

Received: August 29, 1979

PRELIMINARY NOTE

Polyfluorinated Radical Cations

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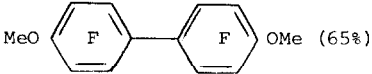
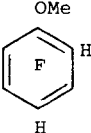
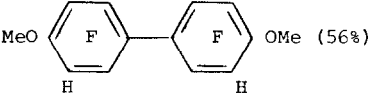
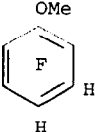
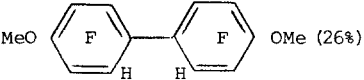
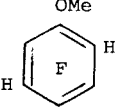

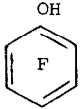
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A study of the effect of fluorine [1] and other halogen atoms [2] on various reactive intermediates is of continued interest. Recently, we described the generation of radical anions by cathodic reduction of polyhalogenated aromatic compounds [3] and radical cations derived from perfluorinated aromatic compounds have been successfully generated by anodic oxidation but at potentials which required the use of exceptional solvents like fluorosulphuric acid [4,5]. We have now demonstrated that the use of methoxy derivatives of highly fluorinated benzenes brings the oxidation potential into a region which allows the use of acetonitrile as solvent. Consequently, we have been able to study the products formed from various methoxypolyfluorobenzenes, as a probe to the structures of the corresponding radical cations, as revealed in the structures of coupled products.

Methoxy derivatives (1-4) were synthesised by reaction of sodium methoxide in methanol with pentafluorobenzene and each of the three isomeric tetrafluorobenzenes. Each derivative (1-4) was oxidised at a voltage within the range of the solvent - electrolyte system (CH_3CN , Et_4NBF_4) and coupled products (1a-3a) were isolated on work up of the corresponding anolyte mixture. In the case of (4), however, no identifiable product could be isolated from the resultant intractable tar. It is surprising, however, that reasonable yields of the coupled products (1a-3a) are isolated because, in each case, these are more readily oxidised (non-reversibly) than the corresponding precursor.

Compound ^a	Anodic Potential ^b (V)	Product ^c (current efficiency)
 (1)	2.4	 (65%) (1a)
 (2)	2.2	 (56%) (2a)
 (3)	2.1	 (26%) (3a)
 (4)	2.2	No identifiable product
 (5)	2.4	 + unidentified material

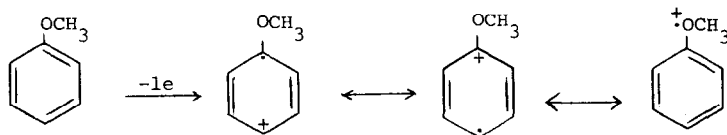
^a N.B. A F in the centre of a ring indicates that all unmarked bonds are to fluorine.

^b Divided cell, Pt anode, against s.c. electrode.

^c Yields after passage of 0.5F mole⁻¹ of substrate.

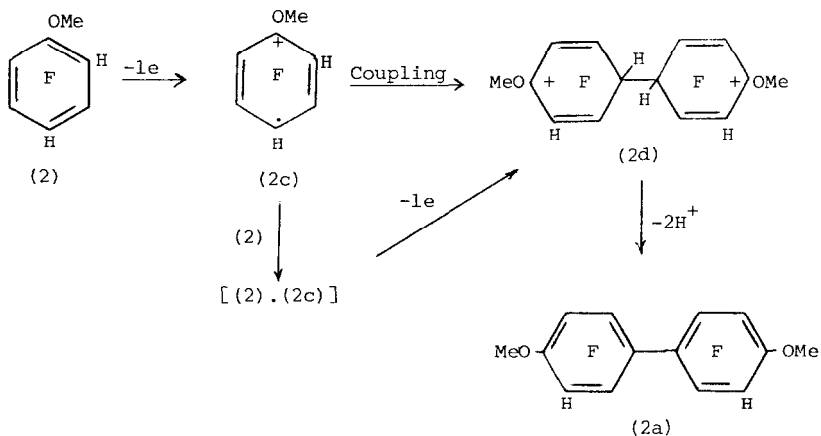
Anodic coupling of aryl methyl ethers is well known but low yields of the coupled products are generally obtained except when unusual solvents are used, e.g. CH₂Cl₂ + CF₃COOH [6,7]. Coupling para- to the ether group is

also observed but no convincing explanation for this orientation has been advanced. In the HOMO's of radical cations derived from aryl methyl ethers, including compounds (1-4), we would anticipate charge and spin density to be greatest at positions ortho- and para- to the ether group, so that coupling through either of these sites might occur. Compounds (1-4), which are all oxidised, present an ideal test of this because a choice of sites is available in (2) but the para-site is actually blocked in (4). Only para-coupling occurs with (2), since (2a) was the only detectable coupled product obtained, but no corresponding coupling occurs with (4), although ortho-sites are clearly available. It could be argued that steric effects inhibit ortho-coupling but we consider this unlikely to account for the considerable difference observed in the products obtained from (2) and (4). Instead, it now seems more reasonable to conclude that spin and charge density is concentrated at the para-positions in radical cations derived from arylmethyl ethers.

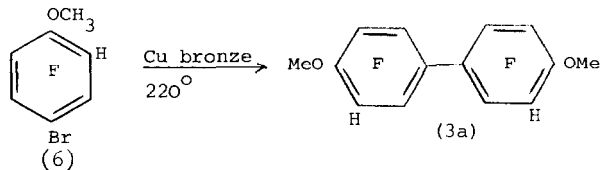


Various mechanisms could be considered for the coupling of compounds (1-3) but there are some points which are relevant. (i) Studies of compounds (1-3) by cyclic voltammetry showed non-reversible oxidation and, consequently, short lifetimes of the derived radical cations. Only (4) gave near-reversible scans. (ii) It is now well established that nucleophilic attack on radical cations can be relatively difficult [8], although observed [9], and therefore a process involving attack of a radical cation on the neutral molecule e.g. (2), (2c) should probably not be given high priority. (iii) Bearing in mind these facts, the most likely coupling process is that involving two radical cations e.g. (2c), or further oxidation of a complex between a radical cation and the neutral molecule e.g. (2), (2c), adsorbed at the anode surface [8]. It is possible to understand the fact that the coupled products e.g. (2a) are not further oxidised because, while adsorbed at the electrode surface, they are probably still in the protonated form e.g. (2d) and only lose protons when they move into the bulk electrolyte.

Pentafluoroanisole (5) is also oxidised and, understandably, no dimers could be isolated; only a trace of pentafluorophenol could be identified in the intractable products.



Starting materials, compounds (1)-(5) were obtained by reactions of the corresponding fluorinated benzenes with sodium methoxide in methanol. Products (1a)[10] and (3a)[11] are known compounds and were identified by comparison of spectra with authentic samples. Compound (2a) is, however, unknown and has been characterised by independent synthesis, starting with the known 4-bromo-2,3,4-tetrafluoroanisole (6) [12].



ACKNOWLEDGEMENTS

We thank the S.R.C. for CASE grants and the Electricity Council for participating in the project. We also thank Dr. O.R. Brown for helpful discussions.

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