POLYFLUOROARYL ORGANOMETALLIC COMPOUNDS

XVII *. 2,4,6-TRIS(TRIFLUOROMETHYL)PHENYLLITHIUM, A STERICALLY CROWDED SYSTEM *

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(Received December 30th, 1986)

Summary

A lithium derivative (3) is generated from 1,3,5-tris(trifluoromethyl)benzene (2) and is shown to be remarkably thermally stable. It is shown that 2 is less acidic than pentafluorobenzene, in competition for butyllithium. A preliminary survey of reactivity shows that 2,4,6-tris(trifluoromethyl)phenyllithium (3) undergoes a variety of transformations including the formation of mercury and copper derivatives, in spite of crowding in the system.

The chemistry of aromatic systems poly-substituted with perfluoroalkyl groups is potentially interesting, although such systems are likely to be comparatively inert to reactions that involve attack on the ring. 2,4,6-Tris(trifluoromethyl)chlorobenzene has been synthesised previously [2] by halogen exchange, using hydrogen fluoride, on the corresponding chlorinated compound and a lithio derivative was generated by chlorine–lithium exchange using butyllithium. Streitwieser and co-workers have determined the acidity of 1,3,5-tris(trifluoromethyl)benzene [3] but there is no report on the generation of a lithio derivative by this route. Here we describe the ready synthesis of 1,3,5-tris(trifluoromethyl)benzene and its conversion to a lithio derivative, which functions to a large extent in a conventional fashion, in spite of the considerable level of crowding around the reaction centre.

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* This paper is dedicated to Professor G.E. Coates, on his 70th birthday, in much appreciation first of his splendidly individual style as a teacher and later of him as a stimulating colleague.

Conversion of carboxyl to trifluoromethyl, using sulphur tetrafluoride is a useful procedure established many years ago by workers at the duPont Co. [4]. Consequently, we have prepared 1,3,5-tris(trifluoromethyl)benzene (2) from benzene-1,3,5-tricarboxylic acid (1), using sulphur tetrafluoride. The product contained acid fluorides that were removed partly by distillation and were re-cycled.
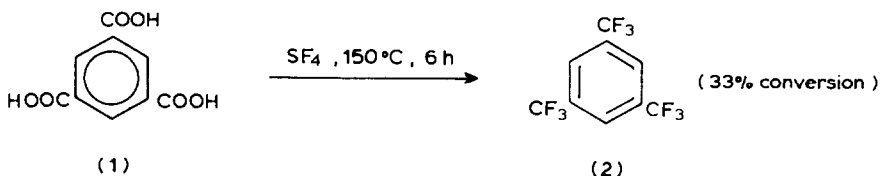

Trifluoromethyl groups have a considerable effect on the acidity of *ortho*-positions [3,5] and consequently, we have found that a lithio derivative 3 is readily formed from 2 by hydrogen–lithium exchange using butyllithium in hexane at room temperature. This exchange is essentially quantitative, as established by quenching with methanol-OD and subsequent mass spectrometric examination of the recovered starting material 2. We have also carried out a competition experiment between 2 and pentafluorobenzene, for a deficiency of butyllithium, at $-65\,^{\circ}$C. A period of 5 h was allowed for equilibrium to be attained and, under these conditions, 88% of the resultant deuterated material was derived from pentafluorobenzene. It may be assumed that the greatest acidifying influence will arise from *ortho*-substituents and so we conclude, therefore, that *ortho*-trifluoromethyl is significantly less acidifying than *ortho*-fluorine in determining C–H acidity; a similar conclusion could be drawn from kinetic acidity data [3].

We have attempted to eliminate lithium fluoride from 3 and, further, to trap a potential intermediate 4, using furan. However, the lithio derivative 3 showed quite ramarkable thermal stability. Starting material 2 was mainly recovered,
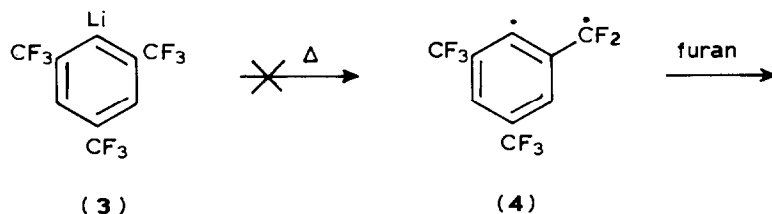

following hydrolysis, even after a sample of 3 had been heated in a sealed tube at $90\,^{\circ}$C. No trapping products were obtained when similar experiments were carried out with added furan.

