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ETHERS AND THEIR SULPHONATED DERIVATIVES

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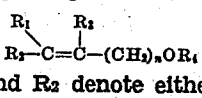
This invention relates to the production of new ethers and their sulphonated derivatives, more particularly to the preparation of sulphonated ethers having wetting and detergent properties.

As is well known, there is a large supply of wetting agents and detergents now on the market. However, many of these substances, particularly those consisting chiefly of esters, are somewhat unstable in alkaline media in which they are frequently employed. Therefore, there has been a demand for wetting agents and detergents which are more stable in alkaline solutions than those now on the market; as yet this demand has not been satisfied from a commercial standpoint.

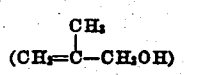
It is an object of this invention to prepare new ethers and their sulphonated derivatives.

It is a further object of this invention to prepare substances having wetting and detergent properties and which are highly stable in alkaline solutions.

In accordance with our invention ethers are prepared having the general formula

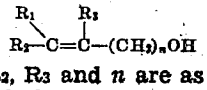


in which R_1 and R_2 denote either hydrogen or alkyl radicals containing not more than 4 carbon atoms; R_3 denotes an alkyl radical containing not more than 6 carbon atoms; R_4 denotes a fatty alcohol radical containing from 6 to 22 carbon atoms, preferably from 8 to 14 carbon atoms, and n is a whole number from 1 to 3. These ethers may, in accordance with our invention, be sulphonated to produce highly surface active agents. For example, the preferred ethers, i. e. those in which R_4 denotes a fatty alcohol radical containing from 8 to 14 carbon atoms, may be sulphonated so as to yield substances having highly effective wetting properties. Sulphonated ethers derived from fatty alcohols containing from 15 to 22 carbon atoms have been found to be effective detergents. The preferred embodiment of our invention involves the preparation of methallyl ethers and their sulphonated derivatives, since these compounds may be prepared from the readily available methallyl alcohol



and since the products obtained from this alcohol have been found to possess particularly excellent properties.

The ethers of our invention may be prepared in any suitable manner known to the art. However, we prefer to prepare these ethers by reacting suitable derivatives of any alcohol having the general formula



in which R_1, R_2, R_3 and n are as above defined, with a fatty alcohol containing from 6 to 22 carbon atoms. The short chain alcohol preferably employed as a starting material in accordance with our invention is methallyl alcohol, since this alcohol is readily available and yields ethers which upon sulphonation gives products having excellent wetting or detergent properties. However, it is to be understood that other alcohols having the above general formula may also be employed; such as, for example, ethallyl alcohol, 2-methyl crotyl alcohol, 3-methyl -3-butene 1-ol and 4-methyl -4-pentene 1-ol.

The fatty alcohol employed as starting material in accordance with our invention may be any of the fatty alcohols containing from 6 to 22 carbon atoms. The particular fatty alcohol employed ordinarily depends upon the nature of the ether or sulphonated ether it is desired to obtain. Thus, for example, we have found that wetting agents are most advantageously prepared by sulphonating ethers of the above type in which the fatty alcohol radicals contain from 8 to 14 carbon atoms; more particularly we have found that a sulphonated lauryl ether prepared from lauryl alcohol in accordance with our invention is a highly effective wetting agent. Sulphonated octyl ethers of our invention are also good wetting agents although these products are not quite as effective as the sulphonated lauryl ethers. On the other hand, we have found that the ethers containing fatty alcohol radicals having from 15 to 22 carbon atoms may be most advantageously employed as detergents; for example, sulphonated cetyl ethers prepared from cetyl alcohol in accordance with our invention have been found to be excellent detergents. Among the other fatty alcohols which may be employed in accordance with our invention may be mentioned 2-ethyl hexane, 2-ol, oleyl alcohol, octadecanol and naphthenyl alcohols.

The ethers of our invention may be prepared by reacting a sodio derivative of an alcohol having the general formula above given with the chloride of a fatty alcohol containing from 6 to 22 carbon atoms, or by reacting the chloride of an alcohol of the above formula with the sodio

derivative of the fatty alcohol. In preparing methallyl ethers in accordance with the preferred embodiment of our invention, we prefer to react methallyl chloride with the sodio derivative of the fatty alcohol since methallyl chloride is easily available. The chlorides of either the short chain or fatty alcohols may easily be prepared in a number of ways; preferably they are prepared by reacting the alcohol with an excess of thionly chloride. In place of the chloride any halide of the alcohol may be employed. The sodio derivatives of the alcohols may be prepared by reacting these alcohols with sodium or in any other suitable manner.

