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"Clayniac"-Catalyzed Epoxidation: The Role of the Aldehyde as Co-Reducer of Molecular Oxygen

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Abstract : *The ability of aliphatic and aromatic aldehydes to serve as the sacrificial auxiliary is measured. This structure-activity relation is consistent with intermediacy of an acylperoxy intermediate. Observed inhibitions by p-benzoquinone, by TEMPO, and by ferrocene carboxaldehyde also point to intervention of a free-radical mechanism*

The accompanying communication describes an efficient and inexpensive procedure for epoxidation[1]. This is an heterogeneous variant to the Mukaiyama method[2]. Olefins, when reacted with O_2 in the presence of clays, can suffer allylic oxidation. A 35 year-old report describes, for instance, the auto-oxidation of α-pinene in the presence of 1% kaolinite into the allylic hydroperoxide, subsequently hydrolyzed into the allylic alcohol[3]. A nice feature of our novel methodology is avoidance of such allylic oxidation. Another feature is mandatory recourse to an aldehyde co-reactant. This aldehyde serves as a sacrificial auxiliary, ending up as the corresponding carboxylic acid. And it needs to be used in stoichiometric amount, typically two or three equivalents. We examine here in more detail the function of the aldehydic co-reducer.

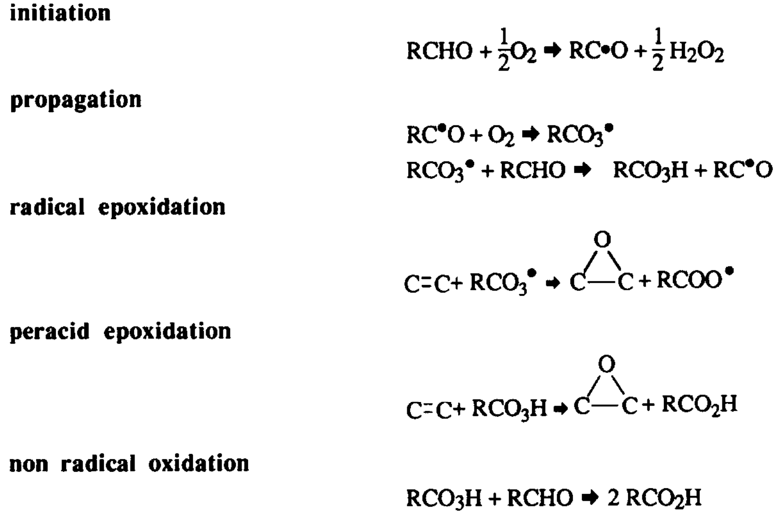
Taking cyclohexene as the test molecule[4], the procedure consists in stirring during 24 h a mixture of cyclohexene (5 mmol), the sacrificial aldehyde (10 mmol), the "clayniac" catalyst [1](25 mg), in methylene chloride (10 mL) under compressed air (10 bar).

We show in Table 1 the ability of various aldehydes to function as sacrificial reducers :

Table 1. Intrinsic ability of various aldehydes to act as co-reducers, when cyclohexene is epoxidized by dioxygen in the presence of "clayniac" as the catalyst.

Aldehyde	**Epoxide Yield, %**	**Relative prowess, %**
Ferrocene carboxaldehyde	0.1	0.14
Piperonal	0.1	0.14
m-Anisaldehyde	0.1	0.14
3-Pyridine carboxaldehyde	0.4	0.65
Phenylpropionaldehyde	2	2.7
Benzaldehyde	3	4.1
Crotonaldehyde	10	14
3-Cyclohexylpropionaldehyde	13	18
Cyclohexane carboxaldehyde	26	36
Pivalaldehyde	46	63
i-Butyraldehyde	73	100

