

Carbon–Carbon Bond Scission during the Reactions of Allylic Hydroperoxides with some Transition Metal Compounds. Results Relevant to a Recent Proposal

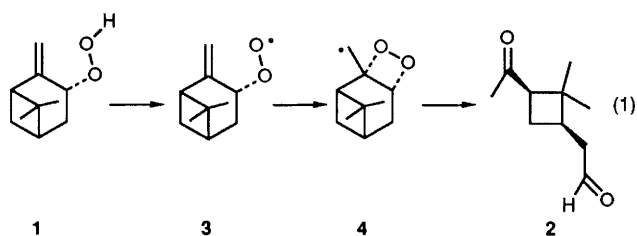
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The proposal that 4-*exo* closure of an allylic peroxy radical can account for the titled reactions of pinocarveyl hydroperoxide has been considered in the light of literature data, along with the results of reactions carried out with a range of alternative copper and iron reagents and with the previously examined reagents in the presence or absence of suitable traps: an acid-catalysed pathway is proposed to account for the observed scission reaction.

Allylic hydroperoxides are, literally, vital intermediates in the aerobic ageing of many natural and synthetic organic materials. Their importance lies not so much in their formation but in their facile breakdown. Such purely homolytic decompositions lead to the propagation of auto-accelerating radical chain oxidations, which can be accompanied by carbon chain scissions: the latter give rise, for example, to losses in the physical performances of rubbers and other polymers,¹ to the generation of objectionable volatiles from rancid foodstuffs,² to the degradation of cellular lipid components³ and to the deterioration of assorted industrial materials.⁴

Such chain scissions are usually described in terms of peroxide homolyses followed by β -scission reactions or by acid-induced heterolytic 'Hock cleavage' reactions. Thus, the recent proposal by Haynes and Vonwiller^{5-7†} of a novel scission pathway, initiated by transition metal ion-catalysed, single-electron redox reactions merits close attention. In that proposal, the conversion of *trans*-pinocarveyl hydroperoxide **1** to pinonyl aldehyde **2** was ascribed⁵ to a sequence in which allylic peroxy radical **3** was held to play a pivotal role [eqn. (1)].



† Note added in proof: It is interesting that the conversion of one of the other examples detailed in refs. 5 and 6 has recently been effected using trifluoroacetic acid (R. J. Roth and N. Acton., *J. Chem. Ed.*, 1991, **68**, 612).

The 4-*exo* closure step to form the dioxetanyl radical **4** is to our knowledge unprecedented and a surprising proposal in view of the report⁸ that the peroxy radical **3**, when generated under autoinitiating conditions (in the presence of dioxygen: an efficient trap for carbon-centred radicals, of which **4** is a representative) underwent Brill–Schenck equilibration [eqn. (2)] via the isomeric peroxy radical **5** to form myrtenal hydroperoxide **6**.

Haynes and Vonwiller suggested that aldehyde **2** was not formed by heterolytic cleavage, but we feel that the following observations support the view that such acid-catalysed Hock cleavage [eqn. (3)] adequately explains the formation of **2** in their reaction systems.

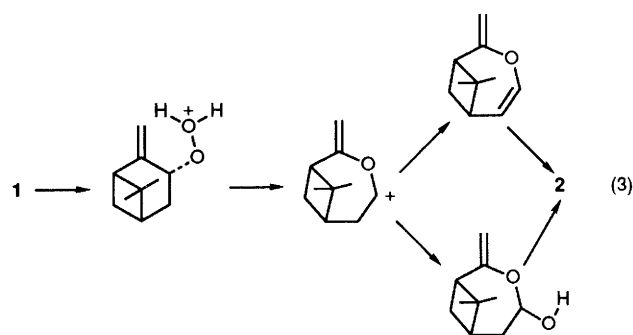
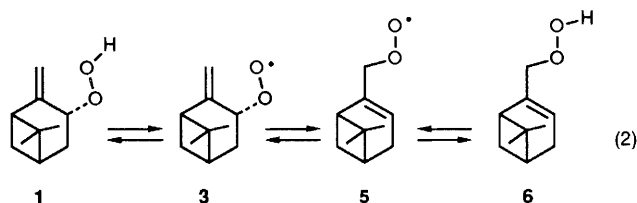
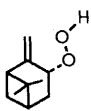
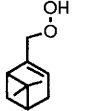

