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Direct Electroreduction or Use of an Electrogenerated Base : Two Ways for the Coupling of Polyhalogenated Compounds with Aldehydes or Ketones.

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Key Words : Polyhalogenated compounds - Electrochemical coupling with aldehydes - Electrogenerated bases.

Abstract : The electrochemical coupling of polyhalogenated compounds with carbonyl compounds is achieved in two ways. A carbanion RX_n^- is generated either by the direct electroreduction of RX_nCl or by deprotonation of RX_nH. In this latter case the base Ph^- is electrogenerated by reduction of iodobenzene. All electrolysis were carried out in an undivided cell fitted with a cadmium-coated cathode and an aluminium or magnesium sacrificial anode.

Introduction :

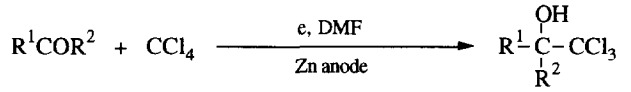
The electroreduction of various organic compounds in the presence of electrophiles gives the corresponding addition or substitution products. In this field, the development of the sacrificial anode technique has proved to be an efficient general method employing very simple devices. Thus a number of reactions have been reported in the last decade, involving the electroreduction of organic halides[1] or pseudo-halides[2,3] and the coupling of the generated carbanions with carbon dioxide, anhydrides, carbonyl compounds, and other electrophiles.

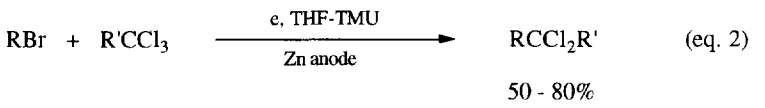
It was recently reported that an additional improvement can be obtained from the use of a Cd-modified cathode[4]. At an electrochemically Cd-coated electrode, the reduction potential of organic halides, notably aryl halides, is shifted to a more positive value (0.3 to 0.6V) than at the uncoated electrode[5]. Besides, no passivation occurs during the electrolyses. We have already shown that when reduced at cadmium coated cathode PhBr or PhI can be used as probase in syntheses involving acidic compounds[6,7].

The present study is devoted to the nucleophilic addition of α-halogenated carbanions RX_n^- to the carbonyl group of aldehydes or ketones. Two ways were investigated in order to produce these carbanions RX_n^-. The first way was the electroreduction of RX_nCl compounds (X=Cl or F). This method has been previously used in this laboratory for the coupling of carbon tetrachloride with carbonyl compounds[8] (equation 1)

[1] FAX. 01 49 78 13 23

and the cross coupling of some substituted trichloromethanes with alkyl bromides[9] (equation 2) .





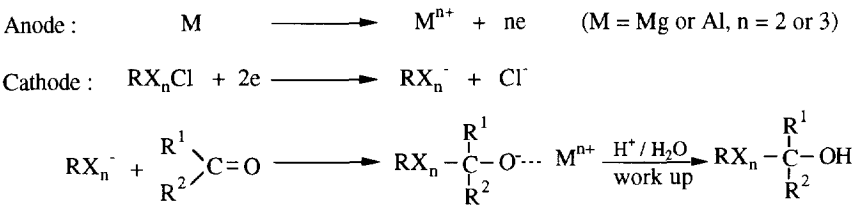
R = $PhCH_2$, CH_2CO_2Me, $CH_3(CH_2)_9$, $CH_2CH{=}CH_2$
R' = Cl, Ph, MeOCO
TMU = tetramethylurea.

For these reactions it was shown that the yields depend on the choice of the anode. Zinc which is compatible only with easily reduced organic substrates gave the best results. Owing to the reduction of Zn^{2+}, a Zn anode is no more suitable when the starting halides are reduced at lower potentials. Consequently we decided to conduct our experiments with a magnesium or aluminium anode.

The second way for generating RX_n^- is an EGB deprotonation of weakly acidic compounds RX_nH (X = Cl or F). In order to compare the results obtained by one or the other way, similar experimental conditions were used.

