Tetrahedron Letters, Vol.31, No.4, pp 463-464, 1990
Printed in Great Britain

0040-4039/90 $3.00 + .00
Pergamon Press plc

A NOVEL APPLICATION OF THE BASE INDUCED MESYL ELIMINATION

M. J. Pestchanker* and O. S. Giordano

Departamento de Química Orgánica, Universidad Nacional de San Luis
Chacabuco y Pedernera, 5700 San Luis, Argentina

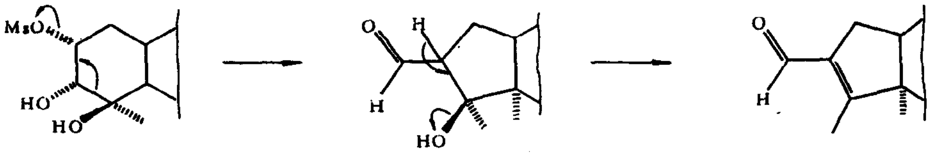
Abstract: The preparation of ketones from *cis* glycols in a two steps process initiated by a mesylation step followed by a base induced elimination is reported.

The use of base induced mesyl elimination is a very well known synthetic tool. The preparation of olefin through the trans elimination of the mesyl group (1), and the formation of epoxides from vic *trans* diols(2) are the most common uses of sach a strategy.

We wish to report here the preparation of ketones from vic *cis* diols by means of sach methodology. Mesylation of *cis* 1,2-cyclohexanodiol(3) affords the monomesyl derivative with the protective group placed on the --OH group in the equatorial position. Cyclohexanone is obtained in variable yields by treatment of this intermediate with NaEtO in EtOH(4). By the application of the same synthetic methodology to 2α, 3α - dihydroxycativic acid methyl ester 1(5), 3-ketocativic acid methyl ester 2 is obtained in good yield. The $NaBH_4$ reduction of 2 affords an 87% of 3β-hydroxycativic acid methyl ester 3.

The transformation 1 3 is similar to the deoxygenation of *cis* diols monotosylates (6), which provides an alternative method for the preparation of deoxy sugars.

The use of this methodology on methyltucumanate 4 (7) affords the rearrangement product 5, which in a subsequent step suffer dehydration of the α ,β -unsaturated aldehyde 6 (scheme 1). This kind of rearrangement has been previously reported (8).

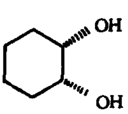
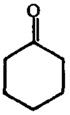
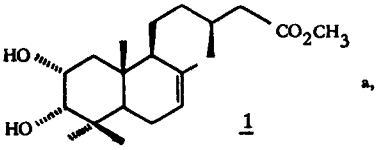
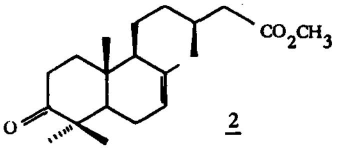
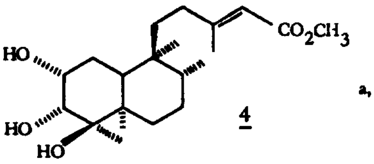
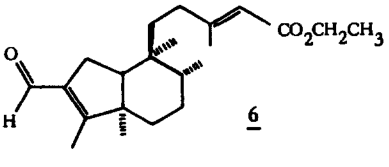
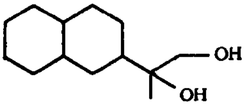
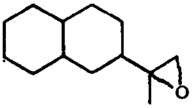


5

Scheme 1

If tedonodiol is used as starting material 7 (9), epoxide 8 is the only product observed, in agreement with (2).

Table 1

Substrate	Conditions	Product	Yield (%)
	a, b		(45 - 67) (4)
 1	a, b	 2	82
 4	a, b	 6	62
 7	a, b	 8	78

a. CH_2Cl_2, MsCl (1 eq.), $N(Et)_3$, 3 h 0°C; b. EtONa (2 eq.), EtOH, 12 h, 25°C.

Acknowledgements: This work was supported by a grant of CONICET of Argentina. We thank Dr. Manuel G. Sierra (IQUIOS - Rosario) for the ^{13}C NMR spectra, to Tec. E. Strazza for the GLC analysis and to Dr. F. Guidugli for the MS. M. J. P. thanks CONICET for a fellowship.

References and Notes

1. Wenkert, E. and Pestchanker, M. J.; J. Org. Chem. 1988, 53, 4875.
2. Furst, A. and Koller, F.; Helv. Chim. Acta, 1947, 30, 1454.
3. Van Rheenan, V.; Kelly, R. C. and Cha, D. Y.; Tetrahedron Lett, 1976, 1973.
4. Yields vary with reaction time and temperature. Yields were determined by GLC.
5. Gianello, J. C., Pestchanker, M. J., Tonn, C. E. and Giordano, O. S.; Phytochemistry, in press.
6. Hanske, F. and Robins, M. J., J. Am. Chem. Soc., 1983, 105, 6736.
7. Rossomando, P., Giordano, O. S., Espineira, J. and Nathan, P. J.; Phytochemistry, 1985, 24, 787.
8. Wendler, R., Hirschmann, N., States, H. and Walker, R.; J. Am. Chem. Soc., 1954, 76, 4013.
9. Guerreiro, E., Kavka, J. and Giordano, O. S.; Anales Asoc. Quím. Argentina, 1979, 67, 119.

(Received in USA 19 September 1989)