

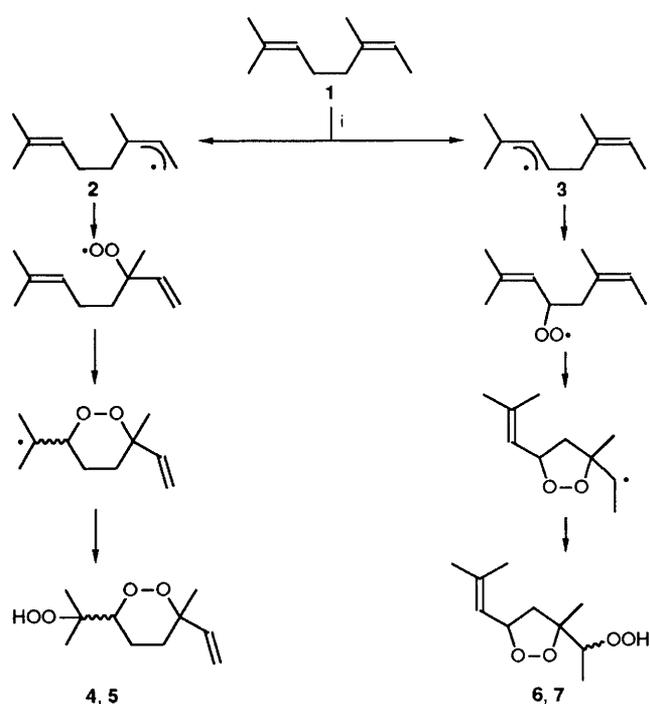
Polyfunctional Peroxides from *tert*-Butyl Hydroperoxide-loaded Autoxidations of Polyunsaturated Substrates and an Assessment of the Rate Constants for Allylic Peroxyl Radical Rearrangements and Peroxyl Radical Ring Closures

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Using the recently-disclosed *tert*-butyl hydroperoxide-loaded autoxidation method, *cis*-2,6-dimethyl-2,6-octadiene and *trans*-5-methyl-1,5,9-decatriene have been converted into hydroperoxy-1,2-dioxanes and hydroperoxy-1,2-dioxolanes: the product ratios from these, and other, reactions permit an assessment of the relative magnitudes of allylic peroxyl radical rearrangements and of peroxyl radical cyclizations.

We recently disclosed¹ conditions under which classical, initiated autoxidation reactions could be modified to provide excellent yields of primary autoxidation products: by carrying out these reactions in media containing high concentrations of *tert*-butyl hydroperoxide, an extra equilibration step relieved substrate-derived peroxyl radicals from the diversion of chain carrying and termination.



Scheme 1 Reagents and conditions: i: 0.02 mol dm⁻³ 1, 1.0 mol dm⁻³ Bu^tO₂H, 1 mmol dm⁻³ initiator (2,2'-azoisobutyronitrile, AIBN or bis-4-*tert*-butylcyclohexylperoxydicarbonate), in 2,2,4-trimethylpentane, O₂, 60 °C, 6–6.5 h

