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An Efficient Inexpensive Electrochemical Preparation of Ruppert's Reagent

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Abstract : The electrochemical reduction of CF_3Br in N,N-dimethylformamide (DMF) in the presence of Me_3SiCl and a sacrificial aluminum anode provides Me_3SiCF_3 in *ca* 90 % faradaic yields.

CF_3SiMe_3 (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 1984[5] indeed involves the use of expensive tris(diethylamino)phosphine (eq 1). An alternative method proposed later involves the use of the costly CF_3I.[6]

$$(Et_2N)_3P + CF_3Br \xrightarrow[-60\,°C]{PhCN} (Et_2N)_3P^+ CF_3^- \xrightarrow{Me_3SiCl} CF_3SiMe_3 \qquad (1)$$

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 CF_3Br and Me_3SiCl in DMF.

The peculiar reactivity of perfluoroalkyl groups, notably CF_3, already investigated by us[8] 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 CF_3Br 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 trifluroacetaldehyde.[9] We now found that Me_3SiCl is reactive enough to nearly suppress this reaction and lead to CF_3SiMe_3 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 cm^2). The solution of DMF (40 ml) containing NBu_4Br (0.05 mol l^{-1}) is first saturated in CF_3Br by bubling it at - 15 °C. The CF_3Br concentration thus obtained is about 0.4 mol l^{-1}. Me_3SiCl (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 Me_3SiCl is then passed at constant current density (1 A/dm^2), and keeping a slow bubling of

CF_3Br and a low - 15 °C temperature during the electrolysis. The progress of the reaction is conveniently monitored by ^{19}F NMR analysis using $PhCF_3$ or CF_3CCl_3 as internal standard.

The mechanism can be described as follows, on the basis of an easier reduction[10] of CF_3Br compared to Me_3SiCl :

$$\begin{array}{lll} \text{anodic reaction} & Al - 3e \longrightarrow & Al^{3+} \\ \text{cathodic reaction} & CF_3Br + 2e \longrightarrow & CF_3^- + Br^- \\ \text{nucleophilic displacement} & CF_3^- + Me_3SiCl \longrightarrow & Me_3SiCF_3 + Cl^- \end{array}$$

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 CF_3SiMe_3, along with $(Me_3Si)_2$ which is formed concurently 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 I_2 at 65 °C for 1.5 h. This is the way already described to cleave the Si-Si bond.[12] Unreacted I_2 can be easily removed by washing with aq 1M $Na_2S_2O_3$. Trap-to-trap distillation can then enable to isolate the Ruppert's reagent as a > 95 % pure product.

Me_3SiCl 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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