1–8 (Table 1), afford the corresponding  $\delta$ - and  $\gamma$ -unsaturated alcohols as main products, in addition to small amounts of saturated alcohols and carbonyl compounds. Alkyl hydroperoxides undergo one-electron reductive decomposition of the peroxy bond with ferrous ion, as in Fenton's reagent, generating the corresponding alkoxy radical 9 (Scheme 2).<sup>10,11</sup> The resulting ferric ion (with stable 3d<sup>5</sup> electron configuration) does not interact with the alkoxy radical. Further fate of the alkoxy radical depends on the nature and structure of the alkyl chain and the reaction conditions. By possessing at least one hydrogen at  $\delta$ -C atom, intramolecular hydrogen abstraction is the preferential route of stabilization of primary and secondary alkoxy radicals, thus generating a  $\delta$ -C radical 10. When the  $\delta$ -carbon radical is generated from alkyl hypochlorites they undergo the chain reaction affording the corresponding 1,4-chlorohydrins;<sup>3,12</sup> nitroso-alcohols are obtained in the Barton's photolysis of alkyl nitrites<sup>1,13</sup> and tetrahydrofuran derivatives are formed in the lead tetraacetate oxidation of alcohols.<sup>3,14</sup> However, the  $\delta$ -carbon radical 10 generated by ferrous ion promoted decomposition of alkyl hydroperoxides, can be oxidatively intercepted by cupric ion affording the corresponding  $\delta$ - and  $\gamma$ -unsaturated alcohols 12 and 13 as final products<sup>8,9</sup> (Scheme 2).



Scheme 1.



Scheme 2.

Interception of the  $\delta$ -C radical by cupric ion, in the intramolecular functionalisation reactions, was also achieved in the photolysis of alkyl nitrites in the presence of cupric acetate<sup>15</sup> and by thermal or ferrous ion induced decomposition of dialkyl peroxides in the presence of cupric acetate.<sup>16,17</sup> However, interception of  $\delta$ -alkyl radical, generated from the alkyl hypohalites or by lead tetraacetate oxidation of alcohols could not be achieved by cupric acetate.

The formation of an olefinic double bond is not a simple elimination reaction, because the main product of intramolecular functionalisation is an unsaturated alcohol possessing a double bond at the  $\delta$ -position **12**, and even a terminal double bond is formed. The ratio of  $\gamma$ - and  $\delta$ -unsaturated alcohols, even if the latter have the less substituted olefinic bond, is between 1 to 4 and 1 to 9; e.g. the ratio of 4-hexen-2-ol (**13**) to 5-hexen-2-ol (**12**), obtained in the decomposition of 2-hexyl hydroperoxide (**2**), is 1 to 6 (Table 1). It means that the formation of the olefinic bond from  $\delta$ -carbon radical **10**, in the oxidative elimination process by cupric acetate involving one inner-sphere electron-transfer process, is not simple elimination, because there is substantial preferentiality of removing a hydrogen from  $\varepsilon$ -C and then from  $\gamma$ -C atom in the open chain hydroperoxides. This electron-transfer elimination process is therefore in accordance with neither Zaitsev's nor Hofmann's rule for introduction of an olefinic double bond in elimination reactions. The oxidation of  $\delta$ -carbon radical **10** (Scheme 2) by cupric ion does not involve the corresponding  $\delta$ -carbonium ion **14**, because if the carbonium ion was involved the more substituted double bond should be formed. Alkyl substituents on the  $\varepsilon$ -C and  $\gamma$ -C atoms do not control the direction of elimination of hydrogen from the adjacent C atom. Cupric ion is responsible for the course of elimination of hydrogen from the adjacent C atom involving alkyl-copper intermediate **11** which undergoes the simultaneous  $C_\delta$ -Cu and  $C_\varepsilon$ -H (or  $C_\gamma$ -H) bonds scission, furnishing the olefinic alcohols (**12** and **13**) and cupric hydride.<sup>18-20</sup> In the alkyl-copper intermediate **11a**, the cupric ion probably is coordinatively attached to the hydroxylic

