Mechanism of Dehydrobromination of β-Bromohydroperoxides

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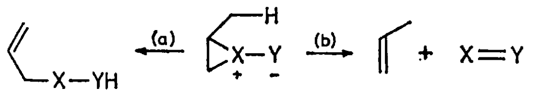
Summary Base-induced dehydrobromination of tetrasubstituted β-bromohydroperoxides to allylic hydroperoxides proceeds without cleavage of the carbon–oxygen bond; this observation excludes intermediate perepoxides and suggests the operation of an intramolecular *E*2 reaction.

Recently we have examined the pathways for decomposition of dipolar species such as (**1**) and established the presence of two competing pathways, (a) and (b).[1–3] With the hope of including in this scheme the as yet unknown perepoxide (**4**) we have examined the base-induced dehydrobromination of β-bromohydroperoxides (**5**)[4] as a possible route to these compounds. However we have demonstrated that conversion of compounds (**5**) into allylic hydroperoxides proceeds without cleavage of carbon–oxygen bonds and therefore cannot proceed through an intermediate perepoxide.



(2) (1) (3)

Scheme

Thus, treatment of isopropylidenecyclohexane[5] with hydrogen peroxide (98%) and a brominating agent at −40° in ether gave a mixture of isomeric products, (**6**) and (**7**). Their structures were determined, as a mixture, by stepwise reduction (trimethyl phosphite) to the bromohydrins followed by debromination (Bu^n_3SnH) to the known carbinols, (**8**) and (**9**). Knowledge of the carbinol ratio, (**8**) : (**9**), enabled us to determine directly the ratio of (**6**) to (**7**) by n.m.r. spectroscopy [*gem*-dimethyl resonances

($CDCl_3$), (**6**) δ 1·87; (**7**) δ 1·50]. By the use of two different brominating agents, *i.e.* *N*-bromosuccinimide (NBS) and 1,3-dibromo-5,5-dimethylhydantoin (DBH) and varying the concentration of hydrogen peroxide we obtained two different mixtures of (**6**) and (**7**). Treatment of each of these with NaOMe (1 equiv.) in MeOH at 0° gave the allylic hydroperoxides (**10**; R = OH) and (**11**; R = OH), which were reduced (trimethyl phosphite) to the corresponding alcohol mixture, (**10**; R = H) and (**11**; R = H). The ratios of allylic hydroperoxides and alcohols were again established by n.m.r. spectroscopy and the results are shown in the Table, along with the result for direct, photosensitized, singlet oxygen addition.

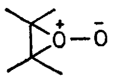
TABLE

Reagent	Product ratio[a,b] (**6**)	(**7**)	(**10**; R = OH)	(**11**; R = OH)
NBS, H_2O_2 (15 equiv.) ..	4	96	5	95
DBH, H_2O_2 (60 equiv.)	21	79	20	80
O_2, Methylene Blue, $h\nu$ ..			80	20

[a] Determined by integration of methyl n.m.r. resonances; accuracy ± 5%; [b] Conversion yields for (**6**), (**7**) and (**10**), (**11**) >93%.

The formation of the allylic hydroperoxides (**10**; R = OH) and (**11**; R = OH) in the same ratio as their precursor bromohydroperoxides (**6**) and (**7**) excludes the possibility of a common intermediate, such as the perepoxide (**12**), and suggests instead an intramolecular *E*2 elimination, as in (**13**), although the corresponding bimolecular process cannot be discounted from our results.

Since widely different isomer ratios of allylic hydroperoxides are obtained from singlet oxygen addition, *cf.* Table, it appears that use of β-bromohydroperoxides may provide a complementary route to allylic hydroperoxides, and thence the corresponding alcohols.



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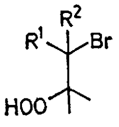

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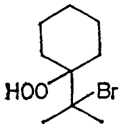

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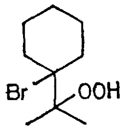

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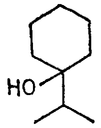

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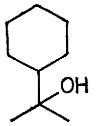

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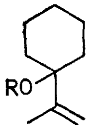

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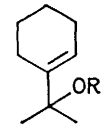

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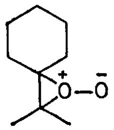

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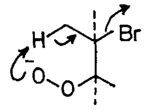

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