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Solid-state conversion of 1,1-diacetates with *N,N'*-dibromo-*N,N'*-1,2-ethanediylbis(*p*-toluenesulfonamide) to aldehydes

Ramin Ghorbani-Vaghei,*[a] Safar-Ali Akbari,[a] Mohammad A. Zolfigol,[a] BiBi Fatemeh Mirjalili[b] and Abdolhamid Bamoniri[c]

[a] *Department of Chemistry, Faculty of Science, Bu-Ali Sina University, 65174 Hamadan, Iran.*
Fax: +98 811 827 2404; e-mail: ghorbani@basu.ac.ir
[b] *Department of Chemistry, Faculty of Science, Yazd University, 89195-741 Yazd, Iran.*
Fax: +98 351 821 0644
[c] *Department of Chemistry, Faculty of Science, Kashan University, 51167 Kashan, Iran.*
Fax: +98 361 555 2930

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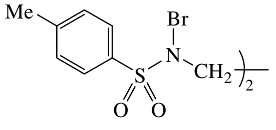
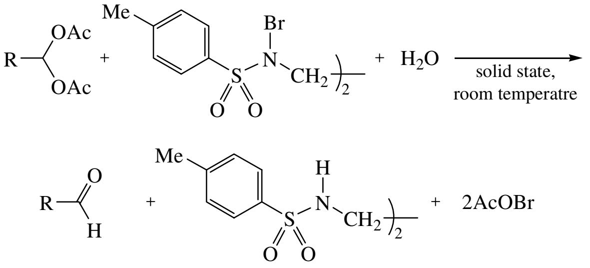
N,N'-Dibromo-*N,N'*-1,2-ethanediylbis(*p*-toluenesulfonamide) can be used for the solid-state conversion of 1,1-diacetates to aldehydes in excellent yields.

1,1-Diacylals are of considerable interest because they are stable under neutral and basic conditions.[1–6] They are important building blocks for the synthesis of dienes in the Diels–Alder reaction.[7] Therefore, the regeneration of carbonyl compounds from 1,1-diacetates is an important reaction in organic chemistry.[8–19] However, these methods involve the use of toxic reagents,[9,13,15] long reaction times,[9,11,16] solvents,[17] microwave irradiation[16,18] and metals.[9,10,13,15] Therefore, we studied the use of *N,N'*-dibromo-*N,N'*-1,2-ethanediylbis(*p*-toluenesulfonamide) (BNBTS)[20–23] for the deprotection of 1,1-diacylals.



BNBTS

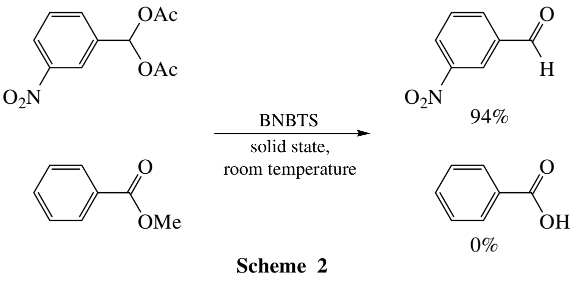
1,1-Diacetates were converted to aldehydes without over-oxidation to carboxylic acids using BNBTS in a solid state (Scheme 1).



Scheme 1

BNBTS, which can be prepared easily, is stable in atmospheric conditions for two months. After completing the reaction, the sulfonamide can be recovered and reused many times without decreasing the yield.

Various acylals were converted to aldehydes in the presence of BNBTS in a solid state (Table 1).† Furthermore, functional groups such as chloro, methoxy, acetoxy and nitro were inert to this reagent and no by-product formation was observed.



Scheme 2

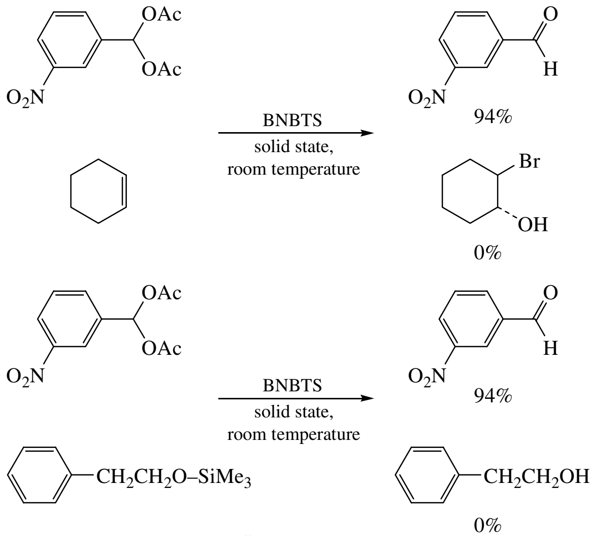
Table 1 Deprotection of acylals with BNBTS in a solid state (reagent/substrate = 1:1).

Entry	R	Product[a]	Time/ min	Yield (%)
1	*m*-$NO_2C_6H_4$	*m*-Nitrobenzaldehyde	3	94
2	*p*-$NO_2C_6H_4$	*p*-Nitrobenzaldehyde	4.5	92
3	*o*-$AcOC_6H_4$	*o*-Acetoxybenzaldehyde	2	98
4	*p*-$AcOC_6H_4$	*p*-Acetoxybenzaldehyde	1.5	98
5	*p*-AcO-*m*-$MeOC_6H_3$	*p*-Acetoxy-*m*-methoxybenzaldehyde	1.5	97
6	*o*-ClC_6H_4	*o*-Chlorobenzaldehyde	4	92
7	Pr^i	Isopropanal	2	90
8	PhCH=CH	Cinnamaldehyde	4	96
9	MeCH=CH	Crotonaldehyde	4	90

[a]Products were characterised by their physical constants, comparison with authentic samples and IR spectra

It is likely that this reagent releases Br^+ *in situ*, which can act as an electrophilic species.[20–23]

Note that esters, isolated double bonds and silyl ethers did not react with this reagent. This procedure shows considerable selectivity between acylal with ester, isolated double bond and



Scheme 3

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† *General procedure for deprotection of acylals with* N,N'*-dibromo-*N,N'*-1,2-ethanediylbis(*p*-toluenesulfonamide)*: acylals (0.5 mmol), BNBTS (0.5 mmol) and a few drops of water were added to a mortar and the mixture was pulverised with a pestle. A spontaneous reaction took place [1.5–4.5 min, Table 1, monitored by TLC (9:1, carbon tetrachloride/acetone)]. After completion of the reaction, CCl_4 (10 ml) was added, and insoluble sulfonamide **1** was removed by filtration. The organic phase was washed with H_2O (10 ml) and dried ($MgSO_4$). After the removal of the solvent in a vacuum, the product was obtained in 90–98% yield.

silyl ether. This was demonstrated by an experiment, in which a mixture of an acylal with an ester was treated with BNBTS at room temperature in a solid state. Only the acylal was selectively oxidised to aldehyde, and the ester remained unchanged (Scheme 2).

Similar competitive reactions between an acylal and an isolated double bond and a silyl ether resulted only in acylal oxidation (Scheme 3).

In conclusion, acylal reactions with BNBTS in a solid state are faster than those with other reagents.[9] Thus, this method is industrially useful and economical.

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