Intramolecular Addition of Alkoxyl Radicals. Part 4.[1] Reductive Cyclisation of Olefinic Hydroperoxides

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Pent-4-enyl hydroperoxide reacts with reducing salts (FeX_2,$TiCl_3$) to afford tetrahydrofurfuryl compounds (halides or dimers) in high yield from the selective cyclisation of the pent-4-enyloxyl radical. Analogous behaviour is observed for photolysis although the yields of cyclic products are lower. The photolysis of hex-5-enyl hydroperoxide does not yield cyclic products but these are observed when this hydroperoxide is reduced by $FeCl_2$. It is suggested that metallic salts are able to complex the alkoxyl radicals thereby making them more electrophilic and hence more prone to cyclise.

The statement made by Waters in 1959[2] that, ' the direct production of organic free radicals by the use of one-electron transferring oxidizing and reducing reagents affords even greater scope for future research ', remains partially true. This can be inferred from the limited number of chapters devoted to these processes in recent books on free radicals.[3] We describe in this paper some observations of the reactivity changes of alkoxyl radicals depending upon whether they are generated under reducing conditions or photochemically.

The reactivity of alkoxyl radicals towards double bonds raises questions that are only partially resolved at this time, such as the origin of the general selectivity in favour of allylic hydrogen abstraction rather than the addition reaction.[4] Better understanding of this behaviour seems necessary in applied chemistry (*e.g.* oxidation processes).[5,6]

The study of the intramolecular behaviour of alkoxyl radicals towards double bonds has already led us to some observations which cast light on this problem, for example in not considering the addition reaction to double bonds as forbidden. Thus photolysis of pent-4-enyl nitrite[7] led selectively to products resulting from the trapping of the tetrahydrofurfuryl radical formed by *exo*-cyclisation[8] of the pent-4-enoxyl radical. The higher homologue, the hex-5-enyl nitrite did not afford any product resulting from intramolecular addition of the alkoxyl radical.[9] These and other results of preparative[1,10] or mechanistic value[11,12] agree qualitatively with those observed for irreversible radical intramolecular addition.[13]

In this paper we describe the behaviour of the olefinic hydroperoxides $RCH{:}CH(CH_2)_nOOH$ (1; $n = 3$, R = H), (2; $n = 3$, R = Me), and (3; $n = 4$, R = H) in the presence of reducing metallic salts able to produce the corresponding alkoxyl radicals.[14] The present results may be considered complementary to those obtained from the peroxyl radicals generated from such olefinic hydroperoxides[15] and which have led recently to fascinating biogenetic schemes.[16,17]

Some results observed when reducing the hydroperoxides (1)—(3) do not agree completely with those for photolysis of the corresponding nitrites and, thus, we have also submitted the hydroperoxides to photolytic cleavage, in order to test if the observed differences originate from the substrates (nitrites of hydroperoxides) or from the initiation mode (photolysis or reduction).

Results and Discussion

Preparation of the Hydroperoxides.—The olefinic hydroperoxides are easily prepared by reacting the corresponding methanesulphonates with a solution of potassium hydroxide in aqueous 30% hydrogen peroxide.[18]

Photolysis of the Hydroperoxides.—The thermal or photolytic homolysis of the O–O bond of hydroperoxides is a well known reaction.[19] The hydroperoxides (1) and (3), in dilute pentane or benzene solution, were illuminated with a diving 150 W high pressure Hanau mercury lamp. The results of chromatographic analysis are reported in Table 1 and the details in the Experimental section. These results are rationalized by Schemes 1 and 2.

Products which are easily rationalized qualitatively by intermolecular reactions of either the alkoxyl (A·) or the hydroxyl radical HO· will not be discussed. It can be concluded from these results that the alkoxyl radicals (A·) behave similarly towards an intramolecular double bond whether they are generated by the photolysis of hydroperoxides or of nitrites. Thus tetrahydrofurfuryl alcohol (7) resulting from the selective *exo*-cyclisation of (A·) to (Cy·5) is obtained from (1). Likewise no products resulting from the cyclisation of (A·) to (Cy·6) or (Cy·7) are observed from the higher homologue (3), in accord with the results for photolysis of the corresponding nitrite.

Reduction of the Hydroperoxides.—We have selected two types of reducing salts, iron(II) halides and titanium(III) chloride. It is well known that iron(II) salts are normally very efficient in reducing hydroperoxides[14] (*e.g.* Fenton's reagent) and that iron(III) salts are able to oxidize a carbon-centred radical, such as the (Cy·) radical resulting from intramolecular addition, by ligand transfer generating a redox chain.[14a] On the other hand, titanium(III) salts are certainly the best reducing agents but the titanium(IV) products once formed normally cannot induce a ligand transfer oxidation.[14a] These conclusions are in accord with the variations observed during the radical cyclisation of olefinic *N*-chloroamines depending on the salts used.[20] We will refer to these results when discussing the cyclisations of the olefinic hydroperoxides.

