A Synthesis of Novel Perfluorodienes

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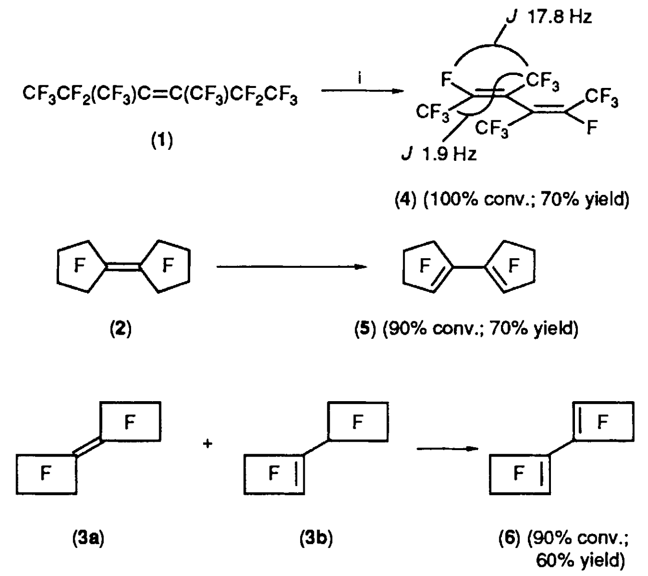
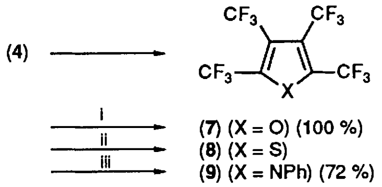
Oligomers of perfluoroalkenes are converted to dienes in good yields, using sodium amalgam; these dienes are highly susceptible to nucleophilic attack and can be excellent sources of heterocycles.

Perfluoro-alkenes and -cycloalkenes may be oligomerised in fluoride ion-induced processes, leading to various synthetically more sophisticated systems;[1] *e.g.* a tetramer (**1**) and other oligomers may be obtained from tetrafluoroethylene,[2] a dimer (**2**) from perfluorocyclopentene,[3] and a mixture of dimers (**3a, 3b**) from perfluorocyclobutene, although the latter are more efficiently synthesised using a pyridine-induced reaction.[3,4]

We have previously explored[5] pyrolytic processes, *e.g.* defluorination over iron, for conversion of (**1**)—(**3**) to the corresponding dienes but this approach can be limited on scale-up and, more serious, is often accompanied by fragmentation and isomerisation, *e.g.* conversion of (**4**) to the corresponding cyclobutene derivative. In electrochemical studies[6] we have established that systems (**1**)—(**3**) are readily reduced albeit in non-reversible processes; indeed, a small amount of the diene (**4**) was obtained from (**1**). However, we



Reagents and conditions: i, Na, Hg (0.5 wt. %), water cooling. F in rings indicates perfluoro substitution.



Reagents and conditions: i, H_2O, K_2CO_3, MeCN, room temp., ii, K_2S, dimethylformamide, room temp.; iii, $PhNH_2$, MeCN, CsF, room temp.

have now been able to synthesise dienes (**4**)—(**6**), in good yields, using an electro-mimetic procedure. For example, simply adding (**1**) slowly to sodium amalgam, with agitation and water cooling but without solvent, gave (**4**) as essentially the only volatile product. Furthermore, (**5**) and (**6**) were also obtained in good yields using analogous procedures and these dienes could be obtained pure by simple crystallisation from remaining (**2**) or (**3**). The NMR data indicate that (**4**) exists in the all-*trans* form.

Thus, we now have an acceptable route to a novel range of electron-deficient dienes and we find that nucleophilic attack occurs readily. Remarkably, in reactions with neutral methanol, (**6**) reacted exothermically while (**5**) reacted over a period of days, in each case giving the corresponding bis(methyl ether) by vinylic displacement of fluoride ion. Diene (**4**), however, required added base to promote the corresponding reaction with methanol. This dramatic difference in reactivity towards MeOH [(**6**) $\gg$ (**5**) $\gg$ (**4**)] provides a nice illustration of the effect of angle strain on nucleophilic attack at unsaturated carbon.

Preliminary investigations demonstrate that (**4**) is an excellent reactant for forming heterocycles, *e.g.* (**7**)—(**9**). Hydrolysis of (**4**) occurs quantitatively, to give the known[7] furan derivative (**7**) and reaction with potassium sulphide gave the thiophene analogue (**8**) which has previously been obtained[8] from the expensive hexafluorobut-2-yne; the pyrrole derivative (**9**) is easily obtained by this route and has previously been synthesised[9] in an approach involving a valence isomer of (**8**).

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