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FLUORINATION OF OLEFINS AND ARENES VIA RADICAL CATIONS

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We have shown that electrolysis of acetonitrile solutions of anthracene compounds that contain fluoride-providing anions results in fluorination at the meso positions in many cases. We have proposed that such reactions occur via attack of the fluoride anions on radical cations formed at the anode. Fluorination occurred when the positive charge of the radical cation was localized but did not occur when delocalization of positive charge occured as with perylene.

Anodic fluorination of 1,1-diphenylethene also occurred via a radical cation intermediate yielding 1,2-difluoro-1,1-diphenylethane and 1,1,4,4-tetraphenylbutadiene as a byproduct. The anodice fluorination of acenaphthylene gave a mixture of the cis and trans 1,2-difluoro addition product.

The reaction of iodine and silver(I) fluoride in acetonitrile yields similar results with PAH. With olefins, however, divergent results were obtained. With iodine and silver fluoride in acetonitrile 1,1-diphenylethene gave 1-fluoro-2-iodo-1,1-diphenylethane, even in the presence of $(CH_3)_4NF \cdot 2HF$ Iodine and silver hydrogen difluoride, however, gave 1,1-difluoro-1,2-diphenylethane. These results are to be contrasted with those with acenaphthylene previously reported.