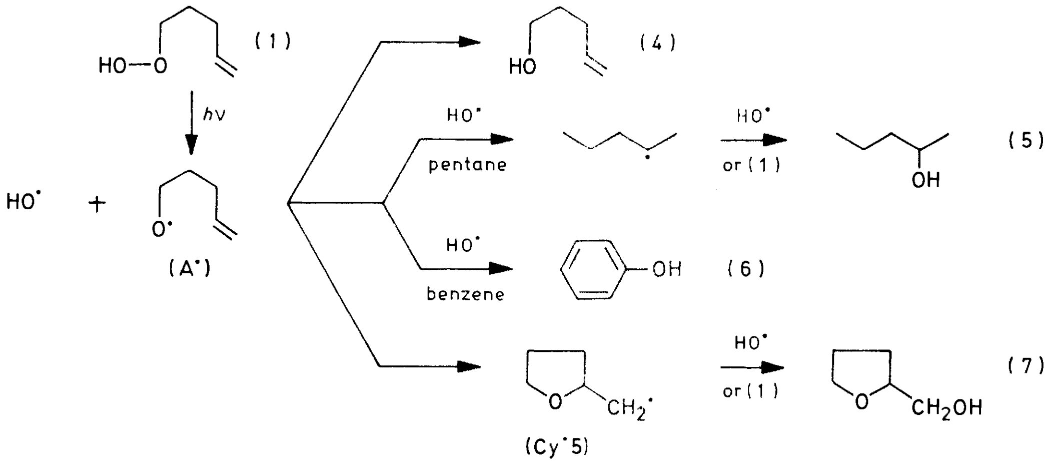
(a) *Reduction of the hydroperoxides* (1) *and* (2). The results obtained by slowly adding a stoicheiometric quantity of reducing salt to the hydroperoxide solution at room temperature are reported in Table 2. The products can be rationalized according to Scheme 3.

The ratio of the expected non-cyclic products (4) and (10) agrees with the relative redox ability of iron and titanium salts. With iron(II) salts the major product from (1) is the tetrahydrofurfuryl halide (11) whose formation is easily rationalized by the selective *exo*-cyclisation of (A·) to (Cy·5) when trapped in a ligand transfer reaction which, as expected,[14a] is more efficient with iodine (73%) than with chlorine (65%).

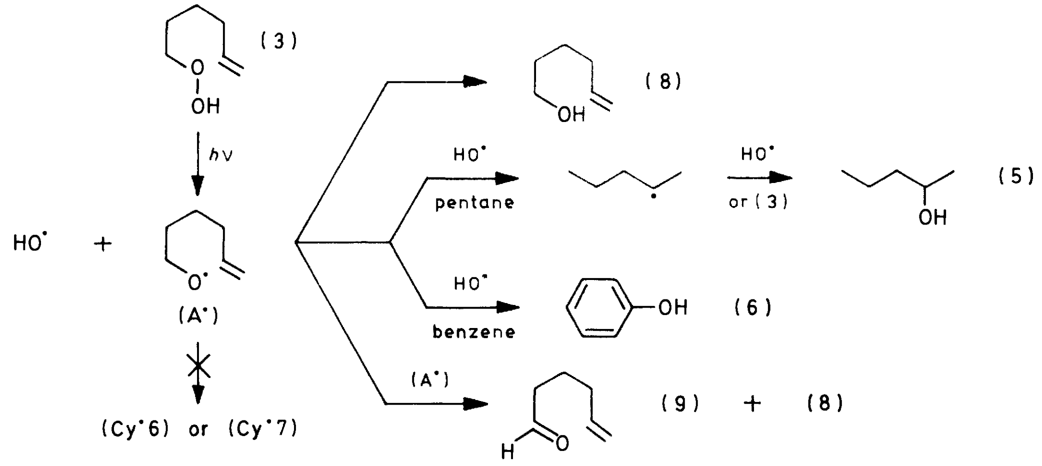
The reduction of the secondary hydroperoxide (2) under analogous conditions by iron(II) chloride gives similar results

Table 1. Photolysis of hydroperoxides (1) and (3)

			Products (%)						
Expt.	Compd.	Solvent	(4)	(5)	(6)	(7)	(8)	(9)	Not investigated
1	(1)	Pentane	32	23		29			16
2	(1)	Benzene	50		39	11			
3	(3)	Pentane		10			60	30	
4	(3)	Benzene			13		44	43	



Scheme 1.



Scheme 2.

