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A MILD AND STEREOSPECIFIC CONVERSION OF VICINAL DIOLS INTO OLEFINS VIA 2-METHOXY-1,3-DIOXOLANE DERIVATIVES

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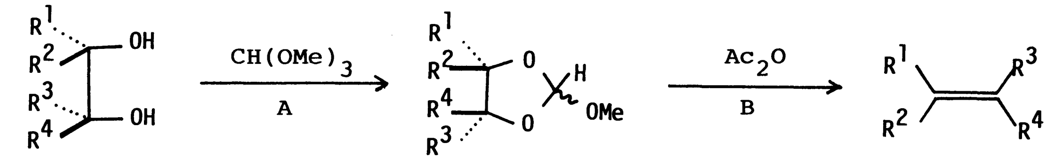
An efficient and practical method for the stereospecific synthesis of olefins from vicinal diols via the corresponding 2-methoxy-1,3-dioxolanes is reported.

In the course of the total synthesis of cycloeudesmol, we encountered the necessity of the efficient conversion of the vicinal diol 1 to the olefin 2 (see entry 7 in Table 1).[1] Although a variety of approaches have already been developed for the conversion of vicinal diols to olefins, only a few possess the mildness, stereospecificity and efficiency necessary for their use in multistep synthesis of complex molecules.[2] The Corey's olefin synthesis by the desulfurization of 1,3-dioxolane-2-thiones with triethyl phosphite or 1,3-dimethyl-2-phenyl-1,3,2-diazaphospholidine is well known,[3] but the method requires expensive thiocarbonyldiimidazole or toxic thiophosgene. On the contrary, the Eastwood's procedure[4] which involves 2-ethoxy-1,3-dioxolanes as intermediates seems to be attractive because triethyl orthoformate which is the reagent necessary for this reaction is very cheap and easy to handle. Unfortunately this procedure is not applicable to the acid sensitive compounds because the reaction conditions require a high reaction temperature under acidic conditions. Actually the application of this method to 1 was unsuccessful. After various fruitless efforts including the olefin synthesis based on 2-dimethylamino-1,3-dioxolane derivatives,[5] we found the efficient method for the conversion of 1 to 2 as shown in Table 1 (entry 7). In this paper we want to demonstrate the applicability of this new method to the wide variety of substrates. The general procedure is shown below.

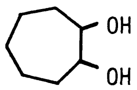
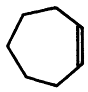
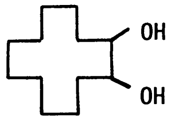
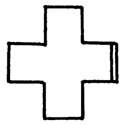
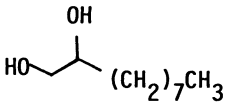
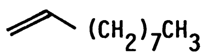
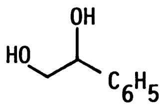
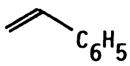
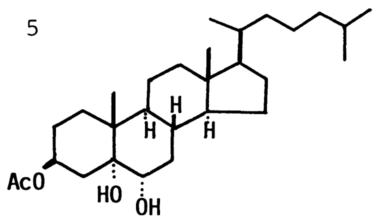
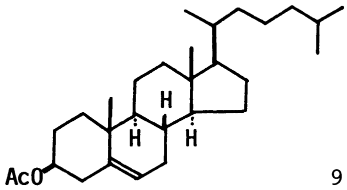
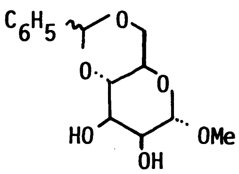
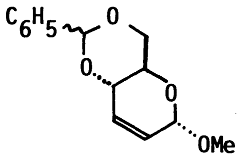
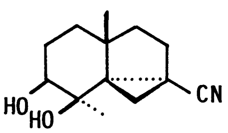
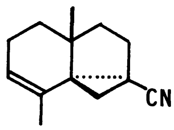
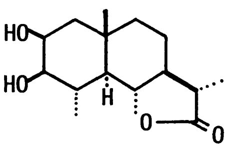
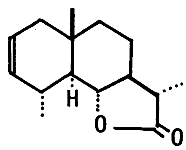
A vicinal diol (1 mmol) was converted into the corresponding 2-methoxy-1,3-dioxolane by treatment with trimethyl orthoformate (5 mmol) in the presence of pyridinium p-toluenesulfonate (PPTS, 0.5 mmol) or p-toluenesulfonic acid (PTS, 0.5 mmol) in THF or dichloromethane (2 mL) under stirring for 12 h at room temperature. The solution was passed through a short column of silica gel (ca. 2 g)[6] and concentrated. The resulting 2-methoxy-1,3-dioxolane was dissolved in acetic anhydride (2 mL) and the solution was refluxed under nitrogen atmosphere and worked up as usual to give the desired olefin.

