REDUCTIVE DEFLUORINATION OF HEXAFLUOROACETONE AND ITS ANIL

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Reductive dehalogenation by the action of metals, which is characteristic for α -halocarbonyl compounds, has not been reported for perfluorinated compounds.

We have found that the reaction of hexafluoroacetone (HFA) with magnesium gives defluorination with the formation of products of the transformations of the enolate of pentafluoroacetone in addition hydrodimerization [1] to give perfluoropinacol (I).

$$(CF_3)_2C = O \xrightarrow{M_{\mathbb{C}}}_{\text{IHF}, -F^-} CF_3C = CF_2 \xrightarrow{\text{HFA}, H^+}_{\downarrow} CF_3COCF_2C(CF_3)_2 \xrightarrow{M_{\mathbb{G}}, H^+}_{\downarrow} CF_3COCFHC(CF_3)_2 \xrightarrow{I}_{\downarrow} (III) OH (III) OH$$

A sample of 6.5 g HFA was added to a mixture of 0.6 g magnesium and 0.2 g HgCl₂ in 25 ml abs. THF below 30°C. After 1 h, the mixture was evaporated in vacuum. Distillation of the residue over conc. H₂SO₄ gave 4.7 g of a mixture containing 52% (I), 22% (II) [2], and 26% (III) as indicated by gas—liquid chromatography. Hydroxyketone (III) was isolated by preparative gas—liquid chromatography, bp 104°C. Found: C 24.76; H 0.81; F 64.14%. Calculated for C₆H₂F₁₀O₂: C 24.32; H 0.68; F 64.19%. PMR spectrum (δ , ppm): 4.5 s (OH), 5.7 d (CH), J = 45 Hz. ¹⁹F NMR spectrum (ppm from CF₃CO₂H): -3.3 m (F¹), -0.2 m (F⁵), 131 m (F²).

In support of this scheme, $CF_3C(OH)=CF_2$ [3] was isolated in 40% yield from the reaction of HFA with Al/HgCl₂ in addition to (I)-(III). The reaction of HFA anil with Zn/HgCl₂ leads to enamine (IV) [4] in 80% yield, mp 70°C (12 mm). PMR spectrum: 4.0 br. s (NH), 6.6 m (Ph). ¹⁹F NMR spectrum: -12.4 d. d (F¹), 1.55 d. q (F³), 3.75 (F²), $J_{F1-F2} = 22.6$, $J_{F1-F3} = J_{F2-F3} =$ 9.8 Hz.



The study of this reaction demonstrates a new approach to the generation of mesomeric anions from fluorine-containing carbonyl compounds and their heteroanalogs.

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