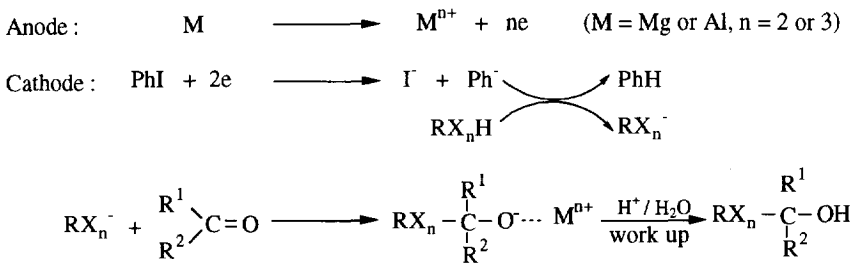
Electrolyses were carried out at room temperature in N,N-dimethylformamide (DMF) at constant current in an undivided cell fitted with a magnesium or aluminium sacrificial anode and a nickel grid cathode freshly coated with an electrolytic deposit of cadmium.

For experiments involving a direct electroreduction of the organic halide, the coupling reaction with a carbonyl compound proceeds according to scheme 1.



Scheme 1

For the EGB mediated syntheses, iodobenzene was used as the probase, according to our preceding work. The reaction pathway corresponds to scheme 2.



Scheme 2

It will be shown that the two routes are of comparable efficiency and can be selected according to the available starting reagent.

Results and discussion :

1) Direct electroreduction.

The results presented in Table 1 show that the coupling between trichlorofluoromethane and aromatic aldehydes (entries 1 - 6) can be obtained with very good yields. Whatever are the nature (electron-releasing or electron-withdrawing) and the position of the substituent on the benzene ring.

The reaction is also efficient with aliphatic aldehydes (Table 1, entry 7). For all these couplings, no difference was observed with either a magnesium or aluminium sacrificial anode.

On the other hand, the reaction was not efficient with ketones, and the expected product was obtained in very low yields (Table 1, entries 8 - 9).

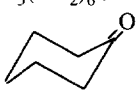
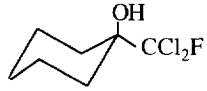
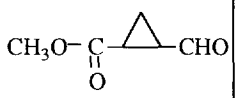
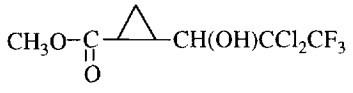
Voltametric experiments showed that the bielectronic non reversible electroreduction of $CFCl_3$ occurs at -1.6V *vs* SCE at a cadmium-coated microelectrode. In agreement with classical data, aromatic aldehydes are reduced at lower potentials ($\approx$ -2V) and we did not observe the reduction of aliphatic aldehydes or ketones. The presence of a carbonyl compound in the solution has no influence on the electrochemical behaviour of $CFCl_3$. This let us assume that electrolyses generate the carbanion $CFCl_2^-$ in all cases. The poor results obtained with ketones which are less electrophilic than aldehydes may be due to a competitive reaction of $CFCl_2^-$. Among various possibilities, we can suppose that $CFCl_2^-$ decomposes into the carben CFCl or couples with DMF since this reaction has been reported for DMF solutions of $CFCl_3$ with zinc powder as reductant[10].

The electroreduction of CF_3CCl_3 also occurs at -1.6 V (as measured by voltametry) and its coupling is achieved with good yields either with aromatic (Table 1, entries 10 - 15) or aliphatic (Table 1 entries 16 - 17) aldehydes. Contrary to that we have observed for $CFCl_3$, the nature of the sacrificial anode has a crucial influence with CF_3CCl_3. Actually, electrolyses involving the same aldehydes as those in entries 10 - 12, 17 (Table 1) but conducted with a magnesium anode instead of aluminium one gave yields which were significantly lower (20 - 50%). One explanation could be that Al^{3+} cations can stabilize the carbanion $CF_3CCl_2^-$ better than Mg^{2+} so avoiding its decomposition into the carbene CF_3CCl. However, no new coupling products have been detected when we added terminal olefins or cyclohexene to the solution in order to give evidence for this assumption. We rather think that Al^{3+} which is a stronger Lewis acid than Mg^{2+} increases the electrophilicity of the carbonyl group. This effect can be compared to that observed by Shono et al. who have previously reported the electroreductive coupling of CF_3CCl_3 with aldehydes in divided cells. Satisfactory yields were obtained only in the presence of an excess of chlorotrimethylsilane (Me_3SiCl)[11].

