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ELECTROPOLYMERISATION OF PERFLUOROCYCLO-ALKENES.

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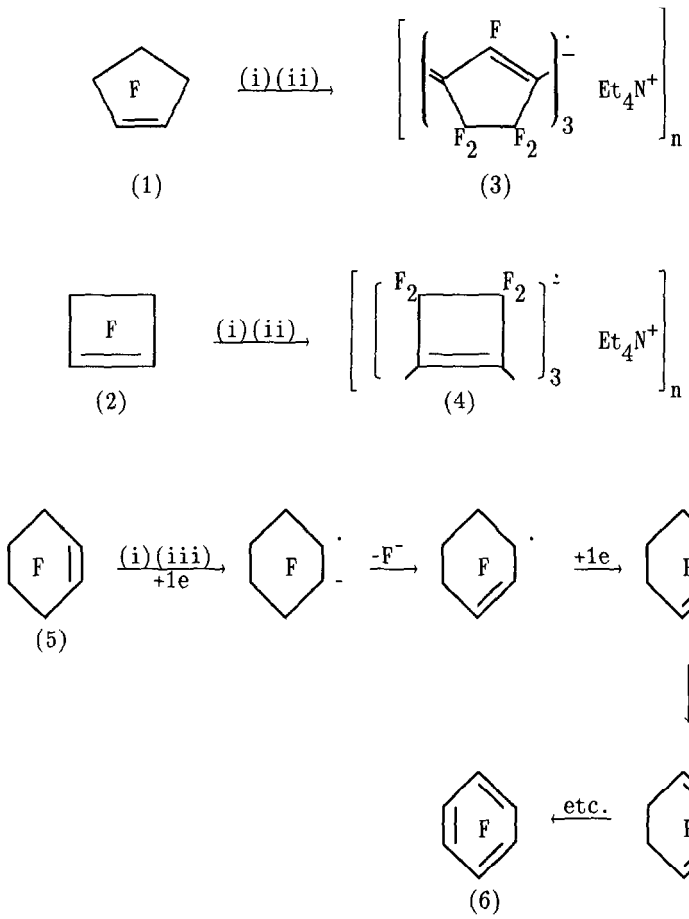
Summary:

Novel conducting materials are obtained by cathodic electropolymerisation of perfluoro-cyclobutene and -cyclopentene.

Fluorinated alkenes are very susceptible to nucleophilic attack[1] and, understandably, they are also susceptible to electrochemical reduction.[2,3] In the course of our investigations on electrochemical reduction of cyclic perfluoroalkenes we made the surprising discovery that polymeric materials are obtained from perfluoro-cyclopentene (1) and -cyclobutene (2), (see Scheme 1). For example, reduction of (1) at a platinum cathode in a divided cell using tetraethylammonium tetrafluoroborate as electrolyte, in either acetonitrile or dimethylformamide, gave lustrous blue-black needles of polymer which grew at the cathode; similar results were obtained using a stirred mercury cathode.

Reaction of perfluorocyclo-butene (2), using the same procedures, gave very similar-looking material. That the materials grow on the cathode in itself suggests that they are conducting, and confirmatory measurement of the conductivity of material derived from (1) gave a value of $10^{-3}\ \Omega^{-1}\ cm^{-1}$. This should be regarded as a minimum value, derived from a multicrystalline sample, and is probably substantially less than the value that would derive from a measurement along a single crystal. These conducting materials are of



Scheme 1.