Reactions with 3 that involve carbon–carbon bond formation are shown in Scheme 1. Steric effects did, however, become apparent by virtue of the fact that we were unable to form either the corresponding ketone with dimethyl carbonate or the benzil derivative with oxallyl dichloride. In both cases, only mono-substitution products 5 and 6 respectively, were obtained. In reaction with acetyl chloride the diketone derivative 7 was obtained as the principal product, obviously produced by an aldol reaction on the initially formed ketone and the product exists principally in the enol form as indicated (7). This is clearly shown by IR and NMR data (see
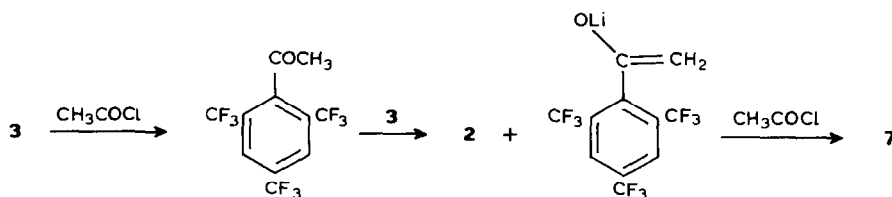
Experimental). However, the chemical shift of OH at 4.85 ppm is clearly not in the strongly hydrogen-bonded region and this must be attributed to the effect of trifluoromethyl, although the reasons for this are not obvious. Carboxylation of 3 to
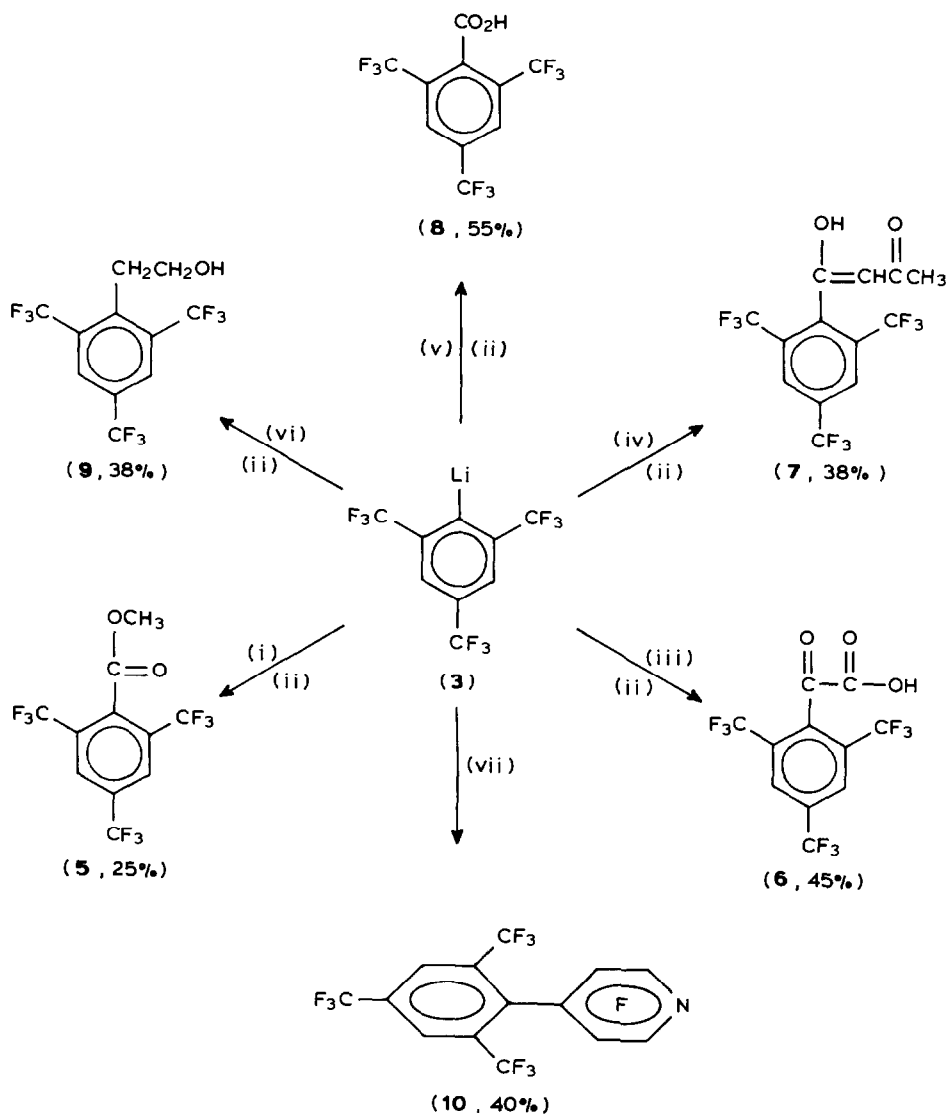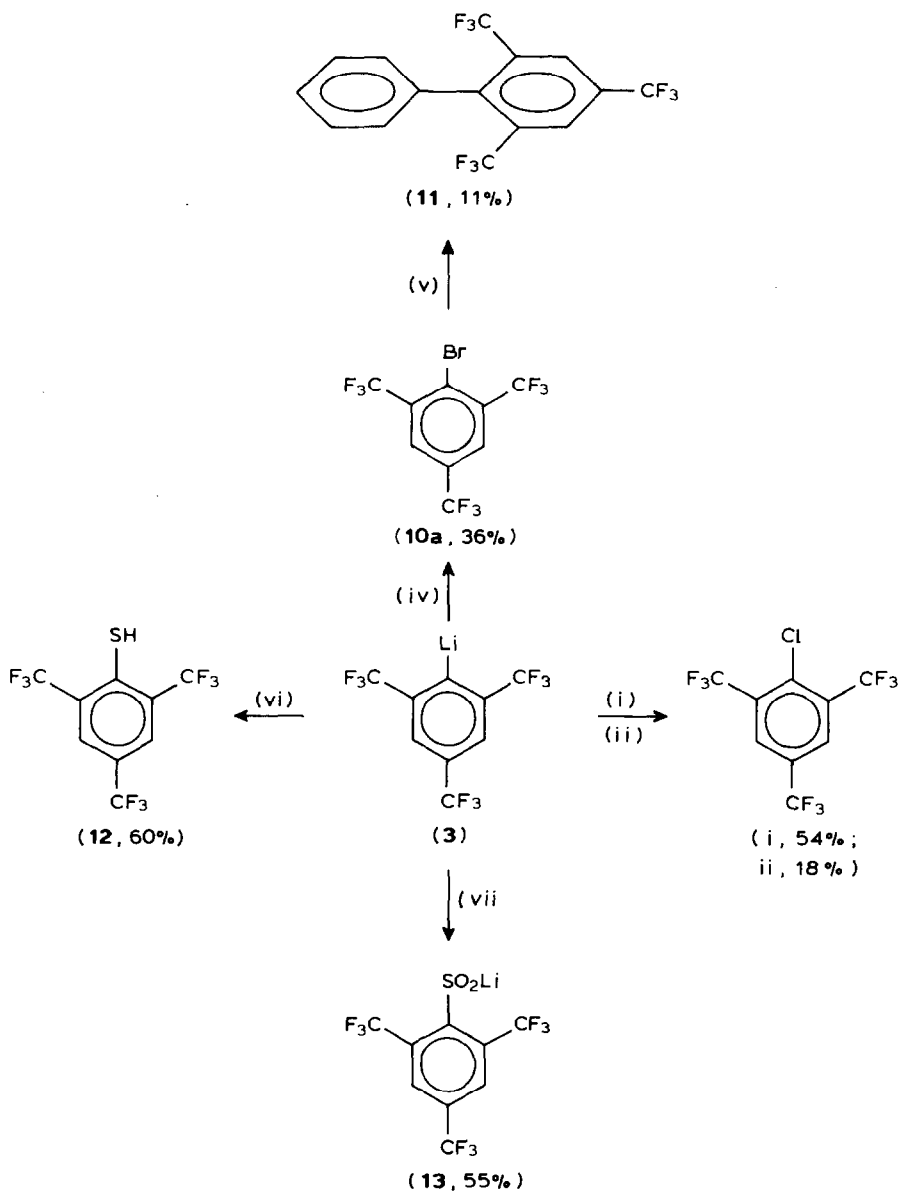

