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Oxidative rearrangement of bicyclo[n.1.0]alkan-1-ols in the presence of oxygen.

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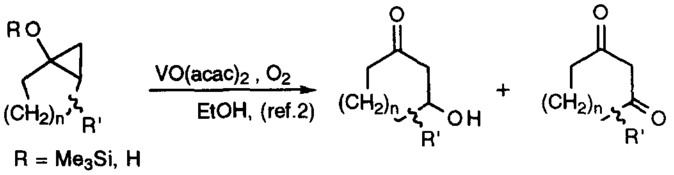
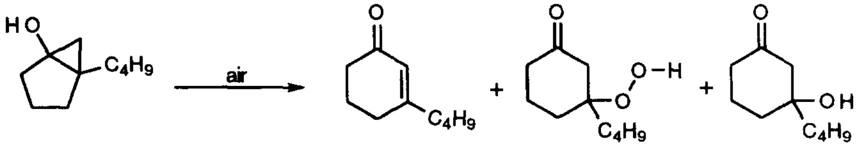
Abstract: Peroxidated compounds were prepared by treatment of ether solutions of bicyclo[n.1.0]alkanols with oxygen in the presence of silica gel, ferric acetylacetonate and light.

In a previous publication we have underlined the instability of bicyclo[3.1.0]hexan-1-ols in the presence of air.[1] A recent communication dealing with transformation in ethanol of bicyclo[n.1.0]alkan-1-ols and their corresponding trimethylsilyl ether into cycloalkan-1,3-diones and/or 3-hydroxycycloalkanones by action of oxygen in the presence of vanadyl acetylacetonate [2] prompts us to report our results.



Upon standing in an open flask on the bench 5-butylbicyclo[3.1.0]hexan-1-ol **1b**, neat or in solution (Et_2O, petroleum ether, acetonitrile, methanol), gives rapidly (1-3 hours) new compounds (TLC). Reaction times for complete transformation of various samples of the same bicyclohexanol **1b** in the same conditions were erratic (from some hours to some days) and silica gel column chromatography of these generally messy reaction mixtures allowed to isolate successively, in various amounts, 3-butylcyclohex-2-enone **2**,[3] 3-butyl-3-hydroperoxycyclohexanone **3b** [3,4] and 3-butyl-3-hydroxycyclohexanone **4b**.[3] Except in methanol the cyclohexenone **2** and the hydroxycyclohexanone **4b** were minor constituents of these reaction mixtures and the yield of the hydroperoxidated compound **3b** was between 25% (in ether) and <5% (in methanol).



1b **2** **3b** **4b**

A more reproducible and fast synthesis of the hydroperoxycyclohexanone was obtained when an etherial solution of the bicyclohexanol **1b** (0.2 M) was stirred under oxygen atmosphere in the presence of silica gel (800 mg for 1 mmol), a catalytic amount of ferric acetylacetonate (4% mol. equivalent) and light (daylight or 100W domestic light bulb at 30 cm). Omission of either of the additives or of light decreased

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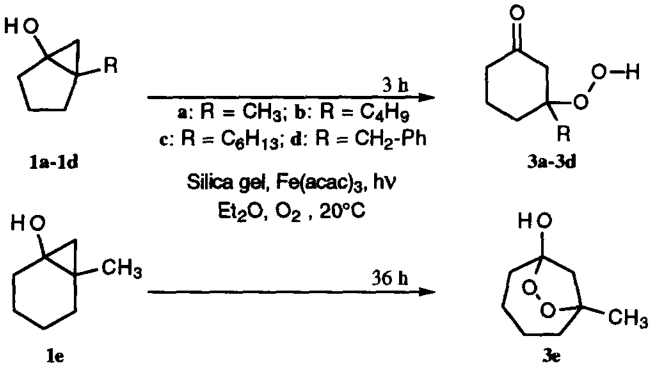
the reaction rate and/or gave a lower yield of the hydroperoxy compound. These reaction conditions were used with the bicyclohexanols **1a** - **1d** and the bicycloheptanol **1e**. In Table I are reported the yields of the peroxidated compounds **3a** - **3e** [5] isolated after silica gel column chromatography.[6]

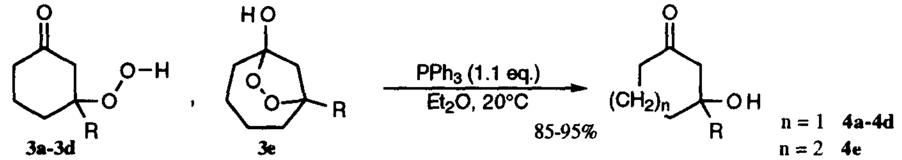
Table 1. Preparation of peroxidated compounds **3a** - **3e**



3	Yield (%)
a	35
b	55
c	68
d	50
e	54

A hydroperoxycyclohexanone form was postulated for the compounds **3a** - **3d** because a carbonyl stretching band ($\nu_{C=O}$= 1715 cm^{-1}) appears in the IR spectrum but an equilibrium of this monocyclic compound with a bicyclic peroxyhemiketal cannot be excluded.

The peroxidated compounds **3a** - **3e** gave a very strong positive test on acidic starch-potassium iodide paper and they were totally transformed into 3-hydroxycycloalkanones **4a** - **4e** by treatment with triphenylphosphine.



The hydroperoxycyclohexanone **3b** was stable in ethanol in the presence of $VO(acac)_2$ and oxygen. However, after addition of the bicyclohexanol **1b** (1 eq.) to this reaction mixture, **3b** was completely transformed after 7 hours and cyclohexenone **2** and hydroxycyclohexanone **4b** were isolated. A quicker (2 hours) simultaneous transformation of **3b** and **1b** in the presence of $VO(acac)_2$ occurred in the absence of oxygen. Although hydroperoxycyclohexanone **3b** was not detected in the vanadyl-catalyzed transformation of **1b** into hydroxycyclohexanone **4b** in the presence of oxygen [2,7] it seems possible that this reaction could occur via such a peroxidated compound.

References and notes

1. Morisson, V.; Barnier, J.-P.; Blanco, L. *Tetrahedron* **1998**, *54*, 7749-7764.
2. Kirihara, M.; Ichinose, M.; Takizawa, S.; Momose, T. *J. Chem. Soc., Chem. Commun.* **1998**, 1691-1692.
3. Rf values on silica-gel plates (pentane/ether: 1/1) **1b**: 0.52; **2**: 0.38; **3b**: 0.33; **4b**: 0.12.
4. The formation of a 3-hydroperoxyalkanoate by treatment of cyclopropanone hemiketal with atmospheric oxygen was reported: Gibson, D.H.; DePuy, C.H. *Tetrahedron Lett.* **1969**, 2203-2206. A cyclic peroxyhemiketal was isolated after photooxygenation of a cyclopropanol derivative in conditions where singlet oxygen could be generated: Scheller, M.-E.; Mathias, P.; Petter, W. *Helv. Chim. Acta* **1984**, *67*, 1748-1754.
5. New compounds were characterized on the basis of IR and NMR spectral data and elemental analysis.
6. In these reaction mixtures the corresponding 3-hydroxycycloalkanone was always obtained (up to 34% in the case of **3a**), along with some cycloalk-2-enone and unidentified by-products.
7. The presence of the enone **2** was also noticed in these conditions.