The ethers of our invention are generally liquids having pleasant odors and yellow to light-brown colors. They are excellent solvents for fatty materials and may also be used as plasticizers for resins and similar compositions, and as textile lubricants. These ethers may be employed as raw materials for the manufacture of plastics since they tend to polymerize upon heating. They may also be used in conjunction with other substances, e. g. with solvents or lubricants, in order to impart their desirable properties thereto.

The ethers obtained as above described may be sulphonated to produce surface active agents having desirable properties. The sulphonation may be carried out in any suitable manner, but preferably the ether is dissolved in a suitable solvent such as acetic anhydride or ethylene dichloride, and sulphuric acid then added to the solution with agitation at a relatively low temperature; the mixture may then be washed with water, neutralized and the sulphonated ether recovered. In place of sulphuric acid, other sulphonating agents such as oleum or chlorsulphonic acid may be employed. It is to be understood that while the products formed by treating the ethers of our invention with sulphonating agents are referred to as "sulphonated" ethers, the term "sulphonated" is used in a broad sense and is intended to cover both sulphated and sulphonated ethers. In view of the varying conditions under which the products of our invention may be prepared and in view of the different characteristics possessed by these products, we are not certain as to whether our products are sulphates or sulphonates or a mixture thereof, and hence do not wish to confine our invention to the production of any particular one of these modifications.

The sulphonated ethers of our invention are capable of a wide variety of uses. As above pointed out, sulphonated ethers having fatty alcohol radicals containing from 8 to 14 carbon atoms are excellent wetting agents, whereas sulphonated ethers having fatty alcohol radicals containing from 15 to 22 carbon atoms have been found to be effective detergents. We have found that the sulphonated methallyl ethers of our invention possess wetting or detergent properties far superior to those of the corresponding sulphonated allyl ethers; in some cases we have found that the allyl ethers are extremely difficult to sulphonate so that surface active agents cannot be obtained therefrom. The sulphonated ethers of our invention may also be employed as foaming agents, softeners and assistants in the cleaning and dyeing of textile material.

The following examples are illustrative of our invention. Amounts are given in parts by weight.

Example I

90 parts of methallyl chloride and 30 parts of the sodio derivative of lauryl alcohol were refluxed for about 12 hours. The reaction mixture was then filtered, diluted with water and extracted with ether. The ether extract was separated from the aqueous mass, dried and the ether removed by distillation. The residue was then vacuum distilled and a product boiling at about 146° C. at 17 mm. pressure was recovered. This product upon analysis proved to be methallyl lauryl ether.

20 parts of methallyl lauryl ether were mixed with 10 parts of 100% sulphuric acid and the mixture agitated at a temperature of about 10° C. for 8 hours. The reaction mass was washed with a 5% sodium chloride solution, neutralized and extracted with ether. The ether extract was separated from the aqueous mass, the ether evaporated therefrom, acetone added to the residue and the acetone partially evaporated. An oily substance separated from the acetone which was extracted with heptane and the extract evaporated to dryness. The residue which remained was sulphonated methallyl lauryl ether.

Solutions of the sulphonated methallyl lauryl ether were prepared and Draves tests were run thereon to determine the wetting properties of the sulphonated ether. The following table shows the results of these tests:

	Strength of solution			
	0.1%	0.2%	0.4%	0.5%
Sinking time.....seconds..	17.2	8.2	6.8	2.6

The excellent wetting properties displayed by this ether were in striking contrast to the behavior displayed by allyl lauryl ether, since this ether was not readily sulphonated and the sulphonation product did not have any appreciable wetting properties.

Example II

4 parts of sodium were dissolved in 85 parts of methallyl alcohol, 30 parts of cetyl bromide were added thereto and the solution refluxed for 8 hours. The reaction mass was washed with water and the excess methallyl alcohol removed by distillation. The residue was then vacuum distilled, whereby a fraction boiling from 155° C. to 159° C. at 2 mm. pressure was obtained; this fraction was found to consist chiefly of methallyl cetyl ether.