As shown in Table 1, the simple cyclic diols (entries 1 and 2) and the acyclic diols (entries 3 and 4) were converted to the corresponding olefins in excellent yields. The diols with a variety of additional groups (entries 5, 6, 7, and 8) were also compatible with the reaction conditions and gave the desired



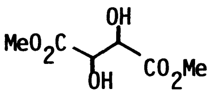
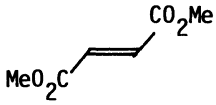
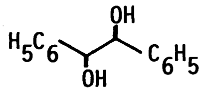
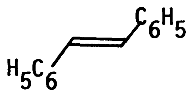
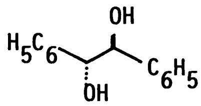
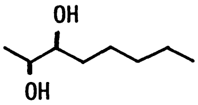
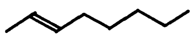
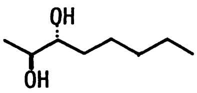
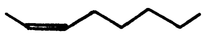
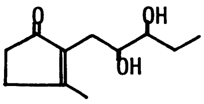
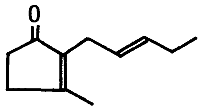
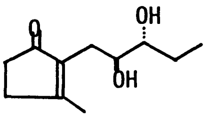
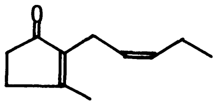
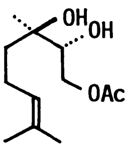
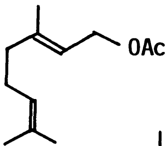
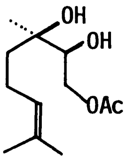
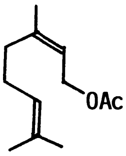
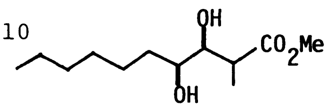
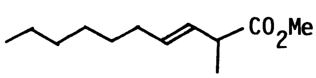
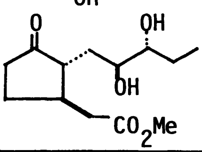
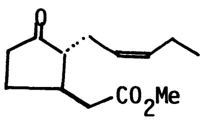
(1)

Table 1. Olefin Synthesis by Deoxygenation of Vicinal Diols[a)]

Entry	Diol[b)]	Conditions in step A[c)]	Conditions in step B	Olefin	Yield of olefin/%
1		PPTS, THF 12 h	sealed tube 140 °C 1.5 h		90[d)]
2		PPTS, THF 5 h	reflux 5 h		96[e)]
3		PPTS, THF 5 h	sealed tube 140 °C 1.5 h		85[d)]
4		PPTS, THF 12 h	reflux 2 h		95[e)]
5		PPTS, CH_2Cl_2 12 h	reflux 5 h		97[e)]
6		PTS, CH_2Cl_2 3 h	reflux 6.5 h		76[e)]
7	 (1)	PPTS, CH_2Cl_2 7 h	reflux 5 h	 (2)	86[e)]
8		PPTS, CH_2Cl_2 12 h	reflux 4 h		78[e)]

a) See Eq. 1. b) Diols in entries 5, 6, and 8 are optically active. c) This step was performed at room temperature. d) Determined by GLC. e) Isolated yield.

Table 2. Stereospecificity in Olefin Synthesis by Deoxygenation of Vicinal Diols[a]

Entry	Diol[b]	Conditions in step A[c]	Conditions in step B	Olefin	Yield of olefin/%
1		PTS CH_2Cl_2	reflux 4 h		95[e]
2		PPTS THF	reflux 6 h		100[e]
3		PPTS THF	reflux 4 h		100[e]
4		PPTS THF	sealed tube 140 °C 2 h		60[d]
5		PPTS THF	seald tube 140 °C 2.5 h		64[d]
6		PPTS THF	reflux 6 h		75[e]
7		PPTS THF	reflux 6 h		75[e]
8		PPTS THF	reflux 6 h		90[e]
9		PPTS THF	reflux 6 h		90[e]
10		PPTS THF	reflux 6 h		100[e]
11		PPTS THF	reflux 6 h		88[e]

a) See Eq. 1. b) Diols indicated here are not optically active except entry 1.
c) This step was performed overnight at room temperature. d) Determined by GLC.
e) Isolated yield.

