The Sulfinatodehalogenation Reaction of α,α-Difluorobenzyl Halides with Sodium Dithionite

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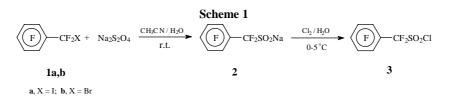
Abstract: The sulfinatodehalogenation reaction of α , α -difluorobenzyl halides, ArCF₂X (Ar = C₆F₅, C₆H₅; X = Br, I), with sodium dithionite took place readily in aqueous acetonitrile under mild conditions, giving the corresponding sodium sulfinate. The 1:1 adducts were obtained when alkenes were added to the reaction system in some cases.

Keywords: Sulfinatodehalogenation, Sodium dithionite, α , α -Difluorobenzyl halide, Alkene.

Since the discovery of the first sulfinatodehalogenation reaction in 1981¹, great efforts have been devoted to this useful reaction. The substrates have been expanded from perfluoroalkyl iodide (R_FI) to per- and poly-fluoroalkyl halides (R_FX, X = Br, I; R_FCCl₃), and many sulfinatodehalogenating reagents such as Na₂S₂O₄, HOCH₂SO₂Na, H₂NC(=NH)SO₂H and Na₂S₂O₅ have been developed². Recently, the sulfinatodehalogenation of 2,2,2-trifluoroethyl halides was accomplished by Chen *et al.*³ However, this reaction is confined to polyhaloalkyl halides till now. The sulfinatodehalogenation reaction of polyhalobenzene and benzyl halides was rarely explored. Herein we report the preliminary results on the sulfinatodehalogenation reaction of some α, α -difluorobenzyl halides with sodium dithionite.

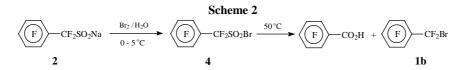
Using acetonitrile as a cosolvent, both heptafluorobenzyl iodide **1a** and bromide **1b** reacted with $Na_2S_2O_4$ readily at room temperature, giving the corresponding sodium sulfinate **2** in high yield (**Scheme 1**). Sodium bicarbonate was added in this reaction to keep the reaction medium slightly basic as usual⁴. The sulfinate was isolated and characterized by converting it to its corresponding sulforyl chloride **3** with chlorine.

Bromination of **2** in aqueous solution with Br_2 at 0-5°C gave the sulfonyl bromide **4**, which was converted to pentafluorobenzoic acid (80%) and heptafluorobenzyl bromide (**1b**, 20%) at 50°C as shown by ¹⁹F NMR (**Scheme 2**).

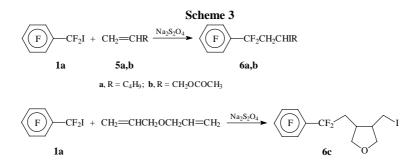


The sulfinatodehalogenation reaction can be successfully applied to perfluoro-benzylation of alkenes. Thus, treatment of **1a** with 1-alkenes **5**, $Na_2S_2O_4$ and $NaHCO_3$ in aqueous acetonitrile at room temperature gave the corresponding 1:1 addutes

6 in 75-86% isolated yield (Scheme 3). When diallyl ether was used in the reaction, the typical cyclized

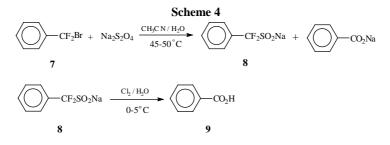


radical adduct 6c was obtained, indicating that a radical intermediate was involved in the above sulfinatodehalogenation reaction. In the case of 1b, the addition reaction did not occur under similar conditions, and compound 2 was formed as the major product.



Similarly, α, α -difluorobenzyl bromide 7 was also able to undergo the sulfinaodehalogenation reaction at 45-50°C to give the sulfinate 8 in 50% isolated yield. Sodium benzoate was formed as a by-product in this reaction (Scheme 4). Unlike compound 2, the reaction of 7 with chlorine in aqueous solution at 0-5°C gave benzoic acid 9 instead of the corresponding sulfonyl chloride.

In conclusion, the sulfinatodehalogenation of some α, α -difluorobenzyl halides has been achieved by reacting with sodium dithionite under mild conditions, providing a facile method for the synthesis of perfluorobenzyl-containing compounds.



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References

- 1. B.N. Huang, W.Y. Huang and C.M. Hu, *Acta Chimica Sinica*, **1981**, *39*, 481. 2. W.Y. Huang and F.H. Wu, *Israel J. Chem.*, **1999**, *39*, 167.
- 3. Z.Y. Long and Q.Y. Chen, Tetrahedron Lett., 1998, 39, 8487.
- 4. W.Y. Huang, B.N. Huang and W. Wang, Acta Chimica Sinica (Engl. Ed.), 1985, 252.

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