Novel Synthesis and Regiospecific Cycloaddition Reactions of Perfluoro-3-methylbut-1-yne

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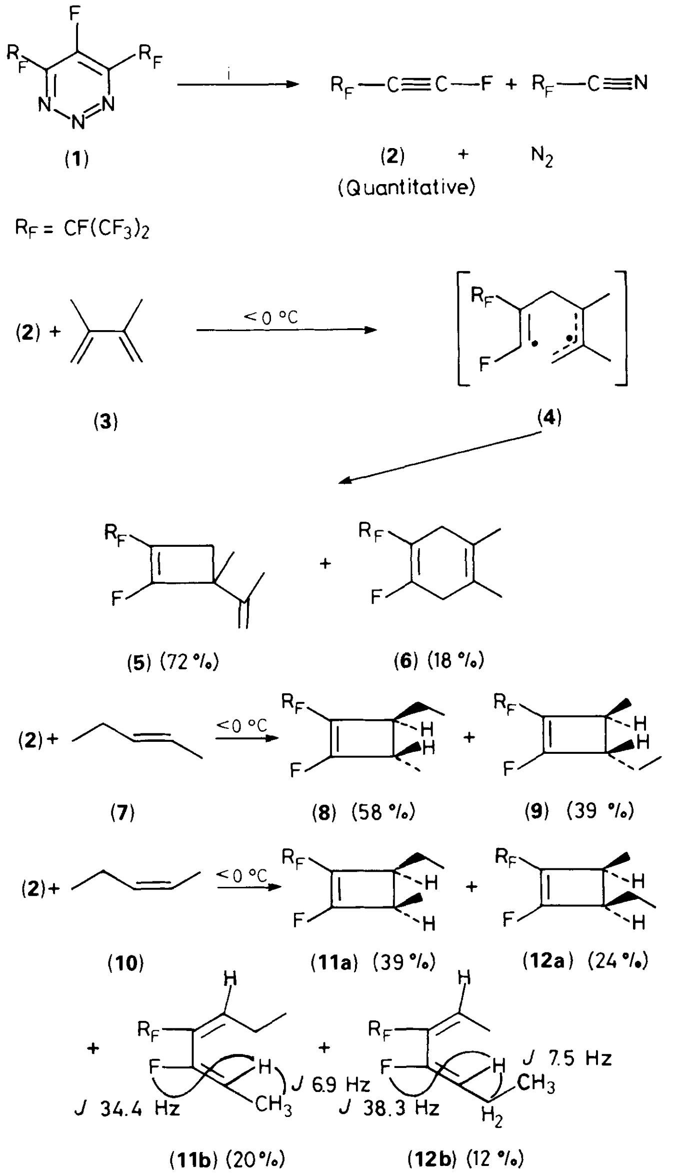
Vacuum pyrolysis of a perfluorodialkyl-1,2,3-triazine (**1**) gives a route to a fluoro-alkyne derivative (**2**), which undergoes novel stereospecific $2\pi + 2\pi$ cycloadditions to (*E*)- and (*Z*)-pentene.

It is well known[1] that fluorine attached directly to an alkyne site, *i.e.* –C≡C–F, is destabilising, *viz.* the explosive instability of difluoroethyne,[2] whereas perfluoroalkyl groups provide systems that are comparatively stable, *e.g.* hexafluorobut-2-yne for which an extensive chemistry is developing.[3,4a] Systems of the type $R_FC{\equiv}CF$ (where R_F is perfluoroalkyl) are of intermediate reactivity and of significant interest, but access to such systems is limited.[4,5]

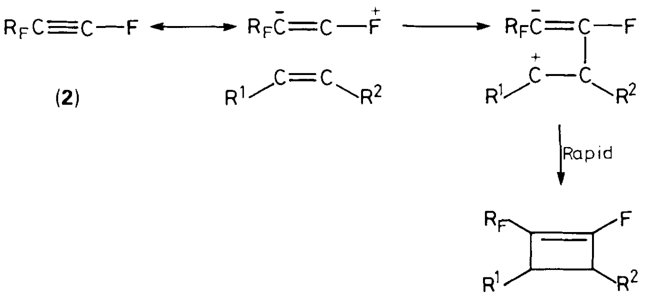
Here, we describe a novel route to perfluoro-3-methylbut-1-yne (**2**), by vacuum pyrolysis of perfluoro-4,6-di-isopropyl-



Scheme 1. *Conditions*: i, 600 °C, 10^{-2} mmHg, short contact, flow system.

1,2,3-triazine (**1**) which has been described recently (Scheme 1).[6] When (**1**) was passed, under vacuum, though a heated quartz tube packed with quartz wool, quantitative conversion to (**2**) occurred. Compound (**2**) can be stored for long periods of time without decomposition, and indeed attempts to promote thermal oligomerisation of (**2**) by heating in a Carius tube to 200 °C resulted in no change.

Compound (**2**) is, however, highly reactive in cycloaddition reactions; reaction with excess 2,3-dimethylbutadiene on warming from liquid air temperature gave quantitative conversion to a product which contained the $2\pi + 2\pi$ product (**5**) and Diels–Alder adduct (**6**). The residue contained uncharacterised products arising from addition of two molar proportions of (**3**) to (**2**). The regiochemistry of the major product (**5**) is consistent with a di-radical intermediate (**4**), although the regiochemistry of addition to the alkyne derivative (**2**) must stem from polarity considerations, *i.e.* the carbon attached to the R_F group in (**2**) will be the more electrophilic.



Scheme 2

Separate reactions with the (*E*)- and (*Z*)-isomers of pent-2-ene (**7**) and (**10**) were quite surprising. The additions were not regiospecific but were highly stereospecific (within limits of detection by capillary g.l.c.); the (*Z*)-isomer (**10**) gave cyclobutene derivatives (**11a**) and (**12a**), and the corresponding butadienes (**11b**) and (**12b**), which occur by regiospecific con-rotatory opening of (**11a**) and (**12a**). The structures (**11b**) and (**12b**) were assigned a stereochemistry on the basis of *J* values, notably characteristic $J_{\mathrm{F,H}}$-*trans*, and the specific ring-opening to give an isomer (**11b**) is most obviously accounted for by minimising interactions between R_F and Et or Me, which become *trans*. The products from (**7**) and (**10**) were scrutinised by capillary g.l.c. and no evidence for the presence of the other stereoisomers was obtained. We conclude, therefore, that these constitute rare examples of stereospecific thermal $2\pi + 2\pi$ cycloaddition reactions and must be considered together with the reported stereospecific additions to ketenes.[7] Arguments advanced to account for these reactions, *i.e.* orthogonal approach of the two sets of π-systems, could of course be applied here, but we consider it more likely that the process is predominantly ionic in character, involving nucleophilic attack by the alkenes (**7**) and (**10**) on (**2**) (Scheme 2).

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