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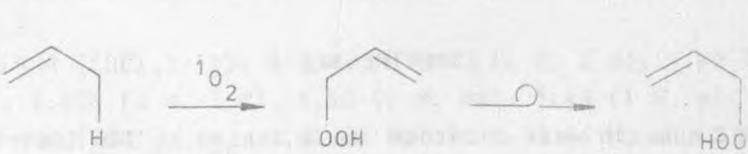
SINGLET OXYGEN OXIDATION OF (E)-2,5-DIMETHYL-3-HEXENE

A solution of (E)-2,5-dimethyl-3-hexene (1) in dichloromethane containing tetraphenylporphine as a photosensitizer was illuminated, under an oxygen atmosphere, with a sodium lamp, and 3-hydroperoxy-2,5-dimethyl-4-hexene (2) was obtained. It partially rearranged in $CDCl_3$, to give a mixture of hydroperoxide (2) and (E)-2-hydroperoxy-2,5-dimethyl-3-hexene (3), in the ratio 2 : 3.

INTRODUCTION

Unsaturated compounds react with the singlet oxygen to give some allyl-type hydroperoxides [1]. In non-polar solvents, these hydroperoxides may then undergo the allylic rearrangement to give the isomeric hydroperoxides [2] (Scheme 1) with structure similar to products of the reaction of unsaturated compounds with the triplet oxygen.

Scheme 1



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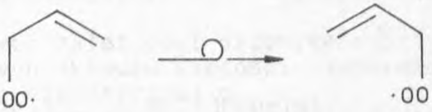
Since only a limited number of examples of such the rearrangement has as yet been reported [2] and ca. one half of them is related to the congeners of cholesterol, I have been anxious to give further few examples of this rearrangement, which might have been helpful for some future mechanistic investigations, particulary in acyclis systems, since it appears that in related rearrangements of β-acyloxyalkyl radicals, different mechanism may apply depending on whether the alkyl moiety is cyclic or acyclic.

These reactions are, generally fairly sensitive to inhibition by phenols, and to acceleration by light and by induced free radical, and they are accepted to follow a radical chain mechanism involving the intermediate allylperoxyl radicals [3], as it is shown in Scheme 2.

Scheme 2



Investigations on the autoxydation of acyclic olefins, unlike to those dealing with cyclic olefins, have been impeded by the unavailability of the pure hydroperoxide products and, consequently, by the lack of a reliable information on their reactivity [2]. The aim of the present study was to obtain a few new hydroperoxides from the oxidation of (E)-2,5-dimethyl-3-hexene, and to study the possible mechanism of their rearrangement.

EXPERIMENTAL

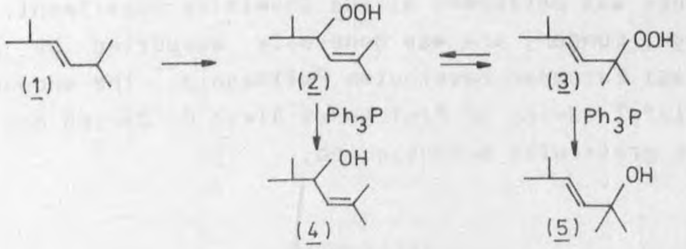
N.m.r. spectra were recorded on a Varian XL 200 instrument, using $CDCl_3$ as a solvent and Me_4Si as an internal standard. (E)-2,5-Dimethyl-3-hexene was a commercial sample (Aldrich); and it was checked for its purity by the n.m.r. spectrometry.

Oxygen was bubbled for 6 h through a solution of the alkene (1 g) and tetraphenylporphine (0.03 g) in dichloromethane (400 cm^3) in a water-cooled flask, which was illuminated a 400 W sodium lamp. The solvent was removed under reduced pressure, and the product was purified by a static distilation below 30°C, followed by chromatography on silica gel (ethyl acetate-light petroleum (1 : 10 v/v) was used as eluant).

RESULTS AND DISCUSSION

A solution of (E)-2,5-dimethyl-3-hexene(1) in dichloromethane containing tetraphenylporphine as photosensitizer was irradiated under an oxygen atmosphere by a sodium lamp. The hydroperoxides 3-hydroperoxy-2,5-dimethyl-4-hexene (2) and (E)-2-hydroperoxy-2,5-dimethyl-3-hexene (3) which were formed and the corresponding alcohols 3-hydroxy-2,5-dimethyl-4-hexene (4), and (E)-2-hydroxy-2,5-dimethyl-3-hexene (5) obtained by the subsequent reduction with triphenylphosphine (Scheme 3) were identified by the ^{1}H.n.m.r. spectroscopy.

Scheme 3



Details of the spectra are given below (chemical shifts in p.p.m.):

δ NMR (CDCl$_3$) (2): 0.934, 0.968 (6 H, 2 d), 1.62 (1 H, m), 1.734, 1.809 (6 H, 2 d), 4.50 (1 H, dd), 5.40 (1 H, m).

δ NMR (CDCl$_3$) (3): 1.01 (6 H, d), 1.33 (6 H, s), 2.08 (1 H, m), 5.60 (2 H, m).

δ (CDCl$_3$) (4): 0.79, 0.95 (6 H, 2 d), 1.47 (1 H, m), 1.65, 1.70 (6 H, 2 d), 3.86 (1 H, dd), 5.09 (1 H, dm).

δ (CDCl$_3$) (5): 0.98 (6 H, d), 1.26 (6 H, s), 1.91 (1 H, m), 5,53 (2 H, m).

Chemical shifts for alcohols (4) and (5) are in agreement with the values reported earlier [5].

The photosensitized oxidation of (E)-2,5-dimethyl-3-hexene (1) has produced, almost exclusively, the monohydroperoxide (2), which was found to be readily isolated and purified by a simple chromatography on silica gel. The compound (2) in $CDCl_3$, rearranged spontaneously to give a mixture of (2) and (3) in the ratio 2 : 3. The reaction was, approximately, of the first order. The mechanism of this reaction is not known, but in the case of hydroperoxides derived from oleic acid and cholesterol [6] it has been shown that they do not incorporate ^{18}O into the product from an atmosphere containing $^{18}O_2$, and it is belived to proceed by a nondissociative, perhaps the pericyclic mechanism which is assumed to be affected by steric effects. Again, the equlibrium composition of the mixture of hydroperoxides would be determined, principally, by steric effects.

Acknowledgment

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UTLENIANIE (E)-2,5-DIMETYLO-3-HEKSENU TLENEM SINGLETOWYM

W wyniku fotochemicznie inicjowanego procesu utleniania (E)-2,5-dimetylo-3-heksenu otrzymano 3-hydroperoksy-2,5-dimetylo-4-heksen. Na podstawie badań ^1H NMR stwierdzono, że ten nowo otrzymany wodoronadtlenek ulega częściowemu samorzutnemu przegrupowaniu w $CDCl_3$ do (E)-2-hydroperoksy-2,5-dimetylo-3-heksenu.