oxygen forming a 6-membered cyclic transition state **11a** (Fig. 1). Formation of a double bond, from the cyclic transition state, rather proceeds through *syn* E2 type of elimination than *anti*-elimination.<sup>10</sup> Preferential expulsion of hydrogen from  $\delta$ -C atom is due to conformational requirements necessary for *syn* E2 elimination because only  $C_\varepsilon$ -H bonds (e.g.  $H^f$ ) can reach eclipsing conformation with  $C_\delta$ -Cu bond (dihedral angle is  $0^\circ$ ). In such conformation the distance between the Cu atom and with it eclipsing hydrogen at  $\varepsilon$ -C atom ( $C_\varepsilon$ -H<sup>f</sup>) is 2.5 Å (by Dreiding's model) allowing proton transfer to the Cu ion. Quasi-axial hydrogens on the  $\gamma$ -C atom ( $H^g$ ), in the cyclic transition state **11a**, cannot reach eclipsing conformation with  $C_\delta$ -Cu bond (dihedral angle is about  $60^\circ$ ) and *syn*-elimination occurs only to a slight extent affording  $\gamma$ -unsaturated alcohol (Table 1). We assume that *anti*-elimination of hydrogen, either from  $\gamma$ -C or  $\varepsilon$ -C atom, is not involved because in such a case we should obtain at least the same ratio of the  $\delta$ - and  $\gamma$ -olefinic alcohols, since quasi-equatorial  $C_\gamma$ -H<sup>g</sup> bond and  $C_\delta$ -Cu bond have dihedral angle of  $180^\circ$  favourable for *anti*-elimination, as well as hydrogens on  $\varepsilon$ -C atom may exist in *anti*-position with  $C_\delta$ -Cu bond.

Evidence supporting the suggested mechanism of this one electron-transfer reaction and double bond formation is the oxidation of  $\delta$ -alkyl radical by cupric acetate was also obtained in the decomposition of alkyl hydroperoxides **5** and **6** (Table 1) having a neopentyl type  $\delta$ -C atom(s). No neopentyl type rearrangement compounds were found among the products of ferrous and cupric ion promoted decomposition of alkyl hydroperoxides **5** and **6** (Schemes 3 and 4), indicating that neopentyl carbonium ion **16** is not involved in the oxidation of

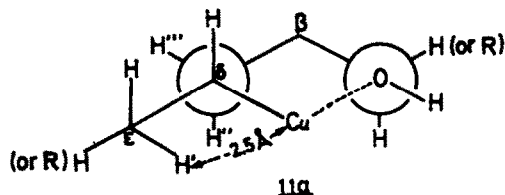
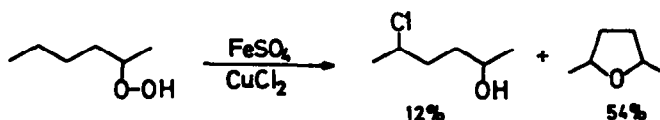


Fig. 1.





Scheme 6.

peaks and also by mass spectrum measurements of ratio of molecular peaks  $m/e$  103 (23) and 102 (22) the isotope effect was determined to be  $k_H/k_D = 6.1$ . This isotope effect indicates that the formation of olefinic double bond in one-electron oxidation of  $\delta$ -carbon radical by cupric ion is concerted E2 type of elimination process and that this electron-transfer reaction does not involve the corresponding  $\delta$ -carbonium ion as an intermediate.

