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REACTION OF PERFLUORO-4-METHYLPENTENE-2 WITH SECONDARY AMINES

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Perfluoro-4-methylpentene-2 [1], an asymmetrical internal perfluoroolefin, reacted with secondary amines such as diethylamine or piperidine to give a terminal enamine [2], which was easily hydrolyzed to the corresponding amide [3]. The reaction mechanism was discussed.

Although a large number of reactions between perfluoroolefins and amines are known, most of the works have dealt with terminal or symmetrical fluoroolefins. On these olefins the simple addition of secondary amines across the double bond is usually observed[1].

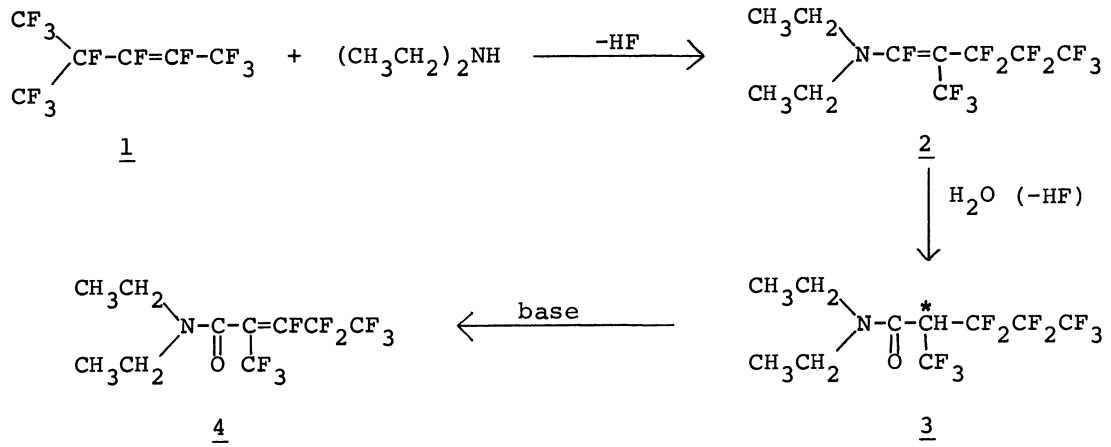
$$CF_2{=}C< \quad + \quad R_2NH \longrightarrow R_2N\text{-}CF_2CH<$$

In this paper, we would like to report an interesting reaction of perfluoro-4-methylpentene-2 [1], an asymmetrical internal olefin, with secondary amines.

When the perfluoroolefin 1, which is a dimer of hexafluoropropene, was allowed to react with two moles of diethylamine in ethyl ether, yellow liquid [2] was obtained as the sole product. This compound was unstable, and when allowed to stand with the atmosphere, it converted to colorless crystals [3]. This conversion was also observed by treating 2 with aqueous hydrochloric acid.

The structures of 2 and 3 were made clear as follows. The ir spectrum of 2 revealed the presence of C=C (1650 cm^{-1}), whereas that of 3 showed the presence of $-\overset{\overset{O}{\|}}{C}-N<$ (1640 cm^{-1}). In the mass spectrum of 3, the molecular peak (M^+ 351) corresponded to the formula $C_{10}H_{11}F_{10}NO$, which agreed with the analytical data. This should have resulted by the addition of diethylamine and water to the olefin, and by the elimination of two moles of hydrogen fluoride therefrom.

The nmr spectra played the most important role for the elucidation of the structures. In the ^1H nmr, CH_3 signals of diethylamino groups in 2 appeared as a triplet at τ 8.8, whereas those in 3 as a quartet at the same place. The latter seemed to be an overlap of two triplet signals, which resulted from the magnetic non-equivalance of the ethyl groups due to the rotational restriction of the $>N-\overset{\overset{O}{\|}}{C}-$ bond[2]. In addition, a multiplet signal at τ 5.8 revealed the presence of one hydrogen atom in



1 2 3 4

the molecular chain of 3.

In the ^{19}F nmr spectrum of the compound 2 four signals appeared at -25.0(4F) +3.5(3F), +25.4(2F) and +47.7(2F) [δ ppm from ext. CF_3CO_2H], which should be due to $\underline{C}F=\underline{C}(\underline{C}F_3)-$, $\underline{C}F_3$, $\underline{C}F_2$ and $\underline{C}F_2$ respectively.