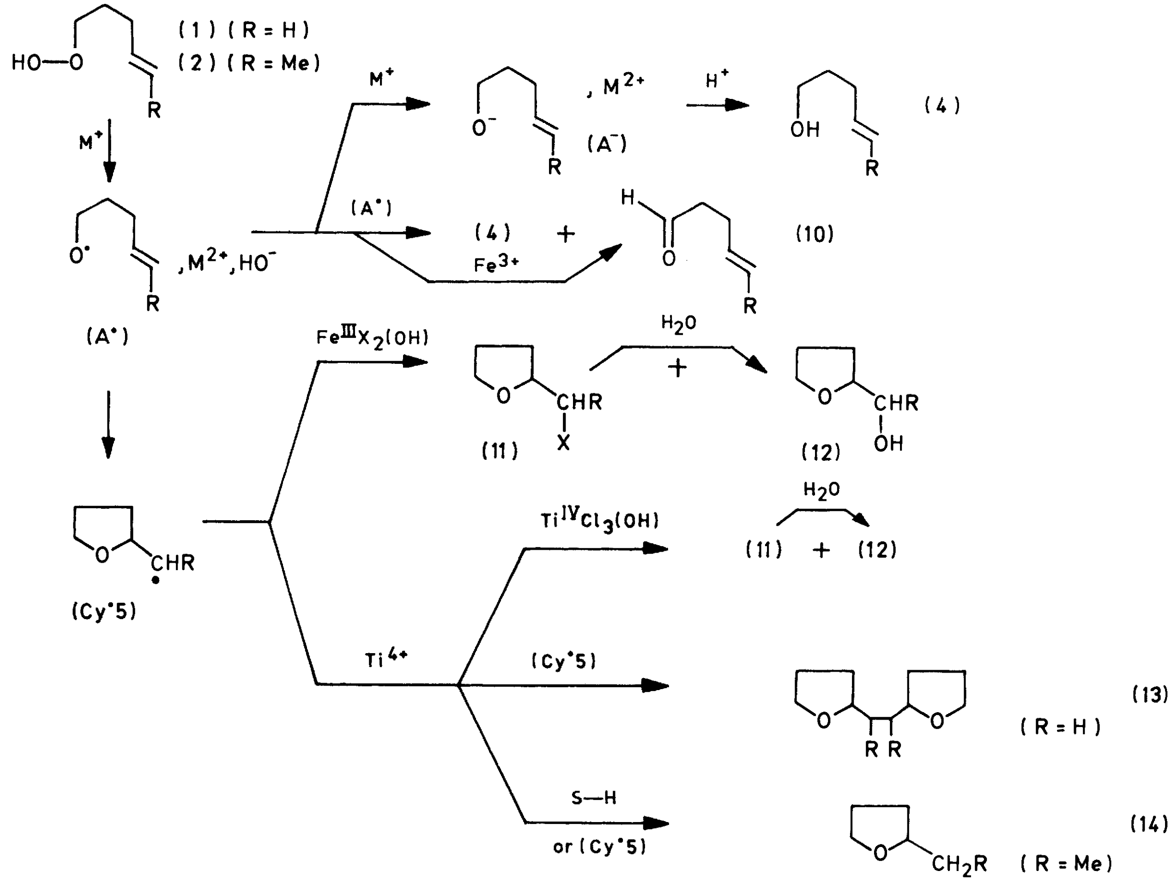
although the intramolecular addition of (A·) is less favoured (48%). Furthermore, in addition to the chloride (11; X = Cl) (19%) that results from chlorine transfer to (Cy·5), the alcohol (12) (29%) is also observed. This could be due to the faster hydrolysis of the chloride, which is now secondary, in the aqueous medium or to an hydroxy transfer to the more oxidable secondary radical (Cy·5; R = Me).

With $TiCl_3$, the major products (11)—(14) (70—86% of the mixture) are cyclic; this can be rationalized as resulting from the radical (Cy·5) formed by cyclisation of (A·). With (1; R = H) the radical (Cy·5) essentially gives the dimer (13) (80% of the mixture). At first sight this is a surprising result, especially when compared to the behaviour of the corresponding olefinic *N*-chloroamines under identical reduction conditions. Then the major product (up to 80%) is the chloromethylpyrrolidine resulting from the aza-analogue of (Cy·5) without yielding any dimer.[21] The origin of this different behaviour may be found in the good ability of *N*-chloroamines to transfer a chlorine atom thereby initiating a free-radical chain reaction.[20] On the other hand the hydroperoxides (contrary to dialkyl peroxides) are known to be unsuitable for the transfer of a hydroxy-group to a carbon-centred radical.[19] Under these conditions the (Cy·5) radical which cannot be oxidized by Ti^{IV} compounds nor undergo a hydroxy transfer reaction from another hydroperoxide molecule, accumulates in the poor hydrogen donor medium used, and gives the dimer (13) as the major product.