When the decomposition of alkyl hydroperoxides was carried out with cupric chloride, instead of cupric acetate, and ferrous sulfate, there also occurred intramolecular functionalisation of  $\delta$ -C atom; however, corresponding cyclic ethers were obtained as major products of the reaction, instead of unsaturated alcohols, in addition to a small amount of 1,4-chlorohydrins (Scheme 6). No traces of tetrahydrofuran derivatives were obtained in the reac-

Table 1. Products of decomposition of alkyl hydroperoxides by ferrous sulfate-cupric acetate reagent

Alkyl hydroperoxides	Products of intramolecular functionalization /yield %/	Corresponding carbonyl compounds and alcohols /yield %/
	<sup>a)</sup>	(7) (19)
		(19) (11)
		(5) (11)
		(27) (40)
		(10) (25)
		(17) (35)
		(27) (35)
		(9) (14)

<sup>a</sup> Carbon-13 NMR showed presence of *cis*- and *trans*-isomers with ratio 1:10.

<sup>b</sup> In the reaction of 2-hexyl hydroperoxide with cupric chloride and ferrous sulfate the intermediary 5-chloro-2-hexanol is converted into 53% yield to mixture of *cis*- and *trans*-2,5-dimethyltetrahydrofuran.

<sup>c</sup> 2-*t*-Butyltetrahydrofuran is obtained only in 2% yield.

<sup>d</sup> 6-Heptenal was isolated in 13% yield.

tions with cupric acetate. The 1,4-chlorohydrins may be the intermediate in the formation of cyclic ethers. It means that the oxidation of  $\delta$ -carbon radical by cupric chloride proceeds by a ligand-transfer process,<sup>10</sup> probably due to greater nucleophilicity of chloride anion as a ligand than acetate ion.

By these two types of oxidative interception reactions of  $\delta$ -carbon radical by cupric ion, two essentially different reaction products can be obtained in fair yields. Unsaturated alcohols with double bond at  $\delta$ -position were obtained involving one inner-sphere electron-transfer oxidation by cupric acetate, while the reaction of alkyl hydroperoxides with ferrous sulfate-cupric chloride reagent, affording 1,4-chlorohydrins (and hence cyclic ether derivatives), proceeds by a ligand-transfer process.

### EXPERIMENTAL

B.ps. are uncorrected. Glc analysis and preparative separations were carried on Varian 1400 and 90-P-3 instruments equipped with columns of 10% Carbowax 20M and 25% XE-60 on Chromosorb P (2 m x 2 mm, 2 m x 6 mm). Calculation of yields were carried out by using an internal standard. IR spectra were recorded on Perkin-Elmer instrument Model 337-Grating (as film or  $\text{CCl}_4$  sols). NMR spectra were recorded on Varian A-60A instrument using  $\text{CCl}_4$  sols. and TMS as internal standard (chemical shifts are reported in  $\delta$  values of ppm units). Mass spectra were performed on Varian-Atlas CH-4 spectrometer. All solvents employed in preparations and decomposition reactions were carefully purified before use. Metal salts were Merck's p.a. purity grade.

**Synthesis of alkyl hydroperoxides.** Aliphatic primary and secondary alkyl hydroperoxides were prepared from the corresponding alkyl methane sulfonates by treatment with an alkaline solon of  $\text{H}_2\text{O}_2$ , according to the procedure described.<sup>22</sup> Purity was checked by KI-treatment and titration of liberated  $\text{I}_2$  with  $\text{Na}_2\text{S}_2\text{O}_3$  standard solon. Cycloheptyl hydroperoxide was made by oxidation of cycloheptylmagnesium chloride with oxygen as described.<sup>23</sup>

