# The Electrochemical Transformation of ααα-Trifluoroacetophenone into Acetophenone; an Unusually Ready Hydrogenolysis of the C–F Bond

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THE electrolytic reduction of ααα-trifluoroacetophenone does not proceed to the expected pinacol, but yields acetophenone and/or acetophenone pinacol depending on the potential employed and the reaction time permitted.

The experimental data and the cited literature, *vide infra*, permit the following conclusions: (*a*) The reduction potential successfully employed for complete hydrogenolysis of all three C–F bonds is substantially below the lowest previously reported; (*b*) the complete hydrogenolysis is not a single step in protic solvents as has been previously proposed; (*c*) the potentials required for the three successive stages of hydrogenolysis must be very nearly the same; and (*d*) hydrogenolysis occurs prior rather than subsequent to pinacolization.

The electrolytic reductions, all under conditions of controlled potential, are summarized in the Table. The general experimental technique has been described;[1] n.m.r. analysis was utilized.[2] All potentials are given relative to an Ag–AgCl reference electrode [saturated KCl, 0·04 v more negative than standard calomel electrode (S.C.E.)], and a pH of *ca.* 4·2 was used.

*Electrolytic reduction of ααα-trifluoroacetophenone*

| Potential (v) | Current (mA) | Time (hr.) | Products[a] |
|---|---|---|---|
| −1·06 | 400 | 9 | 67% acetophenone pinacol |
| −1·06 | 460 | 1 | 14% acetophenone<br>46% α-fluoroacetophenone |
| −1·10 | 200 | 28 | 68% acetophenone pinacol[b]<br><5% acetophenone |
| −1·04 | 710 | 9 | 20% acetophenone pinacol[c] |
| −1·02 | 970 | 3·5 | 63% acetophenone pinacol |
| −0·90 | 300 | 30 | 9% acetophenone pinacol<br>87% acetophenone |
| −0·95 | 450 | 0·5 | 3% acetophenone<br>27% α-fluoroacetophenone<br>>50% starting material |

[a] Recovered starting material is given when present; yields are based on starting ketone. In addition to the products mentioned, an examination for αα-difluoroacetophenone, as well as all the possible carbinols and pinacols, was made on the basis of known or analogous n.m.r. spectra. Di- and tetra-fluoroacetophenone pinacols were eliminated because of absence of any signals (other than due to the monofluoro-ketone and $D_2O$-replaceable hydroxylic protons) in the $\tau$ 3·0—7·1 region. That some hexafluoroacetophenone pinacol was probably present in some cases was suggested by otherwise unexplained exchangeable hydroxylic protons; this could account for a maximum of about 10% of the missing material balance.

[b] 20% Pure racemic acetophenone pinacol formally isolated.

[c] Reverse isotope dilution experiment, [$^{14}$C]-labelled acetophenone pinacols used (*cf.* ref. 1). Only the acetophenone pinacols were investigated.

*Pertinent polarographic data*: An $E_{\frac{1}{2}}$ value of −0·89 v at pH 4·2 was determined for the start of C–F fission; a single wave was found. No evidence for any reducibility at less than the solvent decay limit of −1·3 v was found for either the hexafluoroacetophenone pinacols or the acetophenone pinacols. For comparison, benzyl fluoride and benzotrifluoride showed no reduction to −1·3 v and *p*-trifluoromethylacetophenone was reduced to the corresponding pinacol without C–F fission at −1·15 v (>90% yield in macro runs).

Lund[3] has reported that few $-CF_3$ to $-CH_3$ transformations occur below −2·0 v but that a substituted benzotrifluoride was reducible at pH 6 to the analogous toluene at an $E_{\frac{1}{2}}$ of −1·67 v (*vs.* S.C.E.). Cohen *et al.*[4] studied similar reductions polarographically; the lowest related $E_{\frac{1}{2}}$ values they offer for aqueous media are about −1·70 v (*vs.* a Hg pool anode) with a nonaqueous medium giving even higher values. All aqueous media reductions were reported as single step for complete reduction. Elving and Leone[5] have studied the polarographic reduction of phenacyl fluoride in aqueous alcohol in detail and found the $E_{\frac{1}{2}}$ associated with the C–F fission to be pH dependent on the acid side, reporting values of $-0{\cdot}85$—$0{\cdot}94$ v (*vs.* S.C.E.) for the pH range of 4·0—4·5. These investigators stress the single step total C–F fission of the $CF_3$ group at any potential more negative than that required for the monofluoro-compound.

Our data require the stepwise loss of fluorine; fission of the second C–F bond would appear to be even more readily accomplished than that of the first, while the third C–F bond breaks somewhat less readily. The differences are clearly of the magnitude of hundredths of a volt ($-0{\cdot}89$ *vs.* $-0{\cdot}85$—$0{\cdot}94$, *vide supra*). Involvement of a α-keto-group in this ready hydrogenolysis seems to be indicated.

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