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HEXAFLUOROBENZO[b]FURAN

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Methods for the synthesis of partially fluorinated derivatives of benzo[b] furan, benzo[b] thiophen and indole have been summarised recently[1] but there appears to be no report of the preparation of the perfluoro analogues. The KF exchange process which has been exploited so successfully for the preparation of many perfluoro heterocycles is not suitable since the appropriate perchloro compounds are not readily accessible.

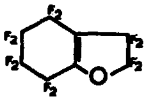
This paper describes the use of a high-valent metal fluoride in the synthesis of hexafluoro benzo[b] furan. Early work with cobalt trifluoride showed that the fluorination of several heterocyles resulted mainly in degradation of the ring systems[2] but the development of complex metal fluoride reagents e.g. caesium tetrafluorocobaltate (III)[3] has provided a route to perfluoroheterocycles in significant yields from hydrocarbon precursors[4].

Benzo[b] furan, synthesised from o-hydroxybenzaldehyde[5], was fluorinated over caesium tetrafluorocobaltate (III) at 380° using a small scale version of the stirred nickel tubular reactors described previously[6]. The composition of the product is recorded in Table 1.

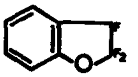
TABLE 1

Tetradecafluorocyclohexane I (13%)

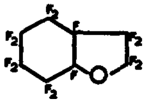
Dodecafluorocyclohexene II (3%)



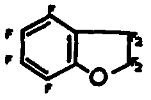
IV[+] (1%)



VII[+] (9%)



III[+] (20%)

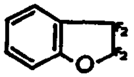


V[+] (20%)

Pentadecafluorooctanoic acid VIII[*] (2%)

Terdecafluorocyclohexylacetic acid IX[+*] (9%)

% by wt. of compound in product.



VI[+] (2%)

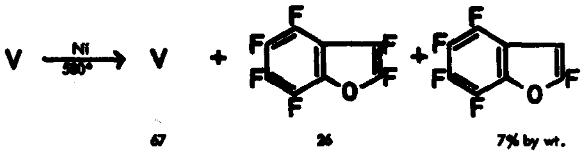
[*] Isolated as methyl ester.

[+] New compounds characterised by elemental analysis and NMR spectroscopy.

The two acidic components were separated from the mixture and esterified, then the neutral components were isolated by fractional distillation and gas liquid chromatography.

Note the absence of hexafluorobenzo[b]furan but that reasonable yields of octafluorobenzo [b] oxalen, V were obtained; a result that parallels that obtained for the fluorination of naphthalene[3]. The pattern of products suggest that fluorination occurs initially in the heterocyclic ring followed by the benzene ring with retention of aromaticity. Compounds I-IV arise from the further fluorination of V.

Many perfluoroarenes are produced by defluorination of a suitable perfluoroalicycle with metals or iron oxide at elevated temperatures[7]. Unfortunately tetradecafluoro-7-oxabicyclo[4,3,0]nonane, III was resistant to defluorination under these conditions. However, hexafluorobenzo[b]furan was prepared by the pyrolytic defluorination of V over nickel gauze at 580°.



Hexafluorobenzo[b]furan is a colourless liquid b.p. 148° which was identified by elemental analysis, mass spectrometry and N.M.R. spectroscopy, the ^{19}F spectrum showing six multiplet signals, each of equal intensity, at 121, 152, 160, 161, 162, 190 p.p.m. upfield from CCl_3F.

Further work is in progress concerning the chemistry of this compound, in particular its reactions with nucleophiles.

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