New prepared alkyl hydroperoxides have the following properties: *iso*-Hexyl hydroperoxide (3) (purity 94%): b.p. 30°/0.04 mm Hg; IR spectrum (film) 3350  $\text{cm}^{-1}$ , 1100  $\text{cm}^{-1}$  and 1010  $\text{cm}^{-1}$ ; NMR spectrum  $\delta = 0.93$  (d 6H),  $\delta = 1.10$ –1.80 (m 5H), and  $\delta = 3.97$  (t 2H). 3,3-Dimethyl-butyl hydroperoxide (5) (94% purity): b.p. 32°/0.04 mm Hg; IR spectrum (film), 3390  $\text{cm}^{-1}$ , 1020  $\text{cm}^{-1}$ ; NMR spectrum  $\delta = 0.91$  (s 9H),  $\delta = 1.50$  (t 2H),  $\delta = 3.90$  (t 2H),  $\delta = 8.40$  (a 1H). 5,5-Dimethylhexyl hydroperoxide (6) (95% purity): b.p. 47°/0.04 mm Hg; IR spectrum (film) 3390  $\text{cm}^{-1}$ , 1040  $\text{cm}^{-1}$  (weak); NMR spectrum,  $\delta = 0.90$  (s 9H),  $\delta = 1.10$ –1.80 (m 6H) and  $\delta = 3.96$  (t 2H). 5,5,5-Trideuterio-*iso*-hexyl hydroperoxide (8): IR spectrum (film) 3350  $\text{cm}^{-1}$ , 2200  $\text{cm}^{-1}$  ( $-\text{CD}_2$ ), 1050  $\text{cm}^{-1}$ ; NMR spectrum  $\delta = 0.92$  (d 3H),  $\delta = 1.10$ –1.80 (m 5H) and  $\delta = 3.98$  (t 2H).

**General procedure for decomposition of alkyl hydroperoxides 1–8.** A mixture of 0.007 mole well powdered crystalline  $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ , 0.018 mole powdered  $\text{Cu}(\text{OAc})_2 \cdot \text{H}_2\text{O}$ , 25 ml AcOH and 3 ml water was stirred under  $\text{N}_2$  for 15 min and then 0.02 mole of alkyl hydroperoxide was slowly added. After addition of peroxide the mixture was stirred at room temp during 1 to 2 hr. Water was added to dissolve inorganic salts and the resultant solon was extracted with ether (3 x 50 ml). The etheral solon was washed with water, sat  $\text{NaHCO}_3$ al and water to remove AcOH, dried over  $\text{K}_2\text{CO}_3$ . The solvent was removed by distillation at atmospheric pressure and the

residue was distilled from a small scale apparatus under reduced pressure. The products were analysed by glc and identified by IR, NMR and mass spectra. Products and their yields are given in Table 1.

**Decomposition of *n*-hexyl hydroperoxide (1).** Reaction was carried out by using 2 g  $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ , 3.25 g  $\text{Cu}(\text{OAc})_2 \cdot \text{H}_2\text{O}$ , 25 ml AcOH, 3 ml water and 2.36 g of *n*-hexyl hydroperoxide (purity 93%), b.p. 30°/0.05 mm Hg.

From the mixture the following products were isolated and characterised: 4-hexenol, IR (film) 3010  $\text{cm}^{-1}$ , 1060  $\text{cm}^{-1}$ , 960  $\text{cm}^{-1}$  (disubstituted olefin); NMR  $\delta = 1.50$ –2.30 (7H),  $\delta = 3.60$  (t 2H) and  $\delta = 5.42$  (m 2H), <sup>13</sup>C NMR showed presence of *cis*- and *trans*-isomers with ratio 1:10; mass spectrum *m/e* 100 (M), 82 and 67. 3-Hexenol, IR (film) 3010  $\text{cm}^{-1}$ , 1050  $\text{cm}^{-1}$  and 970  $\text{cm}^{-1}$ ; NMR  $\delta = 0.90$ –2.40 (7H),  $\delta = 3.50$  (2H) and  $\delta = 5.40$  (2H); mass spectrum *m/e* 100 (M), 82 and 67 (67 is much lower intensity than for 4-hexenol). Satisfactory spectral data were obtained for *n*-hexanol and hexanal, as by-products, and were compared with authentic samples.

