The Reduction of Fluorine-containing Triarylmethanols by Formic Acid

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Triarylmethanols containing one or more fluorine substituents in the *para*-positions are converted by 90% formic acid into a mixture of the fluorine-containing triarylmethane, and a second component in which one fluorine has been replaced by a hydroxy-group. A mechanism is proposed which involves nucleophilic attack by water on the initial carbonium ion (4) with subsequent loss of hydrogen fluoride, to give the diphenyl-*p*-hydroxyphenylmethyl carbonium ion (6) which undergoes hydride transfer with formate to give the product. This mechanism was supported by the isolation of 4-hydroxytriphenylmethanol from the reaction involving 4-fluorotriphenylmethanol. Pentafluorophenyldiphenylmethanol on similar treatment gave 9-(pentafluorophenyl)fluorene, and 2-(trifluoromethyl)triphenylmethanol gave 9-(2-trifluoromethylphenyl)fluorene. Both reactions presumably occur *via* an intramolecular electrophilic aromatic substitution. The ^{19}F and ^{13}C n.m.r. spectra of the triarylmethanes and 9-arylfluorenes are reported and discussed.

THE reduction of triphenylmethanol to triphenylmethane in refluxing aqueous formic acid was discovered *ca.* 75 years ago,[1,2] and has been used sporadically for this and related reactions ever since. There have been several mechanistic studies,[3] and in particular, Stewart[4] showed that the key step involves hydride transfer from formate to the triarylmethyl cation [reactions (1) and (2)].

$$Ar_3COH + HCO_2H \longrightarrow Ar_3C^+ + HCO_2^- + H_2O \quad (1)$$

$$Ar_3C^+ + HCO_2^- \longrightarrow Ar_3CH + CO_2 \quad (2)$$

In a preliminary communication[5] we reported that triarylmethanols containing *para*-fluorine substituents on treatment with formic acid give products in which the fluorine has been replaced by hydroxyl. However, pentafluorophenyldiphenylmethanol on similar treatment gave mainly 9-(pentafluorophenyl)fluorene. In this paper the details of these reactions are described, together with some extensions of the work. The ^{19}F and ^{13}C n.m.r. spectra of a variety of substituted triphenylmethanes and 9-phenylfluorenes are also communicated.

TABLE 1

Products of the reduction of halogenotriarylmethanols by 90% formic acid

Methanol	Reflux time (h)	Products (%)
$4-FC_6H_4C(OH)Ph_2$	2	$4-FC_6H_4CHPh_2$ (65),[6,7] $4-HOC_6H_4CHPh_2$ (35)[8]
$(4-FC_6H_4)_2C(OH)Ph$	1	$(4-FC_6H_4)_2CHPh$ (55),[9] $4-HOC_6H_4CH(Ph)C_6H_4F-4$ (35)
$(4-FC_6H_4)_3COH$	5	$(4-FC_6H_4)_3CH$ (35), $4-HOC_6H_4CH(C_6H_4F-4)_2$ (41)
$(4-ClC_6H_4)_3COH$	14	$(4-ClC_6H_4)_3CH$ (98)[10]
$(4-BrC_6H_4)_3COH$	6	$(4-BrC_6H_4)_3CH$ (63) *,[10]
$3-FC_6H_4C(OH)Ph_2$	1	$3-FC_6H_4CHPh_2$ (80)[7]
$C_6F_5C(OH)Ph_2$	15	$C_6F_5CHPh_2$ (36), 9-(Pentafluorophenyl)fluorene (48)
$2-(CF_3)C_6H_4C(OH)Ph_2$	12	$2-(CF_3)C_6H_4CHPh_2$ (63), 9-(2-trifluoromethylphenyl)fluorene (37)

* 25% $(4-BrC_6H_4)_3COH$ was recovered unchanged.

RESULTS AND DISCUSSION

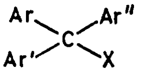
Reaction of Halogen-substituted Triarylmethanols with Formic Acid.—On refluxing 4-fluorotriphenylmethanol with excess of 90% formic acid, hydrogen fluoride was evolved together with carbon dioxide, and a mixture of products was obtained consisting of the 'normal' reduction product, 4-fluorotriphenylmethane (1) and 4-hydroxytriphenylmethane (2). Similarly, 4,4'-difluoro- and 4,4',4''-trifluoro-triphenylmethanol gave mixtures consisting of the normal reduction product and a triarylmethane in which one fluorine had been replaced by a hydroxy-group. On the other hand, 3-fluorotriphenylmethanol and 4,4',4''-trichloro- and 4,4',4''-tribromotriphenylmethanol on similar treatment gave only the 'normal' triarylmethanes. The products, yields, and reaction times are shown in Table 1.

The reaction of 4-fluorotriphenylmethanol was chosen for more detailed study, and the products were quantitatively analysed by h.p.l.c. for a variety of reaction conditions. At longer reaction times (>0.5 h) h.p.l.c. analysis confirmed that (1) and (2) are the major products of the reaction, but showed the presence of one additional minor product (*ca.* 1%) which was not identified. Retention-time comparisons with synthetic 9-(4-fluorophenyl)fluorene demonstrated that none of this material was produced. The yields of the two products were essentially independent of the acid strength in the range 60—99%, although much longer reaction times were required at the lower acid strengths. The proportions of (1) and (2) were also unaffected by added anhydrous sodium formate.