Concerning the nature of the cathode, we have shown that electrolyses of a mixture of CF_3CCl_3 and PhCHO carried out at a nickel grid cathode (not coated with cadmium) yields only 30% of the expected alcohol **10** and a passivation occured in the course of the reaction.

No coupling with ketones or esters was observed. These compounds are not consumed during the electrolyses. This agrees with the result presented in entry 16 (Table 1); the ester group of the substrate is not affected.

Table 1 : Direct electroreductive coupling of polyhalogenated compounds RX_nCl with aldehydes or ketones[b].

N°	RX_nCl	Electrophile	Product		isolated Yield %
1	$CFCl_3$	C_6H_5CHO	$C_6H_5CH(OH)CCl_2F$	**1**	88
2	"	4-$CF_3C_6H_4CHO$	4-$CF_3C_6H_4CH(OH)CCl_2F$	**2**	91
3	"	2-$CF_3C_6H_4CHO$	2-$CF_3C_6H_4CH(OH)CCl_2F$	**3**	86
4	"	4-$CH_3OC_6H_4CHO$	4-$CH_3OC_6H_4CH(OH)CCl_2F$	**4**	72
5	"	3-$CH_3OC_6H_4CHO$	3-$CH_3OC_6H_4CH(OH)CCl_2F$	**5**	74
6	"	2-$CH_3OC_6H_4CHO$	2-$CH_3OC_6H_4CH(OH)CCl_2F$	**6**	80
7	"	$CH_3(CH_2)_6CHO$	$CH_3(CH_2)_6CH(OH)CCl_2F$	**7**	78
8	"			**8**	10[a]
9	"	$C_6H_5COCH_3$	$C_6H_5C(OH)CH_3$ CCl_2F	**9**	11[a]
10	CF_3CCl_3	C_6H_5CHO	$C_6H_5CH(OH)CCl_2CF_3$	**10**	75
11	"	4-$CH_3OC_6H_4CHO$	4-$CH_3OC_6H_4CH(OH)CCl_2CF_3$	**11**	68
12	"	3-$CH_3OC_6H_4CHO$	3-$CH_3OC_6H_4CH(OH)CCl_2CF_3$	**12**	82
13	"	2-$CH_3OC_6H_4CHO$	2-$CH_3OC_6H_4CH(OH)CCl_2CF_3$	**13**	66
14	"	2,6-$Cl_2C_6H_3CHO$	2,6-$Cl_2C_6H_3CH(OH)CCl_2CF_3$	**14**	69
15	"	2,4-$Cl_2C_6H_3CHO$	2,4-$Cl_2C_6H_3CH(OH)CCl_2CF_3$	**15**	71
16	"			**16**	66
17	"	$CH_3(CH_2)_5CHO$	$CH_3(CH_2)_5CH(OH)CCl_2CF_3$	**17**	51

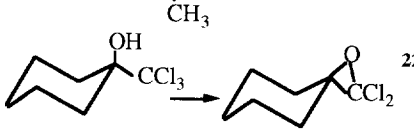
a : approximate G.C. yield, product identified only by GC-SM.
b : the anode was an aluminium rod. For other experimental conditions see the text.

We also noted that the yields decreased when the electrolyses were carried out beyond the consumption of CF_3CCl_3. A further reduction of the coupling product $ArCH(OH)CCl_2CF_3$ (in the form of the alcoholate ion in the solution) is likely involved. We have not for the moment fully investigated this reaction, but GC-SM analysis indicates the presence of a new product which could correspond to the formula $ArCH{=}CClCF_3$.

2) EGB mediated syntheses

The data in Table 2 indicate that the electroreduction of iodobenzene (-1.7 V *vs* SCE from voltametric measurements at a cadmium coated electrode) is a convenient method to generate a carbanion from a weakly acidic compound RX_nH which reacts with aldehydes. Thus when the reactant is CF_3CCl_2H (Table 2, entries 1 - 3, 5) the yields of the coupling products **10** - **12** and **17** are close to those obtained by direct electroreduction of CF_3CCl_3. In this case also, we have observed the crucial role of Al^{3+} cations. Thus **10** was only obtained in 10% yield when a Mg anode was used.

Table 2 : EGB mediated coupling of polyhalogenated compounds RX_nH with electrophiles.