### Decomposition of 2-hexyl hydroperoxide (2)

(a) **With cupric acetate.** The reaction was carried out by using 1.94 g  $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ , 2.78 g  $\text{Cu}(\text{OAc})_2 \cdot \text{H}_2\text{O}$  (both well powdered), 25 ml AcOH, 3 ml water and 2.36 g 2-hexyl hydroperoxide (95% purity), b.p. 28°/0.05 mm Hg. The mixture was stirred under  $\text{N}_2$  for 1 hr and worked up as described. The following products were isolated and identified: 5-hexen-2-ol, IR (film) 3070  $\text{cm}^{-1}$ , 1120  $\text{cm}^{-1}$ , 990  $\text{cm}^{-1}$  and 920  $\text{cm}^{-1}$ , NMR  $\delta = 1.10$  (d 3H),  $\delta = 1.50$  (t 2H),  $\delta = 2.10$  (t 2H),  $\delta = 3.80$  (q 1H),  $\delta = 3.42$  (broad singlet 1H),  $\delta = 5.00$  (m 2H) and  $\delta = 5.70$  (m 1H); mass spectrum *m/e* 100 (M), 82, 68 and 57. 4-Hexen-2-ol, IR (film) 3005  $\text{cm}^{-1}$ , 1080  $\text{cm}^{-1}$ , 1110  $\text{cm}^{-1}$  and 970  $\text{cm}^{-1}$ ; NMR  $\delta = 1.16$  (d 3H),  $\delta = 1.60$  (m 2H),  $\delta = 2.10$  (3H),  $\delta = 3.60$  (q 1H) and  $\delta = 5.37$  (vinyl 2H); mass spectrum *m/e* 100 (M), 56 and 45. 2-Hexanol and 2-hexanone were identified by comparing spectral data with authentic samples.

(b) **With cupric chloride.** A mixture of 1 g  $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ , 1.34 g  $\text{CuCl}_2$ , 20 ml AcOH, 2 ml water and 1.2 g 2-hexyl hydroperoxide was stirred under  $\text{N}_2$  for 2 hrs. From the mixture the following were isolated and identified: 2,5-dimethyltetrahydrofuran (53%) (1:1 mixture of *cis*- and *trans*-isomers), 5-chloro-2-hexanol (12%), 2-hexanol (20%) and 2-hexanone (11%). Spectral data of these products were compared with those of authentic samples; agreement was found to be excellent.

**Decomposition of *iso*-hexyl hydroperoxide (3).** *iso*-Hexyl hydroperoxide (1.2 g); (purity 94%), b.p. 30°/0.1 mm Hg was treated with 1.0 g  $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ , 1.3 g  $\text{Cu}(\text{OAc})_2 \cdot \text{H}_2\text{O}$ , 20 ml AcOH and 1.5 ml water under  $\text{N}_2$  during 1 hr. The following products were isolated by glc as described: 4-methyl-4-pentenol, IR (film) 3055  $\text{cm}^{-1}$ , 1050  $\text{cm}^{-1}$ , 890  $\text{cm}^{-1}$ ; NMR  $\delta = 1.72$  (s 3H),  $\delta = 1.5$ –1.80 (2H),  $\delta = 2.05$  (m 2H),  $\delta = 3.55$  (t 2H) and  $\delta = 4.70$  (s 2H); 4-methyl-3-pentenol was identified by comparing spectral data with sample prepared independently.

**Decomposition of *iso*-amyl hydroperoxide (4).** *iso*-Amyl hydroperoxide (2, 1 g; purity 97%), b.p. 30°/0.03 mm Hg was stirred with 1.9 g  $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ , 2.7 g  $\text{Cu}(\text{OAc})_2 \cdot \text{H}_2\text{O}$ , 25 ml AcOH and 2 ml water for 2 hr under  $\text{N}_2$ . From the mixture the following products were isolated: 3-methyl-3-butenol, IR 3070  $\text{cm}^{-1}$ , 1640  $\text{cm}^{-1}$ , 1050  $\text{cm}^{-1}$  and 890  $\text{cm}^{-1}$ ; NMR  $\delta = 1.72$  (s 3H),  $\delta = 2.22$  (t 2H),  $\delta = 3.60$  (t 2H) and  $\delta = 4.72$  (2H). Saturated alcohol and corresponding aldehyde were identified by comparing spectral data with authentic samples.

