

SYNTHESIS OF SEVEN-MEMBERED HETEROCYCLES CONTAINING FLUOROALKYL GROUPS

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The synthetic utilization of perfluoroolefins for fluorinated heterocycles has considerable interest from pharmaceutical and agrochemical points of view. This work has been extended searching for new heterocycles by having 1-2-methyl-2-pentene 1, one of the two known hexafluoropropene dimers, and 2-2,4-dimethyl-3-heptene 2, one of the three known hexafluoropropene trimers, react with ortho-bifunctional benzenes.

4-Fluoro-2-(F-ethyl)-3-(F-methyl)-1,5-benzoxazepine 3 was prepared by the simple reaction of 1 with 2-aminophenol in the presence of triethylamine in diethyl ether at  $-15 \sim -10^\circ \text{C}$  in 48 % yield. In the NaH-Et<sub>2</sub>O system, catechol reacted with 1 smoothly to produce the corresponding 2,4-difluoro-4-(F-ethyl)-3-(F-methyl)-4H-1,5-benzodioxepin (Y. 44 %) and 2-(F-ethyl)-2-(1-F-methyl-2,2,2-trifluoroethyl)-benzodioxole (Y. 20 %). However, in the case of o-phenylenediamine, 4-(F-ethyl)-3-(F-methyl)-1H-1,5-benzodiazepin-2(3H)-one was obtained in a very poor yield of 6 %.

On the other hand, when 2-2,4-dimethyl-3-heptene 2 was used in the above reactions, new types of heterocycles were obtained. The reaction of 2 was carried out with 2-aminophenol in DMF, giving 7-(F-1-methylethyl)-8-(F-ethyl)-9,14-benzoxazepino[4,3-b]-1,6-benzoxazepine 4 in an yield of 74 %.

When o-phenylenediamine was allowed to react with 2 in DMF, 1H-1,7a-dihydro-7-(F-ethyl)-8-(F-1-methylethyl)-9,14-benzodiazepino[2,3-b]-1,6-benzodiazepine in 54 % yield and 2-(F-1-methylethyl)-3-(F-propylidene)-1,5-benzodiazepine in 30 % yield were produced.

