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STEREOSPECIFIC DEOXYGENATION OF 1,2-DIOLS TO OLEFINS

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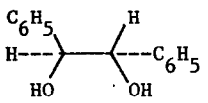
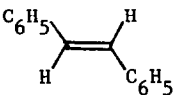
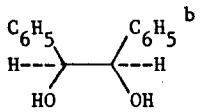
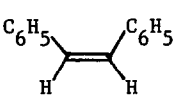
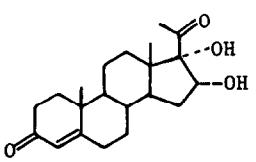
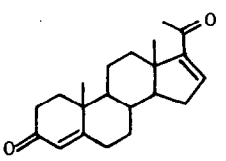
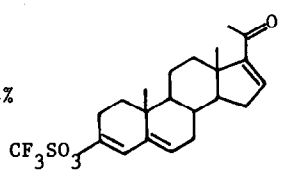
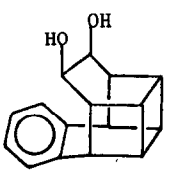
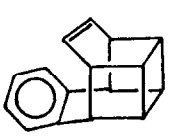
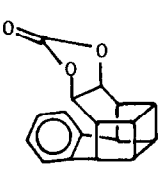
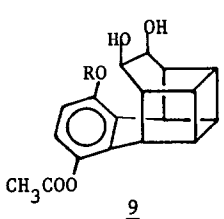
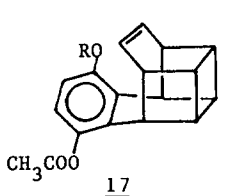
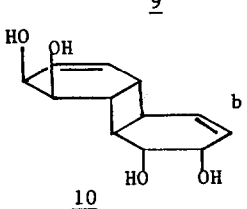
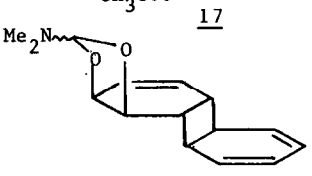
Summary: The 2-dimethylamino-1,3-dioxolane derivatives of 1,2-diols when treated with trifluoromethane sulfonic anhydride and diisopropylethylamine in toluene give the corresponding olefins stereospecifically under mild experimental conditions.

Many methods are known for the conversion of 1,2-diols into the corresponding olefins.[1] Among the notable methods which proceed stereospecifically are a) the desulfurization of 2-thiono-1,3-dioxolanes,[2] b) decompositions of 2-ethoxy-1,3-dioxolanes[3] and c) 2-dimethylamino-1,3-dioxolanes,[4,5] and d) the base-induced elimination of 2-phenyl-1,3-dioxolanes.[6] Methods a-c are usually carried out at temperatures in excess of 100°, while method d employs a very strong base, such as an alkyllithium, for the conversion. In connection with our interest in the synthesis of novel energy-rich compounds of limited thermal stability,[7] we found a need for a mild and stereospecific method for this conversion, where delicate structural and functional features of the parent diol and/or the product may restrict the use of available methods. We wish to report a stereospecific deoxygenation of 1,2-diols which may be achieved at room temperature or slightly above in an essentially neutral medium.

2-Dimethylamino-1,3-dioxolanes (1) have been used successfully by Hanessian, Eastwood, and their coworkers as the intermediate for the conversion of 1,2-diols to the corresponding olefins.[4,5] The elimination proceeds presumably via a quarternary ammonium intermediate using either acetic anhydride at 90-180° or methyl iodide in refluxing toluene. However, if the highly electronegative trifluoromethane sulfonic anhydride is used instead of acetic anhydride, the acidity of 2-proton in the quarternary ammonium intermediate, (2, Scheme 1) will be greatly enhanced. This proton may be removed by a hindered amine, such as diisopropylethylamine, under mild experimental conditions. The ylide intermeidate 3 formed may then undergo fragmentation successively to yield the desired olefin. We indeed found that 2-dimethylamino-1,3-dioxolanes are converted efficiently into olefins in good to excellent yield under these conditions, and the conversion is stereospecific. The results are illustrated in the Table.