N°	RX_nH	Electrophile	Product		isolated Yield %
1	CF_3CCl_2H	C_6H_5CHO	$C_6H_5CH(OH)CCl_2CF_3$	**10**	10[a] / 72[b]
2	"	$4\text{-}CH_3OC_6H_4CHO$	$4\text{-}CH_3OC_6H_4CH(OH)CCl_2CF_3$	**11**	67[b]
3	"	$3\text{-}CH_3OC_6H_4CHO$	$3\text{-}CH_3OC_6H_4CH(OH)CCl_2CF_3$	**12**	81[b]
4	"	$4\text{-}CF_3C_6H_4CHO$	$4\text{-}CF_3C_6H_4CH(OH)CCl_2CF_3$	**18**	58[b]
5	"	$CH_3(CH_2)_5CHO$	$CH_3(CH_2)_5CH(OH)CCl_2CF_3$	**17**	53[b]
6	$HCCl_3$	$CH_3(CH_2)_6CHO$	$CH_3(CH_2)_6CH(OH)CCl_3$	**19**	52[a]
7	"	C_6H_5CHO	$C_6H_5CH(OH)CCl_3$	**20**	61[a]
8	"	$CH_3(CH_2)_5\text{-}C(=O)\text{-}CH_3$	$CH_3(CH_2)_5\text{-}C(OH)(CH_3)\text{-}CCl_3$	**21**	48[a]
9	"			**22**[c]	95[a]
10	"	$C_6H_5CO_2CH_3$	$C_6H_5COCCl_3$	**23**	15[a]
11	$HCCl_2CCl_3$	C_6H_5CHO	$C_6H_5CH(OH)CCl_2CCl_3$	**24**	45[a]
12	$HCCl_2CCl_2H$	C_6H_5CHO	$C_6H_5CH(OH)CCl_2CCl_2H$	**25**	24[a]
			$C_6H_5CH(OH)CCl_2CCl_2CH(OH)C_6H_5$	**26**	31[a]

a : magnesium anode. b : aluminium anode.
c : during the workup the alcohol was wholly converted in the epoxide.

The EGB mediated coupling of chloroform with electrophiles has been previously proposed as an alternative method to chemical reactions using various classical bases ($NaNH_2$, KOH, KOR, ...). Trichloromethylated alcohols have been obtained in a two-step reaction by first electrogenerating the anion of pyrrolidone at a low temperature, in a diaphragm cell, and then coupling chloroform with aldehydes or ketones[12].

We show here that those reactions can be conducted efficiently in one step in an undivided cell at room temperature (Table 2, entries 6 -9). These syntheses can be compared to those involving the direct electroreduction of carbon tetrachloride[8] that we have mentioned in the introduction (equation 1). The two methods give close results.

The EGB mediated coupling of chloroform with an ester of benzoic acid is also possible (Table 2 entry 10) but the yield of the trichloromethyl ketone **23** is low.

The method can be extended to various polyhalogenated compounds, for intance CCl_3CCl_2H (entry 11) or $HCCl_2CCl_2H$ (entry 12). With this latter compound, a mixture of two products (**25** + **26**) was obtained resulting from a single and a double coupling with benzaldehyde.

In conclusion we can say that direct electroreduction of RX_nCl compounds or EGB mediated deprotonation of RX_nH compounds afford two efficient ways for generating the transient carbanions RX_n^- which couple with carbonyl derivatives and especially with aldehydes. Both methods yield valuable polyfonctionalized products in very simple and mild experimental conditions.

Experimental

Electrolysis

The electrochemical cell has been described elsewhere[1]. The cadmium coating of the cylindrical nickel foam cathode (20 cm^2) which surrounds the sacrificial anode was effected by electrolysing a solution of $CdBr_2$ (5.10^{-2} $mol.l^{-1}$) in DMF. A constant current of 0.2 A was applied during 15 mn, then the solution of $CdBr_2$ was removed.

The electrosyntheses were achieved according to the following procedure. In DMF (40 ml) + Bu_4NBF_4 (0.5 g) as supporting electrolyte were added the aldehyde or ketone (20 mmol) and either RX_nCl (20 mmol) or RX_nH (20 mmol) + PhI (20 mmol) in the case of EGB mediated reactions.

A constant current of 0.2 A was applied during 5.6 hours in order to engage 2.1 mol of electrons per mol of RX_nCl or per mol of PhI. GC analysis of samples allowed to check the reaction during the electrolysis.

