The reactions of copper–dibromodifluoromethane–amide systems with alcohols

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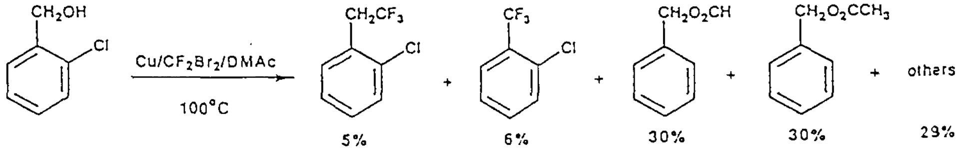
Abstract

1,1,1-Trifluoro-2-arylethanes can be prepared by the trifluoromethyldehydroxylation of benzyl alcohols using the copper–dibromodifluoromethane–amide reaction system, although the yields are low. The mechanism of the reaction may involve chelation of the substrate to copper so that α-substituted benzyl alcohols and most other alcohols are unreactive.

Introduction

Our investigations into the utility of the copper–difluorodihalomethane–amide trifluoromethylating system have shown that reaction occurs with certain chloroaromatic substrates, such as methyl-2-chlorobenzoate, to give various perfluoroalkyl substituted aromatics [1]. 2-Chlorobenzyl alcohol, however, reacted in a totally anomalous manner. The failure to replace chlorine was expected as the CH_2OH moiety is not sufficiently electron withdrawing to activate the molecule towards reaction. However, a reaction did occur and the products identified showed that it is the hydroxy function which is labile to exchange.



Recently there has been significant interest in the CH_2CF_3 substituent, particularly as a result of the often observed increase in the biological activity of specifically fluorinated compounds [2]. Most methods of preparing 1,1,1-trifluoro-2-arylethanes involve harsh conditions and/or low yields [3]. The

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highest yield reported was from the reaction of benzyl bromide with trifluoromethyl iodide and copper powder [4].

Apart from the interest in the trifluoromethylated product, it is intriguing that a hydroxy group is apparently replaced directly by using an organocopper reagent. Previous reports have involved the use of BF_3 as a catalyst, when reaction occurred predominantly at the γ position relative to the OH and benzyl alcohols were found to be inactive [5].

Results and discussion

The yield and product distribution from the reaction of benzyl alcohol with Cu–CF_2Br_2–amide varied considerably with the temperature and solvent employed (see Table 1 and Fig. 1). As a result of these studies, it can be seen that DMF at 80 °C provides the best medium for the production of 1,1,1-trifluoro-2-phenylethane from benzyl alcohol. It should also be noted that there is a distinct cut-off point; no fluorinated products were seen at or below 60 °C. This is probably due to the inability of DMF to react with copper and difluorodibromomethane at these lower temperatures.

The temperature and solvent conditions which gave the best yield of $PhCH_2CF_3$ were used in an investigation of the reactions of other alcohols (Table 2). Only benzyl alcohols with no α substituents and allyl alcohols react: a π system β to the alcohol is essential. Thus PhCH(Me)OH, $PhCMe_2OH$ and Ph_3COH gave the fluoro product (as high as 60% yield of Ph_3CF from Ph_3COH) but no trifluoromethylation. The absence of the π system or its removal to the γ position seems to prevent reaction, so that neither $CH_3(CH_2)_8CH_2OH$ nor $CH_2{=}CHCH_2CH_2OH$ gave any trifluoromethylated product. The C=O π system did not facilitate replacement of the hydroxy group by fluorinated substituents and $CH_3CH_2COCH_2OH$ gave only the formate as the product. A C≡C group β to the alcohol allowed reaction to occur, but a mixture of products was observed so that $PhC{\equiv}CCH_2OH$ gave 1-phenyl-1-trifluoromethyl allene and 1-phenyl-4,4,4-trifluoro-but-1-yne. The formation of allenes by reaction of organometallic reagents with alkynes is well documented [6].

Phenols did not react under these conditions but yielded small quantities of difluoromethoxylated aromatic in addition to many other products.