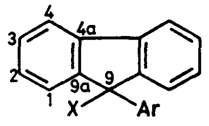
At reaction times < *ca.* 30 min the starting 4-fluorotriphenylmethanol appeared on the chromatogram, accompanied by three additional product peaks, one of which had an extremely long retention time. A reaction lasting 5 min was carried out on a larger scale and separated by column chromatography. Good correlation between the h.p.l.c. chromatogram and the column separation was observed, the starting material and products (1) and (2) were separated together with one of the additional products, which was identified as 4-hydroxytriphenylmethanol (3). The long-retention-time product was not eluted from the column, and the third extra product which was yellow in colour, was in too small a quantity for identification.

TABLE 2

^{19}F Chemical shifts of triarylmethanes, triarylmethanols, 9-arylfluorenes, and 9-aryl-9-hydroxyfluorenes at room temperature



(15)

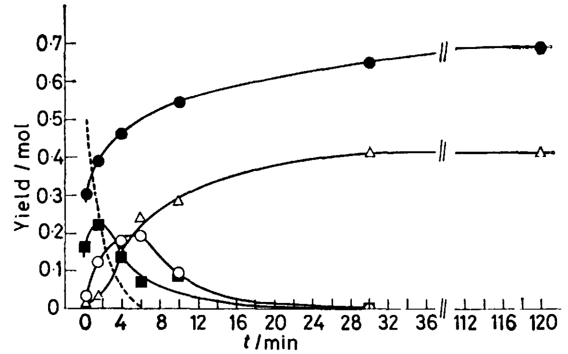


(16)

Compound		ϕ
(15a)	Ar = Ar' = C_6H_5, Ar'' = *p*-FC_6H_4, X = H	116.6
(15b)	Ar = C_6H_5, Ar' = Ar'' = *p*-FC_6H_4, X = H	116.3
(15c)	Ar = Ar' = Ar'' = *p*-FC_6H_4, X = H	115.9
(15d)	Ar = C_6H_5, Ar' = *p*-HOC_6H_4, Ar'' = *p*-FC_6H_4, X = H	116.7
(15e)	Ar = *p*-HOC_6H_4, Ar' = Ar'' = *p*-FC_6H_4, X = H	116.4
(15f)	Ar = Ar' = C_6H_5, Ar'' = *m*-FC_6H_4, X = H	113.8
(15g)	Ar = Ar' = C_6H_5, Ar'' = *p*-FC_6H_4, X = OH	115.6
(15h)	Ar = C_6H_5, Ar' = Ar'' = *p*-FC_6H_4, X = OH	115.1
(15j)	Ar = Ar' = Ar'' = *p*-FC_6H_4, X = OH	114.7
(15k)	Ar = Ar' = C_6H_5, Ar'' = *m*-FC_6H_4, X = OH	114.0
(16a)	Ar = *p*-FC_6H_4, X = H	116.8
(16b)	Ar = *m*-FC_6H_4, X = H	113.5
(16c)	Ar = *p*-FC_6H_4, X = OH	117.0
(16d)	Ar = *m*-FC_6H_4, X = OH	113.8
(15m)	Ar = Ar' = C_6H_5, Ar'' = *o*-$CF_3C_6H_4$, X = H	58.1
(15n)	Ar = Ar' = C_6H_5, Ar'' = *o*-$CF_3C_6H_4$, X = OH	54.4
(16d)	Ar = *o*-$CF_3C_6H_4$, X = H	57.0
(16e)	Ar = *o*-$CF_3C_6H_4$, X = OH	55.2 [a]
(15p)	Ar = Ar' = C_6H_5, Ar'' = C_6F_5, X = OH	137.7 (*o*); 162.4 (*m*); 154.5 (*p*)
(16f)	Ar = C_6F_5, X = H	139.1 (*o*); 161.4 (*m*); 156.0 (*p*) [b] 145.5 (*o*) 162.3
(16g)	Ar = C_6F_5, X = OH	138.3 (*o*); 164.1 (*m*); 158.2 (*p*) [c]

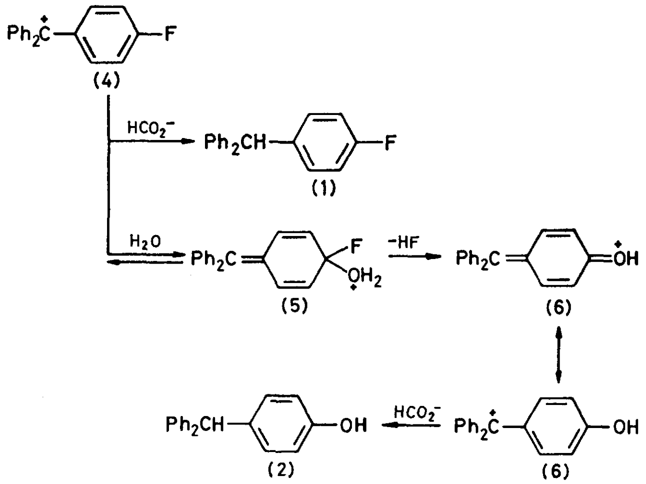
[a] At −45 °C, ϕ 52.3 and 55.8. [b] Shifts were measured at −18 °C. [c] At −45 °C signal for *o*-fluorines is very broad.