The structure-activity correlation is rather clear-cut: aromatic aldehydes ArCHO basically are inefficient auxiliaries; crotonaldehyde is an intermediate case; and aliphatic aldehydes RCHO work best[5]. This is in line with the proposed mechanism for co-oxidation by molecular oxygen of an olefin and an aldehyde, as a radical chain reaction[6] :



initiation

$$\mathrm{RCHO} + \frac{1}{2}\mathrm{O_2} \rightarrow \mathrm{RC{\bullet}O} + \frac{1}{2}\mathrm{H_2O_2}$$

propagation

$$\mathrm{RC^{\bullet}O + O_2 \rightarrow RCO_3^{\bullet}}$$

$$\mathrm{RCO_3^{\bullet} + RCHO \rightarrow RCO_3H + RC^{\bullet}O}$$

radical epoxidation

$$\mathrm{C{=}C + RCO_3^{\bullet} \rightarrow \overset{O}{C{-}C} + RCOO^{\bullet}}$$

peracid epoxidation

$$\mathrm{C{=}C + RCO_3H \rightarrow \overset{O}{C{-}C} + RCO_2H}$$

non radical oxidation

$$\mathrm{RCO_3H + RCHO \rightarrow 2\,RCO_2H}$$

The observed reactivity sequence in Table 1 with "saturated" aldehydes (i-butyraldehyde > pivalaldehyde > cyclohexane carboxaldehyde > 3-cyclohexylpropionaldehyde) is at variance with that reported when the acyl radical RC•O derived from the aldehyde adds to an olefin in a chain reaction[7], which does not appear to be significant under our conditions.

It is to be expected that free radicals of the $RCO_3\cdot$ type be more reactive, because of the lack of resonance stabilization, than free radicals of the $ArCO_3\cdot$ type. Furthermore, a standard free radical trap, such as p-benzoquinone or TEMPO, blocks the reaction[8]. We have also performed a large number of competition experiments between i-butyraldehyde and other aldehydes. We sample for consideration in the following Table 2 the results with equimolar mixtures:

Table 2 - Results from competition experiments with equimolar mixtures of aldehyde X and i-butyraldehyde.

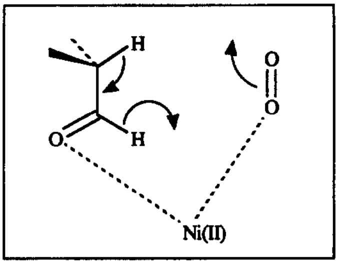
Aldehyde X	Epoxide Yield, %	Calculated Yield [a]
Ferrocene carboxaldehyde	0.6	36.5
Piperonal	26	36.5
m-Anisaldehyde	51	36.5
3-Pyridine carboxaldehyde	48	36.7
Phenylpropionaldehyde	39	37.5
Benzaldehyde	34	38.5
Crotonaldehyde	47	41.5
3-Cyclohexylpropionaldehyde	68	43
Cyclohexane carboxaldehyde	66	49.5
Pivalaldehyde	52	59.5
i-Butyraldehyde	(73)	(73)

[a] assuming additivity of the yields stemming from independent reactions

The lack of correlation between observed and calculated values in Table 2 ($\rho = 0.49$ for 10 data points) is indicative of crossover between the routes followed with each of the two aldehydes, and further supports a chain reaction mechanism. One will note also that ferrocene carboxaldehyde is an inhibitor, presumably because of the very high stability of the corresponding radical.

The reaction site is not exclusively interfacial, as indicated both by the strong inhibition by free-radical traps and by the observation of a reaction, albeit slower, in the absence of the catalyst.

Finally we address the dual question of the role of nickel (II) and of the reason of the superiority of i-butyraldehyde as the oxygen-transfer agent. It is reasonable to surmise attachment of both dioxygen and the aldehydic auxiliary to the metallic center on the catalyst. There is strong recent evidence for the transformation into a singlet oxygen-like active species under these conditions[9]. With singlet oxygen and i-butyraldehyde coordinated onto the metal, we conjecture an ene-type pericyclic process:



(written as concerted, it might occur also by sequential, radical abstraction steps in the ground, triplet state) resulting in the in situ production of hydrogen peroxide and of dimethyl ketene. The former would participate in the olefin epoxidation; while the latter would be unstable and be converted into i-butyric acid during isolation. Ketenes acetylate olefinic hydroperoxides that may be formed as intermediates[3] but the resulting peracetates are very unstable[10].

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