Reaction of Amines with Perfluoroazapropene: Formation of the Novel 4*H*-Pyrido[1,2-*a*]-*s*-triazine System *via* Unsymmetrical Carbodi-imides

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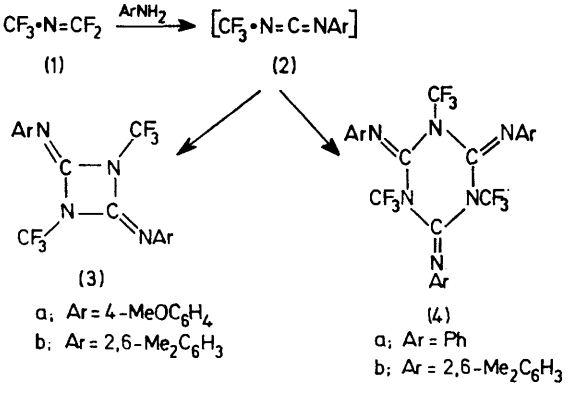
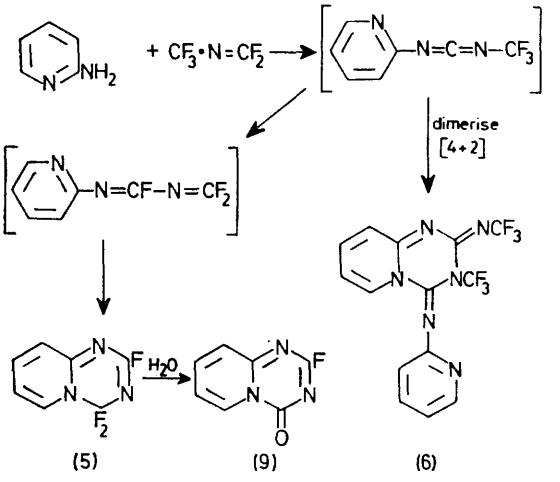
Summary Perfluoroazapropene (**1**) reacts with primary aromatic amines to give intermediate carbodi-imides (**2**) which dimerise or trimerise; intramolecular cyclisation occurs with 2-aminopyridines to give the novel heterocyclic system 4*H*-pyrido[1,2-*a*]-*s*-triazine and with aminopyrazine to give a derivative of 4*H*-pyrazino-[1,2-*a*]-*s*-triazine, respectively.

AROMATIC amines react with hexafluoropropene dimer, $(CF_3)_2C{=}CF{\cdot}C_2F_5$, to give quinolines *via* cyclisation onto the aromatic ring;[1] the formally analogous reaction of such amines with perfluoroazapropene dimer, $(CF_3)_2N{\cdot}CF{=}N{\cdot}CF_3$, now reported, follows a different but equally interesting route. In all cases initial dedimerisation of the dimer[2] occurred to give perfluoroazapropene (**1**) and hence it proved more convenient to treat the amines with (**1**) rather than



SCHEME 1



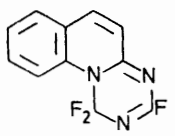
SCHEME 2

with its dimer. Equimolar reactions of (**1**) and primary aromatic amines at 20 °C in the presence of trimethylamine

and with tetrahydrofuran as solvent gave high yields of one or both of a diazetidine (**3**) and a triazine (**4**) (Scheme 1). Thus, 4-methoxyaniline gives the 1,3-diazetidine (**3a**) (72%), whereas aniline gives the hexahydro-*s*-triazine (**4a**) (67%), and 2,6-dimethylaniline gives a mixture of (**3b**) and (**4b**). In no case was the intermediate unsymmetrical carbodi-imide (**2**) isolated; however, pyrolysis at 350 °C of a mixture of (**3b**) and (**4b**) gives (**2**; Ar = 2,6-$Me_2C_6H_3$) which, although stable for several months at 20 °C, is rapidly re-converted into (**3b**) and (**4b**) by the action of triethyl-amine.[3]

2-Aminopyridine gives both the 4*H*-pyrido[1,2-*a*]-*s*-tri-azine (**5**) and its substituted dihydro derivative (**6**) *via* an intramolecular cyclisation and a [4+2] self-addition reaction, respectively, of the intermediate carbodi-imide (Scheme 2). Electron-withdrawing substituents on the pyridine nucleus favour formation of (**6**), whereas electron-donating sub-stituents favour (**5**), as does increasing the amount of solvent. Steric effects are important in suppressing dimerisation of the carbodi-imide: the sole products of the reaction of (**1**) with 2-aminoquinoline and with 2-amino-6-methylpyridine are (**7**) and (**8**), respectively. Although pure (**5**) can be isolated, it is very readily hydrolysed to give (**9**); the 2-F in (**9**) is easily displaced by nucleophiles.

Aminopyrazine gives the 4*H*-pyrazino[1,2-*a*]-*s*-triazine (**10**) (35%) and the dihydro derivative (**11**) (36%), whereas, 3-amino-6-chloropyridazine gives only the pyridazino[1,6-*a*]-*s*-triazine derivative (**12**) in which the 7-F results from nucleophilic displacement of chlorine by the fluoride ion generated *in situ*.



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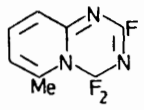

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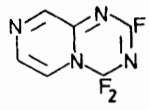

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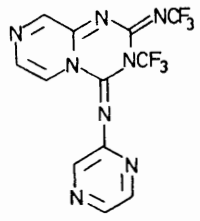

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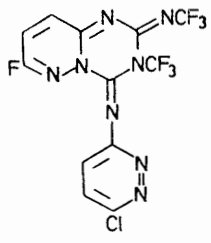

(12)

All the compounds reported have satisfactory elemental analysis and spectroscopic data; mass spectra of (**3**) and (**4**) indicate the structures shown rather than less symmetrical isomers.

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[2] J. A. Young, F. N. Tlumac, and R. D. Dresdner, *J. Org. Chem.*, 1965, **30**, 3524.
[3] K. Hartke and F. Rossbach, *Angew. Chem. Internat. Edn.*, 1968, **7**, 72.