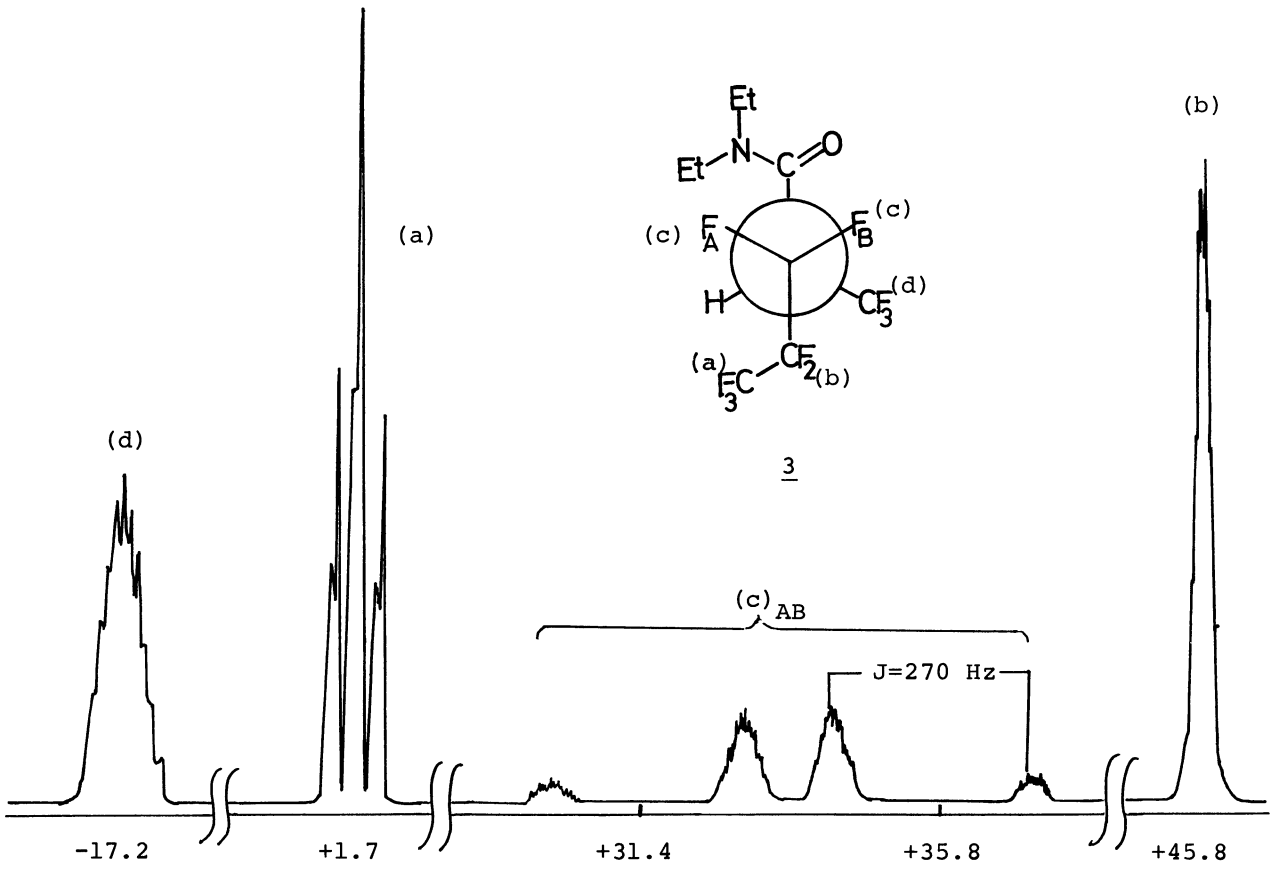
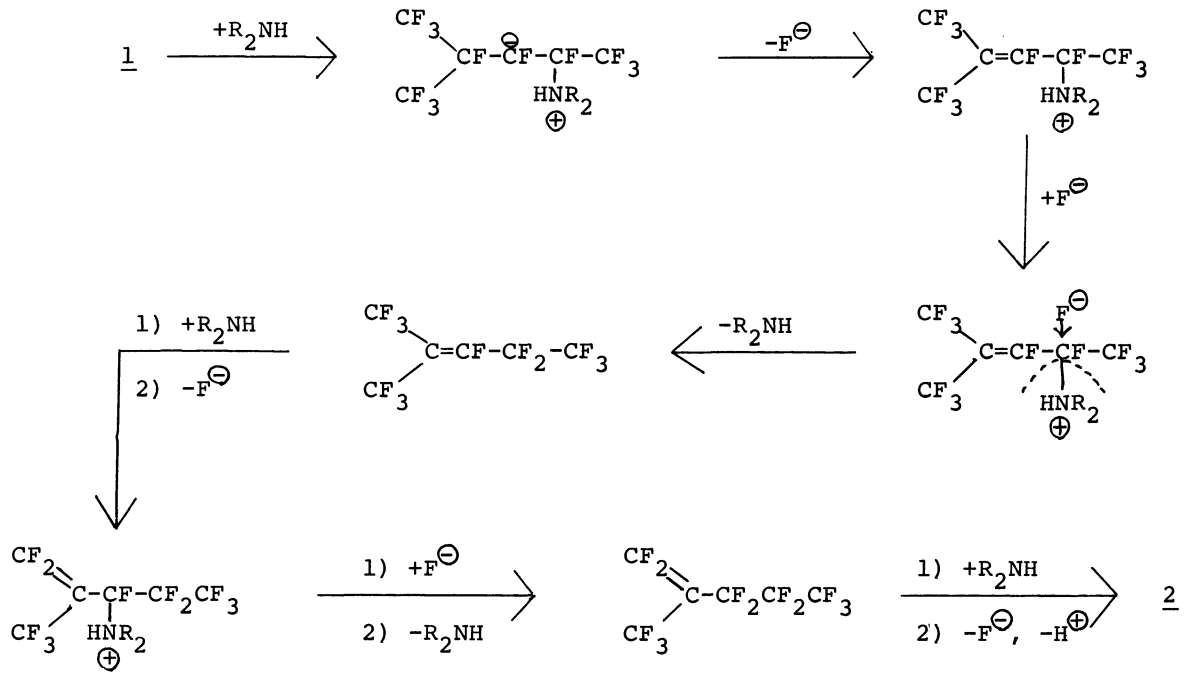


