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PRELIMINARY NOTE

Conversion of Fluorocarbon Olefins into Perfluoro-ketoximes

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SUMMARY

Treatment of perfluoro-2-nitrosopropane and perfluoronitrosocyclobutane with aqueous potassium bisulphite yields the oximes of perfluoroacetone and perfluorocyclobutanone, respectively; the nitroso-compounds are easily prepared <u>via</u> indirect addition of nitrosyl fluoride across the double bonds in perfluoropropene and perfluorocyclobutene.

Whilst investigating the synthesis of fluorocarbon analogues $[R_FN(\dot{O})SO_3^-]$ of Fremy's radical $[\cdot ON(SO_3^-)_2]$ [1] we have stumbled on an attractive alternative [since neither hydrogen fluoride nor hydrogen under pressure is involved (see Route 1)] to the long-established Russian method (Route 2 [2]) for the conversion of perfluoropropene into perfluoroacetone oxime. Application of the method to perfluorocyclobutene provided the oxime of perfluorocyclobutanone (nc) in 45% overall yield (not optimized), so the synthetic route $R_FCF{=}CFR'_F \longrightarrow [R_FCFAgCF_2R'_F] \longrightarrow R_FCF(NO)CF_2R'_F \longrightarrow R_FC({=}NOH)CF_2R'_F$ (R_F = perfluoroalkyl, R'_F = F or perfluoroalkyl, $R_FR'_F$ = α,ω-perfluoropolymethylene) should prove to be a general one in fluorocarbon chemistry.

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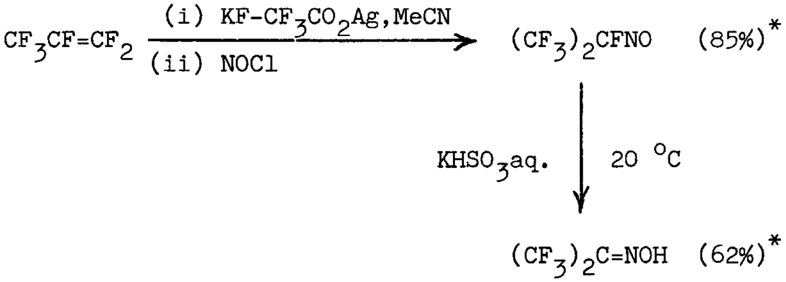
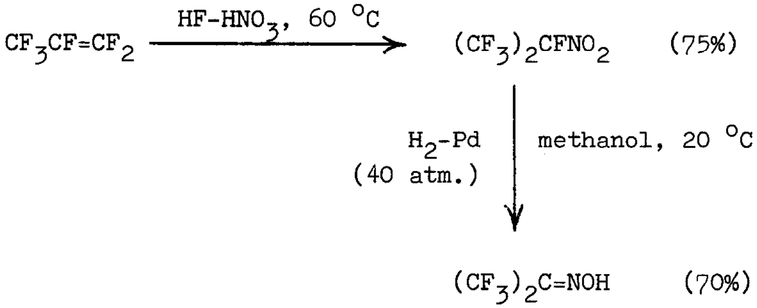


$$\begin{tikzcd}[column sep=large]
CF_3CF{=}CF_2 \arrow[r, "\text{(i) } KF\text{-}CF_3CO_2Ag\text{, }MeCN", "\text{(ii) } NOCl"'] & (CF_3)_2CFNO \quad (85\%)^* \arrow[d, "20\ ^\circ C", "KHSO_3aq."'] \\
 & (CF_3)_2C{=}NOH \quad (62\%)^*
\end{tikzcd}$$

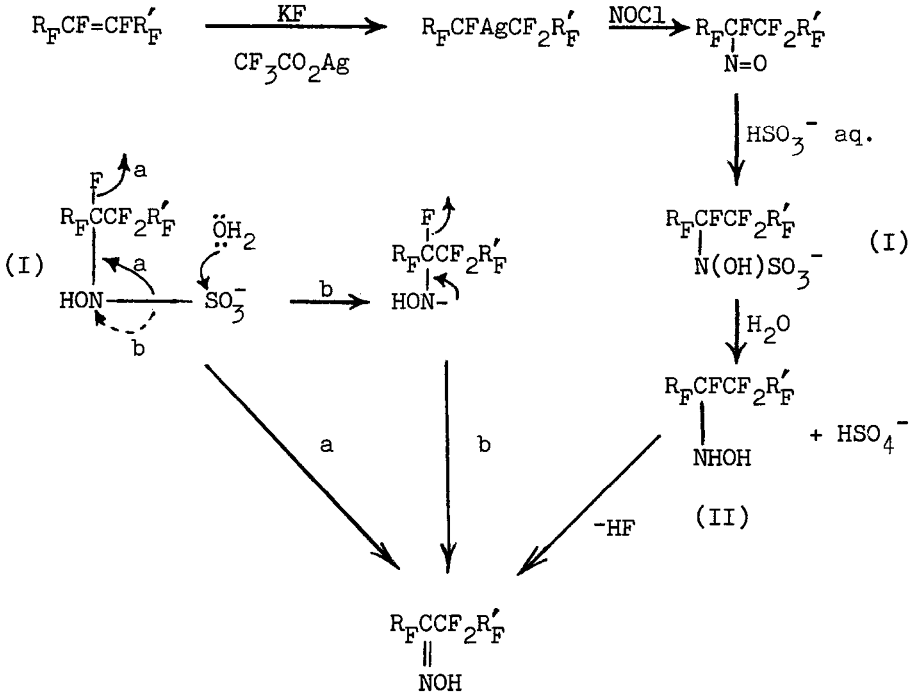
Route 1 (*Yields were not optimized.)



$$\begin{tikzcd}[column sep=large]
CF_3CF{=}CF_2 \arrow[r, "HF\text{-}HNO_3\text{, } 60\ ^\circ C"] & (CF_3)_2CFNO_2 \quad (75\%) \arrow[d, "\text{methanol, } 20\ ^\circ C", "\begin{array}{c}H_2\text{-}Pd\\(40\text{ atm.})\end{array}"'] \\
 & (CF_3)_2C{=}NOH \quad (70\%)
\end{tikzcd}$$

Route 2 [2]

Mechanistically, we suppose that the second stage of the route involves dehydrofluorination of a hydroxylamine (II), although it is conceivable that a more direct defluorosulphonation of the bisulphite addition compound (I) formed initially [_cf_. ref. 1] occurs (see the Scheme). The method employed to convert perfluoropropene and perfluorocyclobutene into the perfluoronitrosoalkane precursors of the oximes stems from other work on perfluoroalkylsilver compounds [3]; we consider it to be more convenient than the perfluoroölefin-NOF-KF route [4] and have also employed it to effect the conversion $(CF_3)_2C{=}CF_2 \longrightarrow (CF_3)_3CNO$.



$R_F = CF_3$, $R'_F = F$; $R_FR'_F = CF_2\text{-}CF_2$

Scheme

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