# Exhaustive hydrodefluorination of aryl trifluoromethyl ketones in a Zn—HOAc—DMF system

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Perfluoroalkyl groups are stable, as a rule, to the action of Zn or even Na in various reaction media.[1] However, a few examples of reductive substitution of α-fluorine atoms in carbonyl compounds and azomethine derivatives are known.[2,3] Boiling of 1,1,1-trifluoroacetophenone or 1,1,1,2,2-pentafluoropropiophenone with Zn in hydrochloric acid causes not only hydrodefluorination of both α-$CF_3$ and α-$CF_2$ fragments, but also reduction of carbonyl groups leading to ethylbenzene or 1,1,1-trifluoro-3-phenylpropane, respectively.[4]

We have found that some aryl trifluoromethyl ketones **1a—d** undergo smooth hydrodefluorination into the corresponding acetyl derivatives **2a—d** when treated with Zn and acetic acid in DMF (Table 1).

$$\underset{\mathbf{1a—d}}{ArCOCF_3} \xrightarrow[DMF]{Zn/HOAc} \underset{\mathbf{2a—d}}{ArCOMe} \qquad (1)$$

The products of the carbonyl group reduction have not been detected. Small amounts (5%) of monofluoro- and difluoromethyl ketones were detected in the reaction mixtures by TLC, $^1$H NMR, and mass spectrometry. Apparently, the process occurs as follows:

$$\mathbf{1} \xrightarrow{H^+} Ar\overset{+}{C}(OH)CF_3 \xrightarrow{e^-} Ar\dot{C}(OH)CF_3 \xrightarrow{e^-} Ar\bar{C}(OH)CF_3 \xrightarrow[-F^-]{} Ar\bar{C}(OH)=CF_2 \longrightarrow ArCOCHF_2 \longrightarrow \cdots \longrightarrow ArCOCH_2F \longrightarrow \cdots \longrightarrow \mathbf{2}$$

Thus, the reaction described is a unique example of regiospecific α-hydrodefluorination of a fluorine-containing moiety in aryl perfluoroalkyl ketones.

**Hydrodefluorination (general procedure).** A mixture of **1** (2 g), Zn dust (5 g), and AcOH (10 mL) in DMF (60 mL) was stirred at 20 or 50 °C (see Table 1). The process was monitored by TCL (benzene/ether, 10/1). The reaction mixture was then poured into water, product **2** was extracted with ether, and purified by recrystallization. Compounds **2** were identified with authentic samples (prepared by acetylation) according to IR, $^1$H NMR, and mass spectral data.

**Table 1.** Properties of compounds **2**

| Compound | Ar | Reaction conditions | | M.p./°C | IR, | $^1$H NMR | Yield |
|---|---|---|---|---|---|---|---|
| | | *t*/h | *T*/°C | | ν(CO)/cm$^{-1}$ | δ(COMe) | (%) |
| **2a** | 4-$Me_2NC_6H_4$ | 1.5 | 50 | 93—94 | 1662 | 2.31 | 78 |
| **2b** | 4-$Ph_2NC_6H_4$ | 0.5 | 50 | 132—133 | 1670 | 2.52 | 90 |
| **2c** | 9-Methylcarbazol-3-yl | 18 | 20 | 95—96 | 1667 | 2.53 | 82 |
| **2d** | 10-Methylphenothiazin-3-yl | 72 | 20 | 100—101 | 1675 | 2.42 | 51 |

## References

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