CHEMISTRY LETTERS, pp. 291-292, 1979. Published by the Chemical Society of Japan

SEVEN-MEMBERED HETEROCYCLES FROM F-2-METHYL-2-PENTENE AND ORTHO-BIFUNCTIONAL BENZENES

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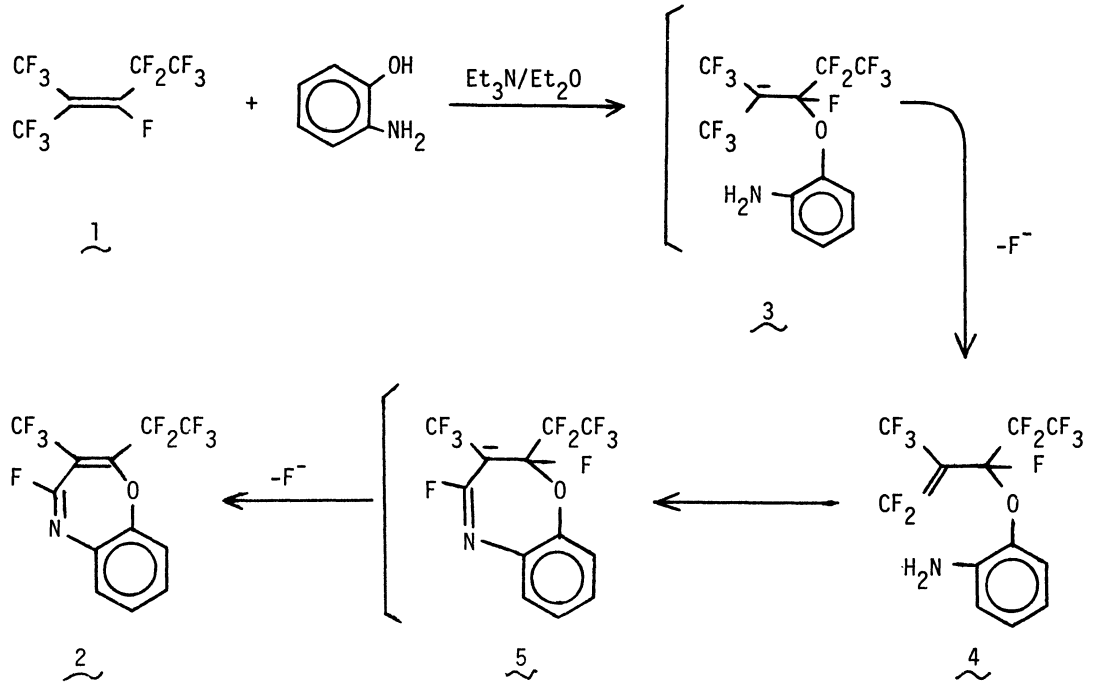
4-Fluoro-2-(F-ethyl)-3-(F-methyl)-1,5-benzoxazepine (**2**) was prepared by a simple reaction of F-2-methyl-2-pentene (**1**) with 2-aminophenol in the presence of triethylamine in diethyl ether. Catechol and o-phenylenediamine similarly reacted with **1** to give corresponding seven-membered heterocyles, i.e., 1,5-benzodioxepin and 1,5-benzodiazepin-2-one derivatives, respectively.

The reactivities of perfluoroolefins to nucleophiles have been studied over the years.[1)] Utilizing these reactivities, we have reported on preparations of some five- and six-membered heterocyclic compounds by the reactions of ortho-bifunctional benzenes with F-propene,[2)] its oxide,[3)] and F-2-methylpropene.[4)] On the other hand, we also demonstrated that arylamines readily attack F-2-methyl-2-pentene (**1**), one of hexafluoropropene dimers, resulting in the formation of fluorinated azetidine and/or quinoline derivatives.[5,6)] These works have now been extended searching for new heterocyclic compounds by having **1** react with ortho-bifunctional benzenes. We wish now to report a novel preparation of seven-membered heterocyclic compounds such as 1,5-benzoxazepine, -benzodioxepin, and -benzodiazepinone by the reactions of **1** with 2-aminophenol, catechol and o-phenylenediamine, respectively.

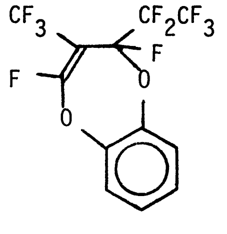
2-Aminophenol reacted with **1** in diethyl ether in the presence of triethylamine. The reaction proceeded smoothly at -15～-10°C, and 4-fluoro-2-(F-ethyl)-3-(F-methyl)-1,5-benzoxazepine (**2**) was obtained as the main product (Y. 48% : bp 60-62°C/ 2 mmHg). The structure of **2** was supported by various spectral data. The ir spectrum showed characteristic absorption bands due to C=N and C=C bonds at 1645 and 1705 cm^{-1} respectively and the ^{1}H nmr spectrum revealed only one signal due to aromatic protons at δ 7.40-6.90. In the ^{19}F nmr spectrum, four signals appeared at δ -50.7, -20.4, 3.7, and 37.3 ppm (upfield from CF_3CO_2H) in the ratios 1 : 3 : 3 : 2. The resonance at δ -50.7 (q) was assigned to -N=C$\underline{F}$-, split by the C$\underline{F}_3$ on the carbon-carbon double bond (J_{F-CF_3} = 15 Hz). The resonance at δ -20.4 was assigned to -C=C-C$\underline{F}_3$, split by all other fluorine nucleus in the molecule ($J_{CF_3-CF_2}$ = 17 Hz, $J_{CF_3-CF_2C\underline{F}_3}$ = 3 Hz). The molecular ion, M$^+$ 349, appeared in the mass spectrum.

The reaction pathway is apparently as shown below. The first step is the nucleophilic attack by the phenoxide ion leading to the carbanion **3**, as in the case of the reaction between **1** and phenol in the presence of triethylamine.[7)] From the carbanion **3**, a fluoride ion was released forming **4**, which is a reactive terminal perfluoroolefin, and it would be attacked nucleophilically by the amino group in the molecule leading to **2** via the carbanion **5**.



A similar type of reaction was observed also between 1 and catechol. In this case, the 2,4-difluoro-4-(F-ethyl)-3-(F-methyl)-4H-1,5-benzodioxepin 6 was obtained in a yield of 44% (bp 94-97°C/ 18 mmHg). Various spectral data, ir, ^{1}H and ^{19}F nmr, and ms, as well as the elemental analysis supported the structure.

The reaction between 1 and o-phenylenediamine also occurred with ease, giving the 1,5-benzodiazepinone compound 7, however, only in a very poor yield (Y. 6% : mp 119-120°C)



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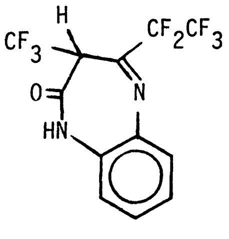

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(Received December 25, 1978)