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Synthesis Of Linear 1-*O*-Dodecylglycerol Ethers Using Allylglycidyl Ether As A Diglycerol Equivalent.

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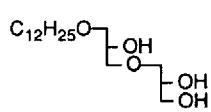
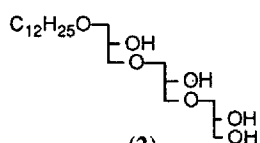
Abstract: *Synthesis of the nonionic surface active agents* (**1**) *and* (**2**) *is described. The scheme uses allyl-glycidyl ether as a diglycerol equivalent circumventing the use of the highly toxic epichlorohydrin.*

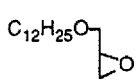
To investigate the solution properties of homogeneous dodecyl polyglycerol ether nonionic surfactants we required the linear 1-*O*-dodecyl-3-*O*-glyceryl glycerol ether (**1**) (dodecyl diglycerol ether) and 1-*O*-dodecyl-3-*O*-(glyceryl-3'-*O*-glyceryl) glycerol ether (**2**) (dodecyl triglycerol ether). Facing the same problem, H. Sagatini *et al* synthesised (**1**) and (**2**) by reacting dodecyl glycidyl ether (**3**) with glycerol and sodium diglycerate, respectively.[1] These procedures, however, do not lead to exclusive formation of the linear compounds although purification of the resultant mixtures by column chromatography gave pure (**1**) (99.7%) and (**2**) (93.4%). T. Hattori and M. Ochiai were able to obtain the linear triglycerol ether of 2,4-*bis*-hydroxy acetophenone from the activated triglycerol ether equivalent (**4**).[2] Linear diglycerol has also been synthesised by epoxidation of allyl ether followed by hydrolysis of the *bis*-epoxide with aqueous sulphuric acid.[3]



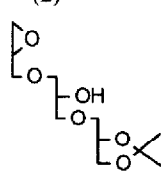
(**1**)



(**2**)



(**3**)

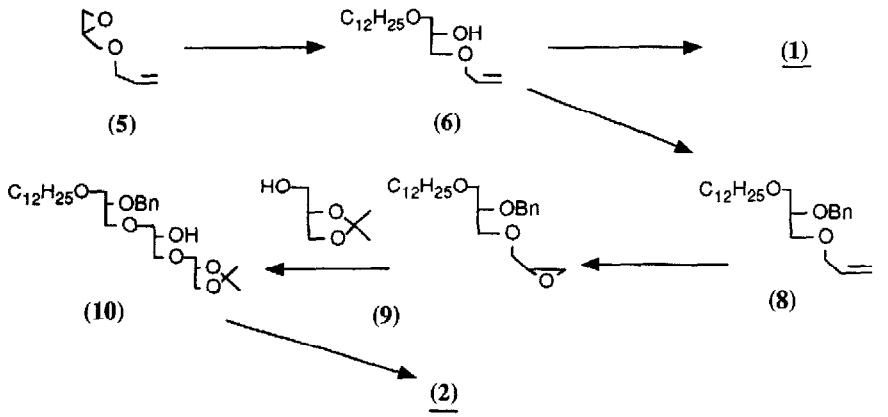


(**4**)

To ensure that we obtained linear (**1**) and (**2**) a synthetic route based upon allylglycidyl ether (**5**) was developed (Scheme).

Nucleophilic attack of the epoxide of (**5**) with dodecyl alcohol under boron trifluoride etherate catalysis gave the common intermediate (**6**) (55-65%). Epoxidation (mcpba) and hydrolysis of (**6**) gave the linear dodecyl diglycerol ether (**1**) in 85% yield.

Since it is possible that the secondary hydroxyl of (**6**) may cause the formation of undesired



Scheme

by-products such as 1,4-dioxanes and branched material, it was protected as its benzyl ether (**8**) (BnCl/18- crown-6/KOH/THF/48h rt). Reaction of the allyl moiety of (**8**) with mcpba gave the epoxide (**9**) in high yield (83%), which was reacted with an 8-fold excess of 2,2-dimethyl-1,3-dioxolane-4-methanol to give the protected triglycerol ether (**10**). Refluxing a solution of (**10**) in 1% TFA/MeOH deprotected the terminal diol in high yield (97%). Palladium hydroxide catalysed hydrogen transfer using cyclohexene in ethanol gave the crude linear triglycerol ether (**2**) (contaminated with glycerol).[4] Purification of this material by column chromatography on silica (10% MeOH/CH_2Cl_2-15% MeOH/CH_2Cl_2) gave (**2**) in 65% yield (purity 99%).[5]

Since allyl glycidyl ether can be obtained from allyl ether, this synthetic scheme circumvents the use of the highly toxic epichloro- hydrin and ensures the linearity of (**1**) and (**2**). Initial observations of the phase behaviour of (**2**) show significant deviations from the study made by T. Hattori *et al* (purity of triglycerol ether 93.4%). It is therefore obvious that highly pure samples are required to obtain meaningful results from solution property studies of these types of materials.

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References

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2. Hattori,T.; Ochiai,M. JP 61,205,277 (**1986**), Chem. Abs. **1987**,*106*,50184.
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4. Hanessian,S.; Liak,T.J.; Vanesse,B. Synthesis,**1981**,396.
5. All materials were analysed by 360 MHz ^1H NMR and the purity of compound (**2**) was determined by normal phase HPLC.

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