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ELECTROCHEMICAL TRIFLUOROMETHYLATION OF CARBONYL COMPOUNDS

S. SIBILLE, S. MCHAREK and J. PERICHON

Laboratoire d'Electrochimie, Catalyse et Synthèse Organique (U.M. n° 28)
C.N.R.S., 2, rue Henri Dunant 94320 THIAIS (France)

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Abstract - The electroreduction of CF_3Br in DMF containing aldehydes or ketones, using a sacrificial zinc anode, affords the corresponding trifluoromethyl alcohols together with the unreactive organozinc species CF_3ZnBr and $(CF_3)_2Zn$. The alcohols are obtained with good yields from aldehydes. With ketones the organozinc species are formed preferentially to the alcohols, but the addition of tetramethylethylene-diamine allows the alcohols to form with moderate yields.

Direct introduction of the trifluoromethyl group on organic molecules from halotrifluoromethanes is a challenge due to the low reactivity or low stability of trifluoromethyl metallic species. However, recent work has pointed out the suitability of the Barbier procedure using zinc powder, trifluorohalomethanes and carbonyl compounds to synthetize trifluoromethyl alcohols (1-4). Whereas interesting yields can be obtained from CF_3I under ultrasonic irradiation(1), CF_3Br is much less reactive, especially when ketones are used as substrates (2), and even in the presence of a catalyst (3), the alcohols do not form with good yields.

We have recently reported that the electrosynthesis of alcohols could be achieved with good yields from organic halides and carbonyl compounds in an undivided cell using sacrificial anodes of magnesium, aluminium or zinc (5). With bromotrifluoromethane a zinc anode was used. The electrochemical reactions can be written as follows :

$$Zn \longrightarrow Zn^{2+} + 2e \quad \text{for the anodic process,}$$

$$CF_3Br + \rangle C{=}O + 2e \longrightarrow CF_3\text{-}\overset{|}{\underset{|}{C}}\text{-}O^- + Br^- \quad \text{for the cathodic one,}$$

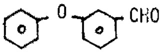
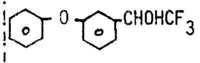
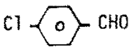
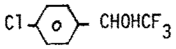
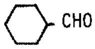
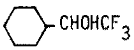
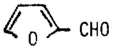
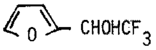
the overall reaction, including the anode consumption being then an electroassisted Barbier reaction :

$$CF_3Br + \rangle C{=}O + Zn \xrightarrow{e} CF_3\text{-}\overset{|}{\underset{|}{C}}\text{-}O^- + Br^- + Zn^{2+}$$

We have shown that the electroreductive coupling of bromotrifluoromethane with such aldehydes as benzaldehyde and octanal gave the expected alcohols with nearly quantitative yields, but poor results were obtained with ketones. In view of the synthetic utility of our electrochemical procedure applied to fluorinated compounds, we now studied the electroreduction of CF_3Br in DMF and its reductive coupling with other aldehydes as well as ketones.

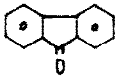
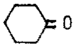
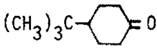
When CF_3Br is allowed to reduce at a nickel cathode in a 0.2-1M aldehyde solution in DMF, using a zinc anode, fluorinated alcohols are formed with excellent chemical (table I) and faradic yields (2.0 to 2.5 F/mole of aldehyde are needed). The use of zinc as anodic material is essential for the coupling process : replacement of zinc by magnesium or aluminium gave very poor results, and, in the case of benzaldehyde, pinacol and benzoin formation occured in large extents.

Table I : Electroreductive coupling of CF_3Br with aldehydes

RCHO	Product	Isolated yield %
PhCHO	$PhCHOHCF_3$	95
		90
		90
		70
$(CH_3)_3CCHO$	$(CH_3)_3CCHOHCF_3$	80
$CH_3(CH_2)_5CHO$	$CH_3(CH_2)_5CHOHCF_3$	80
		50
PhCHO(a)	$PhCHOHCF_3$	21
PhCHO(b)	$PhCHOHCF_3$	33

