Tetrahedron Letters,Vol.30,No.11,pp 1405-1408,1989 0040-4039/89 $3.00 + .00
Printed in Great Britain Pergamon Press plc

MILD HYDROGENOLYSIS PROCESS BY CATALYTIC TRANSFER HYDROGENATION

A. Bianco*, P. Passacantilli and G. Righi

Centro di Studio CNR per la Chimica delle Sostanze Organiche Naturali
Dipartimento di Chimica - Università "La Sapienza"
P.le Aldo Moro n. 5, I-00185 Roma (Italy).

ABSTRACT - A facile hydrogenolysis of allylic acetates was developed with the catalytic transfer hydrogenation using palladium hydroxide on carbon and cyclohexene.

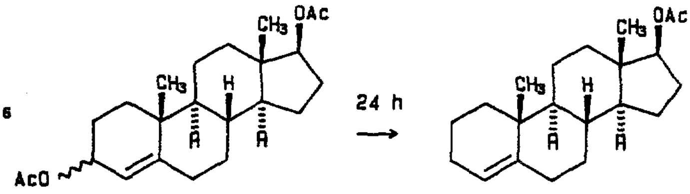
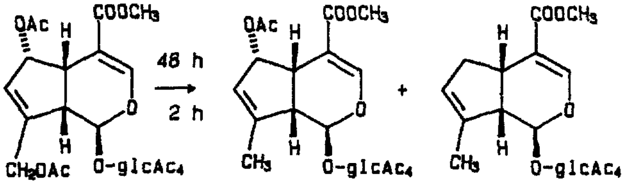
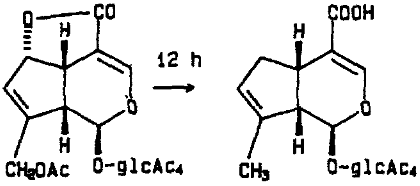
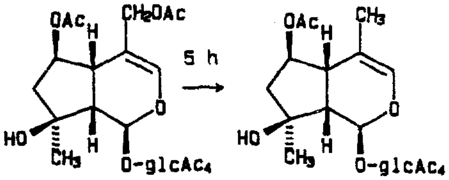
Recently Hanessian and coworkers [1] found that O-benzyl ethers can be efficently cleaved by hydrogenolysis under catalytic transfer hydrogenation [2] using 20% palladium hydroxide on carbon [3] and cyclohexene as the hydrogen donor.

On the contrary we focused our attention on the hydrogenolysis process rather than on the protection/deprotection one; thus we applied this method to the hydrogenolysis of allylic alcohols, via their acetylderivatives, obtaining in very high yields the corresponding olefinic products without saturation of the double bond [4].

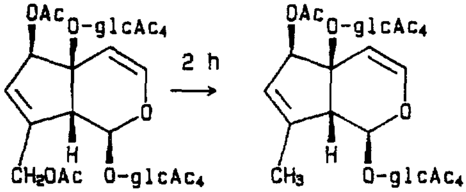
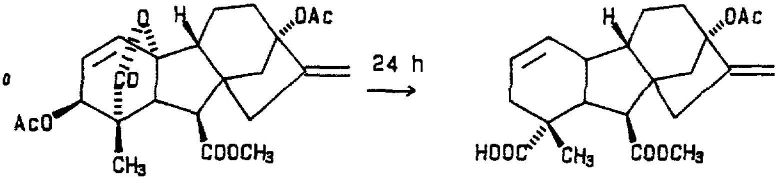
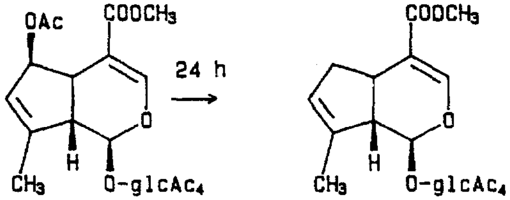
Hydrogenolysis: General Procedure

To a solution of the allylic acetate (1 mmol) in 95% ethanol (10 ml), cyclohexene (5 ml) and 20% $Pd(OH)_2$ on carbon, 50% moist, (1:3 catalyst substrate by weight), are added and the suspension is stirred under reflux for the required period of time (TLC monitoring, see table). The catalyst is then removed by filtration and, after evaporation to dryness, the crude olefin is purified by chromatography. In the table are listed several types of allylic acetates hydrogenolyzed according to this procedure. Yields are calculated after purification.

TABLE

1[6]		65%
2[7]		9% / 80% 50% / --
3[7]		80%
4[8]		100%

TABLE

5[9]		50%
6[10]		35%
7[11]		100%

By examination of the obtained results (see table) it is possible to deduce that the hydrogenolysis reactivity of acetyl groups is related to the nature of the parent alcohols: in fact the ease of hydrogenolysis decreases going from a primary allylic function to a secondary, to a tertiary (entries 2, 5 and 6). However a steric compression increases the reactivity of both secondary and tertiary allylic acetates (entries 3 and 6). Finally, when different alcoholic functions are present, by carefull controlling the reaction time, it is possible to perform a chemoselective hydrogenolysis (entries 2 and 5).

Conclusions

Although various techniques are described for the hydrogenolysis [5], our method offers some advantages. Palladium hydroxide on carbon [3] is a neutral, non pyrophoric catalyst and its use in transfer hydrogenation conditions is useful for small and moderately large scale operations. The selectivity of the reaction can not be achieved under normal hydrogenolysis conditions [5]: isolated and conjugated double bonds, esters, ethers, acetals and glycosidic groups are unaffected.

In conclusion, the favorable catalyst/substrate ratio, the neutral conditions, the compatibility of the conditions with the presence of a variety of other commonly used protecting groups, and the efficacy of the process should encourage its practice in the hydrogenolysis of a variety of natural compounds.

References

1 Hanessian,S., Liak,T.J. and Vanasse B., Synthesis, **1981**, 396.

2 Brieger, B. and Nestrick, T.J., Chem.Rev., **1974**, 74, 563.

3 Pearlman, W.M., Tetrahedron Letters, **1967**, 1663.

4 A preliminary communication appeared at XV Conv.Naz. Div.Chim.Org. S.C.I. , **1985**, Sirmione (Italy), September 22-27, Symposium paper p. 196.

5 For a review see: Augustine, R.L., Catalytic Hydrogenation, M.Dekker, New York, **1965**. Huller, in Patai, The Chemistry of functional groups, Supplement E, Wiley, New York, **1980**; pt.1, pp.515-522.
For a discussion see: Elphimoff-Felkin and Sarda,Org.Synth., **1977**, 56,101.

6 Prepared by $NaBH_4$ reduction of testosterone, followed by acetylation.

7 Bianco A., Guiso M., Iavarone C., Passacantilli P. and Trogolo C., Gazz.Chim. .Ital., **1978**, 108, 13.

8 Agostini A., Guiso M., Marini-Bettolo R. and Martinazzo G., Gazz.Chim.Ital., **1982**, 112, 9.

9 Bianco A., Passacantilli P., Righi G., Nicoletti M. and Serafini M., Phytochemistry, **1986**, 25, 1981.

10 Prepared from giberellin A_3, by diazomethane esterification followed by acetylation.

11 Prepared from shanzhiside Methyl ester (Bianco A., Francesconi A. and Passacantilli P., Phytochemistry, **1981**, 20, 1421) by acetylation followed by dehydration with $POCl_3$/Py.

(Received in UK 27 January 1989)