

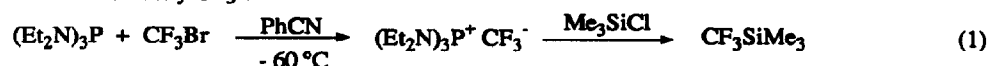
An Efficient Inexpensive Electrochemical Preparation of Ruppert's Reagent

Frédéric Aymard, Jean-Yves Nédélec*, and Jacques Périchon

Laboratoire d'Electrochimie, Catalyse et Synthèse Organique
 CNRS, 2, Rue Henri Dunant, 94320 Thiais, France

Abstract : The electrochemical reduction of CF₃Br in *N,N*-dimethylformamide (DMF) in the presence of Me₃SiCl and a sacrificial aluminum anode provides Me₃SiCF₃ in *ca* 90 % faradaic yields.

CF₃SiMe₃ (Ruppert's reagent) has now become the most convenient reagent for introducing a trifluoromethyl group via the fluoride-ion catalyzed addition to carbonyl^{1,2} or to sulfonyl groups,³ or the Cu-mediated coupling with halocompounds.⁴ Its widespread use, however, remains limited by the lack of convenient and inexpensive method for its preparation. The Ruppert's method published in 1984⁵ indeed involves the use of expensive tris(diethylamino)phosphine (eq 1). An alternative method proposed later involves the use of the costly CF₃I.⁶



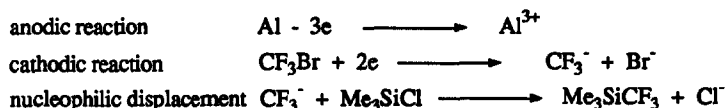
We propose in this note an inexpensive method based on the already described C-Si bond formation by electroreductive cross-coupling between halocompounds and chlorosilanes according to the sacrificial anode process.⁷ We will show that we can now prepare easily and efficiently the Ruppert's reagent by simply reducing electrochemically a mixture of CF₃Br and Me₃SiCl in DMF.

The peculiar reactivity of perfluoroalkyl groups, notably CF₃, already investigated by us⁸ prompted us to select a convenient anode which would not lead to unreactive organometallic intermediates. With respect to this we found that the reduction of CF₃Br in the presence of aluminum anode produces a reactive trifluoromethyl anion without forming an alkyl aluminum intermediate. In the absence of a reactive electrophile the main reaction is the formation of trifluoroacetaldehyde.⁹ We now found that Me₃SiCl is reactive enough to nearly suppress this reaction and lead to CF₃SiMe₃ in *ca* 90 % yield vs the charge passed, according to a two electron reduction process.

The reaction is conducted in a cylindrical undivided cell, fitted with aluminum rod as anode and a nickel foam cathode (area 20 cm²). The solution of DMF (40 ml) containing NBu₄Br (0.05 mol l⁻¹) is first saturated in CF₃Br by bubbling it at -15 °C. The CF₃Br concentration thus obtained is about 0.4 mol l⁻¹. Me₃SiCl (1 mol l⁻¹; 40 mmol) is then added and a charge of *ca* 3500-4000 C corresponding to the conversion of 20 mmol of Me₃SiCl is then passed at constant current density (1 A/dm²), and keeping a slow bubbling of

CF₃Br and a low - 15 °C temperature during the electrolysis. The progress of the reaction is conveniently monitored by ¹⁹F NMR analysis using PhCF₃ or CF₃CCl₃ as internal standard.

The mechanism can be described as follows, on the basis of an easier reduction¹⁰ of CF₃Br compared to Me₃SiCl :



The product was first tentatively isolated from the collected organic phases by trap-to-trap distillation under vacuum (ca 20 mm) with mild warming according to the described procedure.² This led to a mixture of CF₃SiMe₃, along with (Me₃Si)₂ which is formed concurrently in 10-15 %. It was then necessary to remove this by-product and this can be done by simply reacting the crude electrolytic solution with excess I₂ at 65 °C for 1.5 h. This is the way already described to cleave the Si-Si bond.¹² Unreacted I₂ can be easily removed by washing with aq 1M Na₂S₂O₃. Trap-to-trap distillation can then enable to isolate the Ruppert's reagent as a > 95 % pure product.

Me₃SiCl is not easily reduced. Its dimer can however form in the experimental conditions, likely via the formation of the corresponding bromide through a Br-Cl exchange favoured by the presence of aluminum ions, as already observed in the case of alkyl halides.¹³

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