Ceric Ammonium Nitrate Mediated Selective Bromoalkoxylation of Activated Cinnamyl Compounds Using Lithium Bromide

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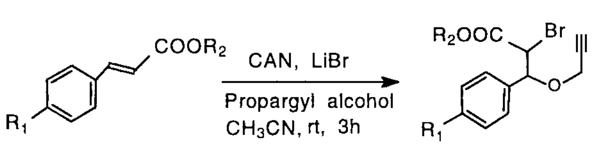
Abstract: Selective bromoalkoxylation of activated cinnamyl systems has been achieved in good yield, using lithium bromide and propargyl alcohol.

Key words: ceric ammonium nitrate, bromoalkoxylation, lithium bromide, selective

In addition to the carbon-carbon bond-forming reactions,[1] ceric ammonium nitrate (CAN) has also been found to be a potential, readily available reagent for various valuable transformations[2] in organic synthesis. Because of our continued interest[3] in exploring CAN as a powerful single electron oxidant, we decided to explore its efficacy in the bromoalkoxylation of cinnamyl compounds using LiBr as the bromine source. Bromoalkoxylation[4] is an important transformation in organic synthesis and the bromoalkoxy compounds can be used as versatile intermediates towards the synthesis of various natural products.[5,6] The bromoethers are generally prepared by the reaction of an olefin with N-bromosuccinimide (NBS) in the presence of an excess of alcohol. Although several CAN mediated organic transformations have been reported in the literature, to our knowledge, bromoalkoxylation of cinnamyl compounds has not yet been explored. We report here a procedure for ceric ammonium nitrate mediated selective bromoalkoxylation of activated cinnamyl compounds using lithium bromide in good yield (Scheme).

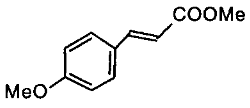
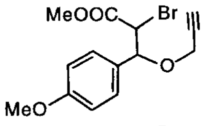
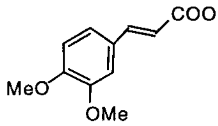
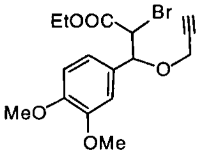
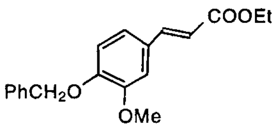
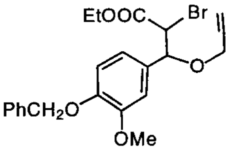
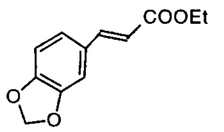
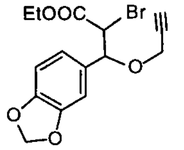
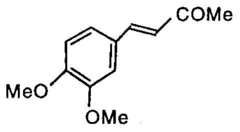
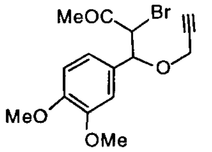
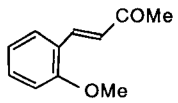
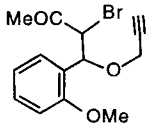


R$_1$ = electron donating group
R$_2$ = Me or Et

Scheme

Thus, a series of activated cinnamyl esters or ketones were subjected to bromoalkoxylation in the presence of CAN and LiBr with an excess of propargyl alcohol at room temperature to furnish the corresponding bromoethers.[7,8] The results are summarised in the Table.

Table CAN mediated bromoalkoxylation of activated cinnamyl compounds

Entry	Substrate	Product	Yield[a]
1			87
2			88
3			88
4			82
5			85
6			79[b]

[a] Yields refer to chromatographically pure isolated products.
[b] Stirring at room temperature for 24 h.

The cation Br$^+$ is generated by the reaction of LiBr with CAN which reacts with the styrenoid double bond and then the addition of alcohol provides the bromo ethers. The reaction is only effective when there is an electron donating group, e.g. a methoxy group in the aromatic moiety either in ortho or para position. Without this aromatic activation the reaction does not proceed at all. As a result, simple methylcinnamate remained unaffected under the reaction conditions.

In conclusion, we developed a selective bromoalkoxylation of activated cinnamyl compounds mediated by ceric ammonium nitrate using lithium bromide in good yield.

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(7) All compounds gave satisfactory spectroscopic data and were compared with the authentic samples.

(8) **General Procedure**: To a magnetically stirred solution of the cinnamyl compound (2.08 mmol), LiBr (2.5 mmol) and propargyl alcohol (1.44 g, 25.7 mmol) in dry acetonitrile (5 ml), a solution of ceric(IV) ammonium nitrate (1.7 g, 3.12 mmol) in acetonotrile (10 ml) was added dropwise at room temperature under nitrogen. The reaction mixture was further stirred for 3 h, and then diluted with ether (15 ml). The organic layer was separated, washed successively with saturated aqueous $NaHCO_3$ solution (3 × 10 ml), water (10 ml) and brine (3 × 10 ml) and then dried over Na_2SO_4. Volatiles were removed under reduced pressure and the residue was purified by chromatography over silica gel to furnish the pure bromoether.

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