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DEPROTECTION OF 1,1-DIACETATES WITH $[\text{NO}^+ \cdot \text{Crown} \cdot \text{H}(\text{NO}_3)_2^-]$

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ABSTRACT

An ionic complex has been obtained from N_2O_4 in the presence of the macrocyclic polyether 18-crown-6. This crystalline compound was used as an effective deprotecting agent for the conversion of 1,1-diacetates to their corresponding aldehydes at room temperature with quantitative yields.

Selective protection and deprotection of functional groups are of great importance in the synthesis of polyfunctional organic molecules. 1,1-Diacetates have found considerable attention during recent years owing to their moderate stability^[1] and ease of preparation.^[1–10] They are also known as interesting alternatives to acetals for the protection of aldehydes and can be

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used as starting materials for the synthesis of valuable intermediate in Diels–Alder cycloaddition reactions.^[11] Regeneration of the original aldehydes from their corresponding 1,1-diacetates is a useful transformation in organic chemistry. The several methods for this purpose have been introduced in the chemical literature.^[1,12–22] In the course of our investigation on the application of Lewis acids as effective catalysts to this transformation,^[23] we were interested to find a completely homogeneous reagent for the conversion of 1,1-diacetates to their corresponding aldehydes. In continuation of our studies on the application of NOX,^[24] N₂O₄,^[25] metal nitrate dinitrogen tetroxide complexes^[26] and transition metal complexes with macrocyclic ethers,^[27] we found that 18-crown-6 gives an ionic complex with N₂O₄ gas as [NO⁺·Crown·H(NO₃)₂[−]] in quantitative yields. By using this new reagent, in this article we now report a simple and convenient method for the conversion of 1,1-diacetates (**1**) to their corresponding aldehydes (**2**) under mild conditions.

A good range of 1,1-diacetates (**1**) with different functional groups were subjected to the deprotection reaction in the presence of [NO⁺·Crown·H(NO₃)₂[−]] (**I**) and dry SiO₂ in dichloromethane. The deprotection reactions were performed under mild conditions at room temperature with quantitative yields (Scheme 1). Unlike the substrates **1a–m**, the reagent was not suitable for deprotection of compound **1n**, the deprotection of this compound was sluggish and a mixture of products was produced.

The deprotection reaction can be readily carried out by placing the complex [NO⁺·Crown·H(NO₃)₂[−]] (**I**), 1,1-diacetates (**1**), dry SiO₂ and CH₂Cl₂ as the solvent in a reaction vessel and efficient stirring of the resulting mixture at room temperature. The reactions were completed after 5 min. The reaction mixture was filtered and dichloromethane was removed by simple distillation over a water bath (40–50°C). Highly pure aldehydes (**2**) were finally obtained by passing the residue through a pad of silica gel.

In conclusion, practical and efficient deprotection of 1,1-diacetates was achieved using the present methodology. The [NO⁺·Crown·H(NO₃)₂[−]] complex, with easy preparation and handling can act as a relatively stable and efficient reagent for this transformation under mild and homogeneous conditions. Meanwhile, 18-crown-6 can be recycled and reused. We believe that the present methodology is an important addition to existing methodologies.

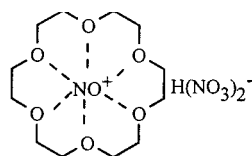
EXPERIMENTAL SECTION

General: Chemicals were purchased from Fluka, Merck, Riedel-dehaen AG and Aldrich chemical companies. Silica gel of mesh 60–70 was

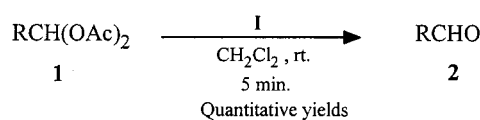


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I



1 or 2	R	1 or 2	R ₁
a	Ph	h	2-O ₂ NC ₆ H ₄
b	2-MeOC ₆ H ₄	i	3-O ₂ NC ₆ H ₄
c	4-MeOC ₆ H ₄	j	4-O ₂ NC ₆ H ₄
d	2,5-(MeO) ₂ C ₆ H ₄	k	4-BrC ₆ H ₄
e	4-MeC ₆ H ₄	l	4-ClC ₆ H ₄
f	5-NO ₂ -2-CH ₃ COC ₆ H ₄	m	5-Me-2-furyl
g	2-CH ₃ CO C ₆ H ₄	n	PhCH=CH ^a

^aThe reaction of this substrate was sluggish.

Scheme 1.

used. The deprotection products were characterized by comparison of their spectral (IR, ¹H-NMR, ¹³C-NMR and TLC) and physical data with the authentic samples. [NO⁺ · Crown · H(NO₃)₂⁻] was synthesized according to the reported procedure,^[28] subjected to a slight modification. Here, we used N₂O₄ gas instead of liquid N₂O₄. Dinitrogen tetroxide (N₂O₄) gas was generated in situ according to our previously reported procedure as follows:^[25,26]

Generation of NO₂-N₂O₄ Gas: Lead(II) nitrate (50 g) was crushed into a powder and was dried in an oven at 120°C for three days. The resulting powder was transferred into a one-necked round-bottomed flask (250 mL) which was equipped with an air condenser and a gas trap containing P₂O₅. The flask was heated by a Bunsen burner to generate a brownish-red NO₂-N₂O₄ gas which was used immediately for the subsequent preparation of [NO⁺ · Crown · H(NO₃)₂⁻].



Preparation of $[\text{NO}^+ \cdot \text{Crown} \cdot \text{H}(\text{NO}_3)_2^-]$: A solution of 18-crown-6 (5.286 g, 0.02 mol) in CH_2Cl_2 (10 mL) was prepared in a three-necked round-bottomed flask (50 mL) equipped with a magnetic stirrer, a gas inlet tube, a thermometer and a drying tube and cooled to -10°C with an ice-salt while being stirred. Generated $\text{NO}_2\text{-N}_2\text{O}_4$ gas was bubbled through this solution 30 min. The solvent was evaporated under vacuum at 20°C to give the $[\text{NO}^+ \cdot \text{Crown} \cdot \text{H}(\text{NO}_3)_2^-]$ complex as a pale yellow deliquescent solid compound **1** [8.380 g, 0.02 mol (~100%)], m.p. $50\text{-}55^\circ\text{C}$ [Lit^[28] m.p. $53\text{-}55^\circ\text{C}$]. $^1\text{H NMR}$ (FT-90 MHz, CDCl_3/TMS): 3.536 (s, 24H), 11.464 (s, 1H).

General Procedure for Deprotection of 1,1-Diacetates: A solution of 1,1-Diacetates (**1**, 1 mmol), $[\text{NO}^+ \cdot \text{Crown} \cdot \text{H}(\text{NO}_3)_2^-]$ (0.523 g, 1.25 mmol) and dry SiO_2 (0.4 g) in dichloromethane (5 mL) was vigorously stirred magnetically at room temperature. The progress of reaction was followed by TLC. The reaction was completed after 5 min. The reaction mixture was filtered. The residue was washed with CH_2Cl_2 (2×5 mL). Dichloromethane was removed by a water bath ($40\text{-}50^\circ\text{C}$) and simple distillation. The residue was passed through a pad of silica gel [eluent: acetone/petroleum ether (10:90)]. The solvent was evaporated and the highly pure aldehydes (**2**) were obtained quantitatively. For recycling 18-crown-6, the pad of silica gel was washed with acetone. Evaporation of acetone gave pure 18-crown-6.

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