Perfluoroalkyl-1,2,3-triazines: Novel Nucleophilic Attack on Ring Nitrogen

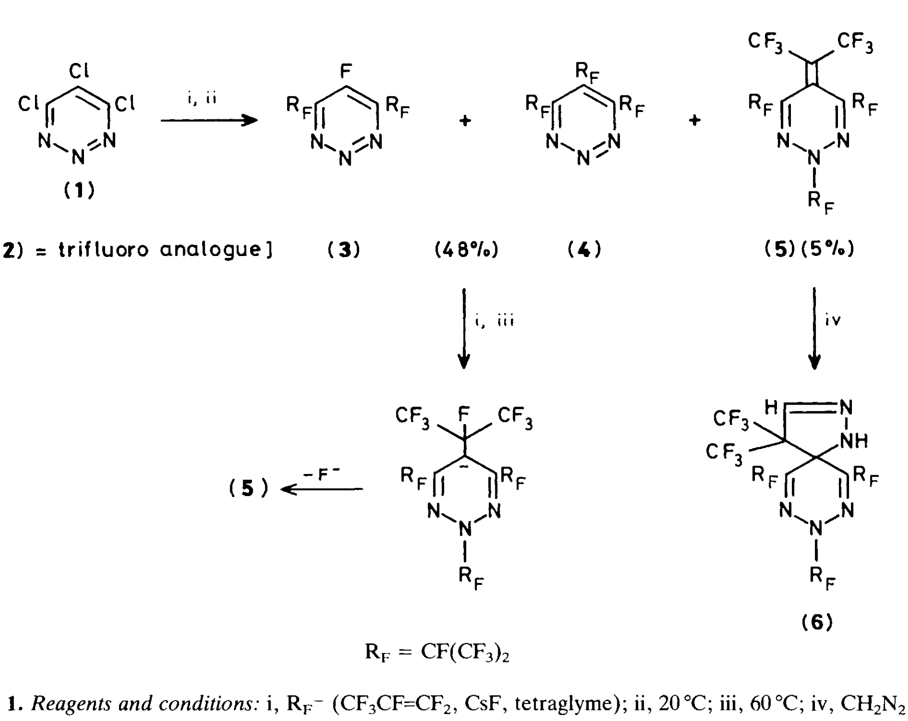
Richard D. Chambers,*[a] Masayuki Tamura,[a] Judith A. K. Howard,[b] and Owen Johnson[b]

[a] *Department of Chemistry, University Science Laboratories, South Road, Durham DH1 3LE, U.K.*
[b] *School of Chemistry, University of Bristol, Bristol BS8 1TS, U.K.*

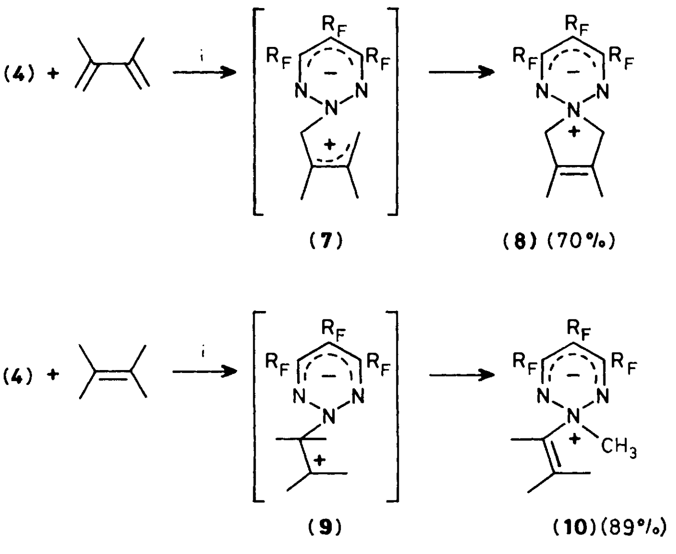
Syntheses of trifluoro- and perfluoroisopropyl-1,2,3-triazine derivatives and the unusual nucleophilic attack by a perfluoroalkyl anion and phenylmagnesium bromide on ring nitrogen are described; cheletropic addition of 2,3-dimethylbutadiene to ring nitrogen and an analogous addition of 2,3-dimethylbut-2-ene occur.

In a series of papers[1] we are describing the synthesis and unusual chemistry of a novel class of 'unnatural products,' the perfluorinated-azines, -diazines, and -triazines. Trifluoro-1,3,5-[2] and -1,2,4-triazines[3] have been described previously, as well as perfluoroalkyl derivatives of these systems.[4,5] However, we now describe an approach to the corresponding derivatives of the extremely interesting 1,2,3-system, starting with the known trichloro-1,2,3-triazine[6] (**1**).

Trifluoro-1,2,3-triazine (**2**) was obtained, by passing (**1**) *via* vacuum transfer over potassium fluoride in two stages, first at 500 °C and then at 600 °C. However, perfluoroalkyl derivatives of the 1,2,3-triazine system may be obtained by direct reaction of (**1**) using, *e.g.* hexafluoropropene, caesium or potassium fluoride, and tetraglyme as solvent, a process developed previously in these laboratories[7] (Scheme 1). At ambient temperatures, a mixture containing (**3**) and (**4**) was obtained, together with the novel product (**5**). The ratios of products depend on the conditions used, but at 60 °C (**5**) became the main product and we have demonstrated, in a separate experiment, that a mixture of (**3**) and (**4**) is converted quantitatively into (**5**), under these conditions. The structure of (**5**) follows partly from the ^{19}F n.m.r. data and, conspicu-



Scheme 1. *Reagents and conditions:* i, R_F^- ($CF_3CF{=}CF_2$, CsF, tetraglyme); ii, 20 °C; iii, 60 °C; iv, CH_2N_2, Et_2O.



Scheme 2. *Conditions:* i, 70 °C, 4 days.

ously, the absence of a 'tertiary' fluorine and the characteristic absorption of $CF_3C{=}C$,[8] at around 60 p.p.m. [61.3 p.p.m. in (**5**)]. Furthermore, double bonds activated by the presence of perfluoroalkyl groups are especially reactive to diazomethane[9] and a Δ^2-pyrazoline (**6**) is a readily produced from (**5**). Compound (**5**) is therefore formed by nucleophilic attack on ring nitrogen in an azine, a process unknown until recently.[10,11]

Remarkably, electron-rich alkenes and dienes react with (**4**) and these reactions may also be regarded as involving nucleophilic attack at nitrogen; *e.g.* dimethylbutadiene gives a product (**8**) in which a unique cheletropic addition to ring nitrogen has occurred (Scheme 2). We are not aware of any other example of this reaction which, of course, is reminiscent of the well-known reaction of sulphur dioxide with butadiene. However, in the formation of (**8**) we suggest a mechanism that involves nucleophilic attack by the diene, possibly involving an intermediate (**7**). The structure of the product (**8**) was confirmed by *X*-ray crystallography.[12] An analogous process may be outlined for reaction of (**4**) with 2,3-dimethylbut-2-ene which gave (**10**) in high yield. The n.m.r. data for (**10**) parallel those for (**8**) but, while (**8**) is colourless, compound (**10**) is green. The most obvious explanation for this difference is that, whereas charge transfer interaction between the hydrocarbon double bond in (**10**) and the triazine ring is possible, such interaction is not possible in (**8**) because the alkene unit is contained in a ring and held away from the triazine ring.

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