A series of reactions lasting different times was then carried out on a small scale and each analysed by h.p.l.c. The combined yield of the two unidentified products was calculated from the difference in the total weight of material used per analysis and the weight of the known components calculated from their peak areas. The results of these experiments, which illustrate the product development with time, are shown in the Figure. Product (3) and the two unidentified products show an initial increase in concentration with time and this is followed by a steady decay until they are completely consumed in 30 min. The growth of product (1) which is more rapid than that of (2) would appear to correlate with the more rapid decay of one or both the unknown intermediates. Likewise, the appearance of (2) correlates with the slower decay of intermediate (3).



Formic acid reduction of 4-fluorotriphenylmethanol. Product development with time. Yields of products given from 1 mol of reactant. Filled circles, $4\text{-}FC_6H_4CHPh_2$; open triangles, $4\text{-}HOC_6H_4CHPh_2$; open circles, $4\text{-}HOC_6H_4C(OH)Ph_2$; filled squares, combined yields of two unidentified products; dashed line records the disappearance of $4\text{-}FC_6H_4C(OH)Ph_2$

We propose that the formation of (2) occurs by the mechanism shown in Scheme 1. Triarylmethanols are substantially dissociated to carbonium ions in formic acid,[4] and the presence of a positively charged group *para*

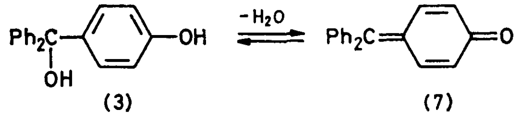


SCHEME 1

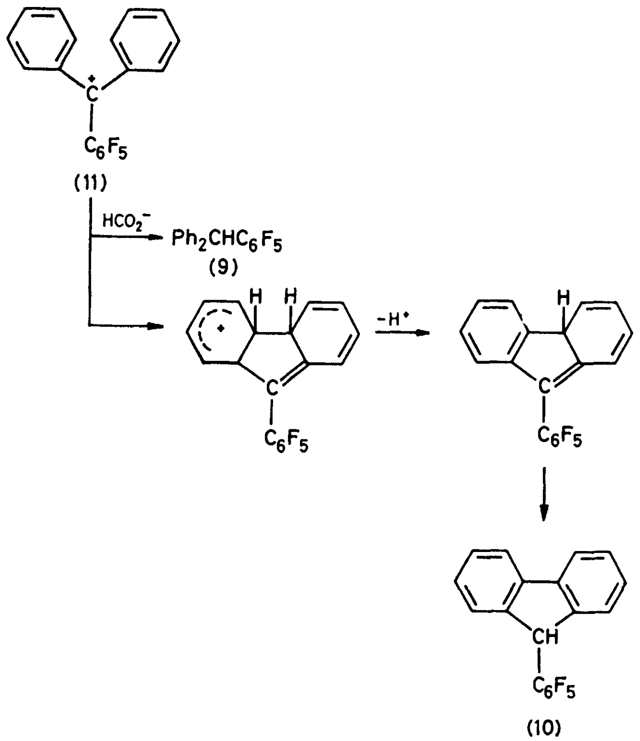
to fluorine in the cation may be expected to activate it to nucleophilic attack by water, which is known to act as a base in formic acid.[4,11] The mechanism of formation of the phenol then involves rapid loss of HF from the initial intermediate (5) to give (6). Intermediate (6) is the ionized form in which 4-hydroxyphenyldiphenylmethanol (3) would exist in acid solution, although it would be isolated and analysed as (3). Hydride transfer to the cation (6) by formate would then account for the formation of phenol (2). Loss of water from (3) or loss of a proton from (6) would give the quinone methide (7), and in fact (3) and (7) are known to interconvert readily.[12] It is possible, therefore, that (7) is one of the two unidentified intermediates, and this view is strengthened by the fact that the one having the shorter retention time was yellow coloured.

Product (1) is clearly formed when the cation (4) undergoes hydride transfer with formate. We speculate that the very long-retention-time unidentified intermediate is in fact the formate salt of (4).

The absence of any variation in the product yields with change in the water concentration in the formic acid indicates either that attack of water on cation (4) is not the rate-limiting step or that there is a sufficient quantity of water, even in 99% formic acid, to make the rate of phenol formation independent of the water concentration. Fluorine displacement from aromatic compounds is known to be several orders of magnitude more rapid than chlorine or bromine displacement.[13] The absence of any halogen substitution in 4,4′,4″-trichloro- and tribromo-triphenylmethanols (see Table 1) is not therefore inconsistent with the proposed mechanism. Similarly, the lack of fluorine replacement in 3-fluorotriphenylmethanol would be expected, since the fluorine is *meta* to the cationic substituent and so would not be activated towards nucleophilic attack by water.



Pentafluorophenyldiphenylmethanol (8) reacted with formic acid to give a mixture of pentafluorophenyldiphenylmethane (9) and 9-(pentafluorophenyl)fluorene (10). The identity of the latter was confirmed by comparing its properties with authentic material synthesized from fluoren-9-one and pentafluorophenylmagnesium bromide, the carbinol first formed being reduced with phosphorus and iodine in glacial acetic acid.[14] Like other 9-arylfluorenes with substituents in the *ortho*-positions of the 9-aryl group (10) shows a temperature-dependent ^{19}F n.m.r. spectrum (see below). It would appear that the pentafluorophenyl group is rotated sufficiently far out of the plane of the carbonium ion (11) so that the positively charged group cannot activate the *para*-fluorine to nucleophilic attack by water. Instead, cation (11) undergoes either hydride transfer to give the triarylmethane (9) or intramolecular electrophilic aromatic substitution as shown in Scheme 2 to give (10).