The behaviour of (2; R = Me) towards $TiCl_3$ seems in

Table 2. Reduction of hydroperoxides (1) and (2)

Expt.	Compd.	Salt	Medium	R	Products (%) (4)	(10)	(11)	(12)	(13)	(14)	Not investigated
5	(1)	$FeCl_2$	H_2SO_4-H_2O	H	10	10	65 (X = Cl)				15
6	(1)	FeI_2	H_2SO_4-H_2O	H	17	10	73 (X = I)				
7	(1)	$TiCl_3$	AcOH-H_2O	H	7		6 (X = Cl)		80		5
8	(2)	$FeCl_2$	AcOH-H_2O	Me	30	22	19 (X = Cl)	29			
9	(2)	$TiCl_3$	AcOH-H_2O	Me	30			30		40	



Scheme 3

accord with this hypothesis although the dimer (13; R = Me) is no longer observed. The assumed intermediate (Cy•5) apparently undergoes a chlorine atom transfer reaction from $Ti^{IV}Cl_3(OH)$ which is followed by hydrolysis (or a direct OH transfer) yielding the alcohol (12) (30%) and a hydrogen atom transfer reaction giving (14) (40%). This could result from the now secondary nature of the (Cy•5) radical causing it to be less able to dimerize for steric reasons but more able to be oxidized. Although not totally satisfying and requiring confirmation, this hypothesis is nevertheless in accord with the peculiar behaviour of (Cy•5) radicals formed during olefinic *N*-chloroamine cyclisations. For instance we have been obliged to conclude that contrary to the findings for primary and secondary radicals, tertiary ones can be oxidized by Ti^{IV} compounds.[22] As regards compound (14) which would be formed from the radical (Cy•5) by hydrogen abstraction, its origin is not obvious but similar products have also been observed in some special cases of $TiCl_3$ reduction of olefinic *N*-chloroamines.[20a,22]

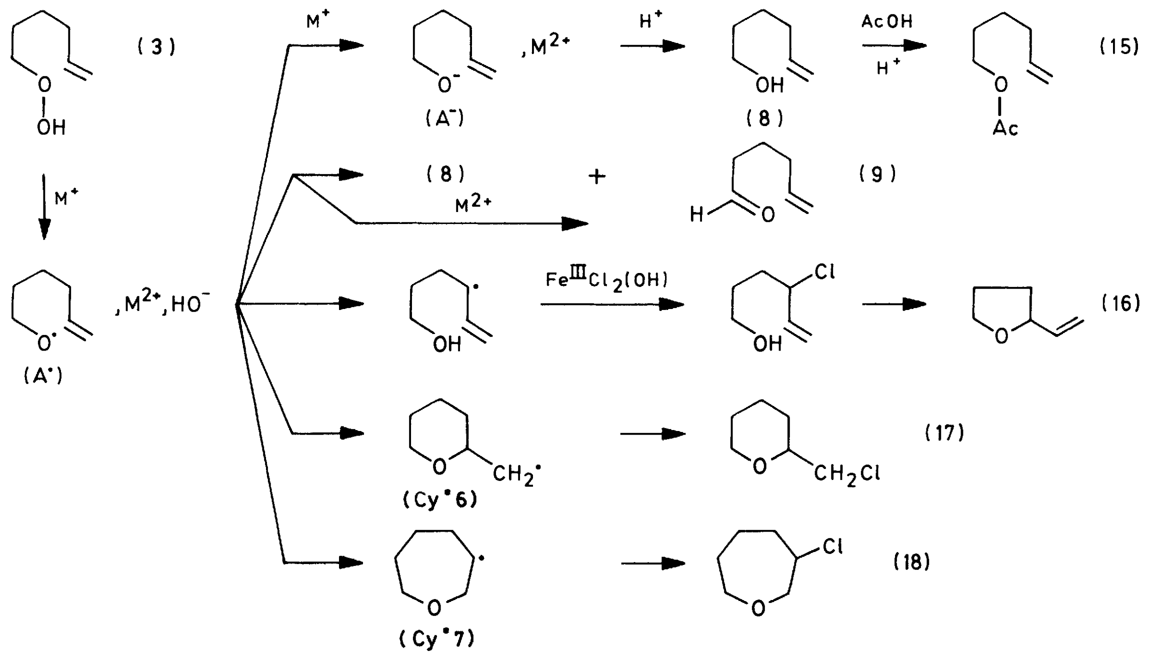
(b) *Reduction of the hydroperoxide* (3). The results obtained by reducing (3) with a stoicheiometric quantity of reducing salt are summarized in Table 3. Although more complicated than previous examples, the products obtained can be easily rationalized according to Scheme 4.

