

## A Direct Route to Fluorinated Cyclopentadienes and Cyclopentadienyl Anions

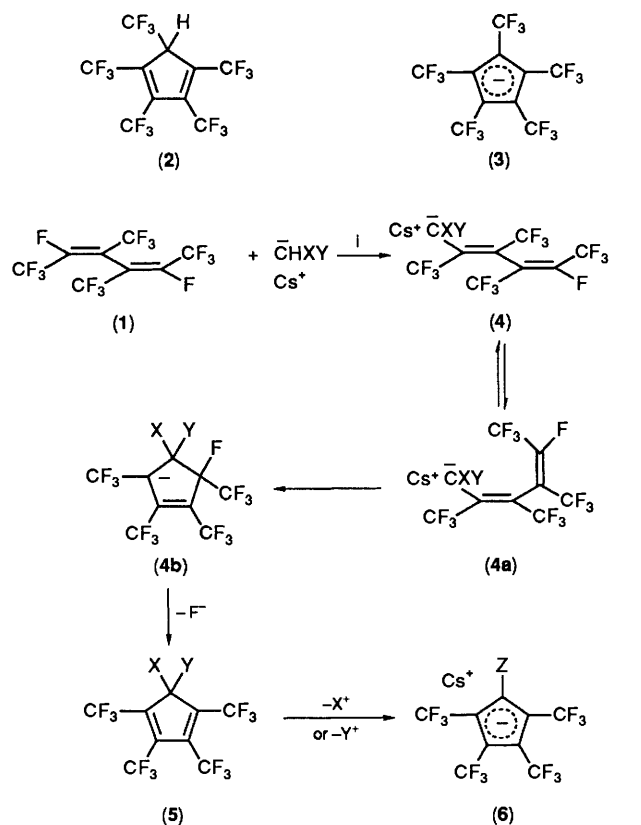
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Fluoride-ion induced reactions of systems  $\text{CH}_2\text{XY}$  with the novel diene  $[\text{CF}_3\text{CF}=\text{C}(\text{CF}_3)]_2$  provides a route to derived cyclopentadienes and cyclopentadienyl anions *via* an unusual cyclisation step.

In an accompanying communication,<sup>1</sup> we described a good synthesis of the interesting fluorinated diene (**1**) and indicated that cyclisation reactions proceed to yield heterocycles. We now describe a novel analogous approach to, hitherto, relatively inaccessible cyclopentadienes and cyclopentadienyl anions derived from (**1**). Laganis and Lemal<sup>2</sup> reported the extremely acidic diene (**2**) by an imaginative but low yield route and observed the derived cyclopentadienyl anion (**3**) in solution; Janulis and Arduengo<sup>3</sup> obtained derivatives using related methodology. It is now established that carbanions

may be generated from suitably acidic systems using fluoride ion<sup>4</sup> and consequently reaction of diene (**1**) with malononitrile, in the presence of caesium fluoride at room temperature, gave rapid reaction. Pentadienyl anions (**4**, **4a**,  $\text{X} = \text{Y} = \text{CN}$ ) were observed in solution by <sup>19</sup>F NMR spectroscopy (stereo-chemistry determined by coupling constants) and then slow cyclisation occurred giving the cyclopentadienyl salt (**6**) but in this case the intermediate diene (**5**;  $\text{X} = \text{Y} = \text{CN}$ ) was not observed. However, when the corresponding reaction was carried out with  $\text{CH}_2\text{XY}$  ( $\text{X} = \text{CN}$ ;  $\text{Y} = \text{tetrafluoro-4-pyridyl}$ ,



$\text{C}_5\text{F}_4\text{N}$ ) then, although the anions (4) were not observed, the cyclopentadiene derivative (5) could actually be isolated and therefore this provides a route to some highly electron-deficient cyclopentadienes, which was a major objective.

Surprisingly, on further reaction, the diene (5) gave a mixture of salts (6) ( $\text{Z} = \text{CN}$  and  $\text{C}_5\text{F}_4\text{N}$ , ca. 3:7), *i.e.* via loss of either CN or  $\text{C}_5\text{F}_4\text{N}$  from (5).

The cyclisation step (4a) to (5) is extremely interesting because, as a 5-*endo-trig* process, it is formally 'disallowed' by the Baldwin rules.<sup>5</sup> It seems more appropriate, therefore, to regard the process as an initial electrocyclic ring closure (4a) to (4b), followed by elimination of fluoride ion, to give (5). What is especially significant is that, while electrocyclic ring closures that are heterocyclic analogues of the conversion (4a) to (4b) are abundant in the literature, we are aware of only one example of an open-chain pentadienyl anion undergoing ring closure to give a carbocyclic system.<sup>7</sup> The mechanism of this reported ring closure was regarded as uncertain,<sup>6</sup> whereas the mechanism seems quite clear for the process (4a) to (5) to (6). The ready loss of CN from (5) may be understood as arising from the ready formation of the fluorinated cyclopentadienyl ( $\text{Cp}_F$ ) anions from (7).

Characterisation of the intermediate ions (4, 4a;  $\text{X} = \text{Y} = \text{CN}$ ) followed from  $^{19}\text{F}$  NMR spectroscopy, which showed appropriate  $J$  values for  $\text{CF}_3\text{-F}$  and  $\text{CF}_3\text{-CF}_3$  coupling; likewise the spectra of ions (6) showed two signals due to  $\text{CF}_3$ , which were multiplets ( $J$  ca. 5 Hz), suggesting that rotation of the groups is restricted. FAB mass spectra are particularly dramatic in that they show the parent ions for (4) and (6) with remarkably little fragmentation in the case of the latter anions (6).  $^{13}\text{C}$  NMR data are also consistent with the assignments.

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## References

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