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OXIDATION OF 1-METHOXYCYCLOPROPANOL BY METAL IONS
IN THE PRESENCE OF OXYGEN AND ACTIVATED OLEFINS

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Previously we described the efficient oxidation of 1-methoxycyclopropanol $\underline{1}$ with Cu^{2+} ions to methyl acrylate $\underline{3}$ and dimethyl adipate $\underline{4}$ via the methyl β -propionate radical $\underline{2}$. It was proved by labelling experiments [3] that the adipate is predominantly formed by addition of radical $\underline{2}$ to the acrylic ester. The oxidation can also be effected with aqueous ferric nitrate but now trimethyl 1,3,6-hexanetricarboxylate and higher telomers are also among the products.

Because β -propionate radicals are not easily accessible from other sources (at least not with avoidance of the competitive generation of isomeric α -propionate radicals), we studied the oxidation of 1-methoxycyclopropanol in the presence of activated olefins as a means of chain lengthening with a three-carbon unit.

When 1 eq. of ferric nitrate in methanol is added to an excess of 3-buten-2-one $\underline{5a}$ ("methyl vinyl ketone") and $\underline{1}$, the product is the expected methyl 6-oxoheptanoate $\underline{6a}$ (yield 30%) $\left\{\delta_{TMS}^{CCl}4\ 3.60\ (s,\ OCH_3,\ 3H),\ 2.06\ (s,\ CH_3^{CO}-,\ 3H),\ 1.5-2.3\ ppm\ (m,\ CH_2,\ 8H)\right\}$. Similarly 2-cyclopentenone gives methyl β -(3-oxocyclopentyl)propionate $\left\{\delta_{TMS}^{CCl}4\ 3.60\ (s,\ OCH_3,\ 3H),\ 1.5-2.5\ ppm\ (m,\ CH_2,\ 11H)\right\}$. Yields are no higher than 30% because of appreciable poly-(-oligo-)merisation (cf. Scheme 1). The yield of $\underline{6a}$ can be increased to 45%, when cupric nitrate

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pyridine complex $(Cu(NO_3)_2, (C_5H_5N)_4)$ is used as the oxident. With 3-penten-2-one 5b and 4-methyl-3-penten-2-one 5c ("mesityl oxide"), the yield of 6b drops to 40% and of 6c to 6%, presumably because of steric and polar effect of the methyl group(s) in 5.

Scheme 1

Scheme 1

OH
$$\frac{Cu^{2^{+}}}{OMe}$$
 $\dot{C}H_{2}CH_{2}CO_{2}Me$ \longrightarrow $H_{2}C = CHCO_{2}Me + (CH_{2})_{4}$ $\dot{C}O_{2}Me$

1 2 3 4

 CH_{3} CH_{2} $CH_{2}CH_{$

In these cases the radical attack takes place exclusively at the β -carbon atom. Consequently, in the resulting radical the free electron is (formally) on the carbon atom next to the carbonyl group; this intermediate is rapidly reduced by Fe²⁺ ion to the corresponding more stable carbanion, which subsequently picks up a proton from the solvent [3].

On adding the radical R' to an excess of butadiene (in MeOH) a resonance stabilised allylic radical 7 is formed, which dimerizes to a mixture of unsaturated C_{14} -diesters 8, 9 and 10 in a ratio of about 19:12:1 (total yield 52%). The IR spectra show the characteristic CO absorptions. Compound 10 has a relatively strong band at 1640 cm⁻¹ (C=CH₂), which is weaker in product 9 and absent in 8. The NMR spectra (CCl₄) show similar absorptions at 8 4.7-5.5 (m, C=CH), 3.60 (s, OCH₃), 1.0-2.4 ppm (m, CH₂). The strong peak in the mass spectrum (parent ion m/e 282) at m/e 141 (35%) of 8, 9 and 10 indicates the same allylic fragment.

The propionate radical R° adds slowly to furan, giving methyl β -(2-furyl)propionate 11 (20%) together with dimethyl adipate (33%). NMR of 11: δ_{TMS}^{CCl} 4 7.25 (d, α CH, 1H), 6.2 and 6.0 (m, β CH, 2H), 3.62 (s, OCH₃, 3H), 2.3-3.1 ppm (m, CH₂, 4H).

The oxidation of 1 with ferric nitrate in an excess of acrylonitrile in methanol yields only polymers. However, with cupric nitrate in an oxygen-free mixture of ammonia and methanol, methyl 5-cyanopentanoate 14 (43%) is obtained. These re-