The expected non-cyclic products (8), (9), and (15) are obtained either with $FeCl_2$ or $TiCl_3$. In this last case, no other products are observed, so that taking into account the solvent changes, the results are analogous to the ones observed from photolysis (Table 1 and Scheme 2).

On the other hand initiation by iron(II) salts yields three new products which can be rationalized as resulting from intramolecular reactions. Thus 1-vinyltetrahydrofuran (16)

Table 3. Reduction of hydroperoxide (3)

				Products (%)						
Expt.	Compd.	Salt	Medium	(8)	(9)	(15)	(16)	(17)	(18)	Not investigated
10	(3)	$FeCl_2$	$AcOH-H_2O$	16	12	25	10	20	13	4
11	(3)	$TiCl_3$	$AcOH-H_2O$	56	27	17				



Scheme 4.

may be obtained by 1,5-allylic hydrogen abstraction followed by chlorine atom transfer from the iron(III) salt and cyclisation. The cyclised products (17) (20%) and (18) (13%) would result from intramolecular addition of the alkoxyl radical (A·) leading to (Cy·6) and (Cy·7) which are themselves oxidised by the iron(III) salt. This behaviour of (A·) observed for the first time needs some comment.

First, it should be observed that the percentages of cyclic products are modest when compared to those obtained from the lower homologues (1) and (2). Of course this behaviour agrees with that observed when the same hydroperoxides (or the corresponding nitrites) are photolysed since no cyclic products were observed from (3) contrary to the results obtained from (1) or (2). But this falls into a more general framework. Indeed it is known that if the hex-5-enyl radical cyclises with a relative rate of 100, the higher homologue, the hept-6-enyl radical cyclises with a relative rate of 2.4.[23] If it is assumed that the alkoxyl radical behaves similarly, particularly because of the related bond lengths C–C· and C–O· and the irreversible nature of the cyclisation of alkoxyl and unstabilized carbon centred radicals,[13b] it can be easily understood that the classical inter- or intra-molecular hydrogen abstractions of the alkoxyl radical are now the major processes.

The second observation is concerned with the non-selectivity observed in the cyclisation process since contrary to the behaviour of the pent-4-enoxyl radical, which cyclized exclusively to (Cy·5) in the *exo*-mode, two products (17) and (18) resulting from the *exo* (Cy·6) and *endo* (Cy·7) radicals are now observed. Once again the quantitative results described for carbon radicals afford some explanation. The relative rates of *exo* : *endo* cyclisations are 47.6 : 1 for the hex-5-enyl radical (hence the practically total *exo*-selectivity) and only 5.7 : 1 for the hept-6-enyl radical.[23] Further examples are known of radicals, apt to behave as hept-6-enyl radicals (similar bond lengths, irreversible cyclisation), which give a mixture of products resulting from (Cy·6) and (Cy·7). This behaviour has been observed with aminyl radicals [24] and even some amidyl radicals lead exclusively to products resulting from the *endo* (Cy·7) radical.[25]

Finally the real question is why are intramolecular addition products of the hex-5-enoxyl radical observed when it is generated from the hydroperoxide (3) by iron(II) salt reduction but not by titanium(III) salt reduction or by photolysis? An answer can be found once again in the behaviour of olefinic *N*-chloroamines. It is true that these compounds, when photolysed in neutral medium, yield cyclic products assumed to result from intramolecular addition of the aminyl radical.[26] Nevertheless the cyclisation process is much more efficient when the aminyl radical is generated from the same *N*-chloroamines with reducing salts.[21b,24] To account for this behaviour it has been proposed that, in this last case, the aminyl radical was complexed by the metallic salt, making it more electrophilic and accordingly more prone to add intra- [20,21a,24] or inter-molecularly [27] to double bonds. The extreme case is the protonated aminyl (aminium) radical which adds very easily to double bonds (although with competing ionic reactions).[28] From the behaviour of the hex-5-enoxyl radical generated from the hydroperoxide by photolysis (no cyclisation observed) or by iron(II) salt reduction (cyclisation products observed) it is quite tempting to propose, by analogy with the behaviour of the aminyl radical, that in the presence of iron salts, the alkoxyl radical is complexed, hence more electrophilic, and able to add intramolecularly. Nevertheless, it should be observed that contrary to aminyl radical behaviour where the nature of the metallic salt (copper, iron, titanium) does not seem to be important [21a] (although subtle differences are sometimes observed [20b]), the complexation of the alkoxyl radical is less efficient with titanium salts (no cyclisation observed) than with iron salts.

The easier intramolecular addition of complexed alkoxyl radicals is also in accord with the behaviour of the pent-4-enoxyl radical: although it cyclises when photochemically generated (Table 1) the percentages of cyclic products are much lower than when generated by reducing metallic salts (Table 2).

