

## New Synthesis of 1,2,3,4-Tetrafluorocarbazoles from Enamines

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**Summary** Condensation of hexafluorobenzene with 1-dialkylaminocyclohexenes gives tetrafluorotetrahydrocarbazoles which are oxidised to tetrafluorocarbazoles by chloranil.

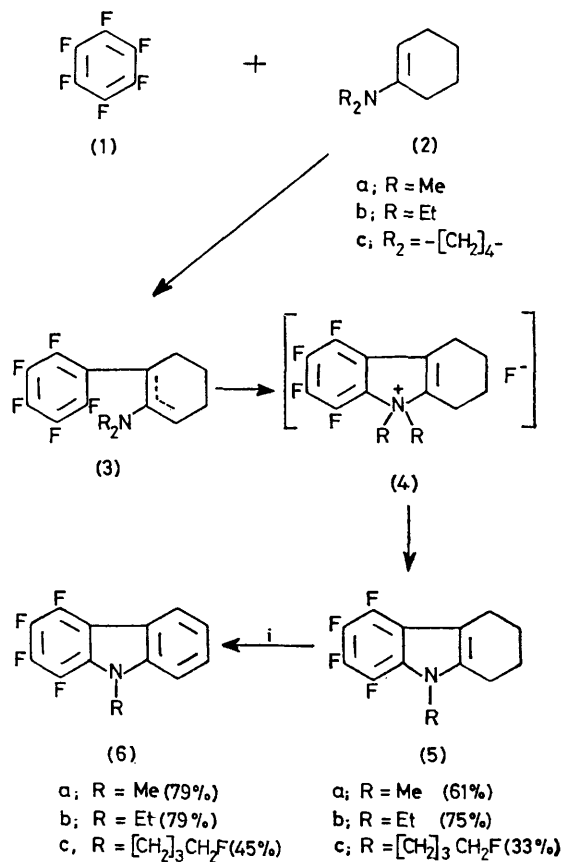
INTRAMOLECULAR nucleophilic substitution of a fluorine atom is the most widely used method for generating poly-fluorinated aromatic heterocyclic compounds.<sup>1</sup> Although a number of fluorinated indole derivatives can be prepared by this method,<sup>2</sup> tetrafluorocarbazole itself can only be obtained by the Fischer reaction<sup>3</sup> starting from tetrafluoroanthranilic acid. Here we report that the arylation of enamines<sup>4</sup> can be accomplished with hexafluorobenzene (1). This reaction provides an easy synthetic route to fluorinated carbazoles.

On refluxing a mixture of (1) and an excess of the enamines (2) C-arylation occurs initially, as shown by <sup>19</sup>F n.m.r. spectroscopy to give the intermediate enamines (3).

On prolonged heating of (3), intramolecular N-arylation then leads to the tetrafluorotetrahydrocarbazole derivatives (5).

The quaternary ammonium salt (4) is presumed to be an intermediate in this reaction which may be dealkylated by fluoride ion.<sup>5</sup> The tetrafluorotetrahydrocarbazoles (5) are readily dehydrogenated by chloranil in refluxing toluene to afford the tetrafluorocarbazoles (6).

This reaction seems to be quite general and can be applied to various enamines and perfluoroarenes leading to numerous fluorinated heterocycles. Some of these derivatives may be useful as <sup>19</sup>F n.m.r. probes in the study of their interactions with nucleic acids.<sup>6</sup>



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<sup>1</sup> P. Tarrant, 'Fluorine Chemistry Reviews,' Marcel Dekker, New York, 1974, vol. 7, ch. 2.

<sup>2</sup> V. P. Petrov, V. A. Barkhash, G. S. Schegoleva, T. D. Petrova, T. I. Savchenko, and G. G. Yakobson, *Doklady Akad. Nauk. S.S.S.R.*, 1968, **178**, 864; A. Filler, S. M. Woods, and A. F. Freudenthal, *J. Org. Chem.*, 1973, **38**, 811.

<sup>3</sup> T. D. Petrova, V. P. Mamaev, and G. G. Yakobson, *Bull. Acad. Sci. U.S.S.R.*, 1969, 609.

<sup>4</sup> M. E. Kuehne, *J. Amer. Chem. Soc.*, 1962, **84**, 837.

<sup>5</sup> For a similar opening of a cyclic ammonium salt with chloride ion, see: J. Ø. Madsen, and S. O. Lawesson, *Bull. Soc. chim. Belges*, 1976, **85**, 805.

<sup>6</sup> Work in progress.