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1-ACYLOXY-2-BUTYNE-4-OLS

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2 Claims. (Cl. 260—488)

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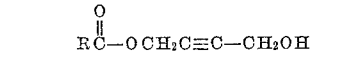
This invention relates to novel half esters of 2-butyne-1,4-diol and the process of producing them.

I have discovered that when 2-butyne-1,4-diol is heated in admixture with an excess of a fatty acid containing 2 or more carbon atoms, only one of the hydroxyl groups of the diol is esterified, resulting in the formation of the half ester of 2-butyne-1,4-diol corresponding to the fatty acid employed.

These novel half esters of 2-butyne-1,4-diol may be represented by the following general formula:



wherein R is aliphatic, and they have been found to be particularly valuable as intermediates in the synthesis of 1-acyloxy-3-butene-2-ones which are readily polymerizable substances whose polymers resemble polyvinyl esters in appearance.

In preparing the novel half esters of 2-butyne-1,4-diol, the acetylenic glycol is mixed with at least one molar equivalent of a fatty acid corresponding to the acid whose half ester is desired, and the mixture heated with stirring until the esterification is complete. A preferred embodiment of the process of the present invention, which is generally applicable to the production of the novel half esters of the present invention, is illustrated in the following example in which the parts are by weight:

Example

A solution of 260 parts of 2-butyne-1,4-diol in 600 parts of glacial acetic acid was treated with stirring under gentle reflux (120–125° C.) for 4 hours. The excess acetic acid was removed by distillation under diminished pressure. The residual liquid was then poured into about 500 parts of water and neutralized with sodium carbonate. The ester layer was separated by extraction with ether. The ether extract was dried over anhydrous sodium sulfate. After removal of the ether by distillation, the 1-acetoxy-4-hydroxy-2-butyne was isolated as a clear liquid, B. P.$_{12}$ 131–132° C.; n_D^{25} 1.4595; d_4^{25} 1.1275.

It will be understood that the foregoing example is illustrative only of a specific embodiment of the present invention and that the procedure therein illustrated is equally applicable to the

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production of half esters of 2-butyne-1,4-diol of a wide variety of fatty acids. As examples of fatty acids whose half esters with 2-butyne-1,4-diol are included within the scope of the present application and which may be produced by the procedures illustrated above, may be mentioned the lower aliphatic acids such as acetic, propionic, butyric, isobutyric and the valeric acids, and also the higher aliphatic acids such as caprylic, capric, lauric, myristic, palmitic, stearic, etc. Of these, the compounds having the widest range of utility are the half esters of the saturated lower aliphatic acids particularly acetic acid, and these lower aliphatic acids, therefore, are preferably employed in practicing the process of the present invention. It should be noted that when formic acid is heated with 2-butyne-1,4-diol, the diformate is obtained, so that the use of formic acid and its half esters with 2-butyne-1,4-diol are not included in the present invention.

As indicated by the foregoing example, at least two molar proportions of fatty acid to each molar proportion of the acetylenic glycol are employed, and preferably somewhat larger amounts up to about ten mols of fatty acid to each mol of the acetylenic glycol are employed, although the process is operative when a large excess of fatty acids (for instance up to a molar ratio of 100:1) is employed. The temperature to which the mixture is heated is not highly critical, but should be sufficient to give a satisfactory rate of reaction. Thus, a temperature of at least 50° C. should be employed and with the lower aliphatic acids, particularly acetic acid, reflux temperature at atmospheric pressure may be used advantageously. Preferably, the reaction is carried out within the range of 100–150° C.

I claim:

1. 1-lower alkanoic acid esters of 2-butyne-1,4-diol wherein the acid radical contains from 2 to 5 carbon atoms.

2. 1-acetoxy-2-butyne-4-ol.

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REFERENCES CITED

The following references are of record in the file of this patent:

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