Pergamon

Tetrahedron Letters, Vol. 35, No. 24, pp. 4193-4196, 1994
Elsevier Science Ltd
Printed in Great Britain
0040-4039/94 $7.00+0.00

0040-4039(94)E0743-H

Catalytic Activity of a Polymerizable tris(β-ketoesterate)Iron(III) Complex towards the Oxidation of Organic Substrates

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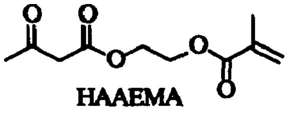
Abstract: The facile oxidation of alkenes, aldehydes, cyclic ketones, alkanes, sulfides and alcohols is achieved by a polymerizable β-ketoesterato complex under Mukaiyama's conditions (atmospheric pressure of molecular oxygen in the presence of a sacrificial aldehyde at room temperature).

Recently Mukaiyama *et al.* have reported a new procedure for the oxidation of organic substrates based on β-diketonato complexes of nickel(II)[1] or iron(III)[2] in the presence of aldehydes (as reductants) and molecular oxygen (as the oxidant). Mukaiyama's oxidation reaction has been applied, by using various catalytic metal centres and experimental conditions, to the synthesis of epoxides from alkenes[1-4], carboxylic acids from aldehydes[4,5], α-hydroxycarbonyl compounds from silyl enol ethers and silyl ketene acetals[6] and esters from ketones[4,7].

In order to realize a heterogeneous analogous of Mukaiyama's system we have synthesized some homoleptic and heteroleptic β-ketoesterate complexes of Cu(II), Ni(II), Co(II) and Fe(III) with the AAEMA ligand (AAEMA= deprotonated form of 2-(acetoacetoxy)ethyl methacrylate)[8,9].



HAAEMA

These complexes are peculiar since they can behave as metallo-organic monomers[9]. The AAEMA ligand, in fact, bears an acrylic "tail" prone to polymerization.

In this letter we report preliminary results obtained by using one of these complexes [e.g. $Fe(AAEMA)_3$, obtained by reaction, in alkaline medium, of $Fe(NO_3)_3$ with HAAEMA], in the presence of a branched chain aldehyde and molecular oxygen, in the oxidation of alkenes, aldehydes, alkanes, sulfides, cyclic ketones and alcohols (fig.1).

In table 1 the results obtained by exposing to oxidizing conditions several different classes of organic compounds are summarized.

The epoxidation of alkenes has been recently shown to occur, at 40°C, under Mukaiyama's conditions also in the absence of metal catalyst[10]. However, experiments carried out in our laboratory demonstrate that when a metal catalyst is present in the reaction medium, the autoxidation of the aldehyde (responsible, via the formation of free peracidic species, of the epoxidation of the olefinic substrate) does not take place to a significant extent[11]. Ethylidenecyclohexane (a prochiral substrate) was smoothly oxidized to its corresponding epoxide[12] with complete conversion and excellent yield (entry 1). Styrene reacted completely after 60 hours yielding 55% styrene oxide and 40 % benzaldehyde (entry 2). Both the aliphatic aldehyde and the aromatic aldehyde tested (*iso*butyraldehyde and benzaldehyde) were readily converted into their corresponding carboxylic acids (entries 3,4).

