

Novel Derivatives of Perfluorocyclobutene

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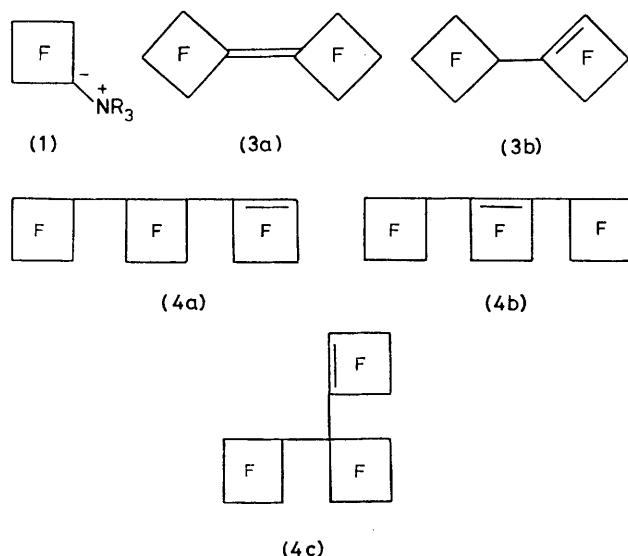
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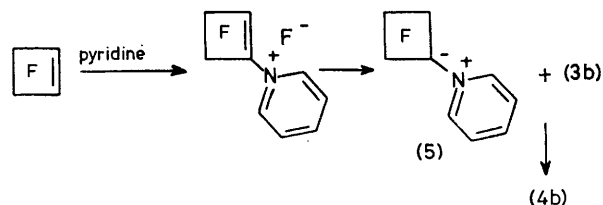
Summary A new trimer, as well as dimers, are formed by a reaction of perfluorocyclobutene with pyridine; the dimers with caesium fluoride give a stable carbanion.

A RECENT description¹ of the isolation of stable ylides (**1**),† obtained by the reactions of trialkylamines with perfluorocyclobutene (**2**), prompts us to report relevant results, concerning the reaction of (**2**) with pyridine.

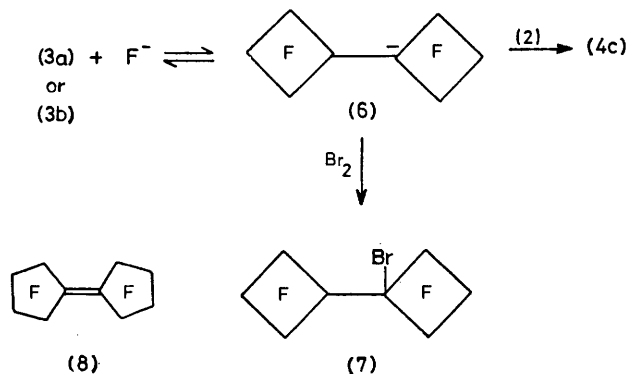


Reaction of (**2**) with pyridine gives a mixture of dimers (**3a**) and (**3b**), and a trimer previously claimed to have the structure (**4a**).² The relative proportions of (**3a**), (**3b**), and (**4a**) vary with the amounts of pyridine used but the total yields are *ca.* 80%. We now find, however, that the trimer has structure (**4b**) rather than (**4a**). This follows simply from the ¹⁹F n.m.r. spectrum which is symmetrical, showing signals corresponding to -CF- (¹⁹F, δ 180 p.p.m.) and three signals characteristic of CF₂ groups contained in a four-membered ring (rel. intensities 1:2:1); a weak i.r. band at 1669 cm⁻¹ was also observed. The structure (**4b**) is in marked contrast to (**4c**), which is the structure of a trimer isolated from the reaction of (**2**) with fluoride ion;³ no (**4c**) has been detected in the reaction with pyridine.

Clearly, different mechanisms must obtain for these processes and formation of (**4b**) is readily rationalized on the basis of reaction of an ylide (**5**), related to (**1**), with the dimer (**3b**). This reaction has been demonstrated in a separate experiment where a mixture of the dimer (**3b**), perfluorocyclobutene (**2**), and pyridine, gave the trimer (**4b**).



We have previously rationalized the formation of (**4c**) on the basis of reaction of an intermediate carbanion (**6**) with perfluorocyclobutene (**2**)³ and we have now established that dimers (**3a**) or (**3b**) do, indeed, form a stable anion (**6**) with caesium fluoride. The carbanion (**6**) has been studied by ¹⁹F n.m.r. spectroscopy, over a temperature range -60 to



+92 °C. Only at the higher temperature did broadening become noticeable and the spectrum is quite different from those of the dimers (**3a**) and (**3b**) but is similar to that of the ylide (**1**).¹ Furthermore, the equilibrium is wholly on the side of the anion (**6**) because no dimers (**3a**) or (**3b**) could be detected. The anion (**6**) may be trapped with (**2**) giving the trimer (**4c**), and with a variety of other trapping agents, including bromine which gave (**7**). The stability of the carbanion (**6**) may be attributed partly to the influence of the cyclobutane ring, as well as the stabilizing influence of the fluorine atoms. This follows from the fact that the bicyclopentylidene system (**8**) did not form an observable anion under comparable conditions. It is probable, therefore, that the orbital associated with the electron-pair in (**6**) has a greater *s*-character imposed by the fact that the associated carbon atom is part of a four-membered ring.

The trimer (**4b**) undergoes a range of novel reactions which are under investigation and will be reported separately.

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† The presence of a F-atom within a ring in structures (**1**)—(**8**) signifies that all unmarked positions in that ring are attached to fluorine.

¹ D. J. Burton, R. D. Howells, and P. D. Vander Valk, *J. Amer. Chem. Soc.*, 1977, **99**, 4830.

² R. L. Pruett, C. T. Bahner, and H. A. Smith, *J. Amer. Chem. Soc.*, 1952, **74**, 1638.

³ R. D. Chambers, M. Y. Gribble, and E. Marper, *J.C.S. Perkin I*, 1973, 1711.