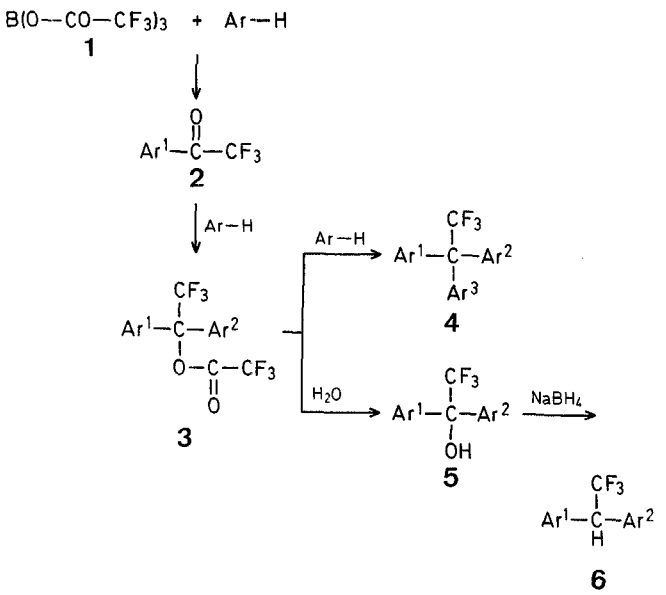

A Simple Method for the Synthesis of 1,1,1-Trifluoro-2,2,2-triarylethanes and 2,2,2-Trifluoro-1,1-diarylethanols using Tris[trifluoroacetoxy]-borane

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Tris[trifluoroacetoxy]-borane (**1**) has been used to remove protecting groups during the synthesis of peptides[1] but no other use has been reported. We have found that a solution of **1** (1 mol) in trifluoroacetic acid can react with aromatic compounds (2 mol) to yield 1,1,1-trifluoro-2,2,2-triarylethanes (**4**) or 2,2,2-trifluoro-1,1-diarylethanols (**5**). The formation of compounds **4** proceeds via the aryl trifluoromethyl ketone **2** and the ester **3** which would hydrolyse to the corresponding alcohol **5** under the conditions of the work-up. Ketones are generally poor alkylating agents and yields are low even with active substrates[2].

The reaction of benzene with **1** gives only traces of the triarylethane **4** and the yield is not improved by heating or prolonged reaction times. More active substrates (toluene, *t*-butylbenzene, and anisole) give **4** in good yields. The reaction with the most reactive substrates (phenol, 1,3-dimethoxybenzene, and 1,2,4-trimethoxybenzene) yielded diarylethanols (**5**). Steric effects appear to be important in determining whether the reaction proceeds to **3** and **4** since the reactions with *m*-xylene and mesitylene do not proceed beyond the corresponding ketones **2**. The reaction of phenol with **1** to produce **5c** required that the reactants were present in equimolar proportions.

While the spectral data confirm the proposed structures, the effect of coupling to fluorine in the ^{13}C-N.M.R. spectra was often difficult to observe due to the low intensity of the signals and overlapping with other bands. In the case of product **5b**, the structure was confirmed by borohydride reduction to the corresponding alkane **6** which showed clearly the coupling to fluorine in the N.M.R. spectra. The reduction, a modification of the procedure of Ref.[3], used a large excess of sodium borohydride. The successful reduction of **5b** shows that borohydride may be used to reduce stabilised carbocations (a solution of **5b** in trifluoroacetic acid is deep red).

1,1,1-Trifluoro-2,2,2-triarylethanes (4) and 2,2,2-Trifluoro-1,1-diarylethanols (5); General Procedure:

Tris[trifluoroacetoxy]-borane (**1**; 5 mmol, or 10 mmol for the reaction with phenol) is dissolved in trifluoroacetic acid (10 ml) and the aromatic compound (10 mmol) is added. The mixture is stirred at room temperature for 18 h and poured into water (20 ml). The product is obtained either by filtration and recrystallisation or by ether extraction (2 × 10 ml) and recrystallisation of the residue obtained by evaporation of the dried (magnesium sulphate) ether extract.

1,1,1-Trifluoro-2,2-bis[2,4,5-trimethoxyphenyl]-ethane (6):

Compound **5b** (0.51 g, 1.18 mmol) is dissolved in trifluoroacetic acid (15 ml) and the solution stirred under nitrogen at room temperature. Sodium borohydride powder (0.42 g, 11.1 mmol) is added in small batches over 30 min. The mixture is stirred for a further 2.5 h, poured into water (30 ml), extracted with ether (2 × 15 ml), and this ethereal layer dried with magnesium sulphate. Removal of the solvent gives an oil which is recrystallised from petroleum ether (b.p. 60–80 °C) to give **6**; yield: 0.38 g (78%); m.p. 69–70 °C.