The alkoxyl radical complexation hypothesis also agrees with a more theoretical analysis of the behaviour of the alkoxyl radical towards the double bond. To rationalize the behaviour of oxygen-centred radicals towards olefins (allylic hydrogen abstraction or addition) it was suggested [4b] and later confirmed [4c] that the addition reaction was easiest when the SOMO energy of the radical was lowest (a notion which overlaps somewhat the electrophilicity concept). Since protonation must lower the SOMO energy of the radical, the fact that protonated alkoxyl radicals add easily to double bonds rather than abstract allylic hydrogen atoms, may be considered as experimental evidence for this hypothesis.[29a,b] Although limited to an e.s.r. study and apparently difficult to use practically,[29c] probably because of the weak basicity of the alkoxyl radical, these results are in accord with the reactivity sequence of addition to the olefinic double bond, namely neutral < complexed < protonated radicals, already proved with aminyl radicals and in agreement with the results of this study.

Conclusions—The reaction of reducing metallic salts with olefinic hydroperoxides gives alkoxyl radicals, able to add intramolecularly to the double bond. The ratio of the resulting cyclic products can be quite high in the case of pent-4-enoxyl radicals which cyclise exclusively in the *exo*-mode. In the case of hex-5-enoxyl radicals the intramolecular addition reaction is again observed although the ratio of cyclic products is much lower and the cyclisation is not selective (*exo*- and *endo*-products). These results are meaningful when compared to those obtained when the same alkoxyl radicals are generated photochemically. Indeed, photochemically generated pent-4-enyloxyl radicals are able to cyclise, but in lower yields and hex-5-enyloxyl radicals do not seem to be able to cyclise. These observations lead to the conclusion that alkoxyl radicals generated in the presence of metallic salts are complexed, thereby making them more electrophilic and thus more able to add intramolecularly to the olefinic double bond.

Experimental

Compounds.—The hydroperoxides (1)—(3) were prepared from the methanesulphonates of the corresponding alcohols which were stirred with hydrogen peroxide in basic medium according to Williams and Mosher.[18] After vacuum distillation, iodometric titration showed the samples to be at least 98% pure. Spectroscopic analysis is in accordance with literature data,[19] $\nu_{max.}$ 3 400—3 380 (OH, s) and 850 and 810 (OO) cm^{-1}; δ *ca.* 9.6 (OOH) and 4.0 (H–COO).

Pent-4-enyl hydroperoxide (1). Pent-4-en-1-ol prepared from tetrahydrofurfuryl alcohol [30] gives the methanesulphonate (94%) with methanesulphonyl chloride in pyridine,[31] b.p. 150—152 °C at 21 mmHg, n_D^{25} 1.4460. The hydroperoxide was then prepared according to Williams and Mosher [18] by dropping a 30% aqueous hydrogen peroxide solution (1.6 mol) and then a 50% potassium hydroxide solution into a solution of the methanesulphonate (0.4 mol) in aqueous (100 ml) methanol (1 000 ml) at 0 °C. The hydroperoxide (1) (61%) was purified by a method using the peroxide hydrogen acidity,[18] extracted, and distilled, b.p. 30—34 °C at 0.04 mmHg, n_D^{25} 1.4334; $\nu_{max.}$ 3 380 (OH), 3 090 ($:CH$), 1 650 ($C{:}C$), 995 and 915 ($CH{:}CH_2$), and 855 and 815 (OO) cm^{-1}; δ 1.4—2.4 (m, 4 H), 3.98 (t, *J* 5 Hz, 2 H), 4.8—6.2 typical of CH_2–CH=CH_2, 3 H), and 9.7br (s, 1 H).

trans-*Hex-4-enyl hydroperoxide* (2). *trans*-Hex-4-enoic acid prepared by malonic synthesis from crotyl bromide (overall yield 60%), b.p. 150—160 °C at 11 mmHg, n_D^{25} 1.4391, was reduced to *trans*-hex-4-en-1-ol by $LiAlH_4$ in ether (95%), b.p. 63.5 °C at 10 mmHg, n_D^{25} 1.4369. The methanesulphonate (61%) was prepared as described above, b.p. 94—96 °C at 0.25 mmHg, n_D^{25} 1.4499, and converted into the hydroperoxide (2) (82%), b.p. 56—58 °C at 3 mmHg, n_D^{25} 1.4411, $\nu_{max.}$ 3 380, 3 040, 970 (γ *trans*-$CH{:}CH$), 855, and 815 cm^{-1}; δ 1.3—2.3 (m, 7 H), 4.0 (t, *J* 5 Hz, 2 H), 5.3—5.6 (m, 2 H), and 9.6br (s, 1 H).

