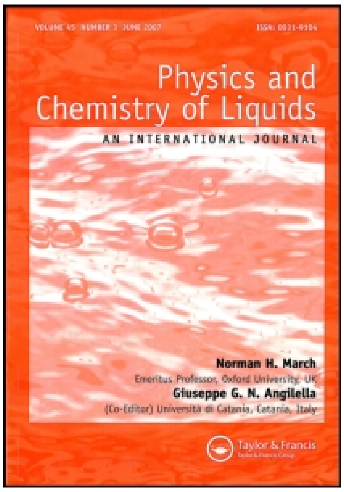

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Wojciech J. Kinart[a]; Andrzej Kinart[a]; Marcin Sendecki[a]
[a] Department of Organic Chemistry, University of Łódź, Narutowicza, Poland

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Lithium perchlorate-catalysed rearrangement of 1-methylcyclohex-2-enylhydroperoxide into 2-methylenecyclohexylhydroperoxide

Wojciech J. Kinart*, Andrzej Kinart and Marcin Sendecki

Department of Organic Chemistry, University of Łódź, Łódź, Narutowicza, Poland

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The catalytic effect of 5 mol dm^{-3} solution of $LiClO_4$ in Et_2O on the rearrangement of 1-methylcyclohex-2-enylhydroperoxide into 2-methylenecyclohexylhydroperoxide has been observed.

Keywords: 1-methyl-1-cyclohexene; photochemical oxidation; lithium perchlorate; rearrangements of hydroperoxides; homogenous catalysis

1. Introduction

Allyl hydroperoxides are important species which are formed when an alkene reacts with either singlet oxygen or tryplet oxygen (autoxidation) [1,2]. In 1958, Schenck [3] showed that the 5α-Δ^6-hydroperoxide, which is formed by singlet oxygenation of cholesterol, rearranged in a non-polar solvent to 7α-Δ^5-hydroperoxide. Several examples of the analogous rearrangements have been recognised and mechanistic investigations for this process have been carried out [4].

We have been continuously interested in the catalysis of hydrogen- and metallo-ene reactions caused by lithium perchlorate, particularly when homopolar enophile is singlet oxygen (O=O) or an azo compound (RN=NR) [5]. We have explained the catalytic effect of $LiClO_4$ as the result of stabilisation of the transition state for reactions with $^1O_2$ and diethyl azodicarboxylate, and in the case of 4-phenyl-1,2,4-triazolone-3,5-dione also by lowering of its highest-occupied molecular orbital (HOMO) [5(a),(b)].

Presently, we have also been anxious to identify an example of the catalysis by lithium perchlorate on the rearrangement of hydoperoxides. Solvent effects in photo-oxidation reactions have puzzled many researchers. Courtneidge compared products of photo-oxidation of 1-methyl-1-cyclohexene (**1**) carried in different solvents [6]. He obtained, as a product of the reaction, a mixture of three hydroperoxides identified as 1-methylcyclohe-2-enylhydroperoxide (**2**), 2-methylenecyclohexylhydroperoxide (**3**) and 2-methylcyclohex-2-enylhydroperoxide (**4**) (Scheme 1). In case of oxidation carried in CH_2Cl_2 (using TPP as sensitiser), the ratio of hydroperoxides **2** : **3** : **4** was equal to 41 : 43 : 16. With increase of the polarity of the solvent, there was an observed increase of the product **2** at the expense of **3**.

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*Corresponding author. Email: ckinart@uni.lodz.pl

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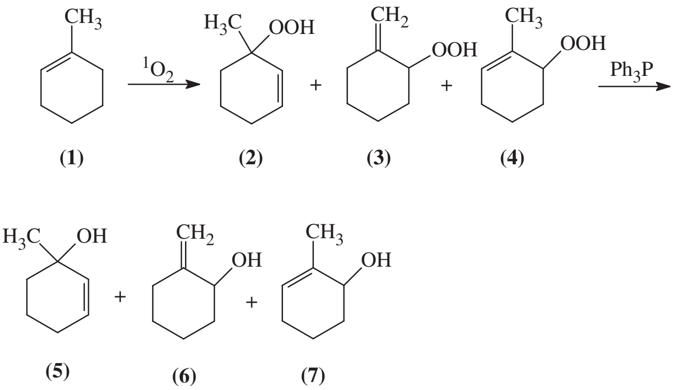

Scheme 1. The products of photo-oxidation of 1-methyl-1-cyclohexene.