$C_{20}H_{23}F_3O_6$	calc.	C 57.69	H 5.57	F 13.69
(416.4)	found	57.86	5.51	13.40

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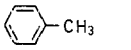
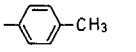
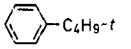
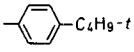
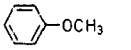
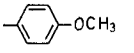
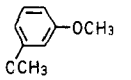
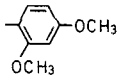
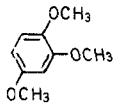
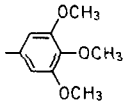
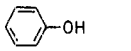
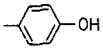
Table 1. 1,1,1-Trifluoro-2,2,2-triarylethanes **(4)** and 2,2,2-Trifluoro-1,1-diarylethanols **(5)**

Reactant Ar—H	Product	Yield [%]	m.p. [°C] (solvent)	Molecular Formula[a]	
	**4a** $Ar^1 = Ar^2 = Ar^3 =$ 	63	204–207° (ethanol/$CHCl_3$)	$C_{23}H_{21}F_3$	(354.4)
	**4b** $Ar^1 = Ar^2 = Ar^3 =$ 	73	250° (dec) (CCl_4)	$C_{32}H_{39}F_3$	(480.7)
	**4c** $Ar^1 = Ar^2 = Ar^3 =$ 	90	196–198° (ethanol)	$C_{23}H_{21}F_3O_3$	(402.4)
	**5a** $Ar^1 = Ar^2 =$ 	82	81–82° (ethanol/H_2O)	$C_{18}H_{21}F_3O_5$	(372.3)
	**5b** $Ar^1 = Ar^2 =$ 	48	104–105° (ethanol/H_2O)	$C_{20}H_{23}F_3O_7$	(432.4)
	**5c**[b] $Ar^1 =$  ; $Ar^2 =$ 	25	173–174° (H_2O)	$C_{14}H_{11}F_3O_3$	(284.2)

[a] The microanalyses showed the following maximum deviations from the calculated values: C, ±0.22; H, ±0.24; F, ±0.40. Exception: **5b**; H, +0.43.

[b] I.R. (Nujol): $\nu = 830$; 750 cm^{-1}.

Table 2. N.M.R.-Spectral Data of Compounds **4, 5,** and **6**

Compound	^{1}H-N.M.R. (Solvent/TMS_{int})[a] δ [ppm]	^{13}C-N.M.R. (Solvent/TMS_{int})[b] δ [ppm]	^{19}F-N.M.R. (Solvent/$F_3C—CHBrCl_{ext}$)[a] δ [ppm]
4a	(CCl_4): 2.33 (s, 3H); 6.90 (s, 4H)	($CDCl_3$): 20.86; 128.8 (q, J = 286.8 Hz); 128.68; 129.91; 137.19; 137.58	(CCl_4): 58.2
4b	(CCl_4): 1.30 (s, 9H); 7.15 (s, 4H)	($CDCl_3$): 31.32; 34.44; 124.48; 128.79 (q, J = 285.8 Hz); 129.65; 137.45; 159.32	(CCl_4): 58.1
4c	(CCl_4): 3.75 (s, 3H); 6.87 (m, 4H)	($CDCl_3$): 55.18; 63.43 (q, J = 23.5 Hz); 113.34; 128.29 (q, J = 285.3 Hz); 131.62; 132.77; 158.84	(CCl_4): 60.1 [$^1J_{^{13}C,^{19}F}$ = 285.7 Hz]
5a	($CDCl_3$): 3.55 (s, 6H); 3.75 (s, 6H); 5.95 (s, 1H, exchanges with D_2O); 6.55 (m, 4H); 7.33 (d, J = 9.3 Hz, 2H)	($CDCl_3$): 55.24; 56.10; 79.96 (q, J = 29.4 Hz); 100.48; 104.32; 120.82; 125.65 (q, J = 286.8 Hz); 129.51; 158.96; 160.65	(acetone): 75.4
5b	($CDCl_3$): 3.55 (s, 6H); 3.83, 3.85 (s, 6H); 5.9 (s, exchanges with D_2O); 6.55 (s, 2H); 7.2 (s, 2H)	(acetone-d_6): 54.80; 55.90; 99.54; 113.58; 120.04; 142.32; 149.89; 151.78	($CDCl_3$): 75.0
5c	(acetone-d_6): 6.7–7.4 (m, 8H); 8.47 (s, 1H, exchanges with D_2O); 8.90 (s, 1H, exchanges with D_2O)	(acetone-d_6): 82.01 (q, J = 27.4 Hz); 115.62; 118.35; 119.84; 124.78; 126.54 (q, J = 289.5 Hz); 128.61; 129.65; 130.63; 157.28; 158.51	(acetone): 75.4
6	($CDCl_3$): 3.75; 3.80; 3.85 (s, 18H); 5.73 (q, J = 10.9 Hz, 1H); 6.55 (s, 2H); 7.00 (s, 2H)	(acetone-d_6): 39.16 (q, J = 27.8 Hz); 56.28; 57.26; 57.45; 99.82; 115.55; 116.46; 128.09 (q, J = 279.4 Hz); 144.28; 151.17; 153.38	($CDCl_3$): 65.3 (d, J = 11.1 Hz)

[a] Recorded on a Perkin-Elmer R12B.

[b] Recorded on a Bruker HX90E.

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