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A READY ROUTE FROM VICINAL CIS-DIOLS TO EPOXIDES

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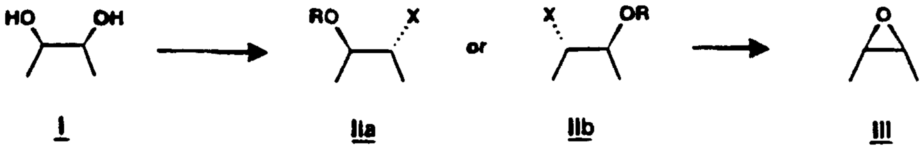
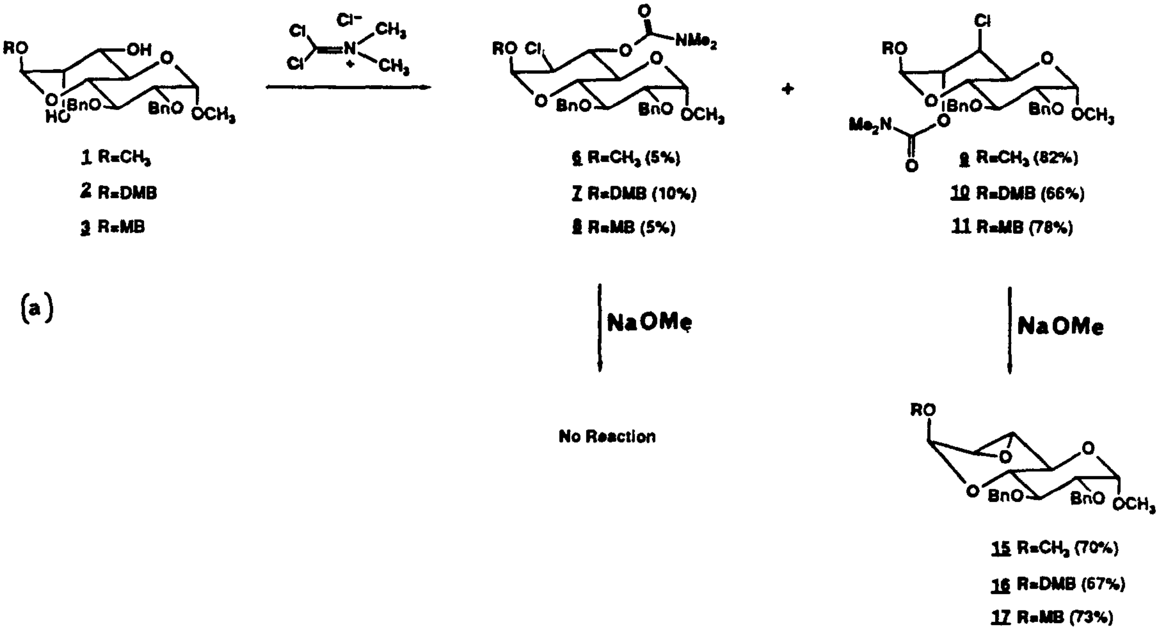
Summary: A two-step procedure for converting a vicinal cis-diol into expoxides is described which involves the preparation of chloro carbamate intermediate by the use of (dichloromethylene)dimethylammonium chloride

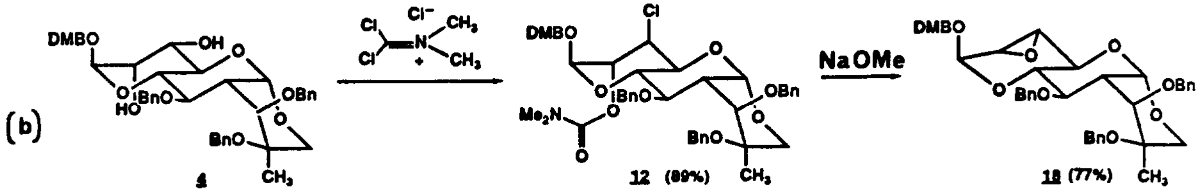
The epoxide functionality is important, not only because it is found in many naturally occurring compounds, but also because of its utility as an agent for chemical transformations.[a] The latter aspect is particularly important in the manipulations of carbohydrate derivatives, where the precursors are usually diols of trans-diaxial or trans-diequatorial orientation.[b] On the other hand, there are no satisfactory routes to epoxides from cis-diols. In this manuscript, we describe a solution to this problem.



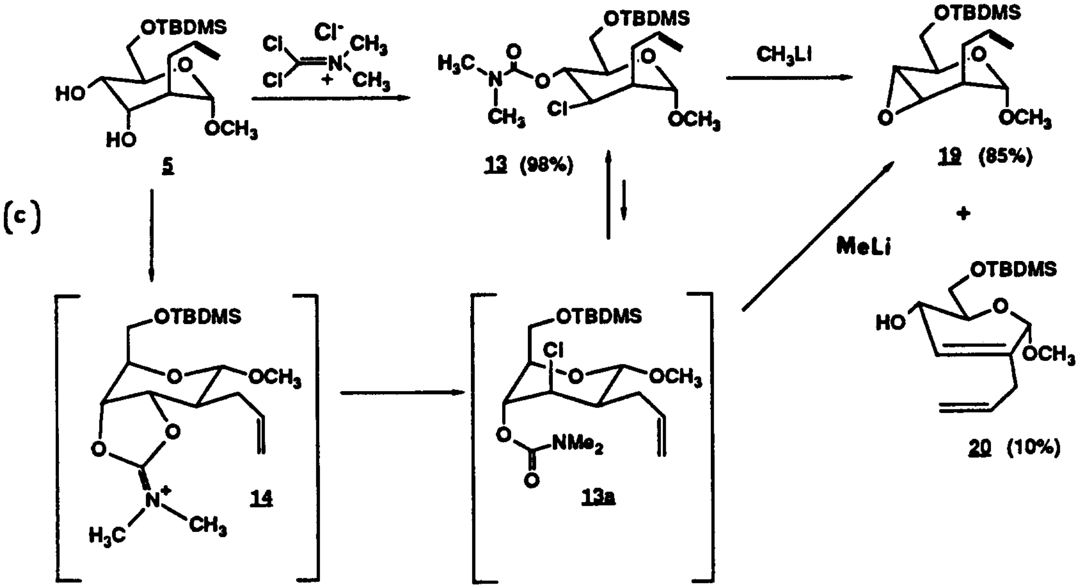
Our requirement was the conversion of a cis-diol such as **I**, specifically into epoxide **III** and this could conceivably be accomplished from either or both of the halohydrins **IIa** and **IIb**. In keeping with the recent study of Stick and co-workers,[c] the cis-diols **1-5**, were treated with phosgene imminium chloride (Viehe's salt)[d] in the presence of triethylamine in refluxing dichloromethane to give the products shown in Table 1. The results are generally in keeping with Stick's observations that the major isomer has trans-diaxial orientation.[c] The formation **13**, although an exception, can be readily rationalized by assuming that the intermediate imminium salt (**14**) reacts from the $^1C_4$ conformation to give **13a** initially, but then adopts the $^4C_1$ conformation shown for the product, **13**.



As can be seen from equations a, b, and c, all compounds with diaxially oriented chloride and carbonate groups reacted smoothly with sodium methoxide to give epoxides in good yields. On the other hand, the corresponding diequatorial analogs **9-11**, which are conformationally immobile because of the trans-ring junction, failed to react under comparable conditions. With regard to compound **13**, epoxide formation in **19** required more



severe conditions, which is consistent with the need for a conformational change to 13a in order to facilitate internal displacement leading to compound 19. A small amount of the elimination product, 20, was also observed.



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