However, Ramamurthy [7] demonstrated that selective oxidation of 1-methylcyclohexene (**1**) within dye cation-exchanged zeolites leads to formation of nearly exclusively 2-methylenecyclohexylhydroperoxide (**3**).

Also, the mechanism of the rearrangements of allylic hydroperoxides puzzled researchers for a long time [4]. Porter [4(d)] proposed that the rearrangement of Δ^{8}-10-hydroperoxide and the Δ^{10}-9-hydroperoxide obtained from the autoxidation of oleic acid involved the cyclic transition state. A similar mechanism involving a sigmatropic [2,3]-rearrangement was suggested by Davies [4(e)] for isomerisation of 5α-hydroperoxy-3β-hydroxycholest-6-ene into 7α-hydroperoxy-3β-hydroxycholest-5-ene, whereas the rearrangement of the last hydroperoxide into 7β-hydroperoxy-3β-hydroxycholes-5-ene was supposed to proceed through a dissociative (S_H1) mechanism [4(e)]. A recent computational study has led to the proposal of an allyl-tryplet dioxygen complex, as an intermediate in the rearrangement of simple allylic hydroperoxides [4(h)].

Previously, we have observed that lithium perchlorate does not affect the rates of Schenck and Smith rearrangements of 5α-hydroperoxide derived from cholesterol [5(a)].

2. Experimental

NMR-spectra were recorded using a Varian Gemini 200BP spectrometer using $CDCl_3$ as solvent.

2.1. *Photo-oxidation*

A solution of 1-methyl-1-cyclohexene (400 mg) and tetraphenylporphine (10 mg) in diethyl ether (5 cm^3) or 5 mol dm^{-3} solution of $LiClO_4$ in Et_2O was vigorously stirred under oxygen while being irradiated for two hours with light from a 400 W sodium lamp. These illuminations were carried out under the same conditions (pressure of oxygen above the solution, intensity of irradiation of the sample, temperature (298 K), etc. were constant). The solvent was removed and the product was identified by NMR. The product of photochemical oxidation was purified by static distillation below 30°C, followed by chromatography on silica gel (ethyl acetate–light petroleum (b.p. 60–80°C) (1/9 v/v) as eluent). The initial products from oxidation consisted of a mixture of **2**, **3** and **4**, but chromatography on silica gel enabled separation of these hydroperoxides. Next, 40 mg of 1-methylcyclohex-2-enylhydroperoxide (**2**) was dissolved in 1 cm^3 of Et_2O and 5 mol dm^{-3}

solution of $LiClO_4$ in Et_2O and was stored for 24 hours at room temperature. The solvent was removed and the product was again identified by NMR. Its reduction with Ph_3P led to the corresponding alcohol.

3. Results and discussion

A solution of 1-methyl-1-cyclohexene (**1**) in Et_2O and 5M solution of $LiClO_4$ in Et_2O containing tetraphenylporphine as photosensitiser was irradiated under an oxygen atmosphere with light from a sodium lamp. The hydroperoxides **2**, **3** and **4**, which were formed, and the corresponding alcohols **5**, **6** and **7**, which were obtained on reduction with triphenylphosphine (Scheme 1), were identified by ^{1}H-NMR spectroscopy. A complete set of characterisation data of compounds **2**–**7** has been given by Courtneidge [6].