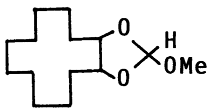
olefins in excellent yields.

Then we studied stereospecificity of this reaction by employing the diols possessing the defined stereochemistry and the results were summarized in Table 2.

The optically active diol (entry 1) and the dl-diol (entry 2) gave trans-olefins. On the contrary, the meso-diol (entry 3) gave the cis-olefin. Analogously threo-diols (entries 4, 6, 8, and 10) gave trans-olefins and erythro-diols (entries 5, 7, 9, and 11) gave cis-olefins. Since no evidence of the formation of isomeric olefins was observed by the careful analysis of the crude products, we concluded that this reaction proceeded in highly stereospecific manner.

To examine the reaction mechanism, we compared the behaviors of 2-methoxy-1,3-dioxolane (3) derived from meso-cyclododecane-1,2-diol in toluene, DMF, and acetic anhydride at their boiling points. The results summerized in Table 3 suggest that

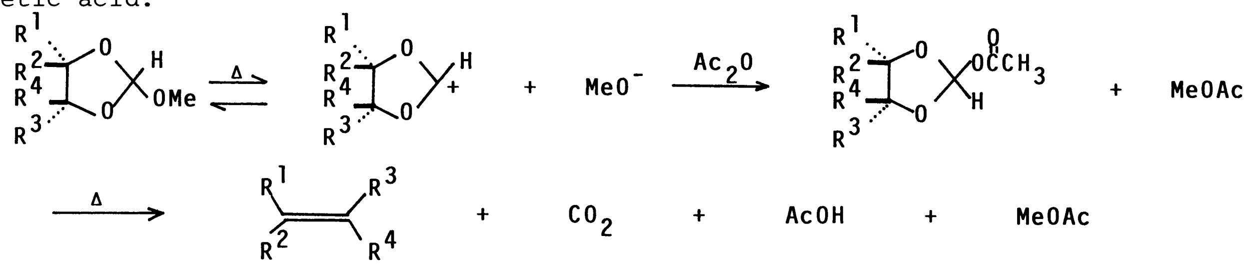
Table 3. The Behaviors of 2-Methoxy-1,3-dioxolane (3) in Toluene, DMF, and Acetic Anhydride under Refluxing for 5 h



3

Solvent	(Reflux temp/°C)	Yield of cis-cyclododecene/%
Toluene	(111)	23 (recovery of 3 77)
DMF	(153)	0 (recovery of 3 100)
Ac_2O	(139)	96

this reaction is not a simple thermal reaction but acetic anhydride plays special role. The possible reaction mechanism is shown in Scheme 1. From thermal equilibrium mixture, methoxy anion is eliminated irreversibly as methyl acetate by acetic anhydride and the carbocation formed is captured by acetoxy anion. The resulting 2-acetoxy-1,3-dioxolane[7)] is thermally decomposed to olefin, carbon dioxide, and acetic acid.[8)] The analogous reaction path has already been proposed by Eastwood to the thermal decomposition of 2-ethoxy-1,3-dioxolanes catalyzed by acetic acid.[4,8)]



Scheme 1.

We thank Dr. Yoshikazu Takagi of T. Hasegawa Co., Ltd., for his kind supply of olefins, the starting materials of vicinal diols employed in this work.

References

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2) E. Block, Org. React., 30, 457-566 (1984) and references cited therein.
3) E. J. Corey and R. A. E. Winter, J. Am. Chem. Soc., 85, 2677 (1963). E. J. Corey and P. B. Hopkins, Tetrahedron Lett., 23, 1979 (1982).
4) G. Crank and F. W. Eastwood, Aust. J. Chem., 17, 1392 (1964); J. S. Josan and F. W. Eastwood, ibid., 21, 2013 (1968).
5) F. W. Eastwood, K. J. Harrington, J. S. Josan, and J. L. Pura, Tetrahedron Lett., 1970, 5233; S. Hanessian, A. Bargiotti, and M. LaRue, Tetrahedron Lett., 1978, 737.
6) This procedure is necessary to eliminate PPTS or PTS from reaction mixture, otherwise the yield of the desired olefin in the next step remarkably decreases.
7) Synthesis and thermal decomposition of 2-acetoxy-1,3-dioxolanes have already been reported; A. P. M. van der Veek and F. H. van Putten, Tetrahedron Lett., 1970, 3951.
8) A stepwise mechanism has been proposed to the thermal decomposition of 2-acetoxy-1,3-dioxolanes; E. Block, Org. React., 30, 481 (1984).

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