Purification and analysis of the products.

After electrolysis, most of the solvent was evaporated under vacuum. The residue was acidified with 6 $mol.L^{-1}$ aqueous hydrochloric acid (50 ml) and extracted twice with diethylether (80 ml). The extracts were washed twice with aqueous sodium hydrogenocarbonate, dried over magnesium sulfate and then evaporated without heating in order to avoid the formation of an epoxide by dehydrochloration of the α-chloroalcohol. The crude product were purified by column chromatography on silica gel (eluant = pentane/ether). Analysis of the products was achieved by ^1H NMR, ^{19}F NMR (δ *vs* $CFCl_3$) and mass spectroscopy. In a large part, the obtained products have not been previously described. Characteristics are given below.

1 : 2,2-dichloro-2-fluoro-1-phenylethanol.
Mass., M/Z(rel. istensity) 156 (M^+ -HO, Cl, 3.3); 107 (68.7); 103 (5.6); 101 (12); 79 (100); 77 (62).
^1H NMR ($CDCl_3$/TMS, 200MHz): 7.4 (m, 5H) ; 5 (dd, 1H, J_1 = 8.5Hz, J_2 = 4.5Hz) ; 4.4 (d, 1H, J_2 = 4.5Hz). ^{19}F NMR ($CDCl_3$/$CFCl_3$): -63.9, (d, J_{F-H} = 7.5Hz). Anal. Calcd for $C_8H_7Cl_2FO$: C, 45.96; H, 3.37; Cl, 33.92; F, 9.09. Found: C, 45.90; H, 3.29; Cl, 33.22; F, 8.84.

2 : 2,2-dichloro-2-fluoro-1-(4-trifluromethylphenyl)ethanol
Mass., M/Z(rel. istensity) 257 (M^+ -F, 5.9); 175 (81.97); 145 (11.27); 127 (100); 101 (9); 69 (9).
^1H NMR ($CDCl_3$/TMS, 200MHz):, 7.51 (s, 4H) ; 5 (dd, 1H, J_1 = 8.07Hz, J_2 = 3.23Hz); 3.5 (d, 1H, J_2 = 3.3Hz). ^{19}F NMR $CDCl_3$, -64.7 , (d, J_{F-H} = 7.7Hz); -62.7, s. Anal. Calcd for $C_9H_6Cl_2F_4O$: C, 39.02; H, 2.18; Cl, 25.59; F, 27.43. Found: C, 39.04; H, 2.21; Cl, 25.30; F, 27.03.

3 : 2,2-dichloro-2-fluoro-1-(2-trifluromethylphenyl)ethanol
Mass., M/Z(rel. istensity) 257 (M^+ -F, 0.58); 193 (14.6); 175 (24); 155 (100); 127 (52.8); 101 (11.9). ^1H NMR ($CDCl_3$/TMS, 200MHz): 8.1 - 7.6 (m, 4H) ; 5.8 (d, 1H, J_{H-F} = 9.7Hz); 4.2 (s, 1H). NMR ^{19}F $CDCl_3$, -65.4 , (d, J_{F-H} = 8.7Hz); -59.7, s. Anal. Calcd for $C_9H_6Cl_2F_4O$: C, 39.02; H, 2.18; Cl, 25.59; F, 27.43. Found: C, 39.08; H, 2.25; Cl, 25.04; F, 26.67.

4: 2,2-dichloro-2-fluoro-1-(4-methoxyphenyl)ethanol
Mass., M/Z(rel. istensity) 219 (M^+ -F, 1.86); 186 (7.97); 165 (29.5); 137 (100); 109 (43.1); 77 (27). ^1H NMR ($CDCl_3$/TMS, 200MHz): 7.3 (d, 2H, J = 8.56Hz) - 6.8 (d, 2H, J = 8.56Hz) ; 5 (d, 1H, J_{H-F} = 8.6Hz); 4.2 (s, 1H); 3.64 (s, 3H). ^{19}F NMR $CDCl_3$, -63.6 , (d, J_{F-H} = 7.2Hz). Calcd for $C_9H_9Cl_2FO_2$: C, 45.22; H, 7.79; Cl, 29.66; F, 7.95. Found: C, 45.16; H, 3.91; Cl, 28.98; F, 7.73.