The initial products from the oxidation carried in Et_2O consisted of a mixture of **2**, **3** and **4** in the ratio 40 : 44 : 16. The analogous ratio of hydroperoxides **2**, **3** and **4** from $5\,\mathrm{mol\,dm^{-3}}$ solution of $LiClO_4$ in Et_2O was equal to 32 : 52 : 16. Additionally, the yield of the reaction carried in 5M solution of $LiClO_4$ in Et_2O increased to 100% in comparison to 55% achieved in pure Et_2O. The outcome of this reaction was different from predicted on the basis of studies carried by Courtneidge [6]. He observed that in polar solvents, the excess of the hydroperoxide **2** was formed at the expense of **3**. We assume that the increase in the yield of **3** at the expense of **2** in the concentrated solution of lithium perchlorate, being considerably more polar medium than pure diethyl ether, is due to the rearrangement of **2** catalysed by $LiClO_4$. When pure hydroperoxide **2** was stored in $5\,\mathrm{mol\,dm^{-3}}$ solution of $LiClO_4$ in Et_2O, it rearranged into **3** within 24 hours. The analogous isomerisation occurs neither in pure Et_2O nor in more polar solvents, like acetone or acetonitrile, even after several days. The studied isomerisation catalysed by $LiClO_4$ is a 1,3-H migration, demonstrating a new example of the counterion effects in reactivity. Although the presentation of its detail mechanism will require further studies, we believe that the perchlorate anion assists the proton transfer in the same way as has been observed in other similar hydrogen migrations [8–12]. In most cases, the active role of the studied anions has here its origin in the formation of ion pairs with the reactants and/or the products. Examples of such processes include the reaction of *trans*-$[FeH(\eta^2-H_2)(dppe)_2]^+$ with triethylamine being accelerated by BF_4^- and PF_6^- [8], the reaction of gold(I)-phosphine catalysed hydroamination of 1,3-dienes by benzyl carbamate facilitated by the presence of OTf^- anions [9], the palladium-catalysed intramolecular arylation taking place in the presence of an excess of carbonate [10], the reaction of 2-pirydylmethyl imidazolium salts with $IrH_5(PPh_3)_2$ leading to chelating NHC complexes being strongly affected by different counterions as Br^-, ${BF_4}^-$, ${PF_6}^-$ and ${SbF_6}^-$ [11], and the acetate-assisted palladium-promoted cyclometalation of dimethylbenzylamine (DMBA-H) [12].

References

[1] M. Prein and W. Adam, Angew. Chem. Int. Ed. Engl. **35**, 477 (1996).
[2] A.G. Leach and K.N. Houk, Chem. Commun. **12**, 1243 (2002).
[3] G.O. Schenck, O.A. Neumüller, and W. Eifeld, Chem. Ber. **618**, 202 (1958).

[4] (a) A.A. Frimer, Chem. Rev. **79**, 359 (1979). (b) W.F. Brill, J. Am. Chem. Soc. **87**, 3286 (1965). (c) W.F. Brill, J. Chem. Soc. Perkin Trans. **2**, 621 (1984). (d) N. Porter and J.S. Wujek, J. Org. Chem. **52**, 5085 (1987). (e) A.G. Davies, I.G.E. Davison, A. Maccoll, M.H. Mruzek, and A.L.J. Beckwith, J. Chem. Soc. Perkin Trans. **2**, 815 (1989). (f) A.G. Davies and W.J. Kinart, J. Chem. Res. (S), 22 (1989). (g) S.L. Boyd, R.J. Boyd, Z. Shi, L.R.C. Barclay and N.A. Porter, J. Am. Chem. Soc. **115**, 687 (1993). (h) S. Olivella and A. Solé, J. Am. Chem. Soc. **125**, 10641 (2003).

[5] (a) A.G. Davies and W.J. Kinart, J. Chem. Soc., Perkin Trans. **2**, 2281 (1993). (b) W.J. Kinart, J. Chem. Res. (S), 486 (1994). (c) W.J. Kinart, I. Tylak and C.M. Kinart, J. Chem. Res. (S), 46 (1999). (d) W.J. Kinart, C.M. Kinart, and I. Tylak, J. Organomet. Chem. **608**, 49 (2000). (e) W.J. Kinart and C.M. Kinart, J. Organomet. Chem. **691**, 1441 (2006).

[6] J.L. Courtneidge, M. Bush, and L.S. Loh, J. Chem. Soc. Perkin Trans. **1**, 1539 (1992).

[7] X. Li and V. Ramamurthy, J. Am. Chem. Soc. **118**, 10666 (1996).

[8] M.G. Basallote, M. Besora, C.E. Castillo, M.J. Fernández-Trujillo, A. Lledós, F. Maseras, and M.A. Máñez, J. Am. Chem. Soc. **129**, 6608 (2007).

[9] G. Kovács, G. Ujaque, and A. Lledós, J. Am. Chem. Soc. **130**, 853 (2008).

[10] D. Garcia-Cuadrado, A.A.C. Braga, F. Maseras, and A.M. Echavarren, J. Am. Chem. Soc. **128**, 1066 (2006).

[11] L.N. Appelhans, D. Zuccaccia, A. Kovacevic, A.R. Chianese, J.R. Miecznikowski, A. Macchioni, E. Clot, O. Eisenstein, and R.H. Crabtree, J. Am. Chem. Soc. **127**, 16299 (2005).

[12] D.L. Davies, S.M.A. Donald, and S.A. Macgregor, J. Am. Chem. Soc. **127**, 13754 (2005).