Hex-5-enyl hydroperoxide (3). Hex-5-en-1-ol prepared from hydroxymethyltetrahydropyran [32] was converted, as previously, into the methanesulphonate (81%), b.p. 155—157 °C, n_D^{25} 1.4479, and then the hydroperoxide (3) (73%), b.p. 46—48 °C at 1.5 mmHg, n_D^{25} 1.4377; $\nu_{max.}$ 3 380, 3 095, 1 660, 1 000, and 915 ($CH{:}CH_2$) cm^{-1}; δ 1.2—1.8 (m, 4 H), 1.8—2.3 (m, 2 H), 3.99 (t, *J* 5 Hz, 2 H), 4.8—6.2 (m, characteristic of CH_2–CH=CH_2, 3 H), and 9.6br (s, 1 H).

Photolysis of Hydroperoxides (1) *and* (3).—Irradiations were performed in a photolysis flask into which was slipped a quartz, water-jacketted immersion well containing a 150 W high pressure Hanau mercury lamp (TQ 150). The lamp was surrounded with a quartz sleeve. The solution was magnetically stirred under nitrogen. When iodometric titration had indicated that the hydroperoxide had disappeared the polymeric material deposited on the lamp and the walls was filtered off and the solvent evaporated. The residual oil was analysed by preparative g.l.c. (30% SE 30). Experimental conditions for experiments 1—4 in Table 1 are as follows: compound (quantity), solvent (quantity), irradiation time, oil weight after solvent evaporation: expt. 1 (1), (3 g, 30 mmol), pentane (2 000 ml), 90 h, 2, 7 g; expt 2 (1) (5 g, 50 mmol), benzene (2 000 ml), 90 h, 3,5 g; expt. 3 (3), (5 g, 43 mmol), pentane (2 000 ml) 48 h, 2.8 g; expt. 4 (3) (5 g, 43 mmol), benzene (2 000 ml), 48 h, 4.3 g. Products (4) and (6)—(8) (Schemes 1 and 2, Table 1) were identified by comparing them with genuine samples. Pentan-2-ol (5) was identified by its i.r. spectrum which was identical with that published and impossible to mistake with that of pentan-3-ol.[33] Hex-5-enal (9) was identified by i.r., $\nu_{max.}$ 3 090 and 3 010 ($CH{:}CH_2$), 2 720 ($HC{:}O$), 1 710 ($C{:}O$), 1 620 ($C{:}C$), 995, and 910 ($CH{:}CH_2$) cm^{-1}.

Metallic Salt Reduction of Hydroperoxides (1)—(3). A stoicheiometric quantity of the solution of the reducing salt was slowly added to the stirred and cooled solution of the hydroperoxide (20—25 °C). After stirring for 2 h, a 10N-sodium hydroxide solution was added with cooling (0—10 °C) and the resulting mixture filtered, extracted with ether, and dried over $MgSO_4$. After solvent evaporation, the oil was analysed by preparative g.l.c. (30% SE 30 or 30% Carbowax 20 M for experiment 10). The details of experiments 5—9 (Table 2, Scheme 3) and 10 and 11 (Table 3, Scheme 4) are as follows: compound, solvent, salt, oil weight after solvent evaporation: expt. 5 (1) (5 g, 50 mmol) in 4M-H_2SO_4 (15 ml), $FeCl_2,4H_2O$ (5 g, 50 mmol) in 4M-H_2SO_4 (35 ml), 4 g; expt. 6, (1), (10 g, 100 mmol) in 4M-H_2SO_4 (30 ml), $FeI_2,4H_2O$ (39 g, 100 mmol) in 4M-H_2SO_4 (130 ml), 13 g; expt. 7, (1), (8.2 g, 80 mmol) in AcOH (50 ml)–H_2O (50 ml), 15% $TiCl_3$ (83 g, 80 mmol) in water, 6.7 g; expt. 8, (2), (6.4 g, 56 mmol) in AcOH (25 ml)–H_2O (25 ml), $FeCl_2,4H_2O$ (11.15 g, 56 mmol) in AcOH (75 ml)–H_2O (75 ml), 4 g; expt. 9, (2), (7 g, 60 mmol) in AcOH (100 ml)–H_2O (100 ml), 15% $TiCl_3$, (62 g, 60 mmol) in H_2O, 4.2 g; expt. 10, (3), (9.1 g, 78.5 mmol) in AcOH (25 ml)–H_2O (25 ml), $FeCl_2,4H_2O$ (15.6 g, 78.5 mmol) in AcOH (40 ml)–H_2O (40 ml), 5.2 g; expt. 11 (3), (23 g, 200 ml) in AcOH (100 ml)–H_2O (100 ml), 15% $TiCl_3$ (317 g, 310 mmol) in H_2O, 14.5 g.

