Synthesis of Fluorinated Dienes and Cyclobutenes

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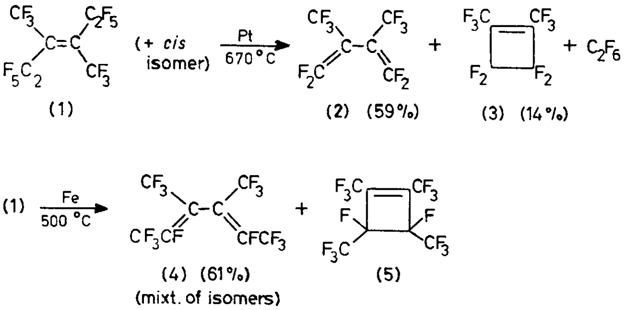
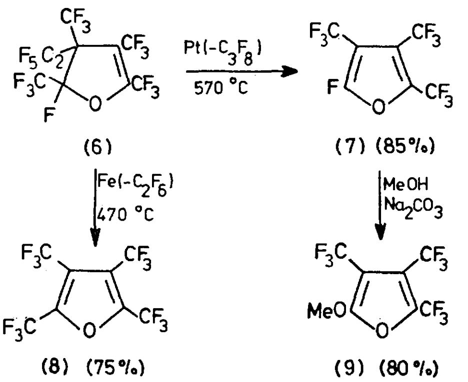
Summary Pyrolysis of some fluorinated alkenes over platinum or iron, gives good yields of dienes and fluorinated furan derivatives.

There are many reports[1] of the pyrolysis of fluorinated organic compounds, including the defluorination of cyclic fluorocarbons over iron to give aromatic compounds.[2] So far, however, these procedures have not seemed valuable for the synthesis of acyclic fluorinated dienes.

The fluorinated alkene (**1**)[3] undergoes a novel fragmentation reaction when passed, in a stream of nitrogen, through a platinum-lined tube at 530—700 °C, giving the diene (**2**),[4] together with lesser amounts of the cyclobutene (**3**). Defluorination of (**1**), over iron filings at 430—500 °C, gave the corresponding diene (**4**),[5] as a mixture of two isomers, and the cyclobutene (**5**). The compounds (**2**), (**3**), (**4**), and (**5**) have been prepared previously but by less accessible routes.

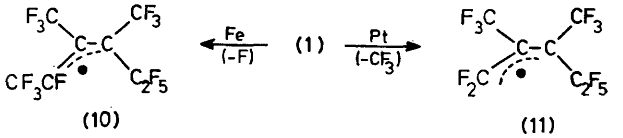




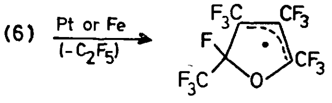
(6) (7) (85%) (8) (75%) (9) (80%)

The derivative (**6**), obtained by a cyclisation process described recently,[6] gave, on passage over platinum at 430—700 °C, the new perfluoro-2,3,4-trimethylfuran (**7**), by elimination of C_3F_8. Pyrolysis of (**6**) over iron at 470 °C, however, led to elimination of the elements of C_2F_6 and provides therefore an alternative synthesis of perfluorotetramethylfuran, reported recently.[6] The structure of (**7**) follows simply by comparison of the ^{19}F n.m.r. spectrum with that of (**8**). Also, displacement of fluorine by methoxy group occurs, giving (**9**).

Clearly, the guiding feature in the eliminations from (**1**) or (**6**) is the formation of corresponding fluorinated allylic radicals (**10**)—(**12**). Loss of CF_3 from (**1**) occurs over platinum but loss of F is obviously preferred over iron, whereas no such alternative is available in reactions of (**6**) and elimination of C_2F_5, as the primary step, takes place over either metal. Subsequent loss of F or CF_3 from (**12**) is, however, determined by the metal.



(10) (11)



(12)

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