TABLE 1

Reaction of benzyl alcohol (5 mmol) with copper (30 mmol) and dibromodifluoromethane (10 mmol) in amide (8 ml) at 100 °C under a N_2 atmosphere (GLC %yield)

Solvent	$BzCF_3$	$BzCF_2CF_3$	BzF	BzOCHO	BzOCOMe	Other
DMF	27	0	23	32	0	19
DMAc	5	0	6	30	30	29
NMP	12	14	0	11	0	55

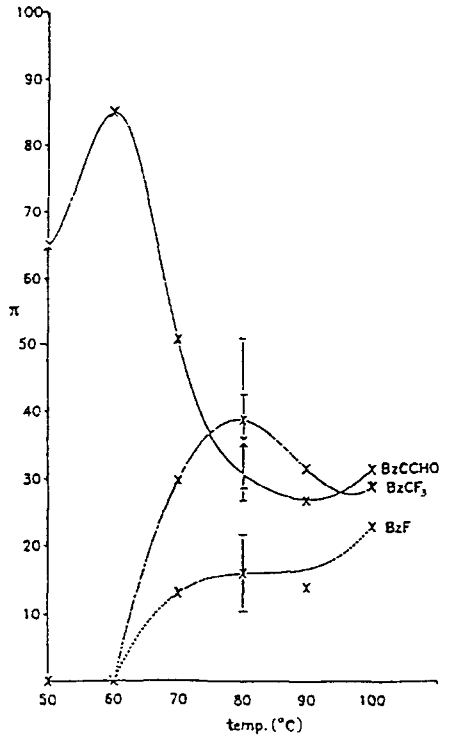

Fig. 1. The reaction of benzyl alcohol with copper, dibromodifluoromethane and DMF (GLC %yields).

TABLE 2

Reaction of alcohol or phenol (5 mmol) with copper (30 mmol) and dibromodifluoromethane (10 mmol) in DMF (8 ml) at 80–85 °C under a N_2 atmosphere (GLC %yield)

Alcohol/phenol	RCF_3	RF	ROCHO	Other
Benzyl alcohol	39 ± 12^a	16 ± 6^a	39 ± 7^a	6 ± 8^a
2-Chlorobenzyl alcohol	12	10	54	0
2-Nitrobenzyl alcohol	$19(11)^b$	3	62	8
3-Nitrobenzyl alcohol	45(23)	3	47	5
4-Nitrobenzyl alcohol	27(2)	0	44	19
Cinnamyl alcohol	(29)	–	–	–
$BzO(CH_2)_5CH{=}CHCH_2OH$	(28)	–	–	–

[a] Range of yields over a series of reactions.
[b] Figures in brackets refer to isolated yield.

2-Hydroxybenzyl alcohol did not react, indicating that phenolic OH is detrimental to reaction.

It is interesting to compare the reactivity of the alcohols with their halo equivalents. Kobayashi *et al.* found that $CuCF_3$ produced from Cu and ICF_3 reacted with benzyl chloride to give a good yield of the corresponding

TABLE 3

Reaction of substrate (5 mmol) with copper (30 mmol) and dibromodifluoromethane (10 mmol) in DMF (8 ml) at 80–85 °C under a N_2 atmosphere (GC %yield)

	RCF_3	$R-C_nF_{2n+1}$	R−F	R−OCHO	Other
BzCl	62	10	–	21	5
BzBr	35	trace	–	26	34
BzF	0	–	–	–	–
BzOH	39 ± 12^a	–	16 ± 6^a	36 ± 7^a	6 ± 8^a
$PhCH=CHCH_2Cl$	8	7	–	–	81
$PhCH=CHCH_2OH$	29	–	6	5	55

[a] Range of yields over a series of experiments.

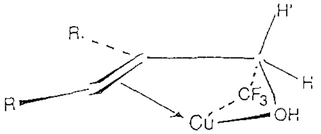

Fig. 2. Proposed transition state for the reaction of trifluoromethyl copper with unsaturated alcohols.

trifluoromethylated compound [4]. However, with the copper–dibromodifluoromethane–amide system, specific reaction does not occur and higher homologues of the trifluoromethylated compounds are observed (Table 3).

