

Antimony Pentafluoride in the Synthesis of Novel Fluoro-alkene Derivatives and a Novel Approach to Conjugated Polymers

Richard D. Chambers,^{a*} Martin Salisbury,^a Glenn Apsey,^a Thomas F. Holmes,^a and Silvana Modena^b

^a Department of Chemistry, University Science Laboratories, South Road, Durham DH1 3LE, U.K.

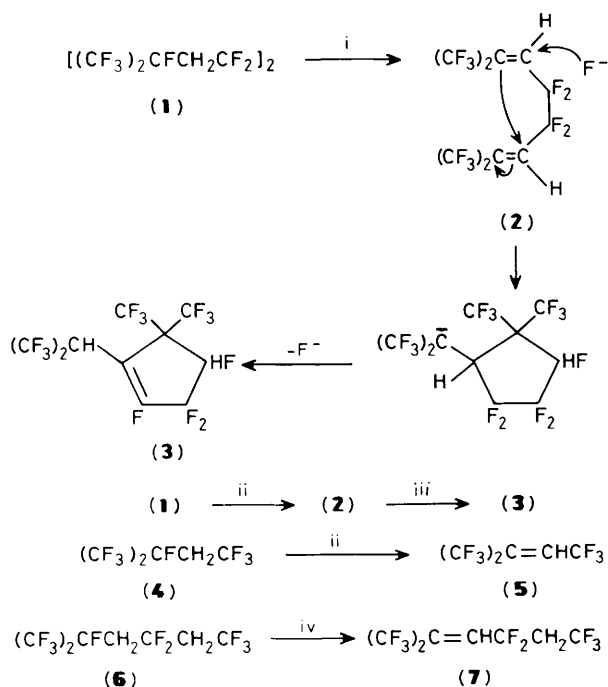
^b Montefluos C.R.S., Via San Pietro 50, I-20021 Bollate, Italy

Elimination of hydrogen fluoride, using antimony pentafluoride, is a useful preparative process for some fluorinated alkenes and presents a new and simple approach to conjugated polymers.

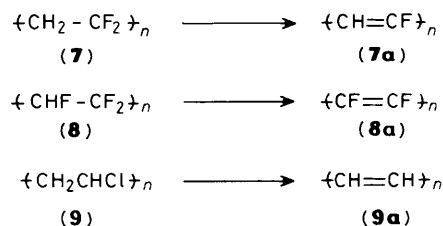
Base-induced β -eliminations are well established processes in the syntheses of alkenes, dienes *etc.*, but corresponding Lewis acid induced eliminations are comparatively neglected because of the obvious limitation that alkenes are usually susceptible to further electrophilic attack. For systems that are resistant to electrophilic attack, such eliminations can be more useful and here we show that elimination of hydrogen fluoride from some fluorohydrocarbons, using antimony pentafluoride, is a very useful preparative process that can be extended to the synthesis of conjugated polymers.

Reaction of compound (1) with tributylamine gave, not the required diene (2), but the cyclic compound (3) because the intermediate (2) undergoes a rapid cyclisation (Scheme 1). In clear contrast, reaction of (1) with antimony pentafluoride gave the diene (2) in essentially quantitative yield; subsequent reaction of (2) with caesium fluoride caused rapid and quantitative conversion to (3). In analogous processes, reactions of (4) and (6) with antimony pentafluoride gave high yields of (5) and (7), respectively.

There is much current interest in conjugated polymers¹ and the effect of replacement of hydrogen by fluorine on the properties of polyacetylene has been speculated upon.^{2,3} Polymerisation of difluoroacetylene has been claimed⁴ and this is surprising, considering the inherent instability of difluoroacetylene.⁵ The reactions of antimony pentafluoride described above suggest an alternative approach to polyacetylene derivatives by effecting elimination from a saturated polymer and we now report that this process is remarkably effective. When a thin film of polyvinylidene fluoride (7) was simply exposed, under high vacuum, to antimony pentafluoride as a vapour, then the film rapidly darkened and went through black to a lustrous black appearance, all at room temperature (Scheme 2). Similarly, polytrifluoroethylene (8) went through the same sequence but this system required heating. In marked contrast, a film of PVC (9) went instantly black, when a vacuum tap was opened to allow vapour contact between antimony pentafluoride and (9). It is clear that extensive elimination occurs in these systems but the products



Scheme 1. Reagents and conditions: i, Bu_3N , $120^\circ C$, 2 h; ii, SbF_5 , $120^\circ C$, 2 h; iii, CsF , sulfolan, $120^\circ C$, 3 h; iv, SbF_5 , $40^\circ C$.



Scheme 2

are not simply (7a)–(9a) since these structures must also contain a number of charged sites. This is evident from the fact that long-lived fluorinated carbocations can be observed in analogous less-conjugated model systems.⁶ Consequently, the i.r. spectrum of the product from PVC resembled closely that recorded for doped polyacetylene, rather than polyacetylene (9a).⁷

These systems may well be difficult to characterise but this procedure offers an extremely simple methodology for generating polyconjugated films or surfaces and it is clear that the electrical properties of these systems should be explored, especially the opportunity for preparing conducting surfaces sandwiching an insulator.

Received, 9th November 1987; Com. 1629

References

- 1 See, for example, W. J. Feast, *Chem. Ind. (London)*, 1985, 263, and references contained.
- 2 T. Yamabe, K. Tanaka, H. Terama, K. Fukui, H. Shirakawa, and S. Ikeda, *Synth. Met.*, 1979–80, **1**, 321.
- 3 S. M. Abdelaty and H. Fukutome, *Progr. Theor. Phys.*, 1986, **75**, 1265.
- 4 M. V. Galakhov, V. A. Petrov, V. I. Bakmutov, G. G. Belenkii, B. A. Kvasov, L. S. German, and E. I. Fedin, *Bull. Acad. Sci. USSR, Div. Chem. Sci.*, 1985, **34**, 279.
- 5 R. D. Chambers, 'Fluorine in Organic Chemistry,' Wiley-Interscience, New York, 1973, p. 190, and references cited therein.
- 6 R. D. Chambers, M. Salisbury, G. Apsey, and G. Moggi, *J. Chem. Soc., Chem. Commun.*, following Communication.
- 7 J. C. W. Chien, 'Polyacetylene Chemistry, Physics, and Material Science,' Academic Press, New York, 1984, p. 412.