SCHEME 2

The mixtures were quantitatively analysed by h.p.l.c., using authentic (9) and (10) for calibration purposes. The chromatograms showed (9) and (10) as the only detectable products. Interestingly, authentic Ph$_2$CHC$_6$F$_5$, prepared by reduction of the carbinol (8) with phosphorus and iodine in acetic acid, was shown to contain a small amount (1.2%) of the fluorene derivative (10), thus indicating that some intramolecular electrophilic substitution occurs in this reaction too.

The reaction mixtures from 3-fluorotriphenylmethanol and 4-fluorotriphenylmethanol (see above) were analysed by h.p.l.c. and shown by comparisons of retention times with those of authentic materials to contain none of the 9-arylfluorene derivatives. In 2-(trifluoromethyl)triphenylmethanol (12) the CF$_3$ group is strongly electron-withdrawing, and also occupies the *ortho*-position. Reduction of this methanol with formic acid again gave a mixture of 2-(trifluoromethyl)triphenylmethane (13) and 9-(2-trifluoromethylphenyl)fluorene (14). This result supports the mechanism (Scheme 2) proposed for fluorene formation. The fluorene (14) also showed a temperature-dependent ^{19}F n.m.r. spectrum.

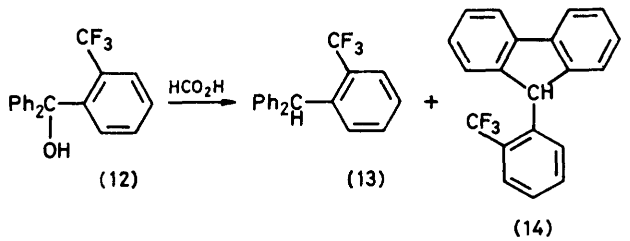


TABLE 3

^{13}C Chemical shifts (J_{CF}/Hz in parentheses) of 9-arylfluorenes and 9-aryl-9-hydroxyfluorenes

	Carbon											
Compound (16)	1	2,3	4	4a	9a	9	1′	2′	3′	4′	5′	6′
Ar = *o*-$CF_3C_6H_4$, X = H	119.6	127.3	125.2	141.0	148.1	49.4	*a*	*a*	124.9	126.2	131.7	130.1
Ar = *m*-FC_6H_4, X = H	119.6	127.2, 127.1	124.9	140.8	146.9	53.9	114.0 (6.8)	115.1 (21.4)	162.8 (247.4)	113.6 (21.2)	129.7 (8.2)	123.7 (0)
Ar = *p*-FC_6H_4, X = H	119.6	127.1	124.9	140.7	147.4	53.5	137.1 (0)	129.5 (7.8)	115.3 (21.4)	161.7 (246.1)		
Ar = C_6F_5, X = H	120.0	127.7, 127.2	123.8	140.9	143.7	42.3	*a*					
Ar = *o*-$CF_3C_6H_4$, X = OH	119.7	128.7, 128.1	124.4	139.5	151.0	65.2	*a*	*a*	127.1	129.9	130.8	126.8
Ar = *m*-FC_6H_4, X = OH	119.6	128.8, 128.1	124.6	139.2	150.0	82.8	145.8 (7.1)	112.5 (23.6)	162.5 (246.0)	113.6 (20.9)	129.1 (8.4)	120.8 (2.6)
Ar = *p*-FC_6H_4, X = OH	119.6	128.7, 128.1	124.6	139.2	150.4	82.8	138.6 (0)	126.9 (8.0)	114.6 (21.4)	161.7 (245.9)		
Ar = C_6F_5, X = OH	120.0	129.5, 128.3	123.7	139.1	147.7	82.0	*a*					

[a] ^{13}C Resonances are not observable under the conditions of a normal proton-noise-decoupled spectrum.

TABLE 4

^{13}Chemical shifts (J_{CF}/Hz in parentheses) of triarylmethanes in CCl_4

Compound (15; X = H)	C_α	C_i	C_o	C_m	C_p
Ar = Ar′ = Ar″ = C_6H_5	56.6	143.6	129.2	127.9	125.9
Ar = Ar′ = Ar″ = *p*-FC_6H_4	54.5	139.0 (3.0)	130.4 (7.7)	115.2 (21.3)	161.4 (247.0)
Ar = Ar′ = Ar″ = *p*-ClC_6H_4	54.9	141.0	130.2	128.5	132.7
Ar = Ar′ = Ar″ = *p*-BrC_6H_4	55.0	141.3	130.5	131.4	120.7
Ar = Ar′ = Ar″ = *p*-$NO_2C_6H_4$ [a]	56.2	149.9	131.4	124.7	148.1
Ar = Ar′ = C_6H_5, Ar″ = *p*-FC_6H_4	55.9	143.4	129.1	128.1	126.3 (Ar, Ar′)
		139.3 (3.0)	130.6 (7.6)	114.8 (21.3)	161.2 (Ar″) (246.0)
Ar = Ar′ = C_6H_5, Ar″ = *m*-FC_6H_4	56.5	142.9	129.1	128.1	126.2 (Ar, Ar′)
		146.4 (6.7)	116.3 (21.7)	162.7 (247.0)	113.0 (Ar″) (21.2)
			124.8 (2.3)	129.3 ($\sim$6.3)	
Ar = Ar′ = C_6H_5, Ar″ = *p*-HOC_6H_4	55.9	143.9	129.1	127.9	125.9 (Ar, Ar′)
		135.8	130.3	114.9	153.7 (Ar″)
Ar = Ar′ = C_6H_5, Ar″ = *o*-$CF_3C_6H_4$	51.6 (1.2)	143.0	129.1	128.0	126.2 (Ar, Ar′)
		142.3		125.6	126.0 (Ar″)
			130.1	132.2	
Ar = C_6H_5, Ar′ = Ar″ = *p*-FC_6H_4	55.2	143.3	129.1	128.2	126.4 (Ar)
		139.2 (3.2)	130.5 (7.8)	115.0 (21.3)	161.3 (Ar′, Ar″) (246.5)
Ar = C_6H_5, Ar′ = *p*-FC_6H_4, Ar″ = *p*-HOC_6H_4	55.1	143.7	129.0	128.0	126.1 (Ar)
		139.5 (2.8)	130.5 ($\sim$9)	114.8 (20.9)	160.9 (Ar′) (253.9)
		135.7	130.2	115.0	153.7 (Ar″)
Ar = Ar′ = *p*-FC_6H_4, Ar″ = *p*-HOC_6H_4	54.3	139.5 (3.0)	130.4 (7.8)	114.9 (21.2)	161.2 (Ar, Ar′) (246.3)
		135.1	130.0	115.1	154.3 (Ar″)