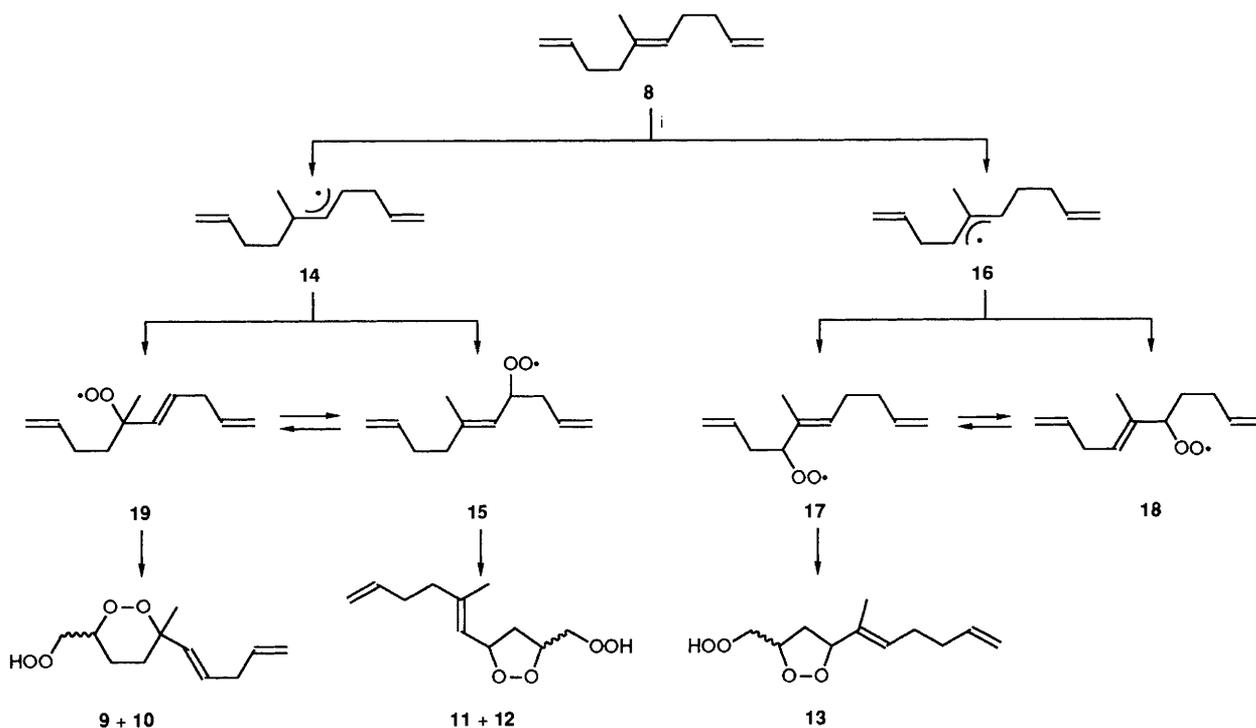
Application of this method to polyunsaturated substrates suggested the prospect of even richer peroxyl radical chemistry and experiment proves this to be the case. Accordingly, reaction of *cis*-2,6-dimethyl-2,6-octadiene 1 under these conditions provides good yields of both hydroperoxy-1,2-dioxanes 4,5 and -dioxolanes 6,7, which are formed by sequences which are depicted in Scheme 1.

Disfavoured abstraction at C-8 competes, because of statistical compensation, with favoured abstraction¹ at C-4. Allylic radicals 2 and 3 then develop *via* non-stereospecific 6-*exo* and stereospecific 5-*exo* closures to give an inseparable, almost equimolar mixture of 1,2-dioxane isomers 4 and 5 and separable, less polar, epimeric 1,2-dioxolanes 6 and 7.

The corresponding reaction (Scheme 2) of *trans*-5-methyl-1,5,9-decatriene, 8,² gave, after HPLC analysis and separation of the principal products (*ca.* 40% conversion with *ca.* 70% of the absorbed oxygen being accounted for by the products described) three fractions containing hydroperoxy-cyclic peroxides, the smallest of which (8%) contained traces of the hydroperoxydioxanes 9 and 10. The others contained hydroperoxy-dioxolanes derived from abstraction at the preferred and the less preferred sites: 11 plus 12 (73%) and 13 (19%).[†]

Consideration of the reactions in Scheme 2, indicates the relative magnitudes of the competing processes: allylic radical 14 preferentially combines with oxygen to give 15 which closes to eventually give 11 and 12, while 16 develops *via* 17 (probably equilibrating with 18) to give essentially only 13.

[†] HPLC separation of the triphenylphosphine-treated material gave samples of isomers 11, 12 and 13 as hydroxydioxolanes (ratio 67:27:10). All materials described herein were fully characterised by ¹H and ¹³C NMR, with appropriate chemical conversions, and, in the case of the hydroperoxydioxanes 9, 10, by independent synthesis using tributyltin hydride-mediated oxygenation of geranyl bromide (using only one equivalent of hydride): a rather inefficient extension of the method of Nakamura *et al.*³ and the comparable reductive oxygenation of allylic organomercury salts by Corey and Walker.⁴