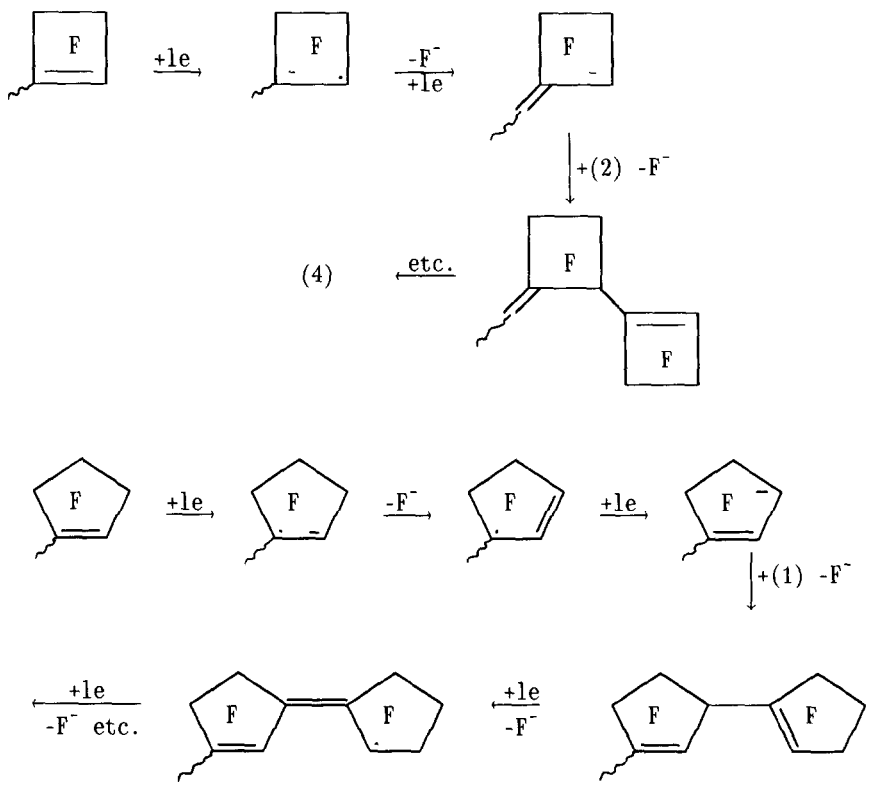
(i) Pt or Hg cathode, divided cell, CH_3CN or D.M.F., Et_4NBF_4,
(ii) -1.9 v (saturated calomel electrode), (iii) -1.6 v (saturated calomel electrode).

particular interest because, so far as we are aware, they are the first such materials to be produced by cathodic electropolymerisation[4] although anodic polymerisations of pyrrole[5] and thiophene[6] are, of course, very well known.

The structures of these bulk materials are not easy to establish but the elemental analyses are quite revealing. Incorporation of tetraethylammonium cations from the supporting electolyte is clearly indicated by the H:N ratios for (3) and (4) and, furthermore, change to tetrabutylammonium tetrafluoroborate gave a H:N ratio corresponding to tetrabutylammonium cations in the polymeric products. A requirement for the presence of tetralkylammonium cations for polymer growth is borne out by the fact that no

polymerisation of (1) or (2) was observed using lithium perchlorate as electrolyte, although polymerisation does occur with tetra-alkylammonium perchlorate. E.S.C.A. data of a thin film of polymer obtained by electropolymerisation of (1)[7] revealed C_{1s} binding energies at least consistent with structure (3) but the limitations of E.S.C.A. for the determination of bulk structure should be borne in mind. Nevertheless, a combination of elemental analysis (which shows a 1:1 ratio, C:F, for the carbon backbone) with these data suggest (3) and (4) as the best interpretations for structure. E.s.r. measurements confirmed the paramagnetic nature of (3) and (4).

Reduction of perfluoro-cyclohexene proceeds in a different manner and is consistent with the findings of earlier workers for the reduction of perfluorocyclohexadienes[2] (see Scheme 1). Formation of hexafluorobenzene (6) at a Pt electrode occurs very smoothly in high yield; no other products were detected and certainly no polymer was observed. This process, together with results obtained by Russian workers on dimerisation of perfluoro-1-alkyl-cyclobutene and -cyclopentene[8] indicate a likely propagation process for the formation of (4) and (3), as shown in Scheme 2.



Scheme 2

The analytical data for (3),(also a 1:1 ratio, C:F, for the carbon backbone), require a greater degree of defluorination than (4), in the polymerisation process.

Further work is proceeding on the characterisation of these interesting new materials.

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