[a] Solvent CD_3COCD_3.

TABLE 5

^{13}C Chemical shifts (J_{CF}/Hz in parentheses) of triarylmethanols in CCl_4

Compound (15; X = OH)	C_α	C_i	C_o	C_m	C_p	Other
Ar = Ar′ = Ar″ = C_6H_5 [a]	82.0	146.9	127.9	127.9	127.2	
Ar = Ar′ = Ar″ = *p*-FC_6H_4	80.7	142.4 (3.2)	129.4 (7.9)	114.7 (21.4)	161.9 (248.1)	
Ar = Ar′ = Ar″ = *p*-ClC_6H_4	80.7	144.3	128.8	128.1	133.6	
Ar = Ar′ = Ar″ = *p*-BrC_6H_4	80.7	144.6	129.2	131.0	121.8	
Ar = Ar′ = Ar″ = *p*-$MeOC_6H_4$	80.6	139.8	128.8	112.7	158.2	54.5 (MeO)
Ar = Ar′ = C_6H_5, Ar″ = *p*-MeC_6H_4	81.4	147.0	127.8	127.8	127.4 (Ar, Ar′)	
		144.1	126.6	128.2	135.9 (Ar″)	20.8 (Me)
Ar = Ar′ = C_6H_5, Ar″ = *p*-FC_6H_4	80.6	146.7	127.7	127.7	127.0 (Ar, Ar′)	
		142.3 (3.1)	129.3 (7.9)	114.6 (21.3)	161.8 (Ar″) (248.6)	
Ar = Ar′ = C_6H_5, Ar″ = *p*-HOC_6H_4	80.2	148.1	127.3	127.6	126.3 (Ar, Ar′)	
		138.2	128.9	114.1	155.9 (Ar″)	
Ar = Ar′ = C_5H_5, Ar″ = *o*-$CF_3C_6H_4$	82.8	147.4	127.6	127.6	127.1 (Ar, Ar′)	
		145.4	*d*	128.4 [c]	127.6 [c] (Ar″)	
			129.9	132.2		
Ar = Ar′ = C_6H_5, Ar″ = *m*-FC_6H_4	81.3	146.5	127.7	127.8	127.0 (Ar, Ar′)	
		149.7 (6.5)	115.0 (22.9)	162.3 (246.4)	113.7 (Ar″) (21.3)	
			123.5 (2.3)	128.7 (7.9)		
Ar = Ar′ = C_6H_5, Ar″ = C_6F_5 [e]	80.8	144.4	128.2	128.2	126.9 (Ar, Ar′)	
		d	*d*	*d*	*d* (Ar″)	
Ar = C_6H_5, Ar′ = Ar″ = *p*-FC_6H_4	81.0	146.7	127.6	127.8	126.9 (Ar)	
		142.5 (3.4)	129.5 (7.9)	114.5 (21.3)	161.8 (Ar′, Ar″) (247.9)	

[a] Solvent $CDCl_3$. [b] Solvent CH_3SOCH_3. [c] Assignments tentative. [d] Resonances not observed. [e] Solvent 1 : 1 CCl_4–$CDCl_3$.

Triphenylmethanol itself is known to undergo cyclization to 9-phenylfluorene under rather harsher conditions than those employed here. Kliegl synthesized 9-phenylfluorene by heating solid triphenylmethanol with crystalline phosphoric acid.[15] Owen and Allen reported the photocyclization of triarylmethanols on photolysis in 99% sulphuric acid.[12] The mechanism they proposed was basically the same as that of Scheme 2, but involved the triplet rather than the ground state of Ar_3C^+.