SCHEME 1. Carbon–carbon bond formation. (i) $(CH_3O)_3CO$; (ii) H_3O^+; (iii) $(COCl)_2$; (iv) CH_3COCl; (v) CO_2; (vi) CH_2CH_2O; (vii) C_5F_5N.

give **8** and reaction with ethylene oxide, to give **9** were not high yield processes. Surprisingly, however, reaction with pentafluoropyridine gave a biaryl **10**.

Exchange of hydrogen in **2** for halogen may be achieved via the lithio derivative **3** (see Scheme 2) and copper coupling of the bromo derivative **10a** also gave a biaryl **11** albeit in low yield. Reactions of **3** with sulphur electrophiles gave **12** and **13**.

Preliminary reactions with metal halides demonstrate that tin, mercury, and

(**11** , 11%)

(v)

Br

(**10a** , 36%)

(iv)

SH   Li   Cl

(vi)   (i) (ii)

(**12** , 60%)   (**3**)   (i , 54% ; ii , 18%)

(vii)

SO$_2$Li

(**13** , 55%)

SCHEME 2. Carbon–halogen and carbon–sulphur bond formation. (i) Cl$_2$; (ii) C$_2$Cl$_6$; (iv) Br$_2$; (v) Cu, C$_6$H$_5$I; (vi) S$_8$, H$_3$O$^+$; (vii) SO$_2$.
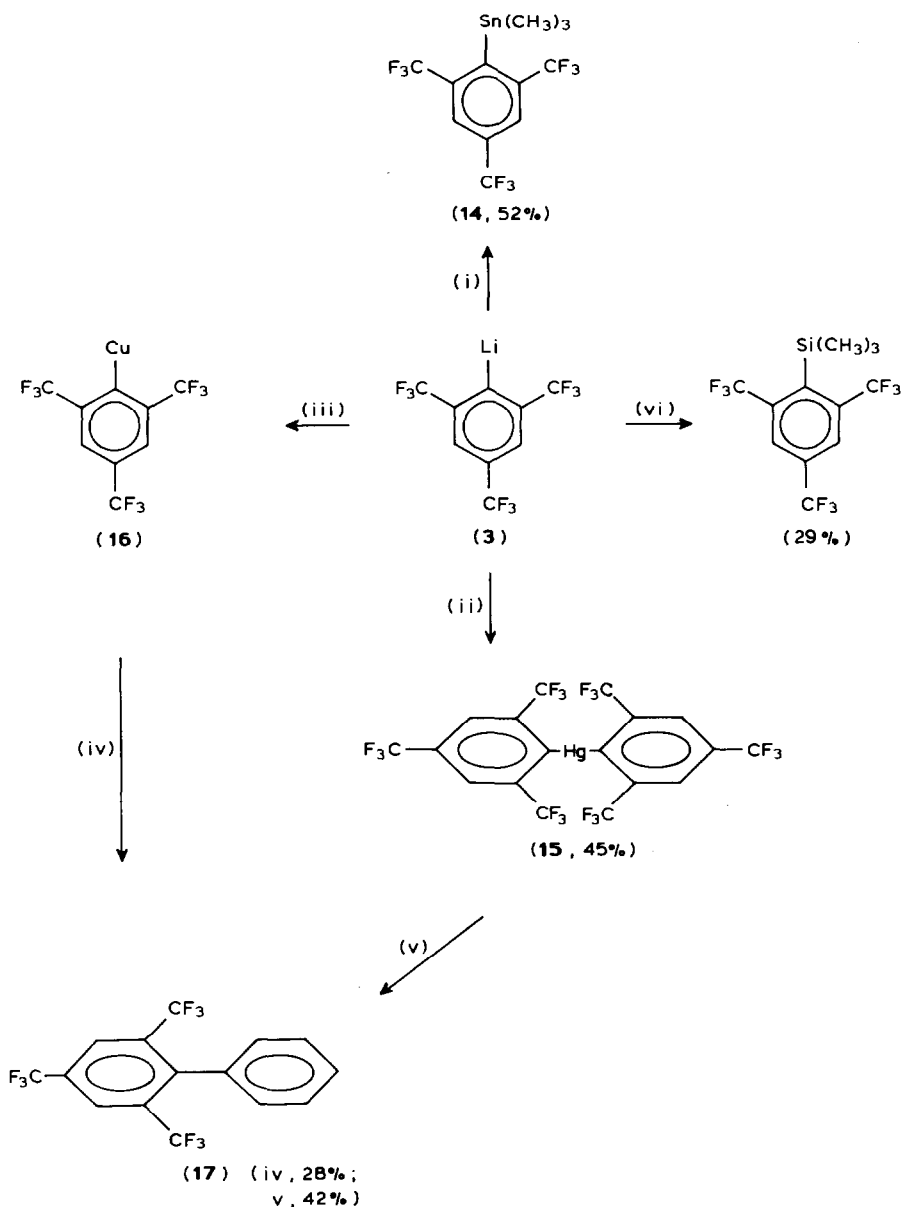
SCHEME 3. Formation of metal and silicon derivatives. (i) $(CH_3)_3SnCl$; (ii) $HgCl_2$; (iii) CuI; (iv) C_6H_5I, DMSO, 100° C; (v) C_6H_5I, Cu, NMP, 141° C; (vi) $(CH_3)_3SiCl$.

copper derivatives may be obtained (Scheme 3) and this is interesting because the 2,4,6-tris(trifluoromethyl)phenyl ligand would appear to be very sterically demanding. The tin and mercury derivatives 14 and 15 are, of course, easily characterised. These derivatives are completely inert to cleavage by electrophiles, quite unlike the reactions of various pentafluorophenyl derivatives of tin [6] and mercury [6,7] which are cleaved by halogens and metal halides, although less readily than phenyl. This is

quite consistent with the fact that, although electrophilic substitution e.g. nitration occurs in pentafluorobenzene [8], we have been quite unable to nitrate 2 under quite drastic conditions. The copper compound is mainly demonstrated by conversion to a biaryl 17. It was demonstrated that reaction of lithio derivative 3 with copper(I) iodide was complete (Gilman test [9]) and a solid was obtained on the addition of dioxane in attempting to apply earlier methodology [10]. This solid had an IR spectrum that compared well with a composite spectrum of dioxane and 2 in Nujol but elemental analysis also demonstrated the presence of lithium and iodine. It is quite probable that, like phenyl [11] and pentafluorophenyl [12] copper, various complexes will be formed depending on the reaction conditions. However, the presence of a copper species is clearly indicated by conversion to a biaryl 17 by reaction with iodobenzene, although in comparatively low yield. Higher yields of 17 were obtained, via the mercurial 15, in reaction with copper (see Scheme 3), and this process must also involve a copper intermediate like 16, although the structure of these species is as yet unknown.

This preliminary survey of the reactions of the lithio derivative 3 is sufficient to indicate the potential use of the latter in the synthesis of systems that may require stabilisation by bulky substituents.

Experimental

Spectroscopic data were obtained using the following spectrometers: IR, Perkin–Elmer 457; mass spectrometry, VG7070E or V.G. Micromass 12B linked with GLC; NMR, Varian EM360L or Bruker WH-360. Trichlorofluoromethane and TMS were used as standards and upfield shifts (ppm) recorded as positive. GLC was carried out using a Pye 104 instrument (flame ionisation detector) with packed columns as follows: Column 05, 5% silicone gum rubber; Column 010, 10% silicone gum rubber; Column 5V, 5% OV101; Column 10V, 10% OV101; Column K, 20% Krytox; and Column P.E.G., 10% polyethylene glycol. Preparative GLC was performed using a Varian Aerograph 920. Carbon, hydrogen, and nitrogen analyses were obtained using a Perkin–Elmer 240 Elemental Analyser.

n-Butyllithium was a commercial sample dispersed as a 1.6 M solution in hexane.