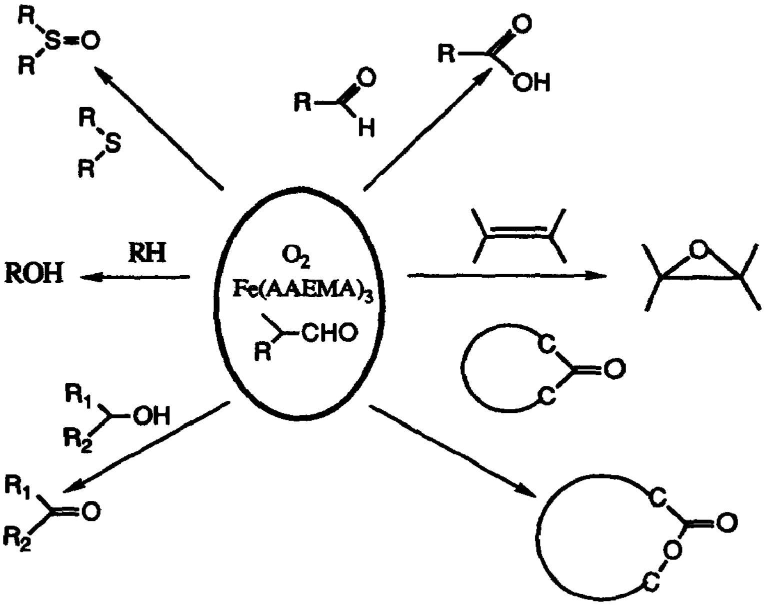


Fig.1

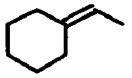
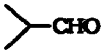
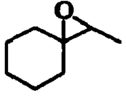
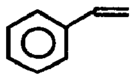
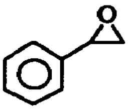
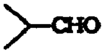
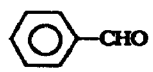
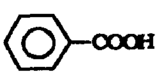
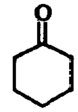
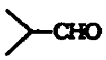
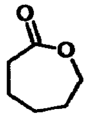
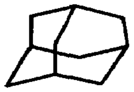
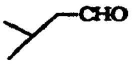
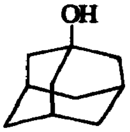
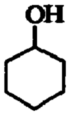
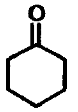
Two ketones were tested in the present oxidation (cyclohexanone and benzophenone). Cyclohexanone was selectively oxidized to ε-caprolactone with conversion as high as 75% (entry 5) while benzophenone did not react at all. A similar behaviour was observed in the Bäyer-Villiger oxidation performed by a Pt(II) complex/H_2O_2 system[13] and in the heteropolyoxometalate/aldehyde/O_2 system[4], where only cyclic ketones were reactive.

The oxidations of adamantane, dimethyl sulfide and cyclohexanol were chosen as representative examples of oxidations of alkanes, sulfides and alcohols respectively.

Among the oxidizing systems effective in the hydroxylation of the alkanes[14], only "dry" ozonization methods[15], HOF/MeCN oxidizing system[16] and dioxiranes[17] proved to be useful for synthetic purposes.

Several catalytic systems based on transition metal complexes have also been studied in the present reaction[18], but none of these is satisfactory from the activity and/or selectivity points of view. Two recent papers report on the aerobic oxidation of alkanes in the presence of a metal centre and an aldehyde[3c,19], but the conversion of adamantane does not exceed 38%. The system Fe(AAEMA)$_3$/*iso*valeraldehyde, herein dealt with, catalyzed the selective monohydroxylation of adamantane to afford 1-adamantanol with a conversion as high as 60% (entry 6).

Table 1. Oxidation reactions with Fe(AAEMA)$_3$ under Mukaiyama's conditions[a].

Entry	Substrate	Sacrificial aldehyde	Time (h)	Conversion (%)	Yield (%)	Product
1			10	100	95	
2		"	40	100	55	
3		none	6	92	83	 [b]
4		none	6	98	95	 [b]
5			36	75	100	
6		 [c]	60	60	99	
7	CH_3-S-CH_3	"	20	15	100	$(CH_3)_2S{=}O$
8		"	48	19	70[d]	

[a] Reaction conditions: 2.5 mmoles substrate, 0.020 mmoles Fe(AAEMA)$_3$, 7.5 mmoles *iso*-butyraldehyde or 15 mmoles *iso*-valeraldehyde (when employed), 10 ml 1,2-dichloroethane in the presence of molecular oxygen (p=1 atm) at room temperature. The products were identified by comparison of their retention times in gas chromatographic analysis and spectroscopic features with those of authentic samples. *Iso*butyric acid or *iso*-valeric acid were the side products deriving from the concurrent oxidation of the sacrificial aldehyde (when employed).

[b] Analyzed as methyl ester after treatment of the reaction mixture with diazomethane.

[c] 37.5 mmoles *iso*valeraldehyde were added as described in the text.

[d] 30% yield in ε-caprolactone was found in the reaction mixture.

As already noticed by Mukaiyama[1b], the oxidation of the target substrate stops when the sacrificial aldehyde is consumed. In order to reach significant conversions even though the oxidation reaction of the substrate is much slower compared to the oxidation of the sacrificial aldehyde, it is necessary to use a many-fold excess of the latter. Another possibility is to add fresh aldehyde when it is consumed, in order to restart the oxidation reaction of the substrate. The oxidation of adamantane was carried out by adding, every 12 hours, 7.5 mmoles of fresh *iso*valeraldehyde and following by GLC the production of the alcohol.

The oxidations of dimethyl sulfide and cyclohexanol were carried out with a six-fold excess of *iso*-valeraldehyde. In the reaction of dimethyl sulfide, however, the small conversion (15%, entry 7) should not be ascribed to the competition between the substrate and the sacrificial aldehyde since, after reaction, most of the *iso*-valeraldehyde was found unreacted.

Cyclohexanol was slowly oxidized into cyclohexanone (entry 8). Consecutive further oxidation into lactone of the cyclohexanone produced, accounts for less than 100% selectivity.

We are indebted to B.Corain and L.Lopez for useful suggestions and kind help. This work was supported by Italian CNR and MURST (Rome).

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12. Ethylidenecyclohexaneoxide: ms (m/e%) 126 (7), 125 (4), 98 (49), 97 (14), 83 (21), 81 (15), 79 (10), 70 (20), 67 (100), 55 (32), 54 (67), 53 (17), 45 (10), 43 (32), 41 (57), 39 (53). ^{1}H NMR($CDCl_3$): δ= 1.28 (d, J=5.55 Hz, 3 H), 1.50-1.60 (m, 8 H)1.65-1.80 (m, 2 H), 2.83 (q, J=5.55 Hz, 1 H);
    ^{13}C NMR ($CDCl_3$): δ=35.6, 34.0, 29.1, 25.8, 25.1, 24.9, 21.7, 13.6 ppm.
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(*Received in UK* 10 *January* 1994; *revised* 6 *April* 1994; *accepted* 15 *April* 1994)