CHEMISTRY LETTERS, pp. 583-586, 1980.

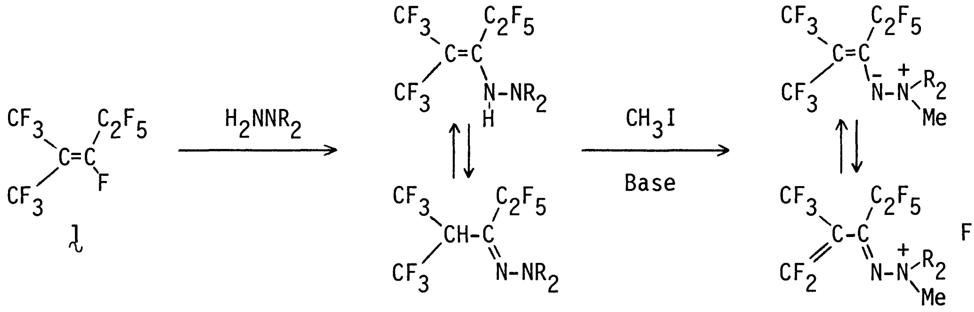
SYNTHESIS OF CYCLIC AMINIMINES WITH PERFLUOROALKYL GROUPS

Isao IKEDA, Takeo TSUKAMOTO, and Mitsuo OKAHARA
Department of Applied Chemistry, Faculty of Engineering,
Osaka University, Yamada-kami, Suita, Osaka 565

Reaction of perfluoro-2-methyl-2-pentene (**1**) with 1,1-dimethylhydrazine gave novel type cyclic aminimines, pyrazolium aminimines, and the reaction scheme was discussed.

The reactivity of **1** with various nucleophiles such as phenoxide, alkoxide, carboxylate and thiophenoxide anions have been recently investigated[1a,b], and a series of substitution products was prepared. In the case of amine as a nucleophile, only the reactions of primary aromatic amines have been reported. The reaction, however, was successive after the substitution reaction, and versatile depending on substrates and reaction conditions[1c,d,e]. On the other hand, the preparation[2] and characterization[3] of aminimines or their derivatives, aminimides, have been studied in our group. Hydrazines were used as the starting materials of these compounds.

In spite of the reactivity of **1** observed in the aromatic amines, the reaction of 1,1-disubstituted hydrazines with **1** was expected to afford the intermediates which might lead to the aminimines stabilized by perfluoroalkyl groups.



On the contrary, 1,1-dimethylhydrazine directly gave new five-membered unsaturated cyclic aminimines (pyrazolium aminimines). Pyrazolium aminimines were recently synthesized *via* propiolic acid hydrazides[4] or from the reaction of β-hydrazinoacrylates with acid chlorides[5], and an attention was collected with respect to the biological activity to some kind of plant[5]. In this letter we will describe a new synthetic method of the compounds of this type and the reaction mechanism.

Thus, a solution of 1 (1.5g, 5mmol) in THF (10ml) and 1,1-dimethylhydrazine (0.6g, 10mmol) were placed in a pressure vessel equipped with a magnetic bar under cooling in a dry ice-acetone bath (-60°C) (procedure 1). After the reaction mixture was stirred at room temperature for a day, the products were checked by glc, which indicated the presence of four kinds of products (2, 4, 6 and 7). The retention times of the compounds in glc increased in the following order, 7 < 2 < 4 < 6. After removing the volatile matter in vacuo, a yellow product, a mixture of 4 and 6 was obtained. Compound 6 was separated by recrystallization from benzene-hexane (2:1) as pale yellow scales (m.p. 132.0∿133.5°C), 4 was fractionated by means of glc as white powder, which sublimes at the temperature above 95°C. Compound 2 was separated by fractional distillation (52.0°C/35mmHg) of the reaction mixture.

Spectroscopic data on these compounds are listed in Table 1.