Mechanistic aspects

From the results described, a β-unsaturated carbon–carbon bond is essential in order for any fluorinated products to be obtained. It was thought initially that the trifluoromethylated product was produced by reaction of trifluoromethyl copper with the formate ester, which is always observed in these reactions. However this is not the case, since benzyl formate did not react under the reaction conditions. The possibility that the desired product was produced by insertion of difluorocarbene (generated by reaction of copper with dibromodifluoromethane [7]) was considered, but benzyl fluoride was also found to be unreactive under the reaction conditions. Since copper is known to form stable complexes with alkenes [8], the most plausible explanation for the formation of the trifluoromethylated compound is that reaction occurs via a transition state of the form shown in Fig. 2.

This proposed transition state does not explain all of the results obtained: in particular, the dramatic effect of replacing one of the α-hydrogen by a methyl group. Steric crowding around the Cu may well be responsible.

The mechanism for the production of alkyl fluorides is also less than obvious. The compound HCF_2NMe_2 (produced by the reaction of $:CF_2$ with DMF [7]) may act as an FAR-type reagent, but on this basis it would be expected that dodecyl alcohol, for example, would react to give fluorinated products. Since this is not the case, an alternative source of fluoride ion seems likely. It has been suggested that copper(I) fluoride (a compound which has never been isolated) is generated by the decomposition of trifluoromethyl copper [9], and it may be that CuF generated in this fashion is responsible for the observed monofluorinated compound via a similar transition state to that suggested for the reaction of $CuCF_3$ with β-unsaturated alcohols.

Formation of the formate is partly due to the reaction of copper(II), DMF and alcohol, *i.e.*

$$\mathrm{BzOH} + \mathrm{Me_2NCHO} \xrightarrow{\mathrm{Cu^{II}}} \mathrm{BzOCHO}$$

However, the yield of formate from this reaction is not as high as that observed for the reaction of benzyl alcohol with copper metal, dibromodifluoromethane and DMF under similar conditions. Also when DMAc was used as the solvent for the reaction of benzyl alcohol with copper(II), only the acetate was formed (both acetate and formate were observed when $Cu/CF_2Br_2/DMAc$ was employed). These observations suggest that free CO is involved in a parallel reaction producing the formate (CO is produced from the reaction of copper, dibromodifluoromethane and DMF [7]). The exact nature of this competing process has yet to be ascertained. It is also relevant to note that formate products are observed in the reaction of benzyl and alkyl halides with $Cu/CF_2Br_2/DMF$.

The other reaction products were of high molecular weight, the only other products identified being diphenylethanes (from benzyl alcohols). This suggests that benzyl radical species are present, although no products arising from hydrogen abstraction were observed.

Conclusions

Although the reactions described probably do not represent the best method of preparing 1,1,1-trifluoro-2-arylethanes, the yields compare well with many published procedures and the reaction is easily carried out and does not require highly toxic reagents. Although the yield is low, the major reaction product (formate) can be easily converted back to the starting material.

The mechanism of the dehydroxylation reaction is unclear but it is likely to involve chelation of the substrate to the copper, as do the copper-catalysed trifluoromethyl dechlorination reactions [1].

Experimental

Equipment

Gas–liquid chromatograms were obtained on a Phillips PU4500 instrument equipped with a Hewlett Packard 3396A integrator. Unless otherwise specified, the column used was OV101 silicon on Chromasorb. Dinitrogen carrier gas and dihydrogen/air flame ionisation detection were employed throughout.

Mass spectra were obtained on a Kratos MS-3074 instrument employing a Hewlett Packard 26296 data station, or by chemical ionisation using a Finnigan MAT 4500 GC–MS instrument.

NMR spectra were obtained on a Bruker WP80SY NMR spectrometer at ambient temperatures. Standards used were tetramethylsilane (^{1}H, internal), trichlorofluoromethane (^{19}F internal) or hexafluorobenzene (^{19}F, external -162.9 ppm), positive shifts to high frequency.

Infrared spectra were recorded on a Perkin-Elmer PE-683 ratio-recording machine interfaced to a PE64K data station.

General procedures

All reactions were carried out under a dinitrogen atmosphere, unless otherwise stated. The dibromodifluoromethane and solvents were all distilled and stored over molecular sieves prior to use. The copper powder used was 200 mesh (Aldrich Chem. Co.). Other chemicals were purchased from Aldrich or Lancaster synthesis and used without further purification.