$$\begin{array}{c} \text{CH}_2\text{CH}_2\text{CO}_2\text{Me} + \text{CH}_2 = \text{CHCN} \\ \hline \\ \text{CH}_2\text{CH}_2\text{CO}_2\text{Me} \\ \hline \\ \text{CH}_2\text{CH}_2\text{CO}_2\text{Me} \\ \hline \\ \text{Or} \text{Fe}^{2^{\bullet}} \\ \hline \\ \frac{12}{} \\ \hline \end{array} \begin{array}{c} \text{CH}_2 = \text{CHCN} \\ \\ \text{CU}^{\bullet} \\ \text{CH}_2\text{CHCN} \\ \text{CH}_2\text{CHCN} \\ \text{CH}_2\text{CO}_2\text{Me} \\ \hline \\ \text{Or} \text{Fe}^{2^{\bullet}} \\ \hline \end{array} \begin{array}{c} \text{CH}_2 = \text{CHCN} \\ \\ \text{CU}^{\bullet} \\ \text{CH}_2\text{CHCN} \\ \text{CH}_2\text{CHCN} \\ \text{CH}_2\text{CO}_2\text{Me} \\ \hline \\ \text{Or} \text{Fe}^{2^{\bullet}} \\ \hline \end{array} \begin{array}{c} \text{CH}_2 = \text{CHCN} \\ \text{CH}_2 = \text{CHCN} \\ \text{Or} \text{Fe}^{2^{\bullet}} \\ \text{CH}_2 = \text{CHCN} \\ \text{CH}_2 = \text{CHCN} \\ \text{CH}_2 = \text{CHCN} \\ \text{Or} \text{Fe}^{2^{\bullet}} \\ \text{Or} \text{Fe}^{2^{\bullet}} \\ \text{CH}_2 = \text{CHCN} \\ \text{CH}_2 = \text{CHCN} \\ \text{CH}_2 = \text{CHCN} \\ \text{CH}_2 = \text{CHCN} \\ \text{Or} \text{Fe}^{2^{\bullet}} \\ \text{Or} \text{Fe}^{2^{\bullet}} \\ \text{CH}_2 = \text{CHCN} \\ \text{CH}_2 = \text{CHCN} \\ \text{Or} \text{Fe}^{2^{\bullet}} \\ \text{CH}_2 = \text{CHCN} \\ \text{CH}_2 = \text{CHCN} \\ \text{Or} \text{Fe}^{2^{\bullet}} \\ \text{CH}_2 = \text{CHCN} \\ \text{CH}_2 = \text{CHCN} \\ \text{Or} \text{Fe}^{2^{\bullet}} \\ \text{CH}_2 = \text{CHCN} \\ \text{CH}_2 = \text{CHCN} \\ \text{CH}_2 = \text{CHCN} \\ \text{Or} \text{Fe}^{2^{\bullet}} \\ \text{CH}_2 = \text{CHCN} \\ \text{Or} \text{Fe}^{2^{\bullet}} \\ \text{CH}_2 = \text{CHCN} \\ \text{Or} \\ \text{CH}_2 = \text{CHCN} \\ \text{OR} \\ \text{CH}_2 = \text{CHCN} \\ \text{OR} \\ \text{CH$$

sults can be explained by assuming that the efficient polymerization initiated by the α -cyanoradical <u>12</u> [4] is suppressed by an even more effective reduction of this radical to the corresponding carbanion <u>13</u>. Presumably this reduction can be effected far more rapidly by the cuprous ion (in ammonia $E_{\text{OX}}^0 = 0.01 \text{ V}$) than by the ferrous ion (in an acidic medium $E_{\text{OX}}^0 = -0.77 \text{ V}$) [5]. Similar results were obtained with a mixture of cupric nitrate and acrylic ester [3].

In the reactions so far described, a reduction and an oxidation of the metal ion are involved, and so the question arises whether the oxidation of the Cu⁺ or Fe²⁺ ion can be achieved by oxygen (rather than by an intermediate radical), thus making the function of the metal ion essentially catalytic in the chain lengthening process. Unfortunately complications arise in practice.

In the presence of 0.05 eq. of ferric nitrate (p_H = 3) in a mixture of 4 eq. of acrylonitrile in methanol, under an oxygen atmosphere, the hemiacetal 1 is converted into dimethyl adipate, methyl β -hydroxypropionate 19 {IR (liq.) 3400 cm⁻¹ (OH), 1720 cm⁻¹ (C=0), 1170-1250 cm⁻¹ (C=0); NMR δ_{TMS}^{CDCl} 3 3.87 (t, OCH₂, 2H), 3.69 (s, OCH₃, 3H), 2.8 (s, OH, 1H), 2.57 ppm (t, COCH₂, 2H)}, dimethyl glutarate 17 (R¹ = CH₃) {IR (liq.), 1730 cm⁻¹ (C=0), 1200 cm⁻¹ (C=0); NMR δ_{TMS}^{CDCl} 3 3.69 (s, OCH₃, 6H), 1.8-2.6 ppm (m, CH₂, 6H)} and polymers. The total yield of identified products is 30-50%. The remarkable "loss" of one carbon atom, involved in the glutarate formation (10-30%) can be explained by the mechanism outlined in Scheme 2 [6]. The oxygen does not exclusively attack ferrous ion, but can also interact with radical 12 with formation of the peroxy radical.

This logically leads via well known steps to the acyl cyanide 16. The presence of this intermediate is supported by the solvent influence: when methanolis replaced by water or ethanol, the product is no longer the methyl glutarate, but the acid and the ethyl ester respectively, by solvolysis of 16. Interestingly with aqueous cupric nitrate (p_H = 3) and oxygen, methyl 5-oxopentanoate $\underline{18}$ and $\underline{17}$ (R^1 = H) are formed in about equal amounts. Again the ability of the cuprous ion (E_{ov}^{O} = -0.15 V [5]) to reduce radicals better than Fe⁺⁺ (<u>i.e.</u> the oxy-radical $\underline{15}$ to the oxoanion, cf. Scheme 2) competes successfully with other radical processes. The ratio in which the esters 17 and 19 are formed depends on the initial oxygen pressure. It varies from 4:6 at 1 atm. 0_2 to 4:1 at 5.10⁻² atm. 0_2 (yield of dimethyl adipate remains constant). Apparently the unstable β-propionate radical R' adds more efficiently to the large excess of acrylonitrile at low 02 concentration than at high O2 concentration, thus giving a relative increase of the more stable α -cyano radical 12 from which the glutarate is formed.

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