(a) an aluminium anode is used instead of zinc
(b) a magnesium anode is used

Table II : Electroreductive coupling of CF_3Br with ketones

Entry	Ketone	Solvent	Alcohol % (isolated yield)
1	PhCOPh	DMF	57 %
2		DMF	30 %
3	$O{=}C(CH_2Cl)_2$	DMF	31 %
4		DMF	5 %
5	$PhCOCH_3$	DMF	5 %
6	$PhCOCH_3$	Pyridine	5 %
7	$PhCOCH_3$	DMF + TMEDA 30 %	16 %
8	$PhCOCH_3$ a)	DMF + TMEDA 30 %	37 %
9		DMF + TMEDA 30 %	25 %
10	$PhCH_2CH_2COCH_3$	DMF + TMEDA 30 %	33 %
11	 a)	DMF + TMEDA 30 %	32 % b)
12	$PhCOCO_2CH_3$	DMF + TMEDA 30 %	45 %

a) 5 mmol $ZnBr_2$ added ; *b) mixture of cis-trans isomers*

In the same conditions, trifluoromethylated alcohols could not be obtained with good yields from ketones, excepted for the easily reducible ones, such as benzophenone, fluorenone or 1,3-dichloroacetone (Table II, entries 1,2,3). With cyclohexanone or acetophenone, yields are about 5 % at 2F/mole. Higher yields (15-20 %) can be obtained by carrying on the electrolysis up to 15-20 F/mole of ketone. The nature of the by-products depends strongly on both the nature of the ketone and the electrolysis conditions. Following the case, large amounts of unreacted ketone are recovered, pinacols are formed (from aromatic ketones) or base-catalyzed condensation occurs (from aliphatic ketones, upon prolonged electrolysis). No degradation of the trifluoromethylalcoholates is noticed, even with very long electrolysis.

Changing DMF by pyridine, which proved to be a better solvent in the Barbier procedure (2) did not give better results (entry 6). The addition to DMF of tetramethylethylene-diamine (TMEDA), a powerful complexing agent for the Zn^{++} cation, led to a great improvement in the yield of alcohol, up to 20 % (entry 7). Moreover, when $ZnBr_2$ was added to the DMF-TMEDA mixture, the yield increased to 35-40 % (Table II, entries 8,11).

Faradic yields are not so good as in the case of aldehydes and up to 6F/mole of ketone can be needed until no more alcoholate forms. The main by-product in the case of acetophenone is pinacol. With aliphatic ketones it is β-cetol or further condensation products, large amounts of unreacted ketone being however always recovered.

Spectroscopic (^{19}F NMR) and electrochemical experiments give some informations about the reduction process of CF_3Br and the role played by Zn(II) ions and TMEDA.

As seen by ^{19}F NMR of the DMF solution, the reduction products, when CF_3Br is allowed to reduce at a nickel cathode, using a zinc anode, are first CHF_3 (δ=78.4 ppm, J_{H-F}=85Hz), arising from residual water, and then the organometallic species $(CF_3)_2Zn$ and CF_3ZnBr, together with fluorinated products arising from attack on DMF. The faradic yield, after 5000 C (quantity of electricity required to reduce 25 mmoles of CF_3Br at 2F/mole) is 70 % for both organozinc compounds.

The ^{19}F NMR chemical shifts (δ=38.7 ppm) of $(CF_3)_2Zn$ and (δ=39.4 ppm) of CF_3ZnBr are consistent with the published observations (6). Upon addition of $ZnBr_2$ to the DMF solution, slow equilibration is observed between both species. We have extracted these organozinc species as a mixture of their pyridine complexes and the ^1H NMR shifts of ligated pyridine are also compatible with previous description (7).

The organozinc complexes are particularly unreactive even towards water ; they are stable for days in DMF, and do not react with benzaldehyde or carbon dioxide, although $PhCHOHCF_3$ and CF_3CO_2H are obtained in high yield when the electrolysis of CF_3Br is performed in the presence of PhCHO or CO_2 (8). Thus they cannot be the intermediates involved in the coupling reaction leading to the fluorinated alcohols.