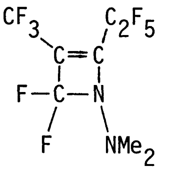
Table 1 Spectral Data of Products

	mass (m/e)	i.r. (cm^{-1})	^{19}F nmr (δppm^*)
(2)	340 (M^+), 320 (M^+-HF) 251 (M^+-HF-CF_3) 221 (M^+-C_2F_5)	1600 ($\nu_{C=N}$)	62.7 (6F, d-t, J_{HF}=9.4Hz, J_{FF}=13.2Hz) 80.1 (3F, s), 106.9 (2F, m)
(4)	320 (M^+), 286 (M^+-F-CH_3) 217 (M^+-F-CH_3-CF_3) 201 (M^+-C_2F_5)	1570 ($\nu_{C=C}$)	51.6 (3F, m), 69.3 (2F, m) 83.3 (3F, s) 116.0 (2F, q, J_{FF}=12.0Hz)
(6)	340 (M^+) 325 (M^+-CH_3) 296 (M^+-NMe_2)	1660 ($\nu_{C=N}$) 1530 ($\nu_{C=C}$)	49.5 (3F, t, J_{FF}=18.6Hz) 81.5 (3F, s) 113.5 (2F, q, J_{FF}=18.6Hz)
(7)	-	-	62.0 (6F, m) 80.9 (3F, t, J_{FF}=11.6Hz) 111.4 (2F, m), 125.4 (2F, m)

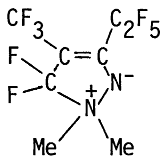
* solvent; acetone-d^6 for 2, 4 and 6, ether for 7
internal standard; CF_3-C_6H_5 at 63.7 ppm (CCl_3F; 0 ppm)

As to 4 and 6, the chemical shifts and coupling constants of ^{19}F nmr are characteristic of the cis-form between CF_3 and C_2F_5. The integral curves suggest that the numbers of fluorine atoms are 10 and 8, respectively. As to 4, one singlet signal of ^1H nmr was observed at 3.38 ppm, which indicates that the two methyl groups are adjacent to the cationic nitrogen. The mass spectral prominent peak of 286 which corresponds to the loss of F and CH_3 is presumably due to the formation of a very stable pyrazolium cation.

These spectral data support that 4 is not a four-membered azetine (4a) but a five-membered cyclic aminimine (4b).



4a



4b

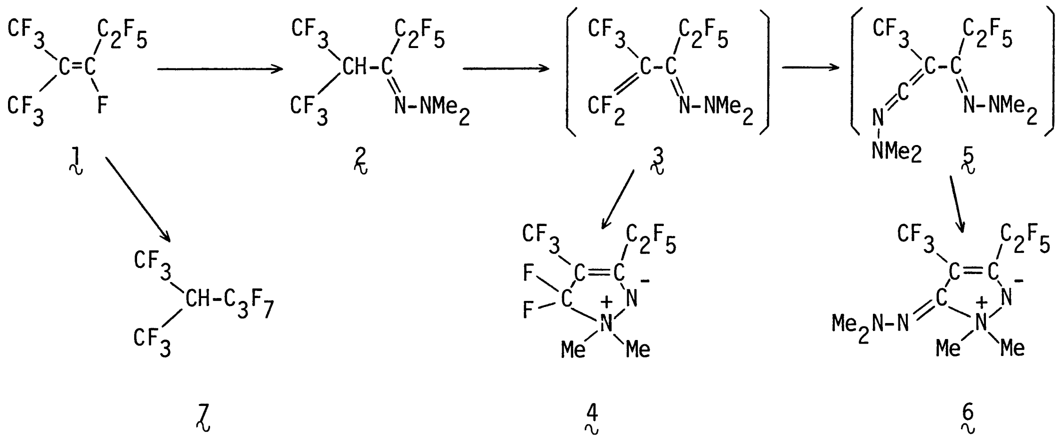
With respect to the ^{1}H nmr spectrum of 6, two singlet signals of the equal magnitude were observed at 2.38 and 3.24 ppm, indicating that 6 containes both dimethylamino group and dimethylammonio group.

Therefore, these two cyclic aminimines were confirmed to be 5,5-difluoro-1,1-dimethyl-3-pentafluoroethyl-4-trifluoromethyl-3-pyrazolium hydroxide inner salt (4) and 1,1-dimethyl-5-dimethylhydrazono-3-pentafluoroethyl-4-trifluoromethyl-3-pyrazolium hydroxide inner salt (6), respectively.

