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Mn (III)-mediated Radical Lactonisation of Allylic Esters of Acetoacetic and Malonic acids

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Summary : $Mn(OAc)_3$ oxidises allyl acetoacetate and allyl malonate to 3-oxa bicyclo (3.1.0) 2-hexanone derivatives whereas under similar experimental conditions cinnamyl and crotyl esters lead to monocyclic γ–lactones derivatives and bis-lactones.

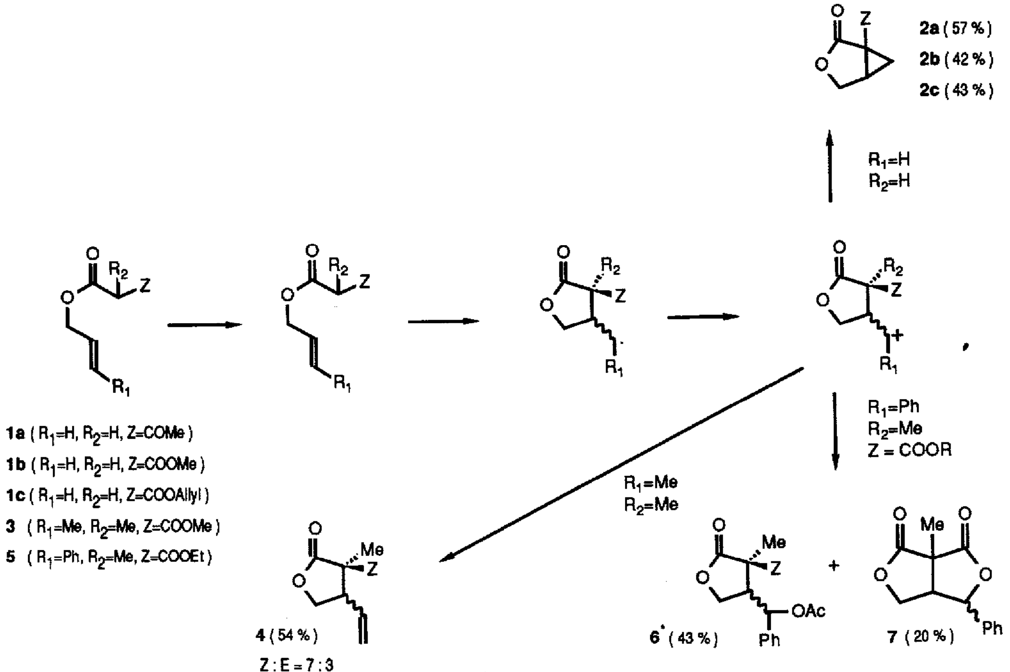
Mn(III)-mediated radical addition of carbonyl compounds to olefins is well known[1a]. Special attention has been devoted to γ- lactones synthesis by intermolecular addition of acids to olefins[1b-k]. Some examples of intramolecular reactions[2] are known , but only one peculiar example of γ-lactone ring closure starting from an ethylenic malonic hemi-ester has been reported[2a]. This appeared as an interesting observation, since previous attempts to obtain free-radical γ-lactone ring closure from such esters, by peroxidic initiation, failed[3a]. Indeed, it has been shown recently that those processes are very slow[3b] .

This paper is concerned with the oxidation of allylic esters of acetoacetic acid and malonic acid . Reactions were performed under the following experimental conditions: the ester (1 eq, 0.4M) in acetic acid, was treated with manganese (III) acetate dihydrate[6] (2 eq by enolisable H) in the presence of copper (II) acetate (1 eq) and potassium acetate (2 eq by enolisable H). The reaction mixture was heated at reflux (β-diesters) or at 75°C (β-ketoester), until the disappearance of the brown dark colour of Mn(III). After extractive work-up, the products were purified by chromatography on silicagel.

Results and proposed mechanism are summarised on scheme 1. We observe exclusive *exo*-cyclisation mode, leading to γ-lactone ring closure. We believe, in agreement with Julia's reports on oxidative cyclisation of ethyl 2-cyano 6-heptenoate in the presence of $CuCl_2$[7b], that fast oxidation of the cyclic carbon radicals prevents reversibility[7] and leads exclusively to five-membered ring products. Under experimental conditions very similar to ours, that is in the presence of one equivalent of $Cu(OAc)_2$, the oxidation of β-keto esters bearing an unsubstituted double bond on the ketone moiety, leads exclusively to phenolic products resulting from the *endo*-cyclisation[4,5].The understanding of this apparent discrepancy would need further studies. The primary cations resulting from **1**, react rapidly with the enolic form of the cyclic β-ketoester or β-diester to close the cyclopropane ring. Similar cyclopropanation has been observed for the copper (II) catalysed addition of ethyl cyanoacetate to various olefins[8]. The secondary radical resulting from **3**, is oxidised to a secondary cation, which is then rapidly deprotonated to give vinyl substituted γ-lactones,the Z and E isomers are produced in the ratio 70:30. The more stabilised benzylic secondary cation, intermediate in the oxidation of **5**, leads to a mixture of diastereoisomeric acetates and bis-lactones. Since diastereoisomeric acetates have not been separated, the stereoselectivity of the cyclisation step is unknown.

Further studies of these reactions are in progress.

Scheme 1



*The product is a mixture of the four possible diastereoisomers.

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