20 parts of the methallyl cetyl ether were mixed with 10 parts of 100% sulphuric acid and the mixture agitated at temperatures between about 25° C. and about 40° C. The sulphonation mass was then washed with water and neutralized with soda. Sodium chloride and acetone were stirred into the washed mass whereupon three layers separated. The acetone layer was withdrawn, filtered and evaporated to dryness whereby sulphonated methallyl cetyl ether was obtained. This ether displayed excellent detergent properties.

Example III

3 parts of sodium were dissolved in 34 parts of methallyl alcohol and 24 parts of a mixture of the chlorides of rice bran alcohols, consisting chiefly of oleyl and linoleyl chlorides and prepared by treating the alcohols with thionyl chloride, were added to the solution. The mixture

was then refluxed for 5 hours. The excess methallyl alcohol was removed by distillation and the residue washed, dried and vacuum distilled, whereby the methallyl ethers of rice bran oil alcohols were recovered. 25 parts of the ethers were mixed with 10 parts of 100% sulphuric acid, the mixture agitated, washed with salt water and extracted with ether. The ether extract was separated from the aqueous mass and the ether evaporated therefrom, whereby the sulphonated ethers were obtained.

Example IV

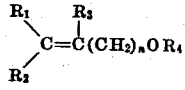
11 parts of sodium were dissolved in 255 parts of methallyl alcohol and 47 parts of octyl chloride were added to the solution. The mixture was then refluxed for 6 hours, the excess methallyl alcohol removed by distillation, water added to the mass and the aqueous mass then extracted with ether. The ether extract was separated from the aqueous mass, the ether evaporated therefrom and the residue vacuum distilled, whereby a fraction having a boiling point of about 100° C. at 12 mm. pressure was recovered. This fraction consisted chiefly of methallyl octyl ether. 7 parts of this ether were then mixed with 10 parts of 85% sulphuric acid at a temperature of about 5° C. and the mixture agitated for a few minutes. At the end of this time the reaction mixture was washed with water and neutralized with soda. The sulphonated product was recovered in the usual manner.

It will be evident from the above description that our invention provides new ethers and their sulphonated derivatives, which, because of their highly valuable properties, will be of great interest, particularly to those engaged in the manufacture and treating of textiles and similar materials.

Since certain changes may be made in the above products and different embodiments of the invention could be made without departing from the scope thereof, it is intended that all matter contained in the above description shall be interpreted as illustrative and not in a limiting sense.

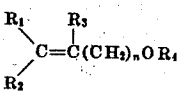
Having described our invention, what we claim as new and desire to secure by Letters Patent is:

1. A composition of matter comprising essentially an ether having the general formula:



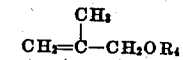
in which R_1 and R_2 denote radicals selected from the group consisting of hydrogen and alkyl radicals containing not more than 4 carbon atoms; R_3 denotes an alkyl radical containing not more than 6 carbon atoms; R_4 denotes a fatty alcohol radical containing from 6 to 22 carbon atoms, and n is a whole number from 1 to 3.

2. A composition of matter comprising essentially an ether having the general formula:



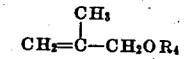
in which R_1 and R_2 denote radicals selected from the group consisting of hydrogen and alkyl radicals containing not more than 4 carbon atoms; R_3 denotes an alkyl radical containing not more than 6 carbon atoms; R_4 denotes a fatty alcohol radical containing from 8 to 14 carbon atoms, and n is a whole number from 1 to 3.

3. A composition of matter comprising essentially an ether having the general formula:



in which R_4 denotes a fatty alcohol radical containing from 6 to 22 carbon atoms.

4. A composition of matter comprising essentially an ether having the general formula:



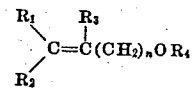
in which R_4 denotes a fatty alcohol radical containing from 8 to 14 carbon atoms.

5. A composition of matter comprising essentially methallyl lauryl ether.

6. A composition of matter comprising essentially methallyl cetyl ether.

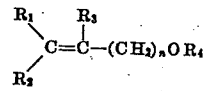
7. A composition of matter comprising essentially methallyl oleyl ether.