Fig 1 ^{19}F nmr spectrum for 3

The pattern of ^{19}F nmr of 3 was more complicated. The signals appeared at -17.2(3F, s), +1.72(3F, t), +34(2F, d of d) and +45.8(2F, s) which were assigned as shown in Fig 1. The $C\underline{F}_2$ signals at $\sim$ +34 ppm appeared as a doublet of doublet, which seemed to have resulted from non-equivalent two fluorine atoms on the same carbon. This suggested that in the compound 3 an asymmetrical carbon* adjascent to the CF_2 is present.

From the spectral data mentioned above we determined the structures of these compounds as the enamine 2 and the amide 3 respectively. Furthermore, by the action of a base on 3, hydrogen fluoride was easily eliminated, giving the amidoolefin 4. The structure of 4 was also clear from ^{19}F nmr, that is, four signals appeared at -17.4(d, $C\underline{F}_3$-C=), +5.2(t, $CF_2C\underline{F}_3$), +38.6(m, C$\underline{F}$) and +42.3(m, $C\underline{F}_2$) ppm.

During the first step of the above reaction, the migration of the double bond within the molecule should have taken place. Such a migration of double bond in the internal perfluoroolefin to the terminal perfluoroolefin is not strange. For example, it is recently reported that fluoride ion catalyses such an isomerization of perfluoroolefins[3]. Although further investigation is necessary in order to elucidate the mechanism of our reaction, it appears that the secondary amine accelerated the migration of the double bond in the following manner.



Thus the addition of secondary amine on fluoroolefin and the elimination of fluoride ion from the adduct, followed by the addition of fluoride ion and the elimination of the secondary amine occurred repeatedly, until the stable terminal enamine 2 was formed. As for the step from 2 to 3, it is well known that fluorinated enamines are hydrolysed easily to afford the corresponding amide[1,4].

When piperidine was used instead of diethylamine in the above reaction, the similar compound which exhibited the same behavior was obtained. The primary amines,

nowever, gave more complicated results, which is now under investigation.

Experimental

To a solution of 1 (28.4 g) in ethyl ether (20 ml) was added diethylamine (13.2 g) under ice-water cooling, and the mixture was allowed to stand overnight at room temperature. The precipitated amine hydrofluoride was filtered off and washed with ether. The filtrate was distilled in a vacuum to give yellow liquid (2, 26.1 g, 82%), bp 95°C/32 mmHg.

When the liquid (3.0 g) was mixed with 10% hydrochloric acid and the whole was left for two days at room temperature. The compound 3 was obtained as colorless needles of mp 62-63°C (2.30 g, 80%). Found : C, 34.07 ; H, 3.13 ; N, 3.94%. Calcd for $C_{10}H_{11}F_{10}NO$: C, 34.25 ; H, 3.14 ; N, 3.99%.

When 1 (6.0 g) and piperidine (3.9 g) were allowed to react in the same manner as above, yellow liquid of bp 114-115°C/26 mmHg (1.1 g) was obtained. The hydrolysis of this compound gave the corresponding amide (0.8 g), which was recrystallized from pertroleum ether giving colorless needles of mp 89-90°c. Found : C, 36.65 ; H, 3.09 ; N, 4.04%. Calcd for $C_{11}H_{11}F_{10}NO$: C, 36.37 ; H, 3.04 ; N, 3.86%.

A mixture of 3 (1.40 g), potassium hydroxide (0.23 g) and ethanol (5 ml) was left at room temperature for 3 hours, and the whole was thrown into water. Oily matter was extracted with ethyl ether, and the solvent was evaporated. The residue (1.30 g) was distilled and the fraction of bp 86-87°C/20 mmHg was collected to give 4. Found : F, 51.8%. Calcd for $C_{10}H_{10}F_9NO$: F, 51.6%.

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