^{13}C *and* ^{19}F *N.M.R. Spectra of Triarylmethanes and* 9-*Arylfluorenes.*—^{19}F Spectra of fluorinated triphenylmethanes, triphenylmethanols, 9-phenylfluorenes, and 9-hydroxy-9-phenylfluorenes are collected in Table 2. In general, the spectra are unremarkable and, in the case of the monofluorophenyl compounds, the signals show appropriate multiplicity, *viz.*, *p*-fluoro-derivatives, a triplet of triplets (J_m *ca.* 8.5, J_o *ca.* 5 Hz) and *m*-fluoro-derivatives a set of eight lines as expected if J_p *ca.* 0 Hz. Compound (15p) has a spectrum typical of molecules containing a pentafluorophenyl group but, in the case of compounds (16f and g), the situation is more complex. At room temperature, the resonance for the *o*-fluorines of (16f) is sufficiently broad as to be almost unobservable and that for the *m*-fluorines is also broadened. As the temperature is raised, the signals sharpen to give a pattern similar to that observed for (15p) and at low temperature five fluorine resonances are observed. These observations are consistent with the *o*- and *m*-fluorine atoms becoming non-equivalent due to restricted rotation about the fluorene-C-9–C-1′- pentafluorophenyl bond. This is a well documented phenomenon.[16–18] For compound (16g), only three fluorine resonances are observed at room temperature but the signal for the *o*-fluorenes is broad at −45°. These spectra are complex and were not analysed further. However, it is clear that the barrier to rotation for 9-pentafluorophenylfluorene is higher than that for 9-hydroxy-9-pentafluorophenylfluorene. This order of ease of rotation is that previously observed in arylfluorenes and hydroxyarylfluorenes by Albert and Rieker.[18] The simpler spectra observed for compound (16e) were subjected to more detailed analysis. In this case, coalescence of the two CF_3 singlets occurred at 23.5 ± 1 °C. At −45 °C a separation of 329 Hz was measured between the singlets which showed a 3 : 2 predominance of one conformer. Such a preponderance has been reported in the case of 9-*o*-tolylfluorene. From the Eyring equation one calculates, using these values of coalescence temperature and chemical shift difference, a value of 53.8 ± 2 kJ mol^{-1} for $\Delta G^{\ddagger}_{23.5}$. No changes were observed in the spectrum of (16d) down to −60 °C. No explanation occurs to us at present to account for the barrier for the hydroxy-derivative being the larger in this case.

^{13}C N.m.r. spectra for the fluorene derivatives, triarylmethanes, and triarylmethanols are listed in Tables 3—5, respectively. Assignments were made using substituent chemical shifts, the assignments of the unsubstituted compounds, and, where appropriate, values of J_{CF}. The observed shifts for the triarylmethanols agree reasonably well with those measured from coupled continuous-wave spectra measured in 1.5M solutions in tetrahydrofuran.[19]

EXPERIMENTAL

^{1}H and ^{19}F n.m.r. spectra were recorded on Varian EM 360 and/or HA-100 instruments at room temperature (unless otherwise stated) with tetramethylsilane as internal standard. ^{13}C N.m.r. spectra were recorded on a Varian CFT 20 spectrometer. Mass spectra were obtained with an A.E.I. MS902 spectrometer. H.p.l.c. analysis was performed on a Pye-Unicam LC3 chromatograph with u.v. detection at 254 nm. Partisil columns of 25 and 50 cm length × 4.6 mm diameter were employed with hexane or 5% (v/v) dioxan–hexane as eluant.

Preparation of Triarylmethanols and 9-*Arylfluorenols.*—4-Fluoro-, 3-fluoro-, and 2-trifluoromethyl-triphenylmethanol and pentafluorophenyldiphenylmethanol were prepared by standard Grignard reactions of benzophenone with the appropriate aryl bromide.[20] The analogous series of 9-arylfluorenols was prepared by similar reactions employing fluoren-9-one. 3,3′,3″-Trifluoro-, 3,3′,3″-trichloro-, and 3,3′,3″-tribromo-triphenylmethanol were prepared from the bromide *p*-XC_6H_4Br and the ester *p*-$XC_6H_4CO_2Me$, where X = F, Cl, or Br. 4,4′-Difluorotriphenylmethanol was prepared by a Grignard reaction of *p*-FC_6H_4Br with ethyl benzoate.

Preparation of Authentic Triarylmethanes and 9-*Arylfluorenes.*[14]—The triarylmethanol or 9-arylfluorenol (1 g), red phosphorus (1 g) and iodine (1 g) were refluxed in glacial acetic acid (20 ml) containing water (2 ml) for 2 h. The solution was filtered into water (200 ml) containing 4 ml of a saturated solution of sodium hydrogensulphite. After 1 h the precipitate was filtered off, or the aqueous phase extracted with ether. The ether extract was then washed with water, sodium hydrogencarbonate solution, and water again. The solid obtained after removal of the ether was then recrystallized.

3-*Fluorotriphenylmethane.* The above method gave a yellow oil which was dissolved in petroleum, from which crystals (70%), m.p. 135—137°, were obtained, (Found: M^+, 262.114 8. Calc. for $^{12}C_{19}{}^1H_{15}{}^{19}F$: M, 262.1 158), ϕ_F 113.8 (8 lines).

2-(*Trifluoromethyl*)*triphenylmethane.* The procedure described above yielded, after recrystallization from petroleum, prisms (65%), m.p. 95 °C (Found: M^+, 312.113 1. $C_{20}H_{15}F_3$ requires M, 312.112 6), ϕ_F 58.1 (s).

Pentafluorophenyldiphenylmethane. The above procedure yielded prisms (50%) after recrystallization from petroleum, m.p. 50—51 °C, *m/e* 334, 314, 313, 311, 293, 257, 256, 255, 238, 237, 207, 206, 188, 187, 167, 166, 165, 153, 152, 115, 78, 77, 65, 63, and 51. H.p.l.c. analysis revealed the presence of 1.2% of 9-(pentafluorophenyl)fluorene.

