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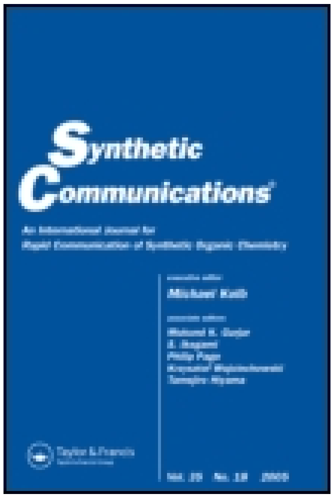

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CERIC AMMONIUM NITRATE AS A CONVENIENT CATALYST FOR PROTECTION OF CARBONYL COMPOUNDS AS 1,3-OXATHIANES

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CERIC AMMONIUM NITRATE AS A CONVENIENT CATALYST FOR PROTECTION OF CARBONYL COMPOUNDS AS 1,3-OXATHIANES

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ABSTRACT

A mild and efficient method for the protection of carbonyl compounds as 1,3-oxathianes has been established by the catalytic use of ceric ammonium nitrate at ambient temperature. While different types of aryl and alkyl ketones and aldehydes were protected smoothly, cyclic aryl ketones and diaryl ketones remained unaffected under the reaction conditions.

Key Words: Ceric ammonium nitrate; Protection; Carbonyl compounds; 1,3-Oxathianes

The great significance of selective introduction and removal of protecting groups in organic synthesis is well established. The success of the

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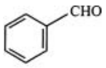
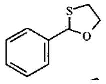
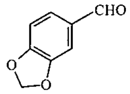
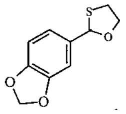
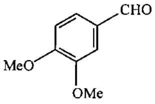
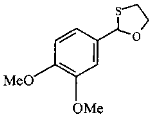
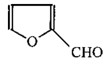
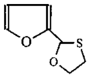
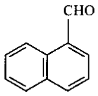
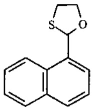
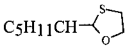
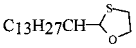
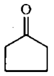
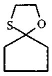
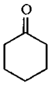
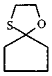
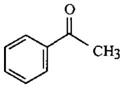
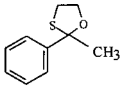
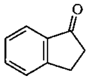
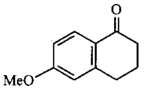
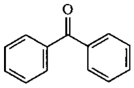
Table 1. CAN-Catalysed Protection of Carbonyl Compounds

Entry	Carbonyl Compounds	Products[a]	Yield (%)[b]
1			81
2			84
3			75
4			89
5			85
6	$C_5H_{11}CHO$		82
7	$C_{13}H_{27}CHO$		81
8			87
9			90
10			85

(*continued*)

Table 1. Continued

Entry	Carbonyl Compounds	Products[a]	Yield (%)[b]
11		No reaction	–
12		No reaction	–
13		No reaction	–

[a]All are isolated yields and are not optimised. [b]All compounds were characterised by IR and ^{1}H NMR spectral data by comparing with authentic samples.[2]

methodology largely depends on the stability of the protecting groups towards different acidic and basic reagents and how easily they can be installed and removed.[1] The protection of a carbonyl group into monothioacetal is widely used in multistep organic synthesis due to its general stability under both acidic and basic conditions.[2] Moreover, 1,3-oxathiane is a versatile synthetic reagent for carbon–carbon bond formations to act as an acyl anion equivalent.[3] In spite of the synthetic importance of monothioacetals, only a very few methods for their preparation have been developed.[2,4,5] But many of these methods suffer from limitations of using stoichiometric reagents or harsh reaction conditions and sometimes cumbersome extraction procedure. So a mild and simple method is still desirable.

In recent years, ceric ammonium nitrate (CAN) has largely been used as an efficient catalyst for the protection of various functional groups which includes our successful achievement towards CAN catalysed protection of alcohols as THP-ethers.[6] Now we report here a mild and efficient method for 1,3-oxathioacetalisation of carbonyl compounds by using a catalytic amount of ceric ammonium nitrate. Both reaction conditions and work-up procedures are mild, simple and convenient. Thus, when various aldehydes or ketones were treated with slight excess of 2-mercaptoethanol in acetonitrile in the presence of a catalytic amount of ceric ammonium nitrate at ambient temperature, the corresponding oxathioacetals were yielded in excellent yields. The results are summarised in Table 1. In general, the reactions were completed within 10 h. Among various solvents attempted acetonitrile was found to be the best one. Most of the aryl and alkyl ketones and aldehydes underwent smooth conversion to monothioacetals, except the cyclic aryl ketones and diaryl ketones. Thus, indanone (Entry 11), 6-methoxy-α-tetralone (Entry 12) and benzophenone (Entry 13) remained unaffected under the reaction conditions even after prolonged (30 h) stirring.

In conclusion, the mild reaction conditions and simple work-up procedures make this methodology an ideal protocol for the protection of various aldehydes and ketones as 1,3-oxathianes.

General Procedure: A mixture of carbonyl compound (3 mmol), 2-mercaptoethanol (3.9 mmol) and CAN (0.3 mmol) in anhydrous acetonitrile (10 mL) was stirred at ambient temperature (30°C) for 10 h under N_2 atmosphere. The reaction mixture was diluted with water (20 mL) and acetonitrile was removed under reduced pressure. The aqueous layer was extracted with ether (3 × 30 mL). The organic layer was washed with 5% aqueous NaOH (3 × 10 mL), brine (3 × 15 mL) and dried (Na_2SO_4). Volatiles were removed under reduced pressure and the yellowish-brown residue was chromatographed over silica-gel (10% ethyl acetate in petroleum ether) to afford the 1,3-oxathiane.

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