An SO Elimination leading to Octafluorodibenzofuran

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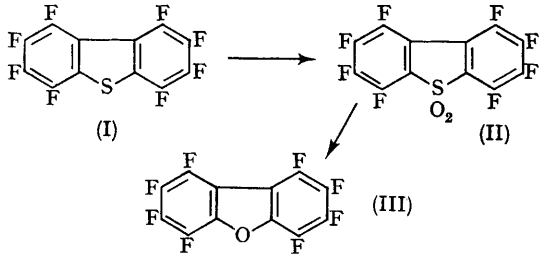
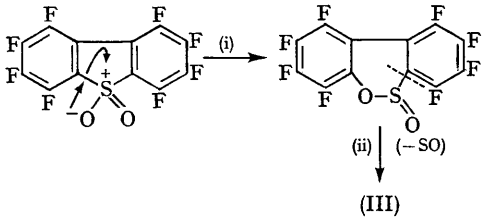
WE recently reported[1] the first synthesis of a perfluorinated compound in the dibenzo-series, octafluorodibenzothiophen (I), and we have



subsequently found that a dioxide (II) can be formed by the reaction of (I) with 85% hydrogen peroxide in trifluoroacetic anhydride, while other methods gave little or incomplete reaction. Current interest in the elimination of sulphur monoxide from sulphones[2] led us to examine the mass spectrum of the dioxide (II) and a large peak at 312 mass units, corresponding to P – SO was observed. Subsequently, we pyrolysed the dioxide (II) and found that the new heterocycle, octafluorodibenzofuran, m.p. 100°, could be isolated in 72% yield. The pyrolysis temperature and conditions were critical; general decomposition occurred on pyrolysis in a sealed tube but, using a flow system, products were obtained which became more simple as the temperature was raised. At 810° octafluorodibenzofuran was obtained in high yield together with small amounts of octafluorodibenzothiophen and a minor unknown impurity. In contrast to these results, pyrolysis of decafluorodiphenyl sulphone (IV), under various conditions, gave only sulphur dioxide elimination, leading to decafluorobiphenyl.

$$(C_6F_5)_2SO_2 \rightarrow C_6F_5{\cdot}C_6F_5$$

The mechanism of the SO elimination possibly involves an intramolecular rearrangement (internal nucleophilic displacement) to an unstable sulphinic ester, followed by SO loss.



Elimination of SO or SO_2 from a compound would then depend on the relative rates of rearrangement (i) to C-S bond cleavage (ii). These possibilities are being investigated.

Octafluorodibenzofuran undergoes nucleophilic substitution by a variety of nucleophiles but the orientation, while of considerable interest, cannot yet be unambiguously assigned.

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[1] R. D. Chambers and J. Cunningham, *Chem. Comm.*, 1966, 469.
[2] Results communicated by J. F. W. McOmie and by M. P. Cava at the Symposium on "Aromaticity", Sheffield, 1966.