5 : 2,2-dichloro-2-fluoro-1-(3-methoxyphenyl)ethanol.
Mass., M/Z(rel. istensity) M^+ 238 (27.3); 217 (5.41); 171 (10); 137 (64.84); 109 (100); 77 (34.13). ^1H NMR ($CDCl_3$/TMS, 200MHz):, 7.2 - 6.8 (m, 4H) ; 5 (dd, 1H, J_1 = 8.45Hz, J_2 = 4.58Hz); 4.2 (d, 1H, J_2 = 4.6Hz); 3.7 (s, 3H). ^{19}F NMR $CDCl_3$, -63.6 , (d, J_{F-H} = 7.2Hz). Calcd for $C_9H_9Cl_2FO_2$: C, 45.22; H, 7.79; Cl, 29.66; F, 7.95. Found: C, 45.11; H, 3.71; Cl, 29.41; F, 7.86.

6 : 2,2-dichloro-2-fluoro-1-(2-methoxyphenyl)ethanol
Mass., M/Z(rel. istensity) M^+ 238 (0.89); 221 (1.78); 175 (22.4); 155 (100); 127 (53); 107 (8.7); 101 (11.9). ^1H NMR ($CDCl_3$/TMS, 200MHz):, 7.4 - 6.7 (m, 4H) ; 5.35 (d, 1H, J_{H-F}= 8.56Hz); 4.2 (s, 1H); 3.7 (s, 3H). ^{19}F NMR $CDCl_3$, -64.1 , (d, J_{F-H} = 9.3Hz). Calcd for $C_9H_9Cl_2FO_2$: C, 45.22; H, 7.79; Cl, 29.66; F, 7.95. Found: C, 45.18; H, 3.92; Cl, 29.32; F, 7.60.

7 : 1,1-dichloro-1-fluorononan-2-ol.
Mass., M/Z(rel. istensity) 178 (M^+ -HO, Cl, 0.92); 129 (5.5); 111 (18.8); 101 (4.6); 83 (8.5); 69 (100). ^1H NMR ($CDCl_3$/TMS, 200MHz): 3.9 (t, 1H, J = 7.44Hz) ; 3 (s, 3H); 1.8 - 1.1 (m, 12H); 0.8 (t, 3H, J = 3.3Hz). ^{19}F NMR $CDCl_3$, -61.5 , (d, J_{F-H} = 8.2Hz). Calcd for $C_9H_{17}Cl_2FO$: C, 46.77; H, 7.41; Cl, 30.68; F, 8.22. Found: C, 46.84; H, 7.25; Cl, 30.05; F, 7.61.

10 : 2,2-dichloro-3,3,3-trifluoro-1-phenylpropanol : R.N. [103654-96-2]
Mass., M/Z(rel. istensity) 107 (M^+ -CCl_2CF_3, 79); 79 (100); 51 (22). ^1H NMR ($CDCl_3$/TMS, 200MHz): 7.5 - 7.2 (m, 5H) ; 5.2 (s, 1H) ; 1.8 - 2.8 (s, 1H). ^{19}F NMR $CDCl_3$, -73.6 , s.

11 : 2,2-dichloro-3,3,3-trifluoro-1-(4-methoxyphenyl)propanol R.N.[103655-02-3]
Mass., M/Z(rel. istensity) 137 (M^+ -CCl_2CF_3, 100); 109 (36); 77 (20). ^1H NMR ($CDCl_3$/TMS, 200MHz): 7.3 (d, 2H, J = 8.8Hz) ; 6.8 (d, 2H, J = 8.8Hz) ; 5.05 (d, 1H, J = 5Hz); 3.7 (s, 3H); 3.4 (d, 1H, J = 5Hz). ^{19}F NMR $CDCl_3$, -73.6 , s.

12 : 2,2-dichloro-3,3,3-trifluoro-1-(3-methoxyphenyl)propanol.
Mass., M/Z(rel. istensity) M^+ 288 (15); 137 (83); 109 (100); 77 (9); 63 (9.7). ^1H NMR ($CDCl_3$/TMS, 200MHz): 7.2 - 6.8 (m, 4H) ; 5.05 (s, 1H); 3.7 (s, 3H); 3.3 (s, 1H). ^{19}F NMR $CDCl_3$, -73.7 , s. Calcd for $C_{10}H_9Cl_2F_3O_2$: C, 41.55; H, 3.14; Cl, 24.53; F, 19.71. Found: C, 41.54; H, 3.24; Cl, 24.41; F, 19.55.

