

SYNTHESIS OF SEVEN-MEMBERED HETEROCYCLES CONTAINING FLUOROALKYL GROUPS

Masamichi Maruta, Satoshi Kubota, Narihiko Yoshimura, Tomoya Kitazume and Nobuo Ishikawa

Department of Chemical Technology, Tokyo Institute of Technology
Ookayama, Meguro-ku, Tokyo, Japan

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 1-2,4-dimethyl-3-heptene 2, one of the three known hexafluoropropene trimers, react with ortho-bifunctional benzenes.

4-Fluoro-2-(1-ethyl)-3-(1-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 $\text{NaH-Et}_2\text{O}$ system, catechol reacted with 1 smoothly to produce the corresponding 2,4-difluoro-4-(1-ethyl)-3-(1-methyl)-4H-1,5-benzodioxepin (Y. 44 %) and 2-(1-ethyl)-2-(1-1-methyl-2,2,2-trifluoroethyl)-benzodioxole (Y. 20 %). However, in the case of o-phenylenediamine, 4-(1-ethyl)-3-(1-methyl)-1H-1,5-benzodiazepin-2(3H)-one was obtained in a very poor yield of 6 %.

On the other hand, when 1-2,4-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-(1-methylethyl)-8-(1-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-(1-ethyl)-8-(1-methylethyl)-9,14-benzodiazepino[2,3-b]-1,6-benzodiazepine in 54 % yield and 2-(1-methylethyl)-3-(1-propylidene)-1,5-benzodiazepine in 30 % yield were produced.

