

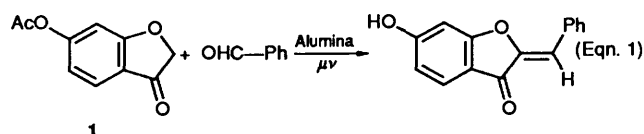
Microwave-assisted Deacetylation on Alumina: a Simple Deprotection Method

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A simple high-yielding method for the deprotection of acetylated phenols and alcohols is described which occurs under mild conditions on an alumina surface using microwave irradiation.

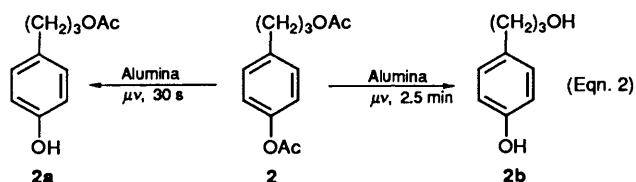
Hydroxy groups protection by acetylation is a common procedure and there are, therefore, numerous methods to achieve it and the deprotection sequence.¹ Recently, we observed that 6-acetoxybenzofuran-3(2*H*)-one **1** underwent concomitant deacetylation during condensation with benzaldehyde on alumina [eqn. (1)].² Since the reaction is, however,



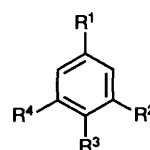
sluggish (3 days for completion) and as a continuation of our studies of reactions on solid surfaces,²⁻⁵ we have developed appropriate conditions to increase the rate of the deacetylation. Here we report a facile and simple procedure to affect the deacetylation of a variety of such esters on neutral alumina under solvent-free conditions, reactions which can be further accelerated safely using an unmodified common household microwave oven.

Microwave heating, used for a wide variety of applications,⁶ has recently found application in polymerizations, depolymerizations, rapid syntheses of organic compounds,⁷ and for the induction of reactions under 'dry' conditions.^{8,9} In the last mentioned, reactants adsorbed on the surface of alumina and silica gel absorb the microwaves whereas the support does not, nor does it restrict their transmission.⁶ Consequently, such supported reagents¹⁰ efficiently induce reactions under safe and simple conditions with domestic microwave ovens instead of specialized commercial microwave systems that require sealed Teflon bombs for solution-phase chemistry.⁷

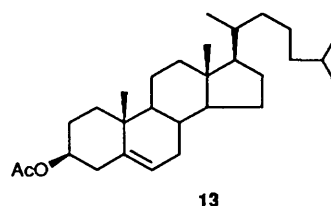
We examined several acetates and now report that this general deacetylation results in rapid formation (2-5 min) in high yield of the corresponding phenols and alcohols under mild and solvent-free conditions on ordinary adsorption grade neutral alumina. As is typically the case,¹¹ the selective deesterification of aryl acetates occurs very rapidly (30 s) as compared to alcoholic acetates (2-3 min) [eqn. (2)]. In-



terestingly, deacetylation of the diacetate **8** is rapid compared to that of the related diacetate **2**. That the effect is not purely thermal¹² is evidenced by comparative deacetylations conducted at the same temperatures with an alternative mode of



	R ¹	R ²	R ³	R ⁴
2	(CH ₂) ₃ OAc	H	OAc	H
3	CHO	H	Oac	H
4	CHO	OMe	OAc	H
5	CH(OAc) ₂	H	Oac	H
6	Ac	H	OAc	H
7	OAc	Ac	H	OAc
8	CH ₂ OAc	H	OAc	H
9	OAc	H	COCH=CHC ₆ H ₄ OAc- <i>p</i>	H
10	CO ₂ Me	H	H	H
11	CO ₂ Me	H	CHO	H
12	CO ₂ H	H	OAc	H



heating; the regeneration of phenolic groups occurs with ease in contrast to alcoholic groups which needed prolonged heating (≥ 40 h) using a conventional oven or oil-bath. We have used the recovered alumina, after washing off the products, several times with no apparent loss of activity. Thus, this solvent-free deprotection process with reusable support is environmentally friendly with no generation of wasteful by-products. Further, the deprotection reaction being fast, no undesirable by-products originating from the arylaldehyde by way of a concomitant Cannizzaro reaction¹³ are observed. The results are summarized in Table 1.

In conclusion, we have developed a simple and economical method for the deacetylation of acetylated phenols and alcohols that occurs under mild conditions using inexpensive aluminium oxide and a household microwave oven as the irradiation source without generation of any chemical waste.

Experimental

Typical Procedure for the Deprotection of Acetyl Esters.—Neutral alumina (4.0 g) was added to a solution of diacetate **2** (0.068 g, 0.29 mmol) dissolved in a minimum of CH₂Cl₂ (1-2 cm³) at room temperature and the reaction mixture was

Table 1 Alumina-mediated cleavage of various acetoxy derivatives

Acetates ^a	Temp. (°C) and conditions ^b	Time	Yield (%) ^c
1	145	10 min	91
2	65	2.5 min	92
2	30	30 s ^e	93 ^e
2	75	40 h ^f	92 ^f
3	75	3 min	92
4	140	8 min	87
5	50	2 min	95
6	80	4 min	91
7	80	4 min ^d	90 ^d
8	35	1 min	89
9	75	3 min	90
10	85	5 min	92
11	75	3 min	82
12	75	3 min ^d	84 ^d
13	130	7 min	96

^a Products exhibited physical and spectral properties in accord with the assigned structures. ^b Acetates adsorbed on commercial neutral alumina (80–200 mesh, ca. 10 g of alumina mmol⁻¹ of esters) were irradiated in an alumina bath inside a microwave oven with turntable at full power (800 W). ^c Isolated and unoptimized yields. ^d Multiple extractions using AcOEt–MeOH (1:1, v/v) are needed for isolation of products bearing polar groups. ^e Cleavage of only phenolic ester group. ^f Complete deacetylation in an oil-bath.

thoroughly mixed using a vortex mixer. The air-dried material, in a small beaker, was placed in an alumina bath inside a microwave oven.⁸ The temperature of the alumina supporting the acetate esters was ca. 50 °C after 2 min of irradiation in an alumina bath (heat sink) inside a Sears Kenmore microwave oven. The product, upon completion of the reaction (2.5 min; followed by TLC examination) was extracted into CH₂Cl₂ (4 × 10 cm³). Evaporation of the extract under reduced pressure yielded essentially the pure product **2b** (0.041 g, 92%). A similar protocol in 30 s afforded the pure monoacetate **2a** (93%). For comparison, similar yields of deacetylated products (obtained either at room temp. or using an oil-bath at 75 °C)¹³ are as follows: **2a**, 48 h at room temp., 3 min at 75 °C; **2b**, 4 days at room temp., 40 h at 75 °C.

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