Electrophilic Aromatic Substitution by the Fluorofullerene $C_{60}F_{18}$

Adam D. Darwish,[a] Anthony G. Avent,[a] Ala'a K. Abdul-Sada,[a] Olga V. Boltalina,[b], Igor Kuvytchko,[b] Ilia Gol'dt,[b]
Peter B. Hitchcock,[a] and Roger Taylor [a]

[a] The Chemistry Laboratory, CPES School, Sussex University, Brighton UK BN1 9QJ
[b] Chemistry Department, Moscow State University, Moscow 119899, Russia

From the reaction of $C_{60}F_{18}$ with various aromatics in the presence of $FeCl_3$ at < 40 °C, we have isolated compounds $C_{60}F_{15}Ar_3$, Ar = phenyl, 4-tolyl, 4-methoxyphenyl, 4-phenoxyphenyl, and 4-chlorophenyl. The reaction rate is little affected by electron supply in the aryl ring, which is attributed to the high reactivity of the electrophile, and consequent low selectivity between the aromatics. Mono- and bis-substitution products, $C_{60}F_{17}Ar$ and $C_{60}F_{16}Ar_2$, respectively, have also been isolated in some cases, the mono-substitution product being the major one for Ar = 2-fluorenyl, 2-biphenylyl, 1- and 2-naphthyl. The 2-naphthyl substituent is able to rotate freely and gives a C_s derivative, whereas rotation of the 1-naphthyl substituent is prevented and the derivative has C_1 symmetry. Reasons will be given for the lack of substitution in either thiophene or azulene. Reaction occurs only when the solutions of the reagents are evaporated to dryness, and the low discrimination between aromatics makes it possible to isolate derivatives having different aryl groups attached to the cage, by reaction with a mixture of aromatics. The effectiveness of catalysts is $SbCl_5 > FeCl_3 > SnCl_4 > TiCl_4$ (completely ineffective) The results provide a basis for a very extensive arylfullerene chemistry.