9-(3-*Fluorophenyl*)*fluorene.* The above procedure yielded needles (70%) after recrystallization from petroleum, m.p. 129—131 °C (Found: M^+, 260.100 8. $^{12}C_{19}{}^1H_{13}{}^{19}F$ requires M, 260.100 1), *m/e* 259, 257, 239, 166, 165, 164, 163, and 130, ϕ_F 113.5 (8 lines).

9-(4-*Fluorophenyl*)*fluorene.* This was prepared by the same method and recrystallized from petroleum in 75% yield, m.p. 108 °C (Found: M^+, 260.101 3. $^{12}C_{19}{}^1H_{13}{}^{19}F$ requires M, 260.100 1), *m/e* 259, 165, 130, 128, 127, 120, 119, and 118, ϕ_F 116.8 (tt).

9-(-2-*Trifluoromethylphenyl*)*fluorene.* This was prepared as above and recrystallized from petroleum in 60% yield, m.p. 120—121 °C (Found: M^+, 310.097 9. $^{12}C_{20}{}^{1}H_{13}{}^{19}F_3$ requires M, 310.096 9), m/e 309, 289, 288, 271, 270, 239, 166, 165, 164, 163, 135, 75, 63, 51, and 50, ϕ_F 57.0 (s).

9-(*Pentafluorophenyl*)*fluorene*. This was prepared as above and recrystallized from ethanol in 64% yield, m.p. 160 °C (Found: M^+, 332.062 5. $^{12}C_{19}{}^{1}H_9{}^{19}F_5$ requires M, 332.062 4), m/e 331, 311, 293, 166, 165, 164, 163, 156, 132, and 64; ^{19}F n.m.r. showed the temperature-dependent spectrum described earlier.

Reaction of 4-*Fluorotriphenylmethanol with Formic Acid.*—4-Fluorotriphenylmethanol (1 g) was dissolved in 90% formic acid to give an orange-yellow solution. The colour darkened on refluxing and then slowly faded away during *ca.* 0.5 h, when CO_2 evolution had virtually ceased. Refluxing was continued for a further 1.5 h when the solution was colourless except for a pale yellow oil on top of the aqueous phase. The condenser was etched at the top by HF and an inorganic solid (probably fluorosilicate) collected in the top of the condenser. The mixture was poured into water (*ca.* 50 ml) which was extracted with ether; the separated ether solution was then washed with water, sodium hydrogencarbonate solution, and then water again and finally dried (Na_2SO_4) before removal of the ether. The residue (0.87 g), a yellow oil, was dissolved in petroleum which deposited yellow crystals of 4-hydroxyphenyldiphenylmethane (0.21 g) on standing, m.p. 96 °C (lit.,[8] 110—112 °C) (Found: C, 87.6; H, 6.2%; M^+, 260.119 8. Calculated for $C_{19}H_{16}O$: C, 87.65; H, 6.2%; M^+, 260.120 1). ν_{OH} 3 390 cm^{-1}. After evaporation of further petroleum a second solid, 4-fluorophenyldiphenylmethane,[6,7] was obtained (0.60 g), m.p. 58°, ϕ_F 116.6 (tt) (Found: M^+, 262.115 0. Calc. for $C_{19}H_{15}F$: M, 262.115 8).

A similar reaction was carried out with a reflux time of 5 min. The residue after the same work-up was chromatographed on silica gel, the column being developed with petroleum containing gradually increasing amounts of ether. $Ph_2CHC_6H_4F$-4, $Ph_2C(OH)C_6H_4F$-4, and Ph_2CH-C_6H_4OH-4 were eluted in the stated order and on increasing the proportion of ether in the solvent to 20% a further component was eluted, 4-hydroxyphenyldiphenylmethanol, m.p. 134° (from petroleum–benzene) (lit.,[20] 139°) (Found: C, 83.7; H, 5.8%; M^+, 276.115 7. Calc. for $C_{19}H_{16}O_2$: C, 82.6; H, 5.85%; M^+, 276.115 0).

Experiments for H.p.l.c. Analysis.—The triarylmethanol (30 mg) was refluxed with formic acid (1 ml) for the required time and the mixture worked up as above. The residue was weighed, dissolved in n-hexane (1 ml) or n-hexane containing 5% dioxan, and 2-μl samples were injected into the h.p.l.c. apparatus. The u.v. detector was calibrated using standardized solutions of authentic materials and product concentrations were determined from peak areas measured by planimetry.

Reaction of 4,4′-*Difluorotriphenylmethanol with Formic Acid.*—The triarylmethanol (3 g) was refluxed with 90% formic acid (50 ml) for 1 h and worked-up as described for 4-fluorotriphenylmethanol. The residue (2.5 g) was dissolved in petroleum–benzene which gave a first crop of crystals and a syrupy residue. The crystals were recrystallised from petroleum, m.p. 87° (Found: C, 82.25; H, 5.15%; M^+, 278.110 9. $C_{19}H_{15}OF$ requires C, 82.0; H, 5.45%; M^+, 278.110 6); ν_{OH} 3 160 cm^{-1}. The ^{13}C n.m.r. spectrum confirmed the structure as 4-*fluorophenyl*-4-*hydroxyphenyl*(*phenyl*)*methanol*. The syrupy residue gave crystals of bis-(4-fluorophenyl)phenylmethane[9] on dissolving in petroleum, m.p. 48° (Found: M^+, 280.107 2. Calc. for $C_{19}H_{14}F_2$: 280.106 3). The structure was confirmed by n.m.r. spectroscopy.