1,3,5-Tris(trifluoromethyl)benzene

(a) Preparation

Trimesic acid (150 g, 0.7 mol) was placed in a 1 l autoclave which was then cooled in liquid nitrogen before addition of sulphur tetrafluoride (500 g, 4.6 mol). The autoclave was sealed, allowed to warm to room temperature and heated at 150°C (6 h). After venting to release unused sulphur tetrafluoride and gaseous products, the liquid contents were poured onto crushed ice to remove unreacted acid and hydrogen fluoride. The lower layer was separated, washed with sodium hydroxide solution (2 M) and dried (MgSO$_4$). Fractional distillation to remove partially fluorinated material yielded a colourless liquid identified as 1,3,5-tris(trifluoromethyl)benzene (64 g, 33%) b.p. 118–120°C (lit. [13], 119.6°C); δ(F) 65.3 (lit. [14], 64.3); δ(H) 8.1 (lit. [14], 8.1); m/e 282 (M^+), 263 ($M^+ - F$), 213 ($M^+ - CF_3$).

(b) Comparison of acidity with that of pentafluorobenzene

A solution of 1,3,5-tris(trifluoromethyl)benzene (0.94 g, 3.3 mmol) and pentafluorobenzene (1.68 g, 10 mmol) in diethyl ether (7 ml) was cooled in an acetone-CO_2 bath and stirred, while butyllithium (8 mmol) in hexane (5 ml) was added dropwise so as to maintain the temperature below $-65\,^{\circ}$C. After stirring for 5 h, methanol-OD (1.5 ml) was added and the mixture allowed to warm to room temperature. The ether/hexane solution was dried ($MgSO_4$) and the solvents removed by distillation before analysis by MS-GLC (Column K, $70\,^{\circ}$C). Comparison of the M^+ and $(M + 1)^+$ peak heights of each component showed that, while 1,3,5-tris(trifluoromethyl)benzene was unchanged, 88% of the pentafluorobenzene had undergone deuterium exchange via the organolithium intermediate.

2,4,6-Tris(trifluoromethyl)phenyllithium

(a) Preparation

A solution of 1,3,5-tris(trifluoromethyl)benzene (2.82 g, 10 mmol) in diethyl ether (7 ml) was stirred under nitrogen at room temperature, while butyllithium (10 mmol) in hexane solution (7 ml) was added, dropwise, so as to prevent vigorous boiling of the ether. Then, the mixture was stirred for a further hour.

Addition of methanol-OD (0.5 ml) and analysis by MS-GLC (Column 010) of the residue, after filtration of lithium methoxide and removal of solvent by distillation, showed that 90% of the 1,3,5-tris(trifluoromethyl)benzene had been converted into the mono-deuterated derivative.

This procedure was repeated at $0\,^{\circ}$C and 66% conversion observed.

(b) Reactions of lithium derivative 3

(i) Chlorine. A gas bulb containing chlorine (300 ml, 13 mmol) was attached to a flask containing 3 (~ 15 mmol) in ether/hexane (1/1, 20 ml), the solution was cooled in liquid air, and then the system was evacuated before the connecting tap was opened, allowing chlorine to condense onto the mixture. After warming, with stirring, to room temperature water was added to dissolve precipitated lithium chloride and the organic layer separated and dried ($MgSO_4$). Removal of the solvents and recovered 1,3,5-tris(trifluoromethyl)benzene by fractional distillation, left a dark residue which was eluted through a silica column with petroleum ether. Removal of the solvent left a colourless liquid identified as 1-chloro-2,4,6-tris(trifluoromethyl)benzene [13] (2.74 g, 66%).

(ii) Hexachloroethane. A solution of hexachloroethane (3.5 g, 15 mmol) in diethyl ether (12 ml) was added to 3 (~ 15 mmol) in ether/hexane (1/1, 20 ml) and the mixture stirred at room temperature (30 min) before addition of water. The organic layer was separated, dried ($MgSO_4$), and the solvent removed by distillation. Analysis by MS-GLC (Column 10V, $100\,^{\circ}$C) showed the residue to contain 1,3,5-tris(trifluoromethyl)benzene, tetrachloroethene, hexachlorethane and chlorinated material. A small quantity of colourless liquid was isolated by fractional distillation ($151\,^{\circ}$C) and identified as 1-chloro-2,4,6-tris(trifluoromethyl)benzene [13] (0.85 g, 18%).

(iii) Bromine. A solution of bromine (1.6 g, 10 mmol) in diethyl ether (7 ml) was added dropwise to 3 (~ 10 mmol) in ether/hexane (1/1, 14 ml). Water was added to dissolve precipitated lithium bromide and the organic layer separated and dried

(MgSO$_4$). The product mixture was separated by fractional distillation and, after removal of the solvent, two fractions were obtained: recovered *1,3,5-tris(trifluoro-methyl)benzene* and a colourless liquid, identified as *1-bromo-2,4,6-tris(trifluoro-methyl)benzene* [14] (0.45 g, 12%), 41–43°C (6 mmHg).

