

## Substitution Reactions of Fluorinated Triarylmethanols in Formic Acid

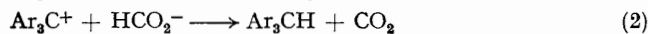
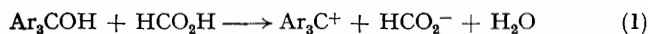
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*Summary* Reaction with formic acid of triarylmethanols containing *para*-fluorine substituents gives, in addition to the expected triarylmethanes, products in which one fluorine has been replaced by a hydroxy-group; in

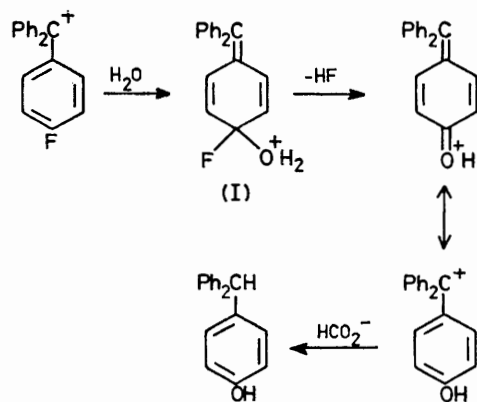
contrast, pentafluorophenyldiphenylmethanol on similar treatment gives the pentafluorophenyldiphenylmethane together with 9-(pentafluorophenyl)-fluorene.

THE efficient reduction of triarylmethanols to triarylmethanes by refluxing in formic acid was discovered about 75 years ago, and has been used sporadically ever since.<sup>1</sup> Stewart<sup>2</sup> showed that the mechanism involves hydride transfer from formate to the triarylmethylcarbonium ion [reactions (1) and (2)].



We found that on refluxing 4-fluoroarylmethanols with excess of 90% formic acid hydrogen fluoride was evolved in addition to carbon dioxide and a mixture of products was obtained consisting of the normal reduction product and a triarylmethane in which one fluorine had been replaced by a hydroxy-group. The products, yields, and reaction times for 4-fluoro-, 4,4'-difluoro-, and 4,4',4''-trifluorotriphenylmethanol are given in the Table. The products of the 4-fluorotriphenylmethanol reaction were quantitatively analysed by high-pressure liquid chromatography which showed their yields to be virtually independent of the acid strength in the range 60–99%, although much longer reaction times were required at the lower strengths. Added sodium formate also had little effect on the product yields.

Triarylmethanols are substantially dissociated to carbonium ions in formic acid,<sup>2</sup> and the presence of a positively charged group *para* to the fluorine in the ion may be expected to activate it to nucleophilic attack by water, which is known to act as a base in formic acid.<sup>2,3</sup> The mechanism of formation of the phenol may well involve rapid loss of hydrogen fluoride from the initial intermediate (I) followed by hydride transfer to the resulting cation by formate (Scheme 1). The absence of any varia-

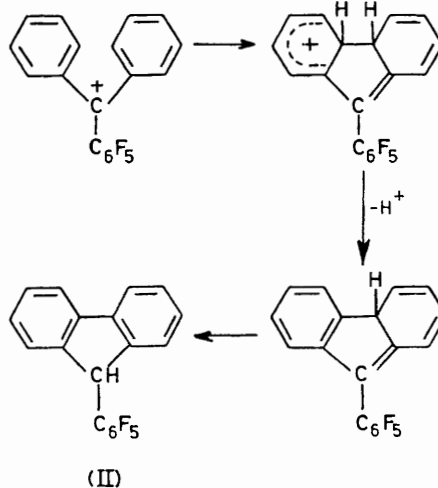


SCHEME 1

tion in the product yields with change in the concentration of water in the formic acid indicates either that the attack of water on the carbonium ion is not the rate-limiting step or that there is a sufficient excess of water, even in 99% formic acid, to make the rate of phenol formation independent of the water concentration.

