Oxidatively Induced Radical Chemistry of Dicarbonyl η^5-Cyclopentadienyl Iron Derivatives of Carboxylic Acids (Fp–Acyl Complexes)

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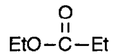
The 17-electron cationic [Fp–acyl] intermediates generated by cerium ammonium nitrate (CAN) oxidation of Fp–acyl complexes in dry acetonitrile undergo a fast homolytic dissociation leading to alkyl radical species whose subsequent fate is dependent on the structural features and reaction conditions.

The oxidation of Fp–acyl complexes (Fp = η^5-cyclopentadienyl iron dicarbonyl) to the corresponding seventeen electron Fp–acyl radical cations, especially by electrochemical[1,2] means, is a well-documented reaction. These cations are rather unstable species as evidenced, *inter alia*, by cyclic voltammetry studies.[1,2] In the presence of strong enough nucleophiles such as alcohols or amines, they are rapidly trapped to give the corresponding esters or amides.[2,3] However, little is known about the chemical evolution of these species, especially regarding the organic part, in poorly nucleophilic media.

During a systematic investigation of the oxidation of several Fp–acyl complexes under diverse conditions, we found that the cerium ammonium nitrate (CAN) oxidation of linear acyl complexes such as **1a**, **2a** or **3a** in dry acetonitrile and at room temperature led to the corresponding esters **4**, **5** and **6** in

EtX

1

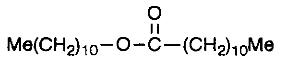


$\mathrm{EtO{-}C({=}O){-}Et}$

4

$\mathrm{Me(CH_2)_{10}X}$

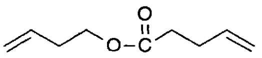
2



$\mathrm{Me(CH_2)_{10}{-}O{-}C({=}O){-}(CH_2)_{10}Me}$

5

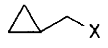
3



6

$\mathrm{Me(CH_2)_8{-}CH{=}CH_2}$

7



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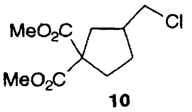

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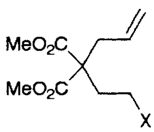

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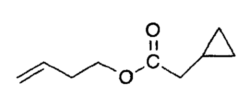

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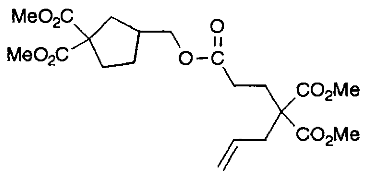

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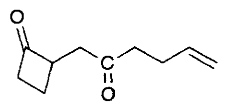

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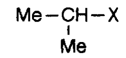
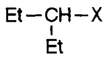


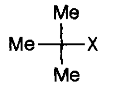
$\mathrm{Me{-}CH(Me){-}X}$

14



$\mathrm{Et{-}CH(Et){-}X}$

15



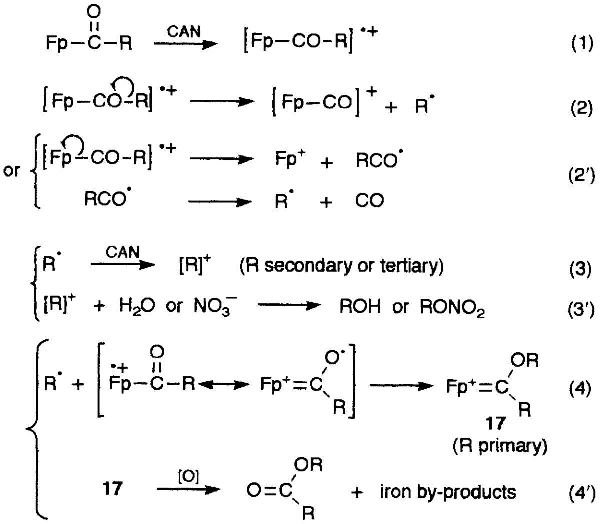
$\mathrm{Me_3C{-}X}$

16

a, X = COFp; **b**, X = Cl; **c**, X = •; **d**, X = $\mathrm{ONO_2}$; **e**, X = OH