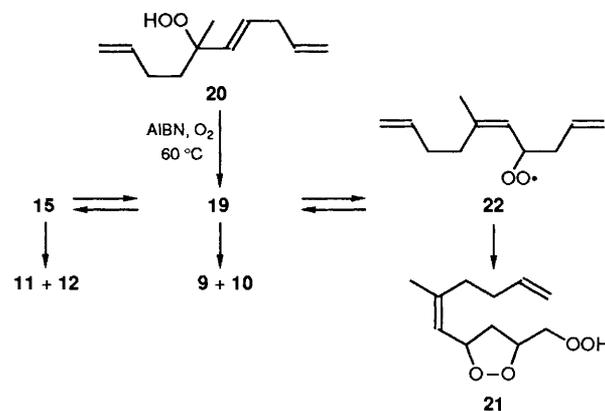
Scheme 2 Reagents and conditions: i, as for Scheme 1

The 5-*exo* peroxy ring closure, like the carbon-centred analogues,⁵ appears to be faster than competing 6-*exo* closures⁶ (although we note that, like the carbon-centred cases, substituent effects might modify this ordering), and the closure of **17** to give **13** supports this view. Furthermore, the plausible equilibration between **17** and **18** indicates that thermoneutral allylic peroxy radical rearrangements (of which this is probably an example) have rate constants comparable with 5-*exo* closures and significantly faster than the competing 6-*exo* closures.

Conversely, however, energetically asymmetric equilibrations (of which that between *secondary*, allylic peroxy **15** and *tertiary*, allylic peroxy **19** is probably an example) seem not to compete with the 5-*exo* closure, as the following appears to demonstrate.

The *tertiary* allylic hydroperoxide **20**,[‡] under oxygen, underwent AIBN-initiated conversion to two groups of hydroperoxy cyclic peroxides that were isolated as hydroperoxides by HPLC (Scheme 3). At ca. 50% conversion the more polar group (41%) was composed of an almost equimolar mixture of hydroperoxydioxanes **9** and **10** (identical, by ¹H NMR with those detected in the minor fraction referred to above), while the less polar group (59%) was comprised principally of three hydroperoxydioxolanes, **11**, **12** and **21** (ratio ca. 78:20:2).

The formation of **9** and **10** in this latter experiment, and the preferential formation of **11** and **12** in both triene reactions, suggest a number of conclusions. Firstly, capture of oxygen by allylic radical **14** at the *secondary* terminus is preferred (a precedent for which might be found in ref. 3); secondly, equilibration of the *tertiary*, allylic peroxy radical **19** to the preferred *trans*, secondary-allylic peroxy radical **15** competes at a rate comparable to the 6-*exo* ring closure of **19**; thirdly, the



Scheme 3

reverse rearrangement (**15** to **19**) is slower than the 5-*exo* ring closure, and finally, rearrangement of **19** to the apparently equally stable *cis*, allylic secondary peroxy **22** is somewhat slower than either rearrangement of **19** to **15** or of cyclisation of **19** onwards to **9** and **10**.

Practically, we find that allylic peroxy radical rearrangements seem faster in cyclic, rather than in acyclic, systems, but attempts to quantify such rates have been frustrated.⁸ However, using the 'radical clock' paradigm, we can use the present results, along with Porter's estimate⁹ for a 5-*exo* peroxy radical closure of $\sim 8 \times 10^2 \text{ s}^{-1}$ at 30 °C, to suggest that both 6-*exo* peroxy radical closures and allylic peroxy rearrangements have rate constants that are about two orders of magnitude lower than the 5-*exo* closure rate. It is interesting to note that the relative 5-*exo* and 6-*exo* peroxy radical closure rates appear to be separated by a ratio similar to that for the carbon-centred analogues:⁵ no doubt similar stereoelectronic control is at work in both cases.

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[‡] Reaction of triene **8** with singlet oxygen gave a readily separable mixture of **20** and an almost equimolar quantity of the *exo*-methylene isomer (*cf.* reactions of other *trans*-trisubstituted alkenes⁷). Similar to *tert*-butylperoxy radicals (Scheme 2) and other electrophiles,² the reaction occurred selectively at the central double bond.

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