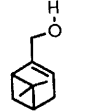

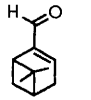
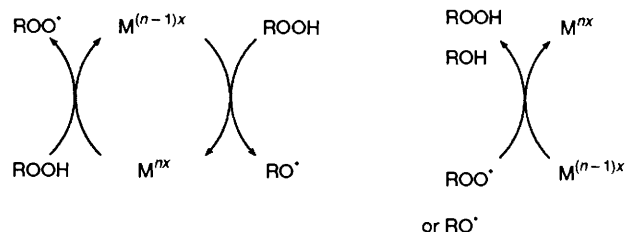


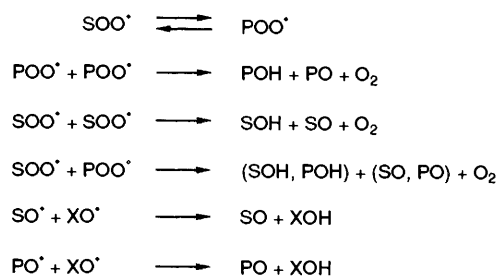
Table 1 Relative ratios for products from the reactions (overnight, at ambient temperature) of copper and iron compounds with *trans*-pinocarveyl hydroperoxide

Metal compound (ligand)	Metal ROOH	Products					
							
aq CuSO ₄ (—)	0.1	88	12	trace	n.d.	trace	n.d.
aq CuSO ₄ (—)	1	54	22	9	trace	9	6
aq CuSO ₄ (—)	10	41	28	10	trace	14	7
CuSO ₄ (am) ^{a,c}	10	42	18	10	2	21	7
CuSO ₄ (py) ^{a,c}	10	2	n.d.	4	n.d.	83	11
Cu(acac) ₂ ^{a,b}	1	19	15	26	7	26	7
aq FeSO ₄ (—)	0.1	71	12	trace	n.d.	18	trace
aq FeSO ₄ (—)	1	32	6	6	n.d.	56	trace
aq FeSO ₄ (—)	10	43	8	10	n.d.	38	2
FeSO ₄ (am) ^c	10	n.d.	n.d.	44	trace	36	n.d.
FeSO ₄ (py) ^c	10	n.d.	n.d.	13	n.d.	83	4
aq Fe ₂ (SO ₄) ₃ (—)	0.1	97	3	trace	n.d.	trace	n.d.
aq Fe ₂ (SO ₄) ₃ (—)	1	97	3	trace	n.d.	trace	n.d.
aq Fe ₂ (SO ₄) ₃ (—)	10	88	12	trace	n.d.	trace	n.d.
Fe ₂ (SO ₄) ₃ (am) ^c	10	94	2	2	n.d.	2	n.d.
Fe ₂ (SO ₄) ₃ (py) ^c	10	43	13	6	n.d.	30	8
Fe(TPP)Cl (—) ^{a,b}	0.03	trace	trace	29	trace	48	23

^a Abbreviations used: am = aqueous ammonia; py = pyridine; acac = pentane-2,4-dionato; TPP = *meso*-tetraphenylporphyrin; n.d. = not detected. ^b 0.05 mol dm⁻³ ROOH in deuteriochloroform. Remainder two phase, aqueous–deuteriochloroform. ^c Ligand/metal = 100.