2-Chlorobenzyl alcohol

Copper powder (1.9 g, 30 mmol) and 2-chlorobenzyl alcohol (0.71 g, 5 mmol) were placed in a 25 ml two-necked flask with condenser attached. After flushing with dinitrogen gas, the solvent, DMAc (7.5 ml) and dibromodifluoromethane (1 ml) were added. The flask was then immersed in an oil bath at 100 °C. After 8 h, GLC analysis showed five peaks, GC–MS analysis identifying the major products as (i) 1,1,1-trifluoro-2-(2-chlorophenyl)ethane [M^+ 194: 196 (19); 194 (54); 174 (5); 127 (36); 125 (100); 109 (7); 89 (11); 63 (7)] and (ii) 2-chlorobenzyl fluoride [M^+ 144: 146 (11); 144 (31); 109 (91); 91 (100); 74 (14); 59 (32); 45 (19)].

Solvent and temperature variations using benzyl alcohol as the substrate

These reactions were carried out in a similar manner as with 2-chlorobenzyl alcohol but with the variations in temperature and solvent as laid out in the text. Unless otherwise stated, reactions were undertaken for 24 h under a dinitrogen atmosphere. Examples of the analysis for each solvent are set out below:

(a) Reaction in DMAc at 100 °C – This reaction was only run for 8 h. After this time GC–MS analysis showed the major products to be (i) 1,1,1-trifluoro-2-phenylethane [M^+ 160: 192 (9); 160 (33); 109 (4); 91 (100); 65 (7); 51 (4); 41 (3)] and (ii) benzyl fluoride [M^+ 110: 110 (45); 109 (100); 91 (18); 83 (12); 63 (8); 51 (10); 39 (11)].

(b) Reaction in DMF at 90 °C – In this reaction, the major products were identified as (i) 1,1,1-trifluoro-2-phenylethane [M^+ 160] and (ii) benzyl fluoride [M^+ 110].

(c) Reaction in NMP at 100 °C – In this reaction the major products were identified as (i) 1,1,1-trifluoro-2-phenylethane [M$^+$ 160] and (ii) benzyl fluoride [M$^+$ 110].

Reaction of various alcohols and phenols with 'CuCF$_3$'

These reactions were carried out in the same manner as with 2-chlorobenzyl alcohol, except that the solvent used was DMF and the oil bath temperature was 80 °C.

2-Nitrobenzyl alcohol

After 24 h, GLC analysis showed four peaks. The major products were identified as (i) 1,1,1-trifluoro-2-(2-nitrophenyl)ethane [M$^+$ 205: 205 (54); 175 (12); 159 (27); 139 (13); 109 (100); 89 (14); 63 (13); 39 (11)] and (ii) 2-nitrobenzyl fluoride [M$^+$155: 156 (8); 155 (100); 125 (10); 109 (49); 97 (30); 83 (76); 63 (17); 57 (17)].

The 1,1,1-trifluoro-2-(2-nitrophenyl)ethane was isolated by column chromatography (silica, 70–230 mesh, using 30% ether/petroleum ether solution). The sample thus obtained was used for NMR analysis. ^{1}H NMR δ: 8.1–8.0 (m); 7.8–7.4 (m); 3.93 (q, 10.4 Hz) ppm. ^{13}C{^{1}H} NMR δ: 150.1 (C–NO$_2$); 133.5 (C–H); 133.3 (C–H); 129.6 (C–H); 125.4 (C–H) and 36.3 (q, 30 Hz CH_2CF_3) ppm. The *C*–CH$_2$ and CF$_3$ carbons were not readily discernible.

3-Nitrobenzyl alcohol

After 24 h reaction, GLC showed two main peaks and GC–MS analysis indicated that these were (i) 1,1,1-trifluoro-2-(3-nitrophenyl)ethane [M$^+$ 205: 205 (67); 159 (43); 139 (28); 119 (15); 109 (100); 83 (9); 63 (12); 39 (9)] and (ii) 3-nitrobenzyl formate [M$^+$ 181: 153 (23); 136 (100); 106 (14); 89 (75); 77 (26); 63 (13); 51 (17); 39 (11)]. ^{19}F NMR spectral analysis of the reaction mixtures showed resonances at -66.6 (t, 10.6 Hz) and -214 (t, 47 Hz).