The differences in reactivity between aldehydes (PhCHO) and ketones ($PhCOCH_3$) are explained by ^{19}F NMR of the DMF solutions containing CF_3Br and the carbonyl compound during electrolysis. Apart the fact that CHF_3 forms in very large amounts when an enolizable ketone is present in the solution, the main difference between aldehydes and ketones is that the organozinc species are formed after the alcohol when the substrate is an aldehyde, and before the alcohol when the substrate is a ketone. Thus the observed reaction products are formed in the following order :

$$CHF_3 + OH^- > RCH(O^-)CF_3 > CHF_3 + \text{enolate} > \text{organozinc species} > R_1R_2\ C(O^-)CF_3$$

Addition of TMEDA to a ketone solution does not affect CHF_3 formation, but enables the alcohol to form before the organozinc species, which can be detected only at the end of the electrolysis, when most of the ketone has been consumed.

Also, the favourable effect of TMEDA upon the coupling reaction may be due to some inhibition in the formation of organozinc species, but the effect of addition of $ZnBr_2$ upon the coupling reaction remains unclear.

Preliminary voltametric experiments show that CF_3Br is a very easily reducible halide ; half-wave potentials at a rotating electrode are very dependent on both the nature of the electrode and the concentration of depolarizer. They range from -1.1 V/ SCE(CF_3Br 10^{-3}M) to -1.6 V/SCE (CF_3Br $2 10^{-2}$M) at a gold electrode, while at a nickel cathode (our working electrode), the wave is very badly defined and extends from -1.3 to -2.0 V/ SCE $ZnBr_2$ reduces in two steps involving bromide exchange at -1.45 V/SCE ($ZnBr_2/Zn\downarrow$) and -1.8 V/ECS ($ZnBr_3^-/Zn\downarrow$). The deposited metal can be oxized -1.1 V/SCE.

In $CF_3Br/ZnBr_2$ mixtures, CF_3Br reduction is inhibited and, on the reverse scan, the reoxidation peak of the deposited metal (Zn) has completely desappeared.

With TMEDA as cosolvent, Zn(II) reduction becomes very irreversible and CF_3Br reduction is also completely inhibited by $ZnBr_2$. The Zn(II) reduction occurs with sudden depassivation of the electrode around -1.7 to -1.9 V/SCE, no reoxidation peak of the deposited metal being observed.

The electrosynthesis of organozinc species using a sacrificial zinc anode has been already described (9) and an anodic mechanism has been proposed. However our results suggest that the formation of organozinc species could be a cathodic process : we propose that, although CF_3Br is very easily reducible, the reducible species in the sacrificial zinc anode system is Zn(II). The highly reactive metal deposit would react with CF_3Br either to form the organozinc species in a classical organometallic way, or to form the addition compound to a reactive carbonyl in a typical Barbier procedure :

$$Zn(II) + 2e \longrightarrow Zn(0)$$

$$\text{followed by : } Zn(0) + CF_3Br \longrightarrow CF_3ZnBr$$

$$\text{or : } Zn(0) + CF_3Br + \rangle C{=}O \longrightarrow CF_3\overset{|}{\underset{|}{C}}-O^- + ZnBr^+$$

The addition of TMEDA would lead to a considerably more active deposit, may be due to the irreversibility of Zn(II)/Zn(0) couple.

In conclusion, the electrochemical addition of the CF_3 moiety from CF_3Br to carbonyl compounds compares favourably with the chemical procedures, leading to secondary alcohols with excellent yields and to tertiary alcohols with lower but still interesting yields. The limitation in the case of the addition to ketones is the formation of trifluoromethyl zinc species.

The importance of the choice of zinc as the anodic material is related to the electrochemical process which could consist in the cathodic deposition of the metal followed by a Barbier-type reaction. Electrochemistry appears then as an interesting and simple way to obtain activated metals. Electrochemical work is actually in progress in order to confirm the proposed mechanism and to find other complexing agents for Zn(II) which would be able to inhibit more strongly the formation of the organozinc species.

EXPERIMENTAL

General Procedure for electrosynthesis

The solvent N,N-dimethylformamide was dried over calcium hydride and distilled over anhydrous copper sulfate, under reduced pressure, before use. The supporting electrolyte (NBu_4Br) and the carbonyl compounds were commercial products. Tetramethylethylenediamine was stored over barium oxide.