For the following generalised reactions **1** = SOOH, **6** = POOH, XO = any oxygen-centred radical in the medium

**Scheme 1** Some hydroperoxide redox-induced radical reactions

Firstly, protic acids (perchloric or trifluoromethanesulfonic) or a 'redox-inactive' Lewis acid (boron trifluoride-ether) very rapidly (in reaction times at ambient temperature of the order of a few minutes) cleanly convert **1** into **2**: the reactions are most facile in acetonitrile (*vide infra*).

We can confirm that aldehyde **2** can be prepared from **1** by two of the transition metal catalysts used by Haynes and Vonwiller. Thus catalytic quantities of copper(II) trifluoromethanesulfonate in acetonitrile or iron(III) chloride bis(etherate) in deuteriochloroform very rapidly (minutes) convert **1** into non-peroxidic materials in which **2** predominated.

Other iron and copper complexes, however, failed to generate even detectable quantities of aldehyde **2** (Table 1), but, rather, the expected products of single-electron redox reactions were slowly produced over periods of hours (some relevant reactions are shown in Scheme 1).

This mechanistic diversity is reminiscent of the distinction made by Gassman and Singleton⁹ between acid-catalysed and radical cation-catalysed Diels–Alder reactions of 1,3-dienes. In that work, 2,6-di-*tert*-butylpyridine was included in reaction mixtures to act as a scavenger for protic acids and thus suppress proton-driven reactions. When we included this proton trap in the reactions of **1** with copper(II) trifluoromethanesulfonate or iron(III) chloride bis(etherate), hydroperoxide conversion was dramatically slowed and only the redox reaction products were obtained (Table 2).

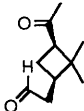
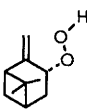
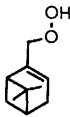

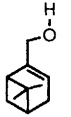


We believe, therefore, that for copper(II) trifluoromethanesulfonate and for iron(III) chloride bis(etherate), traces of strong acid overwhelm the redox-homolytic reactions most usually seen in the reactions of hydroperoxides with variable valence transition metal catalysts and that, therefore, the proposed sequence [eqn. (2)] does not need to be invoked.‡§

It is interesting in this context to recall the reactions of hydroperoxides with some sulfur-based antioxidants¹⁰ where initially slow, apparently radical-mediated reactions oxidise

‡ Hydrolysis by variable amounts of adventitious water might be responsible for the generation of such strong acids: our commercial sample of copper(II) trifluoromethanesulfonate gives an acidic indicator reaction (pH ~ 3.5) when dissolved in water. Accordingly we can expect variable ratios of heterolytic and homolytic reactions in such cases. Consonant with these views are the hygroscopic nature of the solvent in which this reaction most easily occurs (acetonitrile) and the relative suppression of the reaction in either less polar (dichloromethane or deuteriochloroform) or nucleophilic (diethyl ether) solvents.

§ We note that some of the reactions detailed in ref. 6 are not so readily accommodated within a simple picture of fast Hock cleavage: it might be worthwhile investigating those reactions under some of the conditions detailed herein.

Table 2 Relative ratios for products from the reactions of copper and iron compounds with pinocarveyl hydroperoxide in the presence or absence of a proton trap

Metal compound	Solvent (added)	Products						
								
Cu(OT _f) ₂ ^a	MeCN	30	8	3	12	6	30	11
Cu(OT _f) ₂	MeCN	15	12	9	18	5	32	9
Cu(OT _f) ₂	MeCN(DBP) ^a	n.d.	8	17	42	trace	21	13
FeCl ₃ ·(Et ₂ O) ₂	CDCl ₃	94	n.d.	n.d.	n.d.	n.d.	6	n.d.
FeCl ₃ ·(Et ₂ O) ₂	CDCl ₃ (DBP)	n.d.	7	9	21	5	35	23

^a Abbreviations used: OT_f = trifluoromethanesulfonyl, DBP = 2,6-di-*tert*-butylpyridine.

the antioxidants to sulfur-centred acids whereupon much more rapid heterolytic reactions predominate to give familiar, acid-induced carbon-chain scission products.

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