Reduction of 4,4′,4″-*Trifluorotriphenylmethanol with Formic Acid.*—The triarylmethanol (1 g) was refluxed in 90% formic acid (10 ml) until CO_2 evolution ceased and the solution became almost colourless (13 h). The evolution of HF was attested by the etching of the condenser and the deposit of inorganic solid in the condenser top. The mixture was worked up as described above and the yellow gummy residue (0.96 g) was chromatographed on a column of silica gel which was developed with petroleum containing increasing amounts of ether. The first fraction (0.33 g) contained *tris*-(4-*fluorophenyl*)*methane* as a liquid, b.p. 165° at 0.8 mmHg (Found: M^+, 298.097 9. $C_{19}H_{13}F_3$ requires M, 298.096 9). The structure was confirmed by n.m.r. spectroscopy. The second fraction was a yellow gum (0.38 g) which was purified by further chromatography (Found: C, 76.9; H, 4.8%; M^+, 296.100 0. $C_{19}H_{14}F_2O$ requires C, 77.0; H, 4.75%; M^+, 296.101 3), ν_{OH} 3 370 cm^{-1}. The n.m.r. spectra confirmed the structure as *bis*-(4-*fluorophenyl*)-4-*hydroxyphenylmethane*. A third fraction consisting of a red solid (0.01 g) was obtained on adding methanol (2%) to be the solvent, but it was not identified.

Reduction of 4,4′,4″-*Tribromotriphenylmethanol with Formic Acid.*—The triarylmethanol (0.98 g) was refluxed with 90% formic acid for 6 h. No hydrogen bromide was evolved. The product was worked up as described above and gave a yellow gum (0.88 g) which was recrystallized from petroleum to give pale yellow crystals (0.59 g) of $(4\text{-}BrC_6H_4)_3CH$, m.p. 108° (lit., 112—116°).[10] The mass spectrum showed both the original gum and the recrystallized material to contain some unchanged $(4\text{-}BrC_6H_4)_3COH$. From the ^{13}C n.m.r. the proportions of the two components in the original gum were found to be $(4\text{-}BrC_6H_4)_3CH : (4\text{-}BrC_6H_4)_3COH$ 1.7 : 1.0.

Reduction of 3-*Fluorotriphenylmethanol with Formic Acid.*—The triarylmethanol (1 g) was refluxed with 90% formic acid (10 ml) until the colour was discharged (1 h). The usual work-up gave a brown oil (0.77 g) which on recrystallization from petroleum gave $Ph_2CHC_6H_4F$-3, m.p. 135—137° (Found: M^+, 262.114 8. Calc. for $C_{19}H_{15}F$: M, 262.115 8. H.p.l.c. analysis revealed the presence of a minor, unidentified component but retention-time comparison with authentic material showed the absence of 9-(3-fluorophenyl)fluorene.

Reaction of 2-(*Trifluoromethyl*)*triphenylmethanol with Formic Acid.*—The triarylmethanol (0.1 g) was refluxed with 98% formic acid (2 ml) for 12 h and then worked-up as usual to give solid (0.086 g). The mass spectrum showed this to be a mixture of $Ph_2CHC_6H_4CF_3$-2 (Found: M^+, 312.113 8. Calc. for $C_{20}H_{15}F_3$: M, 312.112 6) and 9-(2-trifluoromethylphenyl)fluorene (Found: M^+, 310.096 2. Calc. for $C_{20}H_{13}F_3$: M, 310.096 9). This was confirmed by h.p.l.c. analysis and comparison of the chromatogram with those of authentic materials. The two components have identical retention times, but the detector response from the fluorene is much greater than that from the triarylmethane. The presence of the two components was therefore confirmed from the known amount of material injected and the area of the peak produced.

Reaction of Pentafluorophenyldiphenylmethanol with Formic Acid.—The triarylmethanol (1 g) was refluxed with 90% formic acid for 11 h and the mixture worked-up by the usual procedure to give crude product (0.89 g). The mass spectrum showed the presence of two components, Ph_2CH-

C_6F_5 and 9-(pentafluorophenyl)fluorene. The latter was obtained virtually pure by repeated crystallization from petroleum, m.p. 160 °C (Found: C, 68.35; H, 2.7%; M^+, 332.063 2. $C_{19}H_9F_5$ requires C, 68.68; H, 2.73; M^+, 332.062 4). The crude mixture was quantitatively analysed by h.p.l.c. for the two components (see Table 1).

Reaction of 9-(*Pentafluorophenyl*)*fluorenol with Formic Acid*.—The fluorenol (1 g) was refluxed with 90% formic acid (10 ml) for 19 h and the mixture worked-up as usual to give a syrup (0.9 g) which was recrystallized from petroleum. The mass spectrum showed this to be mainly unchanged fluorenol, with a small amount of 9-(pentafluorophenyl)-fluorene.

Reduction of 4,4′,4″-*Trichlorotriphenylmethanol with Formic Acid*.—The triarylmethanol (0.9 g) was refluxed with 90% formic acid (10 ml) until the colour had virtually disappeared (14 h). The gases evolved were tested for HCl by bubbling through water and then determining the chloride present. None was detected. The product was worked up as for 4-fluorotriphenylmethanol, solid $(4\text{-}ClC_6H_4)_3CH$ being obtained (0.85 g), m.p. 80° (lit.,[10] 92 °C). The structure was confirmed by the mass and n.m.r. spectra.

[9/486 *Received*, 26*th March*, 1979]

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