The electrolysis cell is a cylindric glass vessel (35 to 50 ml). The anode is a commercially available zinc rod (12.7 mm diameter) disposed along the axis of the cell. It is surrounded by a foamy nickel cathode (20 cm^2 area).

To 30 ml DMF or DMF-TMEDA mixture are added NBu_4Br (1 mmol) and the carbonyl compound (20 mmol). The cell is immersed in a cold bath at -10° C in order to avoid excessive heating due to the Joule effect and to ensure sufficient solubility of CF_3Br. CF_3Br is bubbled at atmospheric pressure through the solution. A constant intensity of 0.3A is applied between the two electrodes.

The reaction is followed by GLC analysis and the electrolysis is run until 90 -100 % of the carbonyl compound has disappeared : 4000 to 5000 C (4 to 5 hours) are needed for 20 mmol of aldehyde ; 8000 to 12000 C (8 to 12 hours) for 20 mmol of ketone.

The DMF solution is hydrolyzed with 6N aqueous HCl and extracted with diethylether, the organic phase is washed with water and dried over $MgSO_4$. After removal of the solvent, the crude product is purified by colomn chromatography (silica, pentane : ether 85 : 15). Isolated yields of alcohols are related to the initial carbonyl compound.

Compounds identification

^1H and ^{19}F NMR spectra of the isolated alcohols were recorded on a Varian T60 spectrometer, with Me_4Si or CF_3CO_2H as internal standards. ^{19}F chemical shifts are referenced to $CFCl_3$ (CF_3CO_2H at 76.5 ppm). IR spectra were obtained from a Perkin Elmer 577 spectrophotometer (NaCl disks).

Mass spectra were obtained by using a Finnigan ITD 850 spectrometer connected to a GC chromatograph (DB1 capillary column).

2,2,2-Trifluoro-1-Phenylethanol(4) : ^1H NMR($CDCl_3$) : 7.5-7.4(m, 5H), 5.0(q, 1H), 3.15(OH). ^{19}F NMR($CDCl_3$) : 78.95(d). J_{H-F}=7.5 Hz. Mass : 176(M, 2), 159(M-17, 10), 107(M-69, 100), 79(M-97, 65). IR(neat) : 3400, 1500, 1460, 1270, 1180, 1130 cm^{-1}.

2,2,2-Trifluoro-1-(3-phenoxy-phenyl)ethanol : ^1H NMR($CDCl_3$) : 7.4-6.8(m, 9H), 4.85(q, 1H), 3.65(OH). ^{19}F NMF($CDCl_3$) : 78.4(d). J_{H-F}=7.5 Hz. IR(neat) : 3450, 1585, 1490, 1250, 1180, 1130 cm^{-1} Mass : 268(M, 100), 199(M-69, 30), 171(M-97, 49). Calc. for $C_{14}H_{11}F_3O_2$: C, 62.69 ; H, 4.13 ; F, 21.25 %. Found : C, 62.41 ; H, 4.21 ; F, 21.28 %.

2,2,2-Trifluoro-1-(4-Chlorophenyl)ethanol : ^1H NMR 7.45-7.3(m, 4H), 5.0(q, 1H), 3.1(OH). ^{19}F NMR 79.4(d). J_{H-F}=7 Hz. IR(neat) 3400, 1605, 1500, 1270, 1175, 1135 cm^{-1}. Mass : 210, 212(M, 80, 28), 141, 143(M-69, 100, 79), 113, 115(M-97, 44, 12), 77(97). Calc. for $C_8H_6ClF_3O$: C, 45.63 ; H, 2.87 ; Cl, 16.84 ; F, 27.07 %. Found : C, 45,40 ; H, 3.04 ; Cl, 16.14 ; F, 26.96 %.

1,1,1-Trifluoro-3,3-dimethylbutan -2-ol : ^1H NMR($CDCl_3$) ; 3.6(q, 1H), 2.65(OH), 1.1(s, 9H). ^{19}F NMR($CDCl_3$) : 72.4(d). J_{H-F}=8 Hz. IR(neat) : 3420, 1280, 1165, 1120 cm^{-1}. Mass : 139(M-17, 8), 57(100). Calc. for $C_6H_{11}F_3O$: C, 46.15 ; H, 7.10 ; F, 36.50 %. Found : C, 45.90 ; H, 7.19 ; F, 35.45 %.

