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THREE NEW CONVENIENT PREPARATIONS OF OXETANE

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The most widely used method for the preparation of unsymmetrical oxetanes is the cyclisation of 1,3-halohydrins with alkali When the alcoholic functional group is a primary one, yields are low oxetane itself is obtainable in only 20-25% yields from 3-chloropropan-1-ol,[1,2] but the yield can be improved to 40-45% by the use of the acetate ester of the chlorohydrin, the cyclisation being carried out by the use of a very concentrated solution of sodium hydroxide and potassium hydroxide [2,3] The obvious disadvantage of this method is that the preparation of oxetanes possessing groups sensitive to attack by strong base is impossible

One method which overcomes this difficulty is the elimination of tributyltin bromide from the (bromoalkoxy)tin derivative (3), readily made from the bromohydrin [4]

$$RO(CH_2)_3Br + Bu_3SnOEt \xrightleftharpoons{100^\circ} EtOR + \underset{(3)}{Bu_3SnO(CH_2)_3Br} \xrightarrow{220-240^\circ} Bu_3SnBr +$$

(1) R = H

(2) R = Ac

The published yield of this method is 64%, but we have found that the volatile material obtained after the elimination reaction contains a number of side-products purification by g l c has given us a yield of 25%

The critical stage in this synthesis is the formation of the intermediate (3), and the usefulness of this reaction is limited by the availability of 1,3-bromohydrins. The corresponding bromoacetates can, however, be made from the 1,3-diols by a method analogous to that for chloroacetates,[5] and with ester exchange we have developed three new methods which provide ready access to the formation of oxetanes. In the case of the parent compound, these are as follows

(a) Heating the bromoacetate (2) with tributylethoxytin at 80° for 1 h efficiently achieves an exchange reaction, the ethyl acetate distilling off on raising the temperature to 220° a yield of 40% of oxetane is obtained.

(b) $(Bu_3Sn)_2O + AcO(CH_2)_3Br \rightarrow Bu_3SnOAc + \underset{(3)}{Bu_3SnO(CH_2)_3Br}$

A mixture of bistributyltin oxide and bromoacetate is heated at 80° for 1 h the tributyltin acetate that is formed is a solid, so that heating the mixture containing the intermediate (3) gives material of high purity, yielding 33% of oxetane

(c) $(Bu_3Sn)_2O + 2HO(CH_2)_3Br \rightleftharpoons 2Bu_3SnO(CH_2)_3Br + H_2O$

(3)

Bistributyltin oxide (0 05 mol) is refluxed with bromohydrin (0 1 mol) in dry benzene (40 ml), and the water removed as benzene/water azeotrope After removal of the excess of benzene, heating the residue gives a direct route to oxetane formation with a 20% yield

Another advantage of these methods is that, with the exception of the second, the tributyl tin bromide is recoverable, and can be used to make tributylethoxytin for further work

Oxetane itself presents the least advantageous system for oxetane ring formation in traditional syntheses increased yields are obtained when the alcoholic group is a secondary one,[6] and preliminary work indicates that this is also true for all these new routes to oxetanes.

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