Reaction of Aromatic or Heterocyclic Amines and Perfluoro-2-methylpent-2-ene to give Fused Pyridines, Ketenimines, or Enamines[1]

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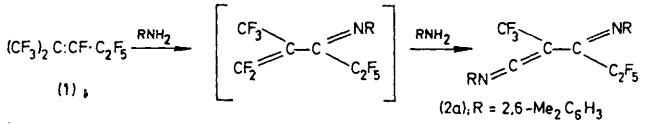
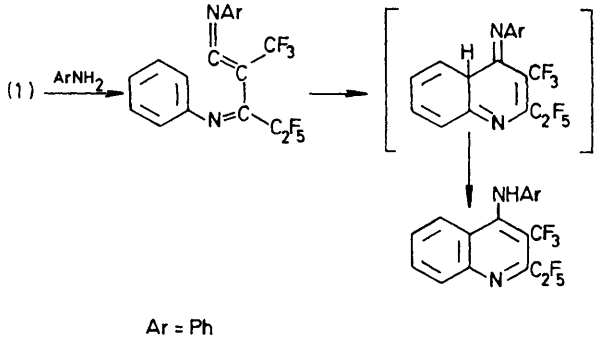
Summary Perfluoro-2-methylpent-2-ene (**1**) reacts with aromatic amines to give high yields of 4-arylaminoquinolines; aminopyridines react similarly to give the corresponding derivatives of either naphthyridine or pyridopyrimidine, whereas aromatic primary amines with substituents in the *ortho*-positions, or t-butylamine, give ketenimines, dialkylamines give enamines, and ammonia gives a dicyano-enamine.

A USEFUL new route is now reported for the synthesis of heterocyclic compounds or ketenimines *via* the reaction of amines with perfluoro-2-methylpent-2-ene (**1**), the dimer readily obtained from hexafluoropropene by the action of fluoride ion.[2]



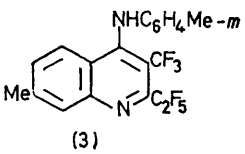
Aromatic primary amines, no ortho-*hydrogen; t-butylamine.* An aromatic amine of this class, typified by 2,6-dimethylaniline, gives an isolable ketenimine (**2a**), ν_{max} 2090 (–N=C=C<) cm^{-1}; t-butylamine gives the analogous ketenimine (**2b**) (85%).

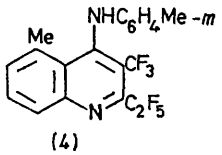
Aromatic primary amines, ortho-*hydrogen available.* High yields of 4-arylaminoquinolines are obtained *via* cyclisation of a ketenimine of type (**2**) (Scheme 1). The reaction takes place particularly readily with aromatic amines in which the aromatic nucleus has electron-donating substituents (alkyl, alkylamino, alkoxy, *etc.*); thus, 2,4-dimethoxyaniline and (**1**) (3 : 1), after reaction for 2 days in tetrahydrofuran solution at 20°, give 74% of analytically pure 4-(2,4-dimethoxyanilino)-6,8-dimethoxy-2-pentafluoroethyl-3-trifluoromethylquinoline. *meta*-Toluidine gives a 30% yield of a 5 : 1 mixture of the quinolines (**3**) and (**4**) illustrating preference for one of the two modes of cyclisation of the ketenimine. α-Naphthylamine similarly affords the 1-azaphenanthrene (**5**).

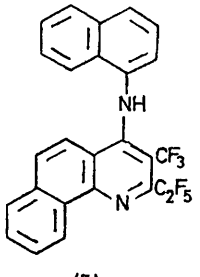


SCHEME 1

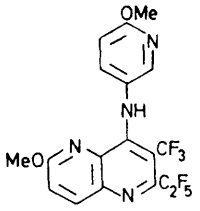
Aminopyridines. 5-Amino-2-methoxypyridine reacted with (**1**) to give [1,5]-naphthyridine (**6**) and not the [1,7]-isomer, *i.e.*, cyclisation takes place at C-2 on the 3-amino-







pyridine nucleus rather than at C-4. With 2-aminopyridines, cyclisation can be envisaged to take place either on the ring-nitrogen or on C-3 to give, respectively, a 4*H*-pyrido[1,2-*a*]pyrimidine or a [1,8]-naphthyridine; both modes of cyclisation have been observed. Thus 2-aminopyridine gave the pyridopyrimidine (**7**) (80%), and although 2-amino-4-methylpyridine reacted similarly, the isomeric 2-amino-6-methylpyridine gave the [1,8]-naphthyridine (**8**).



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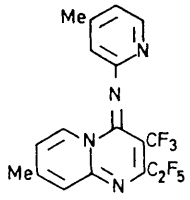

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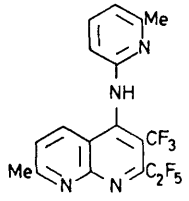
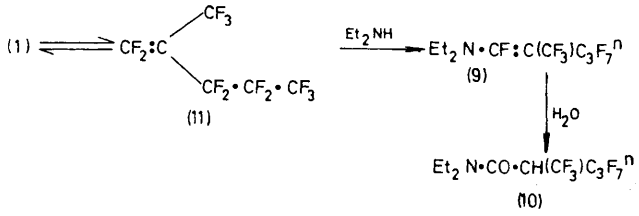


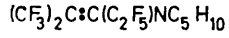
(8)

Dialkylamines. Diethylamine reacts with the olefin (**1**) to give the enamine (**9**) in good yield (Scheme 2), and amide (**10**) is also obtained by ready hydrolysis of (**9**) during work-up. This agrees with a recent publication[3] which showed that compounds (**9**) and (**10**) result from the reaction of diethylamine with perfluoro-4-methylpent-2-ene which must rearrange rapidly to (**1**)[2] and then to (**11**) as soon as fluoride ion is liberated. Olefin (**1**) is attacked at a greater rate by piperidine than it is isomerised by fluoride



SCHEME 2

ion, however, since the main product (86%) is the enamine (**12**); the majority of secondary amines react in this manner.



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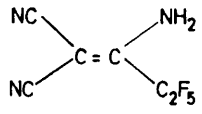

(13)

Ammonia. An almost quantitative yield of the dicyanoenamine (**13**) is obtained, *both* CF_3 groups having been attacked by the nucleophile.

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[1] Presented in part at the 7th International Fluorine Symposium, Santa Cruz, U.S.A., July 1973.
[2] W. Brunskill, W. T. Flowers, R. Gregory, and R. N. Haszeldine, *Chem. Comm.*, 1970, 1444.
[3] G. Tsukamoto and N. Ishikawa, *Chem. Letters*, 1972, 577.