Brown residue from the distillation was chromatographed over silica as described above and a further amount of brominated product was obtained (0.88 g, 24%).

(iv) Trimethyltin chloride. A solution of trimethyltin chloride (2.98 g, 15 mmol) in diethyl ether (10 ml) was added dropwise to 3 (~ 15 mmol) in ether/hexane (1/1, 20 ml) and the mixture stirred overnight before addition of water. The organic layer was separated, dried (MgSO$_4$) under nitrogen, and the volatile materials removed under vacuum leaving a yellow liquid (3.48 g). Distillation yielded a colourless liquid identified as *trimethyl[2,4,6-tris(trifluoromethyl)phenyl]tin*, found: C, 32.4; H, 2.7. C$_{12}$H$_{11}$F$_9$Sn calc: C, 32.43; H, 2.47%; δ(F) 58.7 (6F, CF_3), 64.7 (3F, CF_3); δ(H) 8.1 (2H, CH), 0.8 (9H, CH_3); δ(^{119}Sn) (CDCl$_3$, Sn(CH$_3$)$_4$) 6.98; ν_{max} 3090, 2980, 2910, 1280, 1180, 1130 cm^{-1}; *m/e* 435, 433, 431, 430, 429, 428, 427 (*M$^+$*).

(v) Trimethylsilyl chloride. The reagent (1.88 ml, 15 mmol) was added to 3 (~ 15 mmol) in hexane/ether (1/1, 20 ml) and the mixture stirred overnight before addition of water. The organic layer was separated, dried (MgSO$_4$), and solvents and remaining trimethylsilyl chloride removed by distillation leaving an orange liquid (2.39 g). Analysis of the residue by MS-GLC (Column 10V) showed it to contain three main components, identified from molecular ion peaks and fragmentation patterns as: 1,3,5-tris(trifluoromethyl)benzene; hexamethyl disiloxane, *m/z* 147 (*M$^+$* – CH$_3$), 73 (Si(CH$_3$)$_3$)$^+$; and trimethyl[2,4,6-tris(trifluoromethyl)phenyl]silane, *m/z* 339 (*M$^+$* – CH$_3$), 262 (C$_9$H$_2$F$_8$)$^+$, 73 [Si(CH$_3$)$_3$]$^+$. From GLC the yield was estimated to be 29%.

(vi) Acetyl chloride. The reagent (1.07 ml, 15 mmol) was added to 3 (~ 15 mmol) in hexane/ether (1/1, 20 ml) and the mixture stirred (30 min) before addition of water and extraction of the organic layer into diethyl ether. After drying (MgSO$_4$), solvent was removed by distillation and the residue (3.09 g) analysed by GLC (Column 10V, 100°C) which showed it to contain 1,3,5-tris(trifluoromethyl)benzene (60%) and two other components. The major unknown component was isolated by preparative scale GLC (Column 010) and identified as a colourless liquid *1[2,4,6-tris(trifluoromethyl)phenyl]1,3-butanedione* (0.35 g, 12%); Found: C, 42.3; H, 1.5. C$_{13}$H$_7$F$_9$O$_2$ calc: C, 42.62; H, 1.91%; δ(F) 60.3 (6F, CF_3), 65.4 (3F, CF$_3$); δ(H) 8.3 (2H, *m*-CH), 5.6 (1H, C=CH), 4.8 (1H, C-OH), 2.0 (3H, CH$_3$); δ(^{13}C) (CDCl$_3$) 122.36 (CF_3, q, *J*(C–F) 271.7 Hz) 132.49 (o C-CF$_3$, q, *J*(C–F) 31.6 Hz), 131.88 (*p*-C-CF$_3$, q, *J*(C–F) 34.4 Hz), 126.74 (m-C-H), 107.19 (C=C-H), 21.22 (CH_3), 166.88 (C=O), 143.60 (C=C-OH), 137.05 (C-C-OH); ν_{max} 1770 (C=O), 1700, 1280, 1205, 1140 cm^{-1}; *m/e* 366 (0.5%, *M$^+$*), 43 (100%, CH$_3$CO$^+$).

(vii) Oxalyl dichloride. The reagent (0.64 ml, 7.5 mmol) was added to 3 (~ 15 mmol) in ether/hexane (1/1, 20 ml) and the mixture stirred (30 min) before addition of water and a few drops of conc. hydrochloric acid. The organic material was separated by ether extraction, shaken with aqueous sodium bicarbonate solution to extract any acidic material as its sodium salt and the aqueous layer separated and acidified before ether extraction. The two resulting ether solutions were dried (MgSO$_4$).

Removal of the solvent from the acidic material under reduced pressure left a

solid which was sublimed yielding the white crystalline solid *2-[2,4,6-tris(trifluoro-methyl)phenyl]2-oxoethanoic acid* (1.19 g, 45%), m.p. 113°C; Found: C, 37.1; H, 0.5. $C_{11}H_3F_9O_3$ calc: C, 37.28; H, 0.85%; δ(F) (CDCl$_3$) 58.0 (6F, CF_3), 63.4 (3F, CF_3); δ(H) (CDCl$_3$) 7.7 (2H, *m*-C-*H*), 8.4 (1H, O*H*); ν_{max} 3100 (OH), 1720 (C=O), 1750 (C=O), 1270, 1200 cm^{-1}; *m/e* 335 (1.5%, $M^+ - 19$), 309 (100%, (CF$_3$)$_3$C$_6$H$_2$C=O$^+$).