45–60, 75 and 52% yields respectively.† No other organic by-products were detected in noticeable amounts. The main organometallic product of these reactions was identified (NMR, IR spectroscopy) as the cationic entity $[\mathrm{FpCO}]^+$, present up to 55–70%. $\mathrm{FpONO_2}$ was also usually detected in small amounts (10–20%). When the oxidation of **2a** and **3a** was carried out in the presence of $\mathrm{CCl_4}$ (in a 1:1 v:v MeCN–$\mathrm{CCl_4}$ mixture), exclusive formation of the alkyl chlorides **2b** and **3b** was observed (respective yields: 83 and 80%). Finally, when the oxidation of **2a** was performed in the presence of $\mathrm{Cu(OAc)_2}$ (1 equiv., based on Fp–acyl complex), undec-1-ene **7** was predominantly obtained (65%) together with some ester **5** (16%).

The two latter results are strong indications of a transient formation of alkyl radicals since both carbon tetrachloride[4] and $\mathrm{Cu(OAc)_2}$[5] are well known radical traps leading to alkyl chlorides and alkenes, respectively. The involvement of radical species in the oxidative degradation of Fp–acyl complexes was confirmed by using radical probes. CAN oxidation of Fp–acyl complexes **8a** and **9a** in MeCN–$\mathrm{CCl_4}$ gave alkyl chlorides **3b** (80% yield) and **10** (30% yield) which are the expected products from the rearrangement of a primarily formed cyclopropylmethyl radical **8c** through β-scission of the cyclopropane ring[6–8] and from the rearrangement of a primarily formed γ-ethylenic radical **9c** through 5-*exo-trig*-cyclisation.[6,8] When the reactions were repeated in the absence of carbon tetrachloride, the esters **11** (17% isolated yield) and **12** (49% isolated yield) with a rearranged alkoxy R group were obtained. In the case of **8a**, however, the main reaction product was not the ester **11** but rather surprisingly the cyclobutanone **13**‡ (76% isolated yield).



Scheme 1

When the CAN oxidation in dry acetonitrile was performed on α-branched Fp–acyl complexes (that is on the 2-methylpropanoyl, the 2-ethylbutanoyl and the pivaloyl derivatives **14a–16a**), no carboxylic ester formation could be detected. Instead, formation of nitrate esters **14d** and **15d** in 45 and 40% yield, respectively, was observed with **14a** and **15a** while a mixture of nitrate **16d** (48%) and of alcohol **16e** (32%) was obtained with the pivaloyl complex. Acetone was also formed (20%) in the oxidation of the 2-methylpropanoyl Fp complex. In all these reactions, the main organometallic product (80–90%) of the reaction was the $[\mathrm{Fp{-}CO}]^+$ entity. In the oxidation of **16a** in MeCN–$\mathrm{CCl_4}$, a 70:30 mixture of *tert*-butyl choride **16b** and of *tert*-butyl nitrate **16d** was obtained in 80% overall yield.

The following mechanism (see Scheme 1) is tentatively proposed to account for most of the above observations. Upon mixing CAN and Fp–acyl complexes, almost instantaneous formation of the seventeen electron $[\mathrm{Cp(CO)_2Fe{-}acyl}]^+$ species occurs, which can usually be visualized by the transient appearance of a green colour.[1] At this stage a homolytic dissociative process takes place, leading to alkyl radicals and

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† Fp–acyl complexes have been synthesized by reacting the corresponding acyl chlorides with the Fp anion according to Lapinte's procedure (C. Roger, M-J. Tudoret, V. Guerchais and C. Lapinte, *J. Organomet. Chem.*, 1989, **365**, 347). The oxidation reactions in general were carried out by adding two equiv. of CAN (as a solid) in one portion to a solution of 2 to 2.25 mmol of Fp–acyl complex in 30 ml of dry MeCN under argon. The work-up was done after 10 min of stirring at room temp. Unless otherwise specified, only analytical yields are reported, which are determined by NMR or GC analysis in the presence of a suitable reference (benzene for NMR measurement). Small scale reactions were performed simultaneously in deuteriated acetonitrile (0.06 mmol, of complex in 0.75 ml of solvent) to allow direct NMR measurements. In the case of **2a**, we observed that the yield of ester **5** stays unchanged, regardless of the initial concentration of **2a** (5–75 mmol $\mathrm{dm^{-3}}$).

