Novel Route to Hexafluorobut-2-yne and New Fluorinated Dienes

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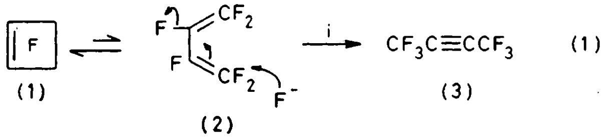
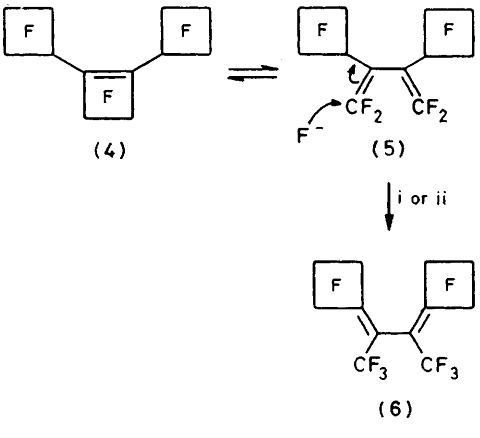
Summary Hexafluorobutyne is made by the passage of perfluorocyclobutene over caesium or potassium fluoride; a dimer (**7**) and trimer (**4**) of perfluorocyclobutene give new dienes.

A whole range of chemistry is developing involving reactions of fluoride ion with unsaturated fluorocarbons[1] and this mirrors some of the vast chemistry of proton-induced reactions of hydrocarbons. Here, we report a synthesis, involving fluoride ion, of the relatively inaccessible hexafluorobut-2-yne, as well as syntheses of some interesting new fluorinated dienes.



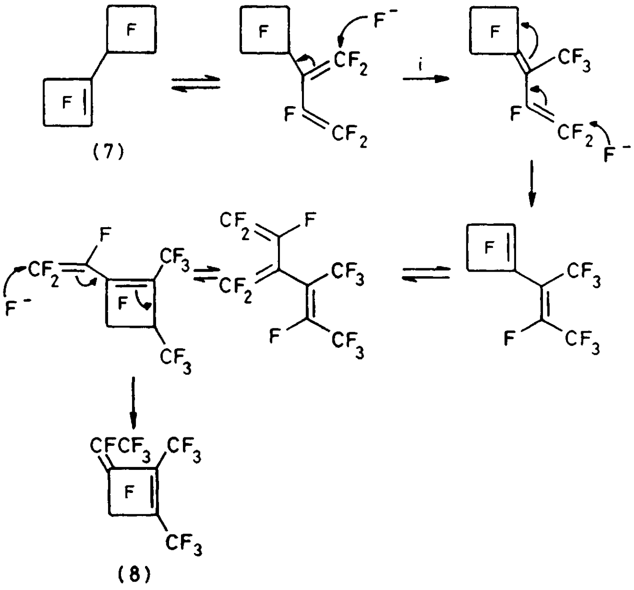
i, CsF or KF, 510–590 °C, flow system in N_2, optimum yields 80–90%.

It has long been established[2] that the cyclobutene–butadiene equilibrium lies, in the fluorinated system (**1**)–(**2**),† predominantly on the side of the cyclic compound (**1**), equation (1). Also, it has been shown[3] that (**2**) is converted into hexafluorobut-2-yne (**3**) by passage, in the vapour phase, over caesium fluoride. Surprisingly, however, these observations have not previously been experimentally related and we now find that (**1**) is converted into (**3**), in good yield, simply by passage over caesium or potassium fluoride. Perfluorocyclobutene is readily available in the laboratory from chlorotrifluoroethylene[4] and, consequently, hexafluorobut-2-yne is now accessible in a convenient laboratory synthesis.



Scheme 1. i, CsF, 510 °C, flow system in N_2, 70% yield; ii, CsF or KF, 300 °C, sealed tube, quantitative.

We have extended this type of reaction to provide a synthesis of the new diene (**6**) from a trimer of (**1**), *i.e.* (**4**).[5] The process can be described as initial ring-opening to (**5**), followed by attack by fluoride ion, see Scheme 1. In this case, however, the intermediate, *i.e.* (**5**), can be isolated from a comparable system excluding fluoride ion. In a sealed-tube reaction, heating (**4**) with caesium or potassium fluoride gave (**6**) essentially quantitatively. More remarkably, passage of the dimer (**7**) over potassium fluoride at 510 °C, gave (**8**) in *ca.* 70% yield, together with minor additional products. At first sight this experimentally simple conversion of (**7**) into (**8**) seems incomprehensible but the mechanism shown in Scheme 2 relates this reaction to the ring-opening processes described above.



Scheme 2. i, KF, 510 °C, flow system in N_2, *ca.* 70% yield.

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† An F inside a ring indicates that all the hydrogen atoms have been substituted by fluorine.

[1] See, *e.g.*, R. D. Chambers, A. A. Lindley, P. D. Philpot, H. C. Fielding, J. Hutchinson, and G. Whittaker, *J.C.S. Perkin I*, 1979, 214, and references contained in this and earlier parts of the series.

[2] J. P. Cheswick, *J. Amer. Chem. Soc.*, 1966, **88**, 4800.

[3] M. T. Miller, W. Frass, and P. R. Resnick, *J. Amer. Chem. Soc.*, 1961, **83**, 1767.

[4] A. L. Henne and R. P. R. Ruh, *J. Amer. Chem. Soc.*, 1947, **69**, 279.

[5] R. D. Chambers, G. Taylor, and R. L. Powell, *J.C.S. Chem. Comm.*, 1978, 433.