Tetrahedron Letters Vol. 22, pp 335 - 336
©Pergamon Press Ltd. 1981. Printed in Great Britain

0040-4039/81/0122-0335$02.00/0

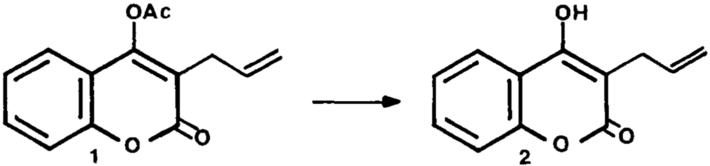
DEACYLATION OF AROMATIC ACETATES. A NEW METHOD OF SELECTIVE PROTECTION OF THE HYDROXYL FUNCTION.

by A.G. González, Z.D. Jorge and H. López Dorta
Departamento de Química Orgánica, Universidad de La Laguna, Instituto
de Productos Naturales Orgánicos, CSIC, La Laguna, Tenerife, Spain.
F. Rodríguez Luis
Departamento de Química Orgánica, Universidad Autónoma de Madrid, Spain.

Abstract.- Acetoxyaromatic compounds are selectively deacylated, via a catalytic-type reaction, to the corresponding phenolic derivatives, by treatment with activated zinc in methanol.

The importance of the protection of hydroxyl functions in the synthesis of complex molecules is well-known[1]. This paper deals with the selective catalytic deacylation of aromatic acetates.

4-Acetoxy-3-allyl-coumarin (1) is an intermediate in our synthesis of C_3-alkylated coumarins[2] and during this work it became necessary to deprotect the C_4 position. This was readily achieved by use of the zinc-silver couple in methanol[3]; deacylation of 4-acetoxy-3-allyl-coumarin (1) gave a practically quantitative yield of (2).

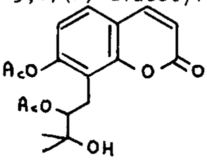
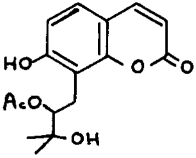
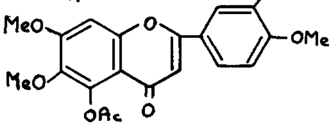
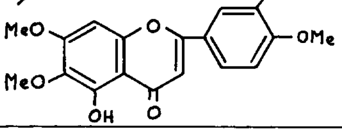


The zinc-copper couple[4] and activated zinc[5] gave similar results, but commercial zinc was completely ineffective. The reaction is hindered by the addition of water and no photochemical-type process is involved.

Representative results are shown in the Table. Reaction in all cases results in almost quantitative deacylation of the aromatic acetates; the reaction is, moreover, highly selective as the reagent does not affect aliphatic acetates.

Research in progress leads us to believe that the process is a catalytic-type methanolysis, since if quantities of zinc of around 25% (16 mg), or less, in moles, are used with regard to the substrate (β-naphthol acetate) (185 mg), the reaction remains quantitative and the zinc is observed not to be consumed during the reaction.

Table

Substrate[6, 7]	product of deacylation by treatment with activated zinc[7].	Yield (%)
4-acetoxy-3-allyl-coumarin	4-hydroxy-3-allyl-coumarin	100
7-acetoxy-coumarin	7-hydroxy-coumarin	97
β-naphthol acetate	β-naphthol	99
α-naphthol acetate	α-naphthol	98
3-acetyl-estrone	estrone	98
3,17(β)-diacetyl-estradiol	17(β)-acetyl-estradiol	98.5
		91
		92

REFERENCES AND NOTES:

1) T.B. Windholz and D.B.R. Johnston, Tetrahedron Lett., 2555 (1967); J.B. Hendrickson and C. Kandall, Ibid, 343 (1970); E.J. Corey and M.G. Bock, Ibid, 3269 (1975); R.C. Ronald, Ibid, 3973 (1975); E.J. Corey, J.L. Gras and P. Ulrich, Ibid, 809 (1976); R.A. Holton and R.G. Davis, Ibid, 533 (1977).
2) A.G. González, Z.D. Jorge, H. López Dorta and F. Rodríguez Luis, results unpublished.
3) R.D. Clark and C.H. Heathcock, J. Org. Chem., 38, 3658 (1973).
4) L.F. Feiser and M. Feiser, "Reagents for Organic Synthesis", Vol. 1, 1293 (1967).
5) *Activation of zinc:* zinc dust (Merck, ∿ 500 mg) is stirred for 4 min with 5 ml of 10% aqueou HCl. The supernatant liquid is decanted and the zinc is washed with acetone (2 x 5 ml), ether (3 x 5 ml) and methanol (2 x 5 ml). The moist activated zinc is added to ∿ 50 mg of the acetylated derivative in 5 ml of Merck analytical quality methanol.

   The reaction having taken place, the zinc was filtered through celite and washed with methanol. The methanol was then evaporated under reduced pressure, the crude residue was partitioned between ether and 10% aqueous HCl. The ether layer is dried and evaporated to yield the deacylated derivative.
6) The acetylated derivatives were prepared by treating the corresponding hydroxylated derivatives with acetic-pyridine at room temperature.
7) The products were identified by NMR, IR and liquid-liquid chromatography and by comparison with authentic samples.

(Received in UK 10 November 1980)