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 F-2-methyl-2-pentene 1, one of the two known hexafluoropropene dimers, and F-2,4-dimethyl-3-heptene 2, one of the three known hexafluoropropene trimers, react with ortho-bifunctional benzenes.

4-Fluoro-2-(E-ethyl)-3-(E-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 to -10 °C in 48% yield. In the NaH-Et₂O system, catechol reacted with 1 smoothly to produce the corresponding 2,4-difluoro-4-(E-ethyl)-3-(E-methyl)-4H-1,5-benzodioxepin (Y. 44%) and 2-(E-ethyl)-2-(1E-methyl-2,2,2-trifluoroethyl)-benzodioxole (Y. 20%). However, in the case of o-phenylenediamine, 4-(E-ethyl)-3-(E-methyl)-1H-1,5-benzodiazepin-2(3H)-one was obtained in a very poor yield of 6%.

On the other hand, when F-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-(E-1-methylethyl)-8-(E-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-(E-ethyl)-8-(E-1-methylethyl)-9,14-benzodiazepino[2,3-b]-1,6-benzodiazepine in 54% yield and 2-(E-1-methylethyl)-3-(E-propylidene)-1,5-benzodiazepine in 30% yield were produced.