The products were isolated by column chromatography (silica, 70–230 mesh and 10% ether/petroleum ether solution). NMR data were obtained on the organofluorine compound. 1,1,1-Trifluoro-2-(3-nitrophenyl)ethane: ^{19}F NMR δ: -66.3 (t, 9.8 Hz) ppm. ^{1}H NMR δ: 8.3–8.1 (m); 7.6–7.5 (m); and 3.5 (q, 10.5) ppm. ^{13}C{^{1}H} NMR δ: 148.6 (C–NO$_2$); 136.4 (C–H); 132.2 (q, 2 Hz); 129.9 (C–H); 125.4 (q, 276 Hz, CF$_3$); 125.2 (C–H); 123.4 (C–H); and 39.9 (q, 30.5 Hz, CH_2CF_3) ppm. MS: Found, 205.03593. $C_8H_8NO_2F_3$, accurate mass 205.035056.

4-Nitrobenzyl alcohol

GLC analysis after 24 h showed three peaks. GC–MS analysis identified the major product as 1,1,1-trifluoro-2-(4-nitrophenyl)ethane [M$^+$ 205: 205 (74); 159 (33); 139 (13); 109 (100); 83 (11); 63 (11); 51 (10); 39 (10)].

The fluorinated product was isolated using a silica column as above. NMR data were obtained on the purified sample. ^{19}F NMR δ: -66.2 (t, 10.9 Hz) ppm. ^{1}H NMR δ: 7.85 (dd, 210 and 8 Hz); and 3.5 (q, 10.5 Hz) ppm.

$^{13}\mathrm{C}\{^{1}\mathrm{H}\}$ NMR δ: 148.0 (C–NO$_2$); 137.3 (C–CH$_2$); 131.2 (C–H); 125 (q, $\sim$280 Hz, CF$_3$); 123.9 (C–H); and 40.0 (q, 30.5 Hz, CH$_2$CF$_3$) ppm. MS: Found, 205.03593. $\mathrm{C_8H_8NO_2F_3}$, accurate mass 205.035056.

Cinnamyl alcohol

GLC and GC–MS analysis identified the major products as (i) 1,1,1-trifluoro-4-phenylbut-3-ene [M$^+$ 186: 186 (29); 118 (17); 117 (100); 116 (17); 115 (72); 91 (32); 63 (12); 39 (11)] and (ii) cinnamyl fluoride [M$^+$ 136: 136 (95); 135 (100); 117 (18); 116 (26); 115 (59); 63 (8); 51 (30); 39 (9)].

The trifluoromethyl compound was isolated by column chromatography (flash silica and hexane). NMR data were obtained on a Bruker 250 MHz machine. $^{19}\mathrm{F}$ NMR δ: -66.8 (t, 10.8) ppm. $^{1}\mathrm{H}$ NMR δ: 7.4–7.2 (m); 6.6 (d, 15 Hz, $\mathrm{Ph{-}CH{=}CH}$); 6.1 (dt, 16 and 7 Hz, $\mathrm{CH{=}\mathit{C}H{-}CH_2}$); and 2.9 (qdd, 10.7, 7 and 1 Hz, $\mathrm{CH{=}CH{-}\mathit{C}H_2{-}CF_3}$) ppm. $^{13}\mathrm{C}\{^{1}\mathrm{H}\}$ NMR δ: 136.76 (C–H); 136.34 (C–C); 128.72 (C–H); 128.19 (C–H); 126.53 (C–H); 126.05 (q, 276 Hz, CF$_3$); 117.26 (q, 3.6 Hz, $\mathrm{\mathit{C}H{-}CH_2CF_3}$); and 37.73 (q, 29.9 Hz, $\mathrm{\mathit{C}H_2CF_3}$) ppm.

