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A MILD AND STEREOSPECIFIC CONVERSION OF VICINAL DIOLS INTO OLEFINS

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There are a large number of methods in the literature for the formation of the synthetically useful olefinic linkage from alcohols, diols and their respective derivatives [1]. In current practice, the deoxygenation of vicinal diols in particular, has been effected either directly in the presence of metals [2], in the form of 5-membered cyclic derivatives by thermal *cis*-elimination [3], or by other procedures [1,4,5]. There is however, a constant demand for mild and stereospecific procedures for converting vicinal diols into the corresponding olefins, particularly in the context of multistep synthesis and polyfunctional compounds, where delicate structural and functional features may restrict the use of available methods. In connection with our interest in the chemistry of amide acetals [6], we describe herein a practical procedure for the conversion of vicinal *cis*-diols in acyclic and cyclic systems, and vicinal *trans*-diols in acyclic systems, into the corresponding olefins in a two-stage, one-pot process, as shown by the preparation of diethyl fumarate from diethyl D-tartrate:

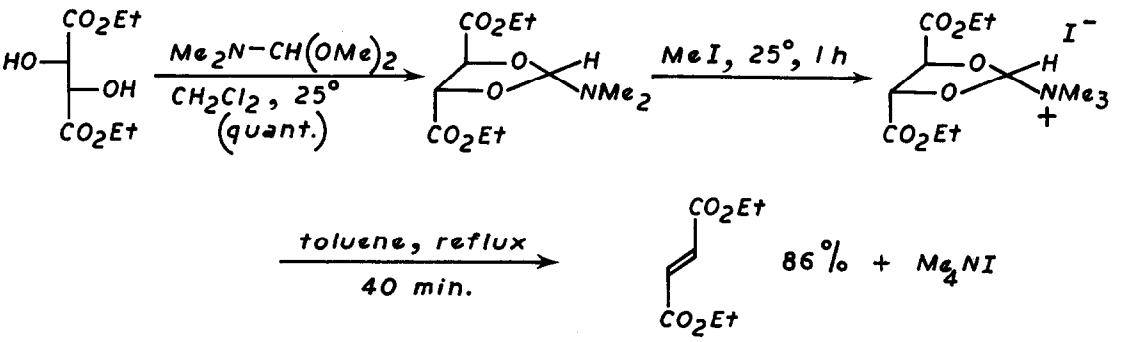
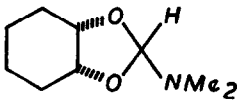
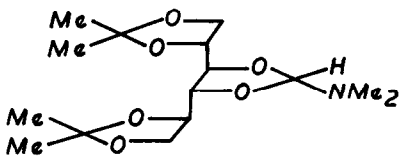
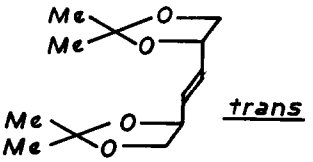
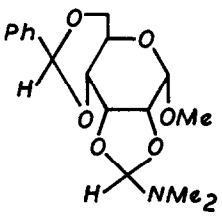
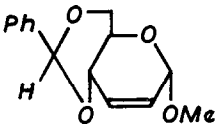
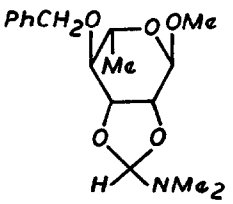
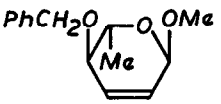
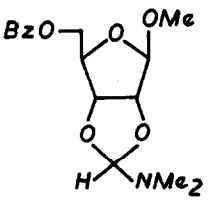


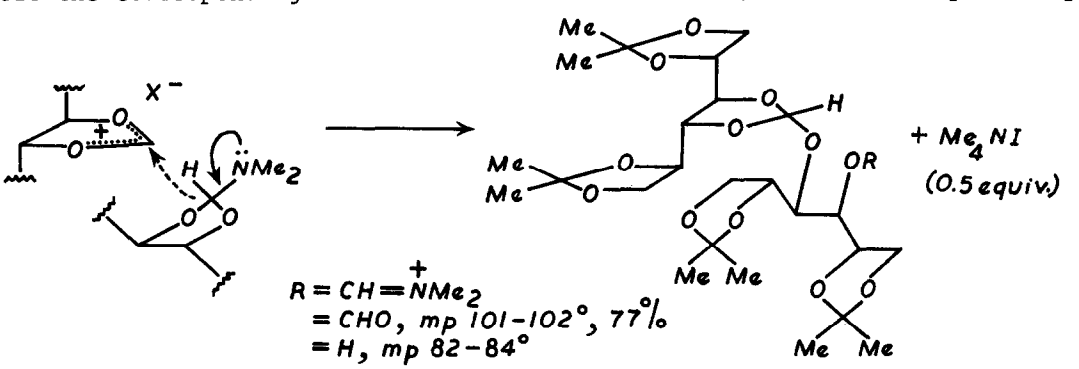
Table 1. Olefins from 1-(dimethylamino)methylene acetals