8. A composition of matter comprising essentially the sulfonation product of an ether having the general formula:



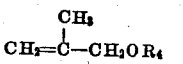
in which R_1 and R_2 denote radicals selected from the group consisting of hydrogen and alkyl radicals containing not more than 4 carbon atoms; R_3 denotes an alkyl radical containing not more than 6 carbon atoms; R_4 denotes a fatty alcohol radical containing from 6 to 22 carbon atoms, and n is a whole number from 1 to 3.

9. A composition of matter comprising essentially the sulphonation product of an ether having the general formula:



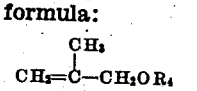
in which R_1 and R_2 denote radicals selected from the group consisting of hydrogen and alkyl radicals containing not more than 4 carbon atoms; R_3 denotes an alkyl radical containing not more than 6 carbon atoms; R_4 denotes a fatty alcohol radical containing from 8 to 14 carbon atoms, and n is a whole number from 1 to 3.

10. A composition of matter comprising essentially the sulphonation product of an ether having the general formula:



in which R_4 denotes a fatty alcohol radical containing from 6 to 22 carbon atoms.

11. A composition of matter comprising essentially the sulphonation product of an ether having the general formula:



in which R_4 denotes a fatty alcohol radical containing from 8 to 14 carbon atoms.

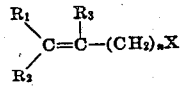
12. A composition of matter comprising essentially sulphonated methallyl lauryl ether.

13. A composition of matter comprising essentially sulphonated methallyl cetyl ether.

14. A composition of matter comprising essentially sulphonated methallyl oleyl ether.

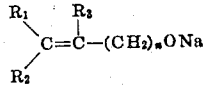
15. A process for the preparation of ethers which comprises reacting a sodio derivative of a fatty alcohol containing from 6 to 22 carbon

atoms with a compound having the general formula:



in which R_1 and R_2 denote radicals selected from the group consisting of hydrogen and alkyl radicals containing not more than 4 carbon atoms; R_3 denotoes an alkyl radical containing not more than 6 carbon atoms; X denotes a halogen atom, and n denotes a whole number from 1 to 3.

16. A process for the preparation of ethers which comprises reacting a halide of a fatty alcohol containing from 6 to 22 carbon atoms with a compound having the general formula:

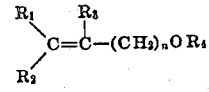


in which R_1 and R_2 denote radicals selected from the group consisting of hydrogen and alkyl radicals containing not more than 4 carbon atoms; R_3 denotes an alkyl radical containing not more than 6 carbon atoms, and n is a whole number from 1 to 3.

17. A process for the preparation of ethers which comprises reacting methallyl chloride with a sodio derivative of an alcohol containing from 8 to 14 carbon atoms.

18. A process for the preparation of ethers which comprises reacting methallyl chloride with the sodio derivative of lauryl alcohol.

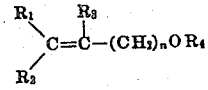
19. A process for the preparation of sulphonated ethers which comprises reacting an ether having the general formula:



in which R_1 and R_2 denote radicals selected from the group consisting of hydrogen and alkyl radicals containing not more than 4 carbon atoms; R_3 denotes an alkyl radical containing not more than 6 carbon atoms; R_4 denotes a fatty alcohol radical containing from 6 to 22 carbon atoms, and n is a whole number from 1 to 3 with a sulphonating agent.

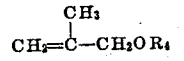
20. A process for the preparation of wetting agents which comprises reacting methallyl lauryl ether with a sulphonating agent.

21. A water-soluble salt of the sulphonation product of an ether having the general formula:



in which R_1 and R_2 denote radicals selected from the group consisting of hydrogen and alkyl radicals containing not more than 4 carbon atoms; R_3 denotes an alkyl radical containing not more than 6 carbon atoms; R_4 denotes a fatty alcohol radical containing from 6 to 22 carbon atoms, and n is a whole number from 1 to 3.

22. A water-soluble salt of the sulphonation product of an ether having the general formula:



in which R_4 denotes a fatty alcohol radical containing from 6 to 22 carbon atoms.

23. A water-soluble salt of sulphonated methallyl lauryl ether.

24. A water-soluble salt of sulphonated methallyl cetyl ether.

25. A water-soluble salt of sulphonated methallyl oleyl ether.

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