

A Novel Annulation Process involving Perfluorocycloalkene Derivatives

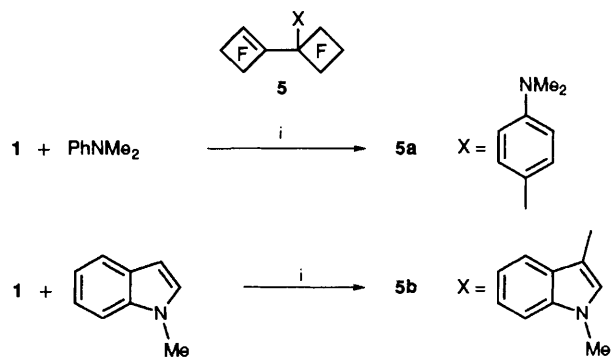
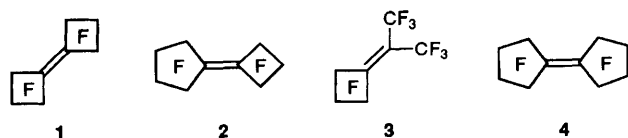
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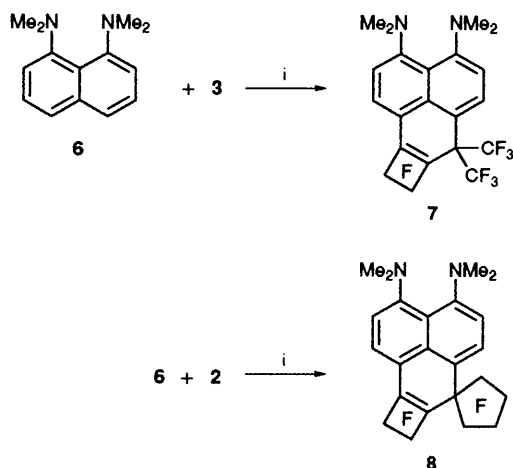
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N,N-Dimethylaniline and *N*-methylindole react as nucleophiles through carbon with perfluorobicyclobutylidene **1**, to give the unusual products **5a** and **5b**; Proton Sponge reacts in an analogous way with the systems **2** and **3** but, in this case, give the novel annelated products **8** and **7**.

Perfluorinated alkenes and cycloalkenes are very susceptible to nucleophilic attack and there is now an extensive literature on the subject,^{1,2} involving a variety of species acting as nucleophiles and a wide range of reactivity of the systems under attack. Considering the fact that aromatic amines are so susceptible to electrophilic attack in the ring, then it is surprising that there are no examples, of which we are aware, where aromatic amines act as *carbon* nucleophiles in reactions with fluorinated alkenes.



Scheme 1 Reagents and conditions: i, MeCN, room temp., overnight

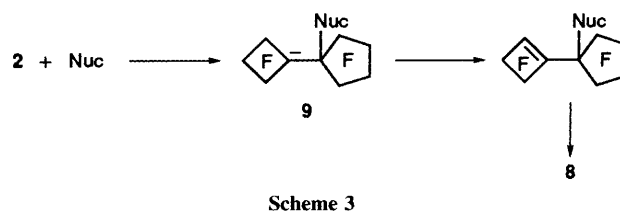


Scheme 2 Reagents and conditions: *i*, MeCN, room temp., overnight

We have previously described syntheses of the novel systems **1**–**4**^{3,4} and, in exploring the chemistry of these compounds, we have now discovered some remarkable examples of attack by aromatic amines acting as carbon nucleophiles. For example, *N,N*-dimethylaniline reacted with perfluorobicyclobutylidene **1**, to give **5a** by nucleophilic attack, accompanied by allylic displacement of fluoride ion; *N*-methylindole reacted in a similar way to give **5b** (Scheme 1).[†]

We have also carried out some reactions with Proton Sponge⁵ **6** and observed some remarkable annelation reactions. Reaction with **3** gave **7**, and **2** gave the analogous product **8** (Scheme 2). In each, the ¹⁹F NMR spectra

[†] Structures were established by a combination of elemental analysis, mass spectrometry and NMR spectroscopy.



Scheme 3

confirmed the structures shown. The regiochemistry is specific and, in each case, reaction appears to proceed *via* initial nucleophilic attack, to place developing negative charge on the carbon atom which is contained in the four-membered ring **9** (Scheme 3). This is understandable because the carbon atom of the small ring is the more electronegative. Analogous reactions have been observed with **4** and Proton Sponge but, in this case, the products showed striking colour changes from solid state to solution and, in some cases, metallic lustre. Further discussion of these systems will be made in a subsequent publication.

Further development of these novel reactions is now taking place.

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References

- 1 R. D. Chambers and R. H. Hobbs, *Adv. Fluorine Chem.*, 1965, **4**, 50.
- 2 R. D. Chambers, *Fluorine in Organic Chemistry*, Wiley-Interscience, New York, 1973.
- 3 R. D. Chambers, G. Taylor and R. L. Powell, *J. Chem. Soc., Perkin Trans. 1*, 1980, 426.
- 4 R. D. Chambers, G. Taylor and R. L. Powell, *J. Chem. Soc., Perkin Trans. 1*, 1980, 429.
- 5 R. W. Alder, P. S. Bowmann, W. R. S. Steele and D. R. Winterman, *J. Chem. Soc., Chem. Commun.*, 1968, 723; H. A. Staab and T. Saupe, *Angew. Chem., Int. Ed. Engl.*, 1988, 865.