1,1,1-Trifluorooctan-2-ol : ^1H NMR($CDCl_3$) : 4.2-3.5(m, 1H),2.8(OH), 1.8-0.8(m, 13H). ^{19}F NMR ($CDCl_3$) : 80.6(d). J_{H-F}=7.5 Hz. IR(neat) : 3380, 1280, 1175, 1145 cm^{-1}. Mass : 97(M-69-18, 16), 70(62), 69(31), 55(100). $CH_3(CH_2)_5CHOHCF_3$ was acetylated (CH_3COCl, pyridine) for elementary analysis. Calc. for $C_{10}H_{17}F_3O_2$: C, 53.09 ; H, 7.57 ; F, 25.19 %. Found : C, 53.40 ; H, 7.54 ; F, 25.25 %.

2,2,2-Trifluoro-1-(2-furyl)-ethanol : ^1H NMR : 7.45(m, 1H), 6.6-6.35(m, 2H), 5.05(q, 1H), 3.3(OH). ^{19}F NMR : 78.4(d). J_{H-F}=7 Hz. IR(neat) : 3390, 1505, 1270, 1180, 1155, 1130 cm^{-1}. Mass : 166(M, 34), 149(M-17, 30), 97(M-69, 100), 69(38). Calc. for $C_6H_5F_3O_2$: C, 43.39 ; H, 3.03 ; F, 34.31 %. Found : C, 43.16 ; H, 3.12 ; F, 34.56 %.

2,2,2-Trifluoro-1-cyclohexylethanol : ^1H NMR($CDCl_3$) : 4.0-3.4(m, 1H), 3.3(OH), 2.1-1.1(m, 11H). ^{19}F NMR : 76.6(d). J_{H-F}= 8 Hz. IR(neat) : 3420, 1455, 1280, 1165, 1130 cm^{-1}. Mass : 165(M-17, 1), 164(M-18, 1.6), 95(M-18-69, 6), 83(71), 55(100). Calc. for $C_8H_{13}F_3O$: C, 52.74 ; H, 7.19 ; F, 31.28 %. Found : C, 53.00 ; H, 7.35 ; F, 30.24 %.

2,2,2-Trifluoromethyl-1,1-diphenylethanol : mp : 73.5-74° C (lit. : 74° C (10)). ^1H NMR : 7.5-7.1(m, 10H), 2.8(OH). ^{19}F NMR : 75.15(s) (lit. : 75 (10)). IR($CDCl_3$) : 3585, 1455, 1280, 1180 cm^{-1} Mass : 252(M, 1.4), 235(M-17, 8), 183(M-69, 87), 105(100).

9-Trifluoromethyl fluoren-9-ol : mp : 83-85° C. ^1H NMR($CDCl_3$) 7.8-7.1(m, 8H), 2.8(OH). ^{19}F NMR ($CDCl_3$) 76.65(s). IR($CDCl_3$) : 3600, 1480, 1460, 1235, 1180 cm^{-1}. Mass : 250(M, 53), 181(M-69, 100), 153(32), 152(35). Calc. for $C_{14}H_9F_3O$: C, 67.20 ; H, 3.62 ; F, 22.78 %. Found : C, 67.43 ; H, 3.77 ; F, 22.34 % .

1,3-dichloro-2 trifluoromethylpropan-2-ol : ^1H NMR : 3.85(s, 4H), 3.15(OH). ^{19}F NMR : 77.5(s). IR(neat) : 3530, 1440, 1325, 1190, 1120 cm^{-1}. Mass : 197, 199, 201(M+1, 28, 14, 3.8), 179(M-17, 8.4) 147, 149(M-CH_2Cl, 39, 10), 127, 129(M-CF_3, 32, 9), 77(100). Calc. for $C_4H_5Cl_2F_3O$: C, 24.39 ; H, 2.56 ; Cl, 35.99 ; F, 28.93 %. Found : C, 23.84 ; H, 2.75 ; Cl, 35.67 ; F, 28.41 %.

