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The formation of peroxides from vinyl ethers in the presence of silica-gel

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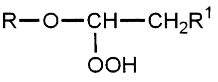
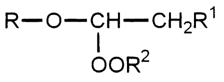
Abstract—Silica-gel containing H_2O_2 or ROOH transforms vinyl alkyl or vinyl aryl ethers into the corresponding α-alkoxy hydroperoxides and dialkyl peroxides under very mild reaction conditions.

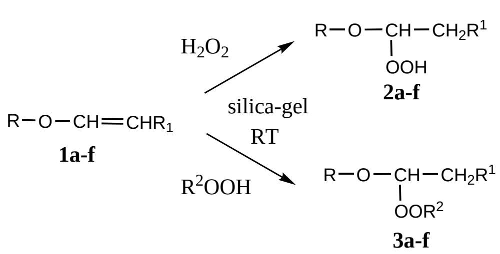
Supported reagents are very important because of their high efficiency and very mild reaction conditions.[1] The use of heterogeneous reactions on solid support is interesting because such reactions can be more selective and milder than ordinary homogeneous reactions. Silica-gel and alumina are among the most important and useful supports for a variety of transformations of functional groups. Some reactions can occur even without solvent.[2] Silica-gel shows catalytic activity and it is known that water present on silica-gel forms silylic acid and so it shows weak acidic character (pH 5.5–7.5).[3,4] For some reactions silica-gel and/or alumina supports are prepared by the sol–gel method because of better surface properties and homogeneity.[5] The amount of water on the surface of solid silica-gel or alumina[6] depends on the activation temperature.

Vinyl alkyl or vinyl aryl ethers, either commercially available or prepared by a known procedure,[7] were transformed into the corresponding α-alkoxy hydroperoxides and α-alkoxy dialkyl peroxides at room temperature (Table 1). For this purpose we first deactivated the silica-gel by heating it to a high temperature. Hot silica-gel must be cooled down to room temperature in a dessicator (with phosphorus pentoxide) or in a dry box and then poured into the ethereal solution of hydrogen peroxide or alkyl peroxide. The ether was then completely removed under vacuum at room temperature.

Table 1. The yields of the corresponding peroxides

Compound	Product yield (%)[a]		
	 $\mathrm{R{-}O{-}\underset{\displaystyle OOH}{CH}{-}CH_2R^1}$	 $\mathrm{R{-}O{-}\underset{\displaystyle OOR^2}{CH}{-}CH_2R^1}$	
Vinyl ether	R^2	*t*-Bu	Cumyl
1a	30	20	18
1b	45	32	30
1c	42	30	25
1d	40	28	22
1e	35	26	20
1f	36	35	32

[a] The yields were determined by NMR integration and iodometry (the purity of isolated peroxides was 95–97%).



1a: R=Et, R^1=H
1b: R=Et, R^1=Me
1c: R=Ph(Me)CH, R^1=H
1d: R=Ph(Me)CH, R^1=Me
1e: R-R^1=$CH_2CH_2CH_2$
1f: R-R^1=$CH_2(CH_2)_2CH_2$

R^2= *t*-Bu, cumyl

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Vinyl ethers were dissolved in an appropriate dry non-polar solvent (e.g. *n*-hexane, *n*-pentane, toluene, benzene) and applied to the top of a column filled with the silica-gel and the same non-polar solvent. Elution was carried out using the same solvent. The products were immediately adsorbed on silica-gel and desorpted with more polar solvents (e.g. diethyl ether, methyl acetate, ethyl acetate). When we dissolved the starting compounds in polar solvents no transformations of the vinyl ethers was observed. In the case of bad deactivation of the silica-gel we isolated the corresponding alcohols and carbonyl compounds. Water present on the silica-gel was being added to the vinylic double bond under the mildly acidic conditions caused by the silylic acid. It is known that transformations of ethers and acetals are catalyzed by acids ($pK_a<3$), which are much stronger than the silylic acid formed on the silica-gel.[8–10]

We can conclude that transformations on silica-gel are very important because of the very mild reaction conditions and the high yield of eluted compound. The procedure for these transformations is very simple and occurs during the elution time. Without silica-gel, no reactions were observed.

For characterization of the peroxides we prepared authentic samples by known procedures from the corresponding ketals[11] or by conventional acid-catalyzed transformation of vinyl ethers into hydroperoxides.[12] All products were characterized by NMR Brucker Avance DPX300 and GC–MS Hewlett Packard 6890 (with library of MS spectra – NBS75).

Acknowledgements

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