‡ Compound **13** was isolated by flash chromatography and fully characterized by mass, IR, ^{1}H and ^{13}C NMR spectroscopy. Its identity was further confirmed by comparison with an authentic sample prepared according to Trost methodology (B. M. Trost and M. J. Bogdanowicz, *J. Am. Chem. Soc.*, 1973, **95**, 5321): 3-oxohept-7-enal (prepared and used as its 3-ethylene ketal derivative) was condensed with diphenylcyclopropylsulphonium tetrafluoroborate (KOH, dimethyl sulphoxide). The resulting cyclopropane spiroepoxide was rearranged to cyclobutanone ($\mathrm{LiPF_6}$, benzene, reflux 16 h); the ethylene ketal group is removed during the work-up ($\mathrm{HBF_4{-}H_2O}$) of the spiroepoxide.

$[Fp–CO]^+$.§ Secondary and tertiary radicals formed from α-branched Fp–acyl complexes are then rapidly oxidized to the corresponding cations whose trapping by nitrate anions or adventitious water leads to the observed reaction products. Rather than being converted to primary cations, the less oxidizable[5] primary radicals produced in the homolytic dissociation of linear Fp–acyl complexes, in the absence of radical traps such as CCl_4, react with the seventeen electron Fp–acyl radical cationic species to give the cationic iron alkoxy–carbene (Fischer type) complexes **17**. These complexes are finally rapidly converted to esters RCO_2R and iron by-products. We have checked that $[Fp{=}C(OEt)Me]^+\ BF_4^-$[9] immediately decomposes to ethyl acetate in dichloromethane or acetonitrile solutions containing CAN.

An alternative (ionic) route to Fischer complexes **17**, involving an attack of primary alkyl cations on Fp–acyl complexes, may be ruled out on the following grounds: (*i*) the alkylation of Fp–acyl complexes by triethyloxonium tetrafluoroborate is already a slow process, requiring several hours at room temperature. *N*-Ethyl acetonitrilium tetrafluoroborate was independently prepared[10] and we found that its reaction with Fp–COMe, both in acetonitrile or in dichloromethane is still slower, if it occurs at all; (*ii*) in the case of **9a**, the intermediacy of carbocationic species would more likely result in the formation of a rearranged product with a six-[11] rather than a five-membered ring.

Finally, at the present stage of our investigations, we think that the formation of the cyclobutanone **13** could follow from an internal rearrangement of the radical cation of **8a**, involving carbonyl insertion in the cyclopropane ring.

In conclusion, this work shows that the CAN oxidation of Fp derivatives of aliphatic carboxylic acids, in the absence of nucleophiles, brings about a radical process leading ultimately to the ester RCO_2R. In that process the seventeen electron $[Fp–acyl]^+$ radical cationic species act both as radical sources and as radical traps. Provided that the reaction conditions are optimized, Fp–acyl complexes or other structurally related organometallic species could constitute, in the future, a new source of alkyl radical (especially of primary ones) for use in organic synthesis.

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§ In this step, the stability of the $[Fp–CO]^+$ cationic entity (see N. Grice, S. C. Kao and R. Pettit, *J. Am. Chem. Soc.*, 1979, **101**, 1627) would act as the driving force of the reaction. Another possibility which cannot be discarded at the present stage of our investigations is a homolytic cleavage of the iron–carbon bond leading to Fp^+ and the acyl radical. The acyl radical would then decarbonylate (P. Delduc, C. Tailhan and S. Zard, *J. Chem. Soc., Chem. Commun.*, 1988, 308 and references cited therein) to an alkyl radical. The Fp^+ cation is known to undergo a disproportionation reaction leading to $[FpCO]^+$ (W. P. Giering and M. Rosenblum, *J. Chem. Soc., Chem. Commun.*, 1971, 441).

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