The doublet coupling (9.4Hz) of signal of six fluorine atoms at 62.7 ppm suggests the existence of $(CF_3)_2CH$- group in 2. Compound 7^6 was identified by comparison of the glc and the ^{19}F nmr spectrum^7 of the authentic sample, $(CF_3)_2CHC_3F_7$.

In procedure 1, 4 and 6 were produced in 35% and 18% yield based on 1, respectively^8. When a solution of 1 (1.5g, 5mmol) in THF (5ml) was added dropwise into that of the hydrazine (0.6g, 10mmol) in THF (5ml) suspended with NaH (0.24g, 10mmol) for 30 min. at room temperature, 6 and 4 were obtained in 51 and 23% yield, respectively, after one day.

In order to clarify the reaction route, 2 and 4 were isolated separately to serve for the further reaction. In the presence of an excess amount of NaH, 2 dissolved in diethyl ether changed to 4 as a sole product. In the presence of an excess amount of 1,1-dimethylhydrazine, 2 dissolved in diethyl ether disappeared completely after two hours at room temperature to give predominantly 6 together with a small amount of 4. On the other hand, 4 was recovered quantitatively after the treatment in the same reaction conditions that employed for 2. The reaction scheme is considered as follows.



In the first step of the reaction a nucleophilic attack by the hydrazine to 1 results in displacement with the fluorine atom at the olefinic carbon atom of 1, and then migration of the proton occurs to give 2. After elimination of HF from 2, the intermediate 3 generated is attacked intra- or intermolecularly by the nitrogen atom. If the reaction occurs intramolecularly, 4 is produced. But the intermolecular attack of the hydrazine to 3 gives 6 *via* 5. Compound 7 is generated from 1 by the addition of HF, which is released when 2, 4 and 6 are produced respectively.

The stability of the aminimines may be a result of the electron-withdrawing effect of the perfluoroalkyl groups and the delocalization of lone paired electrons of the anionic nitrogen coupled by the presence of α,β-unsaturated linkage. Thus, the substitution by 1,1-dimethylhydrazine, followed by the elimination of HF and the cyclization gave the novel compounds, pyrazolium cyclic aminimines, containing perfluoroalkyl groups as the ring substituents.

References and Notes

1. a) N. Ishikawa and A. Nagashima, Bull. Chem. Soc. Japan, 49, 502 (1976).
   b) S. Yanagida, Y. Noji, and M. Okahara, Tetrahedron Lett., 1977, 2337.
   c) N. Ishikawa, A. Nagashima, and A. Sekiya, Chem. Lett., 1974, 1225.
   d) N. Ishikawa and A. Nagashima, Bull. Chem. Soc. Japan, 49, 1085 (1976).
   e) M. Maruta T. Kitazume, S. Kubota, N. Yoshimura, and N. Ishikawa, Chem. Lett., 1979, 291.
2. I. Ikeda, T. Katsura, and M. Okahara, J. Am. Oil Chemists' Soc., 53, 537 (1976).
3. a) I. Ikeda, T. Katsura, and M. Okahara, J. Am. Oil Chemists' Soc., 55, 293 (1978).
   b) I. Ikeda, Y. Machii, and M. Okahara, Synthesis, 1978, 301.
4. a) W.J.S. Lockley and W. Lwowski, Tetrahedron Lett., 1974, 4263.
   b) W. Sucrow and M. Slopianka, Chem. Ber., 111, 780 (1978).
5. Grohe, Klaus, Ger. Offen., 2741482.
6. Compound 7 was isolated as a solution in ether by distillation (33.5°C/760mmHg) of the reaction mixture of a different run for the convenience. reaction conditions; 1 (1.5g, 5mmol), 1,1-dimethylhydrazine (0.3g, 5mmol), ether (10ml)
7. N. Ishikawa and A. Sekiya, Nippon Kagaku Kaishi, 1972, 2214.
8. The yields were calculated from the integral curves of 4 and 6 in the ^{19}F nmr of the reaction mixture in which an equal molar amount of benzotrifuloride to that of 1 used was added as the internal standard.

(Received February 25, 1980)