

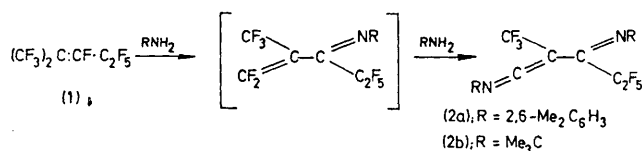
Reaction of Aromatic or Heterocyclic Amines and Perfluoro-2-methylpent-2-ene to give Fused Pyridines, Ketenimines, or Enamines¹

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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.

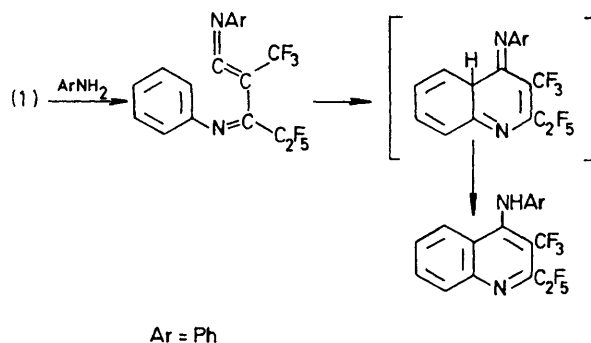
A USEFUL new route is now reported for the synthesis of heterocyclic compounds or ketenimines *via* the reaction of amines with perfluoro-2-methylpent-2-ene (**1**), the dimer readily obtained from hexafluoropropene by the action of fluoride ion.²



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 ($-\text{N}=\text{C}=\text{C}-$) cm^{-1} ; *t*-butylamine gives the analogous ketenimine (**2b**) (85%).

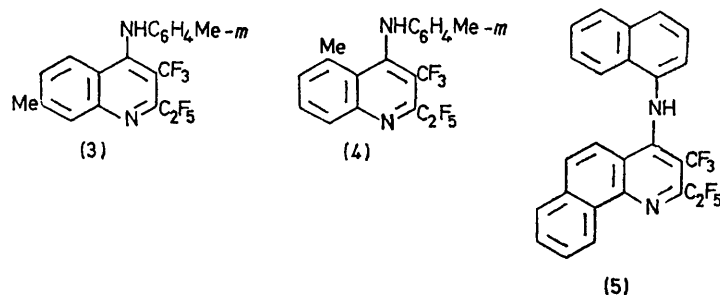
Aromatic primary amines, *ortho*-hydrogen available. High yields of 4-arylaminoquinolines are obtained *via* cyclisation of a ketenimine of type (2) (Scheme 1). The reaction takes place particularly readily with aromatic amines in which the aromatic nucleus has electron-donating substituents (alkyl, 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**).

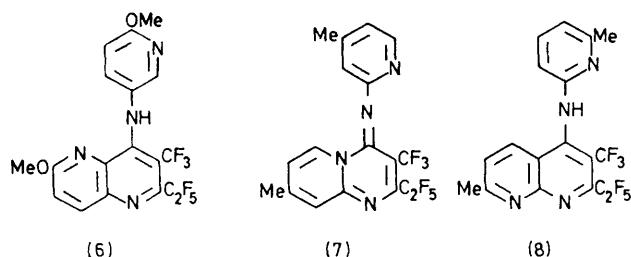


SCHEME 1

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-

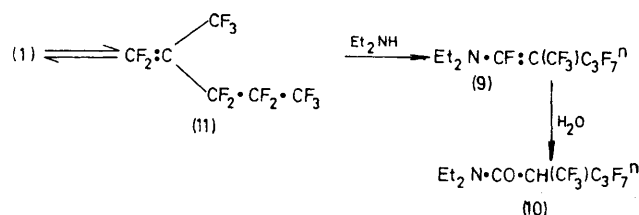


pyridine nucleus rather than at C-4. With 2-aminopyridines, cyclisation can be envisaged to take place either on the ring-nitrogen or on C-3 to give, respectively, a 4*H*-pyrido[1,2-*a*]pyrimidine or a [1,8]-naphthyridine; both modes of cyclisation have been observed. Thus 2-aminopyridine gave the pyridopyrimidine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



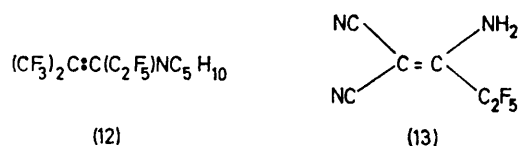
Dialkylamines. Diethylamine reacts with the olefin (1) to give the enamine (9) in good yield (Scheme 2), and amide (10) is also obtained by ready hydrolysis of (9) during work-up. This agrees with a recent publication³ which showed that compounds (9) and (10) result from the reaction of diethylamine 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.



Ammonia. An almost quantitative yield of the dicyanoenamine (13) is obtained, both CF₃ 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.