13 : 2,2-dichloro-3,3,3-trifluoro-1-(2-methoxyphenyl)propanol.R.N.[103674-94-8].
Mass., M/Z(rel. istensity) 137(M^+ -CCl_2CF_3, 100); 107 (65); 79 (18); 77 (26); 69 (9). ^1H NMR ($CDCl_3$/TMS, 200MHz): 7.5 - 6.8 (m, 4H) ; 5.6 (s, 1H) ; 4.3 (s, 1H); 3.7 (s, 3H). ^{19}F NMR $CDCl_3$, -73.6 , s.

14 : 2,2-dichloro-1-(2-6-dichlorophenyl))-3,3,3-trifluoropropanol.
Mass., M/Z(rel. istensity) 272 (M^+ -HO, Cl, 2); 177 (74.34); 175 (100); 149 (5); 111 (51.6); 75 (63.85). ^1H NMR ($CDCl_3$/TMS, 200MHz): 7.27 - 7.06 (m, 3H) ; 6.1 (d, J = 10.8 Hz, 1H) ; 4.4 (d, J = 10.8 Hz, 1H). ^{19}F NMR $CDCl_3$, -76.2 , s. Calcd for $C_9H_5Cl_4F_3O_2$: C, 32.96; H, 1.54; Cl, 43.24; F, 17.38. Found: C, 33.01; H, 1.64; Cl, 42.75; F, 16.70.

15 : 2,2-dichloro-1-(2-4-dichlorophenyl))-3,3,3-trifluoropropanol.
Mass., M/Z(rel. istensity) 177 (M^+ - CCl_2CF_3, 90); 175 (100); 149 (13); 111 (53); 75 (17). NMR ^1H ($CDCl_3$/TMS, 200MHz): 7.7 - 7.2 (m, 3H) ; 5.8 (s, 1H) ; 3.3 (s, 1H). NMR ^{19}F $CDCl_3$, -73.6 , s.

16 : methyl-(2-[2,2-dichloro-3,3,3-trifluoro-1-hydroxypropyl]) cyclopropanecarboxylate.
Mass., M/Z(rel. istensity) 228 (M^+ - OH, Cl, 31); 197 (68.45); 169 (21.41); 133 (100); 113 (81); 69 (50.21). ^1HNMR ($CDCl_3$/TMS, 200MHz): 4.3 (dd, 1H, J_1 = 8.7Hz, J_2 = 7.3Hz) ; 4 (dt, 1H, J_1 = 8.7Hz, J_3 = 6.8Hz); 3.86 (d, 1H, J_2 = 7.3Hz); 3.7 (s, 3H); 1.8, (m, 1H); 1.1 (m, 2H). ^{19}F NMR $CDCl_3$, -74.2 , s. Calcd for $C_9H_9Cl_2F_3O_3$: C, 34.19; H, 3.23; Cl, 25.23; F, 20.28. Found: C, 34.28; H, 3.34; Cl, 24.91; F, 19.85.

17 : 2,2-dichloro-1,1,1-trifluorononan-3-ol. R.N. [111748-95-9]
Mass., M/Z(rel. istensity) 237 (M^+ -CH_3CH_2, 39); 195 (3); 167 (25); 153 (12); 151 (24.3); 139 (38.7); 69 (57); 55 (100). ^1H NMR ($CDCl_3$/TMS, 200MHz): 3.95 (d, 1H, J = 7.5Hz) ; 2.4 (s, 1H); 2 -1.1 (m, 12H) ; 0.9 (t, 3H, J = 3.5Hz). ^{19}F NMR $CDCl_3$, -73.95 , s.

18 : 2,2-dichloro-3,3,3-trifluoro-1-(4-trifluoromethylphenyl)propanol.
Mass., M/Z(rel. istensity) 257(M^+ -CF_3, 1.29); 236 (1.72); 204 (10.44); 164 (100). ^1H NMR ($CDCl_3$/TMS, 200MHz): 7.5 (s, 4H) ; 5.2 (d, 1H, J = 5.4Hz) ; 3.15 (d, 1H, J = 5.4Hz). ^{19}F NMR $CDCl_3$, -73.6 , s ; -62.5, s. Calcd for $C_{10}H_6Cl_2F_3O$: C, 36.72; H, 1.85; Cl, 21.68; F, 34.86. Found: C, 36.69; H, 1.95; Cl, 21.72; F, 34.80.