	Acetal[a]	Conditions (MeI, toluene, reflux)	Olefin	Yield
1.	 oil (ref. 7)	neat, 100° [c]		90%
2.	 mp 46-47° (ref. 8)	5-10 min.	 trans	95% [d]
3.	 mp 101-102°	neat, 120°		85% [e]
4.	 oil	30 min.		95% [f]
5.	 oil	30 min.		89% [g]

a. Only one diastereomer is shown, b. yields are for isolated products; entries 3, 4, 5 by short column chromatography, c. salt heated gradually to 100°; product isolated by distillation, d. by direct crystallization; mp 82°, $[\alpha]_D$ + 60° (Chf) (ref. 5,8), e. salt heated gradually to 120° (bath temp.); mp 117-118°, $[\alpha]_D$ + 128.5° (Chf) (ref. 9), f. syrup; $[\alpha]_D$ - 105° (Chf) (ref. 10), g. chromatographically homogeneous syrup; mp 62-63° after chromatography (~25%) (ref. 10).

First, the diol (1 mmole) is converted into the corresponding 1-dimethylamino(methylene)acetal [12] (quant.), by treatment with excess N,N-dimethylformamide dimethylacetal (2-10 equiv) in dichloromethane. The solution is evaporated to dryness, the acetal is dissolved in toluene (6 ml) and excess methyl iodide (4 ml) is added. The resulting trimethylalkylammonium salt precipitates within a short period of time, and the suspension is heated at reflux (5-60 min) to give the olefin. As seen in Table 1, a variety of functional groups are compatible with the reaction conditions, which are essentially neutral, and the yields are consistently high. It is of interest that the *trans*-olefin in entry 2 had been previously prepared [8] by treatment of the crystalline acetal with acetic anhydride (130°, 3 h). The formation of olefins from the corresponding 1-dimethylamino(methylene)acetals takes place only after heating the preformed trimethylalkylammonium salts [13] and the rate and method of formation seems to depend on the geometric constraints in the substrate (see entry 3), among other factors [14]. The intervention of a carbenic intermediate [3,8] or a concerted process is under study.

In connection with these studies, we also report that when reactions were conducted at room temperature in the presence of an alcohol (18 h), or in refluxing toluene (2 h), but in the presence of 4A molecular sieves (2 g) and a limited amount of methyl iodide (0.25-0.5 ml), the major products were the corresponding orthoester derivatives [15,12] (R = H; CHO respectively).



A mixed orthoester derivative was similarly obtained with the acetal in entry 4 (presumably a 2-formate)[16], oil (55%); $[\alpha]_D^{25}$ - 115° ($CHCl_3$). Deformylation (NaOMe, MeOH) gave the corresponding crystalline derivative, mp 166-168°; $[\alpha]_D^{25}$ - 86° ($CHCl_3$).

Presumably, in these cases, reaction occurs between unalkylated acetal and its acyloxonium counterpart, to give initially, an iminium salt, which eventually leads to the formate ester [17].

Olefin formation from 1-dimethylamino(methylene)acetals as described in this paper, nicely complements the Tipson-Cohen procedure [5] which requires the presence of vicinal organic sulfonate esters (NaI, Zn, DMF,reflux,2-5 h, ref. 5, 9) and the Corey-Winter procedure [3] utilizing vicinal thionocarbonate derivatives ($P(OMe)_3$, reflux, 3 days, ref. 9, 10). It offers in addition, the advantages of simplicity of operation ,mildness and efficacy [18].

References and notes

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13. The corresponding 1-dimethylamino(ethylidene) acetals did not give olefins, but underwent hydrolysis during workup to the corresponding vicinal hydroxyacetates [6] as expected.
14. Other diols having a variety of functional and stereochemical features are being investigated.
15. See for example, W. Tritschler and S. Kabusz, Synthesis, 32 (1972).
16. Attachment is tentatively assumed to be via the C-3 hydroxyl group of the rhamnose unit, the formate ester being at C-2, based on a stereoselective attack by the C-3 oxygen (with cleavage of the quasi equatorial C-3-O bond), on the dioxolenium carbon atom of another unit (see ref. 17).
17. S. Hanessian and J. Banoub, Tetrahedron Lett., 661 (1976).

18. We thank the Farmitalia Co. (Milan) and the Ministère de l'Education du Québec for financial support and the NRCC for a fellowship (M. LaRue).

New compounds had elemental analysis and spectroscopic characteristics that were in accord with their respective structures.