1-Trifluoromehtyl-1-phenylethanol$^{(4)}$: ^{1}H NMR : 7.7-7.2(m, 5H), 3.2(OH), 1.7(3H). ^{19}F NMR : 81.6(s) IR(neat) : 3440, 1290, 1275, 1170 cm^{-1}. Mass : 173(M-17, 4), 121(M-69, 100), 105(22), 91(6), 77(25).

2-Trifluoromethyl-4-phenylbutan-2-ol : ^{1}H NMR : 7.4-7.15(5H), 3.0-2.6(m,2H), 2.25(OH), 2.2-1.8(m, 2H), 1.4(s, 3H). ^{19}F NMR : 83.55(s). IR(neat) : 3460, 1270, 1175, 1105 cm^{-1}. Mass : 218(M,11) 200(M-18, 25), 149(M-69, 1.8), 131(M-69-18, 85), 105(28), 91(100). Calc. for $C_{11}H_{13}F_3O$: C, 60.54 ; H, 6.00 ; F, 26.12 %. Found : C, 60.57 ; H, 6.28 ; F, 25.22 %.

1-Trifluoromethylcyclohexanol : mp 61.62° C. ^{1}H NMR($CDCl_3$) : 2.15(OH), 2.1-1.4(m, 10H). ^{19}F NMR($CDCl_3$) : 85.8(s). IR($CDCl_3$) : 3600, 1315, 1255, 1200, 1160 cm^{-1}. Mass : 99(M-69, 97), 81(M-69-18, 100), 69(14), 55(31). Calc. for $C_7H_{11}F_3O$: C, 49.99 ; H, 6.59 ; F, 33.89 %. Found : C, 49.91 ; H, 6.39 ; F, 34.20 %.

4-t-butyl-1-trifluoromethylcyclohexanol : The two isomers have been isolated in the ratio 80:20. Major isomer : mp 95.96° C. ^{1}H NMR : 2.3-2.1(m, 2H), 2.0(OH), 1.7-1.2(m,7H), 0.85(s,9H). ^{19}F NMR : 78.1(s) IR($CDCl_3$) : 3600, 1310, 1230, 1185, 1125, 1085 cm^{-1}.

Minor isomer : mp 49.50° C. ^{1}H NMR : 1.9-0.9(m, 9H), 1.7(OH), 0.85(s, 9H). ^{19}F NMR : 85.6(s). IR.($CDCl_3$) : 3600, 1315, 1260, 1180, 1130, 1115 cm^{-1}.

Mass (both isomers) : 57(100), 41(49). Calc. for $C_{11}H_{19}F_3O$: C, 58.91 ; H, 8.54 ; F, 25.41 %. Found (mixture of both isomers) : C, 58.52 ; H, 8.36 ; F, 25.38 %.

3,3,3-Trifluoro-2-phenyl-2-propanoic acid, methyl ester : ^{1}H NMR ($CDCl_3$) 7.9-7.7(m, 2H), 7.5-7.3 (m, 3H), 4.3(OH), 3.95(s, 3H). ^{19}F NMR($CDCl_3$) : 77.3(s). IR(neat) : 3480, 1750, 1245, 1175, 1135 cm^{-1}. Mass : 234(M, 12), 217(M-17, 26), 175(M-59, 24), 165(M-69, 2.5), 105(100), 77(22). Calc. for $C_{10}H_9F_3O_3$: C, 51.13 ; H, 3.87 ; F, 24.34 %. Found : C, 51.00 ; H, 3.91 ; F, 24.52.

Organozinc complexes

^{19}F NMR spectra were recorded at different times directly on aliquots of the electrolyzed solution, with $C_6H_5CF_3$ added for internal calibration ($PhCF_3$ at 63.7 ppm). At 5000 C , the DMF solution was rapidly hydrolyzed with diluted (2N) aqueous HCl and extracted with chloroform. 10 ml pyridine was added to the organic layer which was washed twice with water. Low pressure distillation gives a pale brown solid residue which was washed with benzene.

^{19}F NMR($CDCl_3$) : δ_{CF_3} = 39.1 and 39.6 (relative intensities $^1/3$: $^2/3$), corresponding to a 1:4 mixture of $(CF_3)_2Zn$ and CF_3ZnBr. ^{1}H NMR($CDCl_3$) : 8.8-8.5(2H), 8.2-7.8(1H), 7.7-7.4(2H).

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