(viii) Dimethyl carbonate. The reagent (1.35 ml, 15 mmol) was added to **3** ($\sim$ 15 mmol) in ether/hexane (1/1, 20 ml) and the mixture stirred (30 min) before addition of sulphuric acid (2 *M*). The organic material was extracted into ether, dried (MgSO$_4$), and the solvent removed by distillation. Analysis of the residue by GLC (Column 010, 125–150°C) showed it to consist of two components, which were separated by fractional distillation and shown to be 1,3,5-tris(trifluoromethyl)-benzene, and a white solid identified as methyl-2,4,6-tris(trifluoromethyl)benzoate (0.2 g, 4%), δ(F) (CDCl$_3$) 62.3 (6F, CF_3), 65.6 (3F, CF$_3$); δ(H) (CDCl$_3$) 8.2 (2H, *m*-C-H), 4.0 (3H, CH$_3$O); *m/e* 340 (0.6%, M^+), 309 (100%, (CF$_3$)$_3$C$_6$H$_2$C=O$^+$).

(ix) Ethylene oxide. A glass bulb containing ethylene oxide (600 ml, 26 mmol) was attached to a flask containing **3** ($\sim$ 15 mmol) in hexane/ether (1/1, 20 mmol), the solution cooled in liquid nitrogen, and the system evacuated before a connecting tap was opened allowing the ethylene oxide to condense onto the ether solution. After stirring (1 h) hydrochloric acid (2 *M*) was added and the organic material extracted into ether. Removal of the solvent under reduced pressure left a yellow powder from which was sublimed (90°C) a white solid. On recrystallisation from petroleum ether (60/80) a white crystalline solid was obtained, identified as *2-[2,4,6-tris(trifluoromethyl)phenyl]ethanol* (1.7 g, 35%), m.p. 74–75°C; Found: C, 40.6; H, 2.2. $C_{11}H_7F_9O$ calc: C, 40.49; H, 2.15%); δ(F) (CDCl$_3$) 59.3 (6F, CF$_3$), 63.6 (3F, CF$_3$); δ(H) (CDCl$_3$) 8.1 (2H, *m*-C-*H*), 4.9 (1H, O*H*), 2.8 (2H, C*H*$_2$), 2.2 (2H, C*H*$_2$); ν_{max} 3280 (OH), 2900 (CH$_2$), 1280, 1240, 1200, 1180, 1165, 1120 cm^{-1}; *m/e* 309 (1.7%, $M^+ - $ OH), 276 (93.8%), 31 (100%).

(x) Carbon dioxide. Excess solid carbon dioxide was added to **3** ($\sim$ 10 mmol) in hexane/ether (1/1, 10 ml) and the mixture stirred until it attained room temperature. Water was added and the ether layer separated and dried (MgSO$_4$) before removal of the solvent under reduced pressure. The residue was analysed by GLC (Column 010) and shown by comparison with the authentic material to be 1,3,5-tris(trifluoromethyl)benzene. The aqueous layer was acidified (dil. HCl) and ether extracted. Removal of solvent under reduced pressure left a white crystalline solid which was dried under vacuum and recrystallised from benzene/petroleum ether 40/60 (1/1) before identification as 2,4,6-tris(trifluoromethyl)benzoic acid [15] (1.49 g, 46%), m.p. 185–186°C; equivalent weight 324.

(xi) Sulphur dioxide. A gas bulb containing sulphur dioxide (600 ml, 26 mmol) was attached to a flask containing **3** ($\sim$ 15 mmol) in hexane/ether (1/1, 20 ml), the solution was cooled in liquid nitrogen and the system evacuated before allowing the sulphur dioxide to condense onto the ethereal solution. After warming to room temperature the dense precipitate was filtered, washed with ether and air dried. The cream powder gave a positive Smiles test [16] and was identified as lithium 2,4,6-tris(trifluoromethyl)phenyl sulphinate (2.92 g, 55%); δ(F) [(CD$_3$)$_2$CO] 55.7 (6F, CF_3), 64.2 (3F, CF$_3$); *m/e* 329 (C$_9$H$_2$F$_9$SO$^+$), 262 (100%, C$_9$F$_8$H$_2^+$).

(xii) Sulphur. The reagent (0.48 g, 15 mmol) was added to **3** ($\sim$ 15 mmol) in ether/hexane (1/1, 20 ml) and the mixture stirred (1 h) before addition of sulphuric acid (2 *M*). The organic material was extracted into ether solution, dried (MgSO$_4$),

and solvent removed by distillation. Analysis of the residue by GLC (Column 010, 150°C) showed one product had been formed in 60% yield. A pungent smelling colourless liquid was isolated by preparative-scale GLC (Column 010) and identified as *2,4,6-tris(trifluoromethyl)benzene-thiol*, (Found: C, 34.7; H, 0.8. $C_9H_3F_9S$ calc: C, 34.39; H, 0.96%); δ(F) 64.7 (6F, CF_3), 65.7 (3F, CF_3); δ(H) 8.0 (2H, *m*-C-H), 4.3 (S*H*); ν_{max} 3100, 2630 (S–H), 1620, 1580, 1470, 1270, 1200, 1130 cm^{-1}; m/z 314 (40%, M^+), 294 (100%).