8-Hydroxyoct-6-enyl benzyl ether

This material was prepared from 6-hydroxyhexylbenzyl ether, which was obtained from the Wellcome Foundation, by standard chemical procedures. After 16 h at 80 °C, the organic compounds were extracted into ether and the solvent removed by washing with water. The trifluoromethylated compound was isolated by column chromatography and identified by NMR spectroscopy as $\mathrm{BzO(CH_2)_5CH{=}CHCH_2CF_3}$. $^{19}\mathrm{F}$ NMR δ: -67.3 (t, 10.8 Hz) ppm. $^{1}\mathrm{H}$ NMR δ: 7.3 (m); 5.7 (dt, 15 and 7 Hz, $\mathrm{CH{=}\mathit{C}H{-}CH_2}$); 5.4 (dtt, 15, 7 and 1.5 Hz, $\mathrm{CH_2CH_2{-}\mathit{C}H{=}CH}$); 4.3 (s, PhCH$_2$); 3.4 (t, $\mathrm{O\mathit{C}H_2CH_2}$); 2.7 (qdd, 10.7, 7 and 1 Hz, $\mathrm{\mathit{C}H{=}CH{-}CH_2CF_3}$); 2.0 (m, CH$_2$); 1.6 (m, CH$_2$); and 1.34 (m, CH$_2$) ppm. $^{13}\mathrm{C}\{^{1}\mathrm{J}\}$ NMR δ: 138.7 (C–H); 138.3 (C–C); 128.4 (C–H); 127.7 (C–H); 127.5 (C–H); 117.6 (q, 3.5 Hz, C–H); 72.9 (CH$_2$); 70.3 (CH$_2$); 37.4 (q, 29.6, CH$_2$CF$_3$); 32.5 (CH$_2$); 29.6 (CH$_2$); 28.8 (CH$_2$); and 26.0 (CH$_2$) ppm. The CF$_3$ peaks were not easily discernible.

Phenylpropargyl alcohol

After 8 h, the organic compounds were extracted into ether and the ether layer washed with further portions of water. Analysis by TLC showed three spots, two of which originated from the starting material. A silica column was run, and NMR spectra obtained for the first fraction. $^{19}\mathrm{F}$ NMR δ: -61.0 (t, CF$_3$?); -67.0 (t, CF$_3$?); -82.8 (s, CF$_2$CF$_3$?); -108.9 (s, CF$_2$CF$_3$) ppm. $^{1}\mathrm{H}$ NMR δ: 7.2–7.5 (m); 5.5 (s); 3.2 (q) ppm + others. $^{13}\mathrm{C}\{^{1}\mathrm{H}\}$ NMR δ: a large number of peaks in the aromatic region (120–135 ppm); 83.3 ($\mathrm{CH_2{=}C{=}C}$); and 26.9 (q, 35 Hz, $\mathrm{\mathit{C}H_2CF_3}$) ppm. GC–MS (CI) showed peaks with M$^+$ +1 of 185 ($\mathrm{Ph{-}C{\equiv}C{-}CH_2CF_3}$ or isomer); 235 ($\mathrm{Ph{-}C{\equiv}C{-}CH_2CF_2CF_3}$ or isomer); and 285 ($\mathrm{Ph{-}C{\equiv}CH_2CF_2CF_2CF_3}$ or isomer). IR spectroscopy showed, amongst other peaks, two peaks at 1960 and 1930 cm^{-1}, indicative of an allene.

1-Phenylethan-1-ol

GLC analysis showed four peaks for a 24 h sample. GC–MS analysis identified the fluorine-containing product as 1-fluoro-1-phenylethane: M^+ 124: 124 (23); 104 (100); 89 (2); 78 (29); 63 (4); 51 (14); 39(5); ^{19}F NMR spectroscopy indicated a peak at -167.1 (dq, 48 and 24 Hz) ppm.

2-Phenylpropan-2-ol

After 8 h, GLC analysis showed five peaks. GC–MS analysis showed the fluorine-containing product to be 2-fluoro-2-phenylpropane: M^+ 138: 138 (21); 123 (100); 103 (25); 91 (4); 77 (15); 63 (3); 51 (15); 39 (7). ^{19}F NMR spectroscopy of the reaction mixtures showed a large number of peaks, the main ones being -91.3; -89.5; and -142 (septet, 22 Hz) ppm.

Triphenylmethanol

After 24 h, GLC analysis showed two peaks. GC–MS analysis identified the fluorine-containing product as triphenylfluoromethane [M^+ 262: 262 (48); 243 (8); 185 (100); 165 (30); 105 (4); 77 (4); 51 (3)]. ^{19}F NMR spectroscopy showed a peak at -126.5 ppm.