**Decomposition of 3,3-dimethylbutyl hydroperoxide (5).** The reaction was carried out by using 2.36 g 3,3-dimethylbutyl hydroperoxide (purity 94%), 2.22 g  $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ , 2.91 g  $\text{Cu}(\text{OAc})_2 \cdot \text{H}_2\text{O}$ , 25 ml AcOH and

3 ml water. The mixture was stirred under  $N_2$  for 2 hr and worked up as before. The products were isolated by glc and identified by IR, NMR and mass spectra. 3,3-Dimethyltetrahydrofuran: IR (film)  $1075\text{ cm}^{-1}$  (C—O stretch.); NMR  $\delta = 1.10$  (s 6H),  $\delta = 1.63$  (t 2H),  $\delta = 3.30$  (s 2H) and  $3.75$  (t 2H); mass spectrum  $m/e$  100 (M), 85, 70 and 55. For the 3,3-dimethylbutanal and 3,3-dimethylbutanol spectral data were in full agreement with authentic samples.

**Decomposition of 5,5-dimethylhexyl hydroperoxide (6).** The mixture of 1.46 g 5,5-dimethylhexyl hydroperoxide (95% purity), b.p.  $50^\circ/0.04\text{ mm Hg}$ , 1.11 g  $FeSO_4 \cdot 7H_2O$ , 1.45 g  $Cu(OAc)_2 \cdot H_2O$ , 12 ml AcOH and 1.5 ml water was stirred, at room temp under  $N_2$  for 1.5 hr. The mixture was worked up as described and the following compounds isolated by glc: 5,5-dimethyl-3-hexenol, IR (film)  $3020\text{ cm}^{-1}$  (vinyl C—H),  $980\text{ cm}^{-1}$  (trans disubstituted olefin); NMR  $\delta = 1.00$  (s 9H),  $\delta = 2.17$  (q 2H),  $\delta = 3.50$  (t 2H) and  $5.30$  (vinyl 2H).

**Decomposition of cycloheptyl hydroperoxide (7).** A mixture of 1.9 g  $FeSO_4 \cdot 7H_2O$ , 2.70 g  $Cu(OAc)_2 \cdot H_2O$ , 25 ml AcOH, 2 ml water and 2.60 g cycloheptyl hydroperoxide (89% purity) b.p.  $30^\circ/0.05\text{ mm Hg}$ , was stirred under  $N_2$  for 1 hr. 4-Cycloheptenol was isolated from the mixture by glc and characterized by IR (film)  $3005\text{ cm}^{-1}$ ,  $1640\text{ cm}^{-1}$ ,  $1045\text{ cm}^{-1}$  and  $710\text{ cm}^{-1}$ ; NMR  $\delta = 1.4$ – $2.4$  (broad multiplet 8H),  $\delta = 3.78$  (m 1H),  $\delta = 5.75$  (2H); mass spectrum is in accordance with the proposed structure. However, isomeric 3-cycloheptenol was not isolated as a pure compound, because it was contaminated with isomeric 4-cycloheptenol, but all spectral data supported the proposed structure. 6-Heptenal: IR  $3065\text{ cm}^{-1}$ ,  $2710\text{ cm}^{-1}$ ,  $1720\text{ cm}^{-1}$ ,  $1640\text{ cm}^{-1}$ ,  $995\text{ cm}^{-1}$  and  $920\text{ cm}^{-1}$ ; NMR  $\delta = 1.30$ – $1.70$  (m 4H),  $\delta = 1.90$ – $2.60$  (m 4H),  $\delta = 5.02$  (m 2H),  $\delta = 5.70$  (m 1H),  $\delta = 7.50$  offset 140 Hz (1H); 2,4-dinitrophenylhydrazone m.p.  $95^\circ\text{C}$ . Satisfactory spectral data were obtained for cycloheptanol and cycloheptanone.