19 : 1,1,1-trichlorononan-2-ol. R.N. [4776-43-6]
Mass., M/Z(rel. istensity) 211 (M^+ -Cl, 15.67); 195 (3.83); 180 (2.15); 112 (21.12); 72 (100); 56 (20.04). ^1H NMR ($CDCl_3$/TMS, 200MHz): 3.9 (dd, 1H, J_1 = 9.4Hz, J_2 = 10Hz) ; 3.3 (s, 1H); 2 - 0,8 (m, 15H).

20 : 1,1,1-trichloro-2-phenylethan-2-ol : R.N. [53495-27-5]
Mass., M/Z(rel. istensity) 189 (M^+ -Cl, 1,31); 125 (19.82); 107 (78.41); 79 (100); 77 (50.53). NMR ^1H ($CDCl_3$/TMS, 200MHz): 7.4 - 7.2 (m, 5H) ; 5 (s, 1H) ; 4.1 (s, 1H).

21 : 2-methyl-1,1,1-trichlorooctan-2-ol. R.N.[99064-60-5]
Mass., M/Z(rel. istensity) 211 (M^+ -Cl, 5,65); 198 (2.12); 184 (5.15); 148 (20.22); 126 (6.71); 112 (21.06); 72 (100); 55 (12.37). ^1H NMR ($CDCl_3$/TMS, 200MHz): 3.2 (s, 1H); 2 (t, 2H, J = 8Hz); 1.4 - 0.8 (m, 11H).

22 : 1,1-dichloro-2-oxaspiro [2,5] octane.
Mass., M/Z(rel. istensity) 181 (M^+, 0.55); 165 (32.31); 145 (3.56); 127 (5.91); 99 (28.77); 81 (100). ^1H NMR ($CDCl_3$/TMS, 200MHz): 1.2 - 0.8 (m, 10H). Calcd for $C_7H_{10}Cl_2O$: C, 46.44; H, 5.57; Cl, 39.16. Found: C, 46.41; H, 5.30; Cl, 38.87.

23 : phenyltrichloromethyl ketone. R.N. [2902-69-4]
Mass., M/Z(rel. istensity) 187 (M^+ -Cl, 2.61); 152 (21.11); 105 (100); 83 (34.81); 77 (8.9). ^1H NMR ($CDCl_3$/TMS, 200MHz): 7.4 - 6.9 (m, 5H).

24 : 2,2,3,3,3-pentachloro-1-phenyl-propanol.
Mass., M/Z(rel. istensity) 306 (M^+, 0.82); 271 (1.01); 229 (3.45); 107 (64.11); 79 (100); 77 (35.78). ^1H NMR ($CDCl_3$/TMS, 200MHz): 7.2 - 6.9 (m, 5H) ; 5.1 (s, 1H) ; 4.8 (s, 1H).

25 : 2,2,3,3-tetrachloro-1-phenylpropanol.
Mass., M/Z(rel. istensity) 195 (M^+ -C_6H_5, 1.85); 165 (1.01); 107 (58.59); 79 (100); 77 (66). ^1H NMR ($CDCl_3$/TMS, 200MHz): 7.3 - 6.9 (m, 5H) ; 4.85 (s, 1H) ; 4.5 (s, 1H) ; 2,7 (s, 1H).

26 : 2,2,3,3-tetrahloro-1,4-diphenylbutan-1,4-diol.
Mass., M/Z(rel. istensity) 343 (M^+ -Cl, 2.03); 303 (2.44); 197 (100); 107 (60.98); 79 (81); 77 (34.15). ^1H NMR ($CDCl_3$/TMS, 200MHz): 7.3 - 6.8 (m, 10H) ; 4.51 (s, 2H); 3.35 (s, 2H). Calcd for $C_{16}H_{14}Cl_4O_2$: C, 50.56; H, 3.71; Cl, 37.31. Found: C, 50.72; H, 3.65; Cl, 37.88.

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