4,4',4''-Trichloro- and 4,4',4''-tribromo-triphenylmethanols were converted solely into the corresponding triarylmethanes on similar treatment, and no chlorine or bromine displacement took place (see Table). These results are not inconsistent with the proposed mechanism since fluorine displacement from aromatic compounds by nucleophiles is known to be several orders of magnitude more rapid than chlorine or bromine displacement.<sup>4</sup>

Pentafluorophenyldiphenylmethanol reacted to give a mixture of pentafluorophenyldiphenylmethane and 9-(pentafluorophenyl)-fluorene (II). The identity of the latter was confirmed by comparing its properties with authentic material synthesised from fluoren-9-one and pentafluorophenylmagnesium bromide, the carbinol first formed being reduced with phosphorus and iodine in glacial acetic acid. Like other 9-arylfluorenes with substituents in the *ortho*-positions of the 9-aryl group,<sup>5</sup> (II) shows a temperature dependent <sup>19</sup>F n.m.r. spectrum owing to restricted rotation. This gives a hint as to the origin of the intriguing difference in behaviour of the pentafluorophenyl- and 4-fluorophenyl-compounds. It appears that the pentafluorophenyl group is rotated sufficiently far out of the plane of the carbonium ion so that the positively charged group cannot activate the *para*-fluorine. The mechanism of fluorene formation probably involves an



SCHEME 2

TABLE  
Products of the reduction of halogenotriarylmethanols by 90% formic acid

Methanol	Reflux time/h	Products <sup>a</sup> (yield/%)
4-FC <sub>6</sub> H <sub>4</sub> C(OH)Ph <sub>2</sub>	2	4-FC <sub>6</sub> H <sub>4</sub> CHPh <sub>2</sub> (65), 4-HOC <sub>6</sub> H <sub>4</sub> CHPh <sub>2</sub> (35)
(4-FC <sub>6</sub> H <sub>4</sub> ) <sub>2</sub> C(OH)Ph	1	(4-FC <sub>6</sub> H <sub>4</sub> ) <sub>2</sub> CHPh (55), 4-HOC <sub>6</sub> H <sub>4</sub> CH(Ph)C <sub>6</sub> H <sub>4</sub> F-4 (35)
(4-FC <sub>6</sub> H <sub>4</sub> ) <sub>3</sub> COH	5	(4-FC <sub>6</sub> H <sub>4</sub> ) <sub>3</sub> CH (35), 4-HOC <sub>6</sub> H <sub>4</sub> CH(C <sub>6</sub> H <sub>4</sub> F-4) <sub>2</sub> (41)
(4-ClC <sub>6</sub> H <sub>4</sub> ) <sub>3</sub> COH	14	(4-ClC <sub>6</sub> H <sub>4</sub> ) <sub>3</sub> CH (98)
(4-BrC <sub>6</sub> H <sub>4</sub> ) <sub>3</sub> COH	6	(4-BrC <sub>6</sub> H <sub>4</sub> ) <sub>3</sub> CH (63) <sup>b</sup>
C <sub>6</sub> F <sub>5</sub> C(OH)Ph <sub>2</sub>	15	C <sub>6</sub> F <sub>5</sub> CHPh <sub>2</sub> (30), (II) (60).

<sup>a</sup> Satisfactory analytical and spectroscopic data were obtained for new compounds. <sup>b</sup> 25% of the methanol was recovered.

intramolecular electrophilic aromatic substitution as shown in Scheme 2. This reaction bears a strong resemblance to the production of 9-phenylfluorene by heating triphenylmethanol in phosphoric acid, as reported by Kliegl.<sup>6</sup> It is also analogous to the photocyclization of triarylmethanols in sulphuric acid observed by Owen and Allen.<sup>7</sup>

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<sup>2</sup> R. Stewart, *Canad. J. Chem.*, 1957, **35**, 766.

<sup>3</sup> L. P. Hammett and N. Dietz, *J. Amer. Chem. Soc.*, 1930, **52**, 4795.

<sup>4</sup> J. Miller, 'Aromatic Nucleophilic Substitution,' Elsevier, London, 1968, p. 139.

<sup>5</sup> T. H. Siddall and W. E. Stewart, *J. Org. Chem.*, 1969, **34**, 233; K. D. Bartle, P. M. G. Bavin, D. W. Jones, and R. L'amie, *Tetrahedron*, 1970, **26**, 911.

<sup>6</sup> A. Kliegl, *Ber.*, 1905, **38**, 287.

<sup>7</sup> E. D. Owen and D. M. Allen, *J.C.S. Perkin II*, 1973, 95.