(xiii) Pentafluoropyridine. The reagent (2.54 g, 15 mmol) was added to 3 (~ 15 mmol) in ether/hexane (1/1, 20 ml) and the mixture stirred at room temperature (1 h) and refluxed (1 h). Water was added and the organic material extracted into ether and dried (MgSO$_4$). After removal of solvent by distillation the residue was analysed by GLC (Column 010, 145°C) and one product observed in 40% yield. A white crystalline solid was isolated by preparative-scale GLC (Column 010) and identified as *2,3,5,6-tetrafluoro-4-[2,4,6-tris(trifluoromethyl)phenyl]pyridine*, (Found: C, 39.0; H, 0.6; N, 3.0; $C_{14}H_2F_{13}N$ calc: C, 38.99; H, 0.46; N, 3.25%); δ(F) (CDCl$_3$) 61.0 (6F, CF_3), 63.4 (3F, CF_3), 89.4 (2F, m, 2,5-C-*F*), 140.0 (2F, m, 3,6-C-*F*); ν_{max} 3060, 1620, 1460, 1280, 1210, 1135 cm^{-1}; m/e 431 (M^+).

Mercury and copper derivatives

(a) Bis[2,4,6-tris(trifluoromethyl)phenyl]mercury

(i) Preparation. Mercury(II) chloride (2.03 g, 7.5 mmol) in ether (20 ml) was added to a solution of 3 (~ 15 mmol) in hexane/ether (1/1, 20 ml) and the mixture stirred at room temperature (3 d). The solution was poured onto ice and a yellow-white crystalline solid was filtered and dried under suction. Sublimation (60°C, < 1 mmHg) produced a white solid which was recrystallised from chloroform/ethanol yielding *bis[2,4,6-tris(trifluoromethyl)phenyl]mercury* (2.59 g, 45%), m.p. 78–80°C, Found: C, 27.9; H, 0.2. $C_{18}H_4HgF_{18}$ calc: C, 28.35; H, 0.52%); δ(F) (CDCl$_3$) 61 (6F, CF_3), 63.6 (3F, CF_3); δ(H) 8.1 (2H, *m*-C-H); δ(^{13}C) 123.76 (*o*-CF_3, q, *J*(C–F) 268.5), 122.76 (*p*-CF_3, q, *J*(C–F) 277.1), 139.67 (*o*-*C*-CF$_3$, q, *J*(C–F) 32.2), 131.86 (*p*-*C*-CF$_3$, q, *J*(C–F) 33.5), 125.55 (*C*-H), 163.50 (*C*-Hg); m/e 764, 763, 762, 761, 760) (M^+), (485, 483, 482, 481, 480, 479) ((CF$_3$)$_3$C$_6$H$_2$Hg$^+$), 281 (100%).

(ii) Reaction with iodobenzene. A mixture containing bis-2,4,6-tris(trifluoromethyl)phenylmercury (2.07 g, 2.7 mmol), iodobenzene (1.07 g, 5.25 mmol), copper powder (0.89 g, 14 mmol) and n-methylpyrrolidinone (9 ml) was stirred at 141°C under nitrogen (3 h). The product mixture was analysed by MS-GLC (Column P.E.G., 150°C) and ^{19}F NMR, and the components identified as: 1,3,5-tris(trifluoromethyl)benzene, iodobenzene, and 2,4,6-tris(trifluoromethyl)biphenyl, δ(F) 58.7 (6F, CF_3), 64 (3F, CF_3); m/e 358 (100%, M^+). The yield of biphenyl was calculated from GLC to be 42%.

(b) "2,4,6-Tris(trifluoromethyl)phenyl copper"

(i) Formation and coupling with iodobenzene. A solution of 3 (~ 10 mmol) in ether/hexane (1/1, 14 ml) was prepared as described previously. A small sample was removed for a Gilman Colour Test [9] and the resulting green colouration showed that the lithium derivative was present. Copper(I) iodide (1.91 g, 10 mmol) was then added and the solution stirred for 24 h until the colour test was negative.

Iodobenzene (2.04 g, 10 mmol) and dioxane (15 ml) were added to the mixture and the ether removed by distillation under nitrogen. The residue was heated at $100\,^\circ C$ (48 h) before addition of ammonium chloride and ammonia solution to dissolve the copper salts. Organic material was extracted into ether solution, dried ($MgSO_4$), and analysed by MS-GLC (Column 010, $140\,^\circ C$) and ^{19}F NMR (after removal of ether). The components were identified as: 1,3,5-tris(trifluoromethyl)-benzene (28%), iodobenzene (36%), and 2,4,6-tris(trifluoromethyl)biphenyl, (36%); δ(F) 59.5 (6F, CF_3), 64.7 (3F, CF_3); m/e 358 (M^+).

Acknowledgement

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