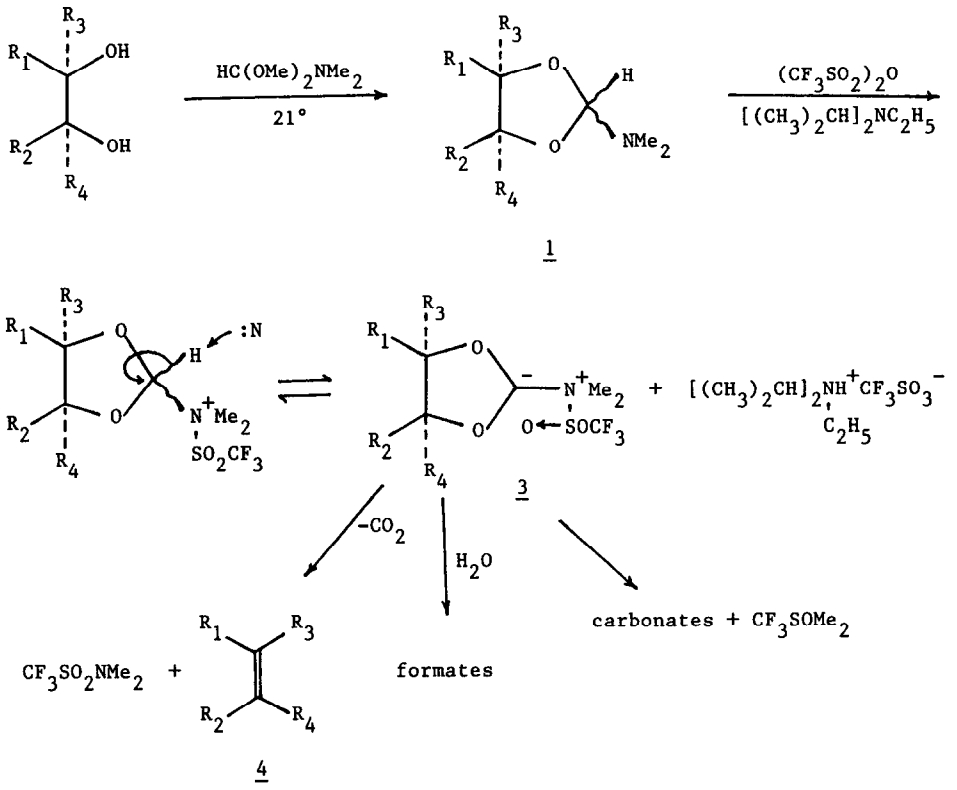
The dimethylaminodioxolanes (1) were prepared as mixtures of stereoisomers (1:1) in quantitative yield by treating the diol with an excess of neat N,N-dimethylformamide dimethyl acetal for one hour at 21°, followed by evaporation under reduced pressure. The crude dioxolanes were dissolved in dry toluene (~0.03 M) containing 4 equivalents of diisopropylethylamine. A solution

Table. Conversion of 1,2-Diols to Olefins via 2-Dimethylamino-1,3-Dioxolanes[a]

Diols	Temperature	Products/Yields			
 5	21°	 11	87%	Monoformate of 5	10%
	50°		94%		5%
 6 [b]	21°	 12	75%	Monoformate of 6	14%
	50°		85%		7%
 7	50°	 13	24%	 14	45%
 8	0°	 15	25%	 16	70%
	50°		61%		1%
 9	50°	 17	40%		
 10 [b]	21°	 18	65%[c]		

[a] All new products except 18 have been characterized by elemental and spectral analyses.
[b] One equivalent of triflic anhydride and 2.2 equivalents of the amine were used in order to minimize the isomerization of cis-stilbene or to yield 18. [c] Spectral yield.

Scheme 1



of trifluoromethane sulfonic anhydride (0.015 M, 2 equivalents) in dry toluene was then added with vigorous stirring. After 20-30 minutes, the reaction mixture was diluted with ether, washed with aqueous $NaHCO_3$ and dried. The ethereal solution was evaporated and the products were isolated from the residue by chromatography over silica gel.

The stereospecificity of this reaction is illustrated by the deoxygenation of (±)- and meso-dihydrobenzoins (5 and 6)[8] to yield the corresponding stilbenes (11 and 12) in excellent yield. In contrast to the reaction of 1 with acetic anhydride, in which the isomerization of cis-stilbene to trans-stilbene occurs above 90°,[5] the isomerization was not detected in our procedure. 16α,17α-Dihydroxyprogesterone (7) afforded 16-dehydroprogesterone (13) and its enol trifluoromethane sulfonate (14), mp 137-9°. The formation of enol trifluoromethane sulfonate under these reaction conditions is known in the literature,[9] and 14 may be hydrolyzed to the corresponding ketone 13 in refluxing 0.1 N KOH in $THF/H_2O/DMSO$ (3:6:1). The reaction was also successfully applied to the synthesis of the heat-labile cage olefins 15 and 17. Olefin 15 was synthesized previously in poor yield (10-15%) by the lead tetraacetate induced bis-decarboxylation of the corresponding diacid at 72-75°, in which both a rearranged product and its decomposition product are the major products in this reaction.[7a] Furthermore, lead tetraacetate induced bis-decarboxylation of 1,2-diacids is known to require carefully-controlled experimental conditions.

Recently, the reaction was further extended to the synthesis of the heat-labile dioxy-derivative 18, which could not be synthesized by existing deoxygenation procedures. When the base-induced elimination of 2-phenyl-1,3-dioxolanes[6] was applied to 10, the phenyldioxolane fragmented to yield phenol and benzene instead.[7d]

The mechanism of formation of olefins from dioxolanes has been reviewed by Bloch.[10] The formation of these products may be formulated via an ylide intermidiate 3 which subsequently fragments to form the olefin. The fragmentation is more important at higher temperatures, while by-product formation becomes more important at lower temperatures. The detailed mechanism and scope of this reaction are currently under investigation.

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