Dodecyl alcohol

After 8 h, GC–MS (CI) analysis showed one major peak with $M^+ +1$ equal to 215. ^1H NMR δ: 7.9; 4.0; 3.4; 1.6; 1.2; and 0.7 ppm. $^{13}C\{^1H\}$ NMR δ: peaks at 160.7 ($C{=}O$), 63.6 ($\mathit{C}H_2OCHO$) and a large number of other peaks in the 31–13 ppm region.

2-Oxobutan-1-ol

After 24 h, GLC analysis showed two peaks. These were identified by GC–MS analysis as 1-(2-oxobutanyl) formate and 2-oxobutan-1-ol. ^{19}F NMR spectroscopy of the reaction mixtures showed a number of peaks, none of which were significant.

But-1-en-4-ol

After 24 h, GLC analysis showed a very large number of peaks, some of which were identified by GC–MS as buta-1,4-diene, 1,1,1-trifluoropent-4-ene and difluoropentadiene(?) ^{19}F NMR spectroscopy of the reaction mixtures showed a number of peaks, none of which were significant in size.

2-Nitrophenol

After 8 h, GLC analysis showed four peaks; three of these were identified by GC–MS as benzoxazole, 2-nitrophenol and 2-(difluoromethoxy)-nitrobenzene.

Catechol

After 8 h, there were a large number of products as identified by GLC methods. GC–MS analysis identified some of these as 2-(difluoromethoxy)phenol, 2-hydroxyphenyl formate and diphenyl ether carbonate. ^{19}F NMR spectroscopy showed a peak at -71.7 (d, 88.8 Hz) ppm.

Benzyl formate

GLC analysis and ^{19}F NMR spectroscopy showed that no reaction had occurred after 24 h.

Benzyl fluoride

GLC analysis and ^{19}F NMR spectroscopy showed that no reaction had occurred after 24 h.

Benzyl chloride

After 24 h, GLC analysis showed seven peaks. GC–MS identified the fluorine-containing products as (i) 1,1,1-trifluoro-2-phenylethane [M^+ 160], (ii) 1,1,1,2,2-pentafluoro-3-phenylethene [M^+ 210], (iii) 1,1,1,2,2,3,3-heptafluoro-4-phenylbutane [M^+ 260: 260 (20); 91 (100); 65 (4); 51 (3) and (iv) 1,1,1,2,2,3,3,4,4-nonafluoro-5-phenylpropane [M^+ 310: 310 (15); 91 (100); 65 (7); 51 (3)].

Benzyl bromide

After 24 h, GC analysis showed three peaks. GC–MS analysis identified the major peak as a mixture of 1,1,1-trifluoro-2-phenylethane [M^+ 160: 160 (35); 141 (7); 109 (7); 91 (100); 65 (13); 1(8)] and 1,1,1,2,2-pentafluoro-2-phenylethane [M^+ 210: 210 (26); 91 (100); 77 (3); 69 (4); 65 (13); 51 (8); 39 (8)].

Cinnamyl chloride

After 8 h, GLC analysis indicated that a large number of products had been formed. GC–MS cross-scan report showed all homologues from 1-phenyl-3-trifluoromethyl prop-1-ene (M^+ 186) to 1-phenyl-3-perfluorononyl prop-1-ene (M^+ 586). A full MS analysis was obtained for 1-phenyl-3-perfluoropropylprop-1-ene [M^+ 386: 386 (284); 336 (2); 146 (4); 117 (100); 91 (9); 69 (8); 51 (3)]. Also identified was 1,6-diphenylhexa-1,5-diene [M^+ 234: 234 (3); 117 (100); 91 (9); 77 (2); 65 (2); 51 (2); 39 (2)].

Chlorododecane

GLC analysis and ^{19}F NMR spectroscopy showed that no reaction had occurred.

Other reactions

To investigate the effect of copper and its salts, benzyl alcohol (5 mmol) and copper, copper(I) chloride or copper(II) chloride (30 mmol) were heated in DMF or DMAc (8 ml) at 80 °C. The products were identified by GLC and GC–MS analyses.

Acknowledgements

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