The products isolated from pent-4-enyl hydroperoxide (1) have been identified as follows: pent-4-en-1-ol (4; R = H) and tetrahydrofurfuryl chloride (11; R = H, X = Cl) by comparison with authentic material; pent-4-enal (10; R = H), $\nu_{max.}$ 3 080 and 3 030 ($CH{:}CH_2$), 2 720 (HC:O), 1 720 (C:O), 1 640 (C:C), 995, and 915 ($CH{:}CH_2$) cm^{-1}; tetrahydrofurfuryl iodide (11; R = H, X = I), b.p. 30—32 °C at 0.2 mmHg, n_D^{25} 1.5374, $\nu_{max.}$ 1 100 and 1 055 (CO, s) and 605 (CI) cm^{-1}; δ 1.5—2.3 (m, 4 H), 3.0—3.2 (m, 2 H, CH_2I), and 3.6—4.2 (m, 3 H, CH_2–O–CH); bis-1,2-tetrahydrofurylethane (13; R = H), $\nu_{max.}$ 1 065 and 1 045 cm^{-1} (CO, s); δ 1.1—2.5 (m, 12 H) and 3.3—4.1 (m, 6 H); *m/e* 170 (M^+, 16%), 142 (65), 127 (29), 97 (30), 85 (65), 84 (53), 72 (49), 71 (100), 70 (55), 67 (34), 55 (46), 54 (34), 43 (76), 42 (57), 41 (39), 39 (55), 30 (36), 28 (83), and 18 (42). I.r. and n.m.r. spectra agree with those described for the same product (13; R = H) obtained by lead tetra-acetate oxidation of decane-1,10-diol.[34]

From *trans*-hex-4-enyl hydroperoxide, *trans*-hex-4-en-1-ol (4; R = Me) was identified by comparison with an authentic sample; hex-4-enal (10; R = Me) by i.r., $\nu_{max.}$ 3 030 (:CH), 2 730 (HC:O), 1 730 (C:O, s), 1 650 (C:C, sh.), and 970 (γ *trans* CH:CH) cm^{-1}; 2-ethyltetrahydrofuran (14; R = Me) by i.r., $\nu_{max.}$ 1 080 (s, sh at 1 095), and 1 045 (s, sh at 1 035) cm^{-1}, and n.m.r., δ 0.8—1.1 (t, *J* 7 Hz, 3 H), 1.2—2.1 (m, 6 H), and 3.4—4.0 (m, 3 H); 2-chloroethyltetrahydrofuran (11; R = Me, X = Cl) by i.r., $\nu_{max.}$ 1 075 (s), 1 040 (s), and 685 (CCl) cm^{-1}, and n.m.r., δ 1.48 (d, *J* 6 Hz, 3 H), 1.65—2.2 (m, 4 H), and 3.65—4.2 (m, 4 H); and 2-hydroxyethyltetrahydrofuran (12; R = Me) by i.r., $\nu_{max.}$ 3 450 and 1 065 (s, sh at 1 090 and 1 040) cm^{-1}, and n.m.r., δ 1.13 (d, *J* 6 Hz, 3 H), 1.5—2.1 (m, 5 H), and 3.45—4.2 (m, 4 H).

From hex-5-enyl hydroperoxide (3), hex-5-en-1-ol (8) and hex-5-enal (9) were identical with samples obtained by photolysis. 2-Chloromethyltetrahydropyran (17) was identical with an authentic sample. Hex-5-enyl acetate (15) had $\nu_{max.}$ 3 080 (:CH), 1 740 (C:O), 1 640 (C:C), 1 240 (CO, s), 995, and 915 ($CH{:}CH_2$) cm^{-1}; δ 1.3—1.8 (m, 4 H), 1.95 (s, 3 H), 1.9—2.3 (m, 2 H), 4.0 (t, *J* 6 Hz, 2 H), and 4.75—6.2 (m, 3 H, characteristic of CH_2–CH=CH_2). 2-Vinyltetrahydrofuran (16) had $\nu_{max.}$ 3 080, 3 010, 1 640 (s, sh at 1 090 and 1 040), 995, and 920 cm^{-1}; δ 1.3—2.2 (m, 4 H), 3.5—3.95 (m, 2 H), 4.0—4.45 (q, 1 H), and 4.85—6.1 (m, 3 H, characteristic of $CH{:}CH_2$). 3-Chloro-1-oxacycloheptane (18) had $\nu_{max.}$ 1 140, 1 120, and 760 cm^{-1}; δ 1.3—2.4 (m, 6 H) and 3.2—4.2 (m, 5 H); *m/e* 134 (M^+, 6% with isotopic peak at 136 in the ratio 100 : 33), 104 (12), 102 (38, methanol loss), 98 (10, chlorine loss), 69 (19), 68 (46), 67 (19), 55 (17), 42 (100), 41 (34), 39 (17), and 27 (14).

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