**Synthesis of 5,5,5-trideuterio-iso-hexyl hydroperoxide (8).** Alkylation of diethyl methylmalonate (13 g) was carried out by 10 g of trideuteriomethyl iodide in the presence of 1.74 g Na in 65 ml abs EtOH.<sup>24</sup> Diethyl trideuterio-methyl-methyl malonate, b.p.  $40$ – $42^\circ/0.1\text{ mm Hg}$ , was obtained in 91% yield (13 g), with satisfactory spectral data (IR: 2240, 2120 and  $2070\text{ cm}^{-1}$  for  $GD_3$ ). Decarboxylation of this malonic ester was carried out by NaCl (5 g) in wet dimethyl sulfoxide (65 ml) at  $155^\circ$ <sup>25</sup> and ethyl  $\alpha$ -trideuteriomethylpropionate was obtained in 78% yield (6.4 g), b.p.  $110^\circ$ . Reduction of this ester with LAH, tosylation<sup>26</sup> of the corresponding alcohol and solvolysis in KI solon<sup>27</sup> yielded 2-trideuteriomethylpropyl iodide (5.1 g). Alkylation of diethyl malonate (4.80 g) was repeated but now with 5.1 g of 2-trideuteriomethylpropyl iodide in 30 ml dry EtOH and 0.7 g Na,<sup>24</sup> alkylated malonic ester was obtained in 86% yield (4.9 g) with satisfactory spectral evidence for this structure. Decarboxylation was carried out in the same manner as described with 75% yield.<sup>25</sup> After reduction by LAH, 1.7 g of 5,5,5-trideuterio-iso-hexanol was obtained in all over yield from  $CD_3I$  of 22% with correct IR, NMR and mass spectra: IR (film)  $3300\text{ cm}^{-1}$ ,  $2200\text{ cm}^{-1}$  and  $2060\text{ cm}^{-1}$  (for  $-CD_3$ ),  $1050\text{ cm}^{-1}$ ; NMR  $\delta = 0.88$  (d 3H),  $\delta = 1.00$ – $1.80$  (m 5H) and  $\delta = 3.55$  (2H); mass spectrum  $m/e$  105 (M), 90, 88 and 87. 5,5,5-Trideuterio-iso-hexyl hydroperoxide was prepared as described for iso-hexyl hydroperoxide.

**Decomposition of 5,5,5-trideuterio-iso-hexyl hydroperoxide (8).** The mixture of 0.45 g  $FeSO_4 \cdot 7H_2O$ , 0.65 g  $Cu(OAc)_2 \cdot H_2O$ , 10 ml AcOH, 0.3 ml water and 0.57 g 5,5,5-trideuterio-iso-hexyl hydroperoxide was stirred under  $N_2$  for 1.5 hr. Two isotopically isomeric unsaturated alcohols (23) and (22) were isolated by glc as a mixture: IR (film)  $3040\text{ cm}^{-1}$ ,  $2055\text{ cm}^{-1}$ ,  $2185\text{ cm}^{-1}$  and

$2210\text{ cm}^{-1}$  (last three peaks for C—D),  $1050\text{ cm}^{-1}$  and  $890\text{ cm}^{-1}$ ; NMR spectrum consisted peak characteristic for isotopically isomeric alcohols, but integral of peaks for  $CH_2$ — (from 22) and peaks for vinyl protons (from 23) showed the ratio of these two isomeric alcohols to be 14:86. The same ratio of isotopically isomeric alcohols 23 and 22 have been obtained and by mass spectrum, intensity of molecular peaks  $m/e$  102 (from 22) and 103 (from 23) showed the ratio to be 4:24.5. Determination of isotope effect by both methods gave the same value for  $k_H/k_D = 6.1$ . 4-Trideuteriomethyl-3-pentenol (24) was not isolated and it was identified by comparing the retention time (on glc) with corresponding compound obtained in the decomposition of iso-hexyl hydroperoxide.

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