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An Alternative New Route to Perfluorovinylamines. Pyrolysis of an Alkali Metal Salt of Perfluoro(3-dialkylamino-propionic acids)

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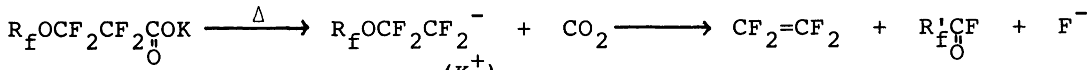
An alternative new route to give various kinds of perfluorovinylamines is described, which involves a pyrolysis of an alkali metal salt of perfluoro(3-dialkylamino-propionic acids) instead of using that of perfluoro(2-dialkylamino-propionic acids).

The thermal decomposition of alkali metal salts both of perfluorocarboxylic acids(1) and perfluorosulfinic acids(2) has been known to produce high yields of perfluoroolefins by the extrusion either of carbon dioxide or sulfur dioxide, respectively. An important application of this method is exemplified by an industrial preparation of perfluorovinylethers from an alkali metal salt of perfluoro(2-alkoxy-propionic acids)(1).(3) In contrast, that of perfluoro(3-alkoxy-propionic acids)(2), which is an isomer of 1, has rarely been used as their precursors, because it undergoes destructive fragmentation on pyrolysis yielding tetrafluoroethylene and a lower homologues of perfluoroacid fluorides as the principal products.



$$R_fOCF_2CF_2\underset{\overset{\|}{O}}{C}OK \xrightarrow{\Delta} R_fOCF_2CF_2^- + CO_2 \longrightarrow CF_2{=}CF_2 + R_f'\underset{\overset{\|}{O}}{C}F + F^-$$

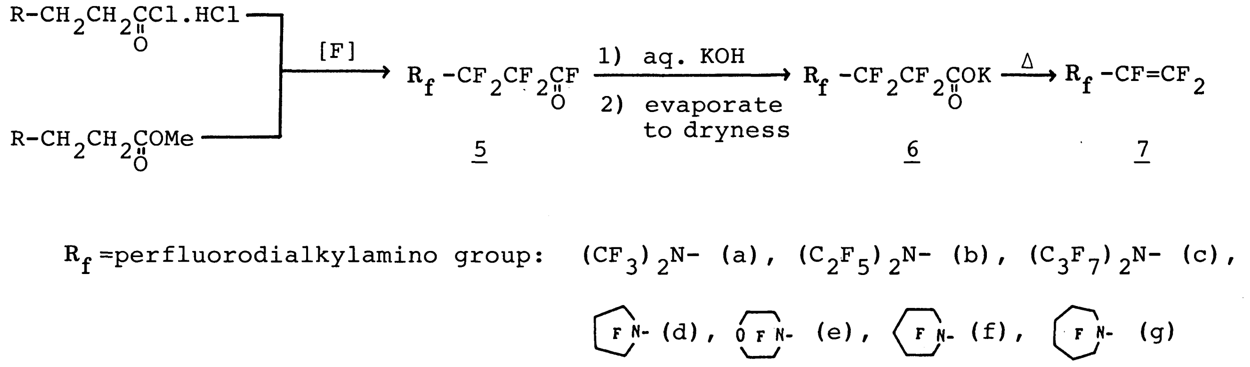
(2) (3) (K^+)

R_f, R_f'=perfluoroalkyl group

Scheme 1.

Recent examination(4) on the pyrolysis of Na salt of 3-oxa-11-chloro-eicosafluoroundecane sulfinate substantiated the results obtained from 2 that the perfluorocarbanion (equivalent to 3 in Scheme 1) involving an oxygen atom at the 3-position was very apt to docompose into degradation products.

In the preceding paper,(5) it was shown that various kinds of perfluorovinylamines could be obtained with only one-step by the pyrolytic reaction of an alkali metal salt of perfluoro(2-dialkylamino-propionic acids)(4)(Previous Route). However, it has a limitation to the kind of perfluorovinylamines due to the availability of the precursor. Perfluorovinylamines having higher homologues of aliphatic perfluorodialkylamino group remained unsurveyed yet due to the difficult synthesis of the starting perfluoro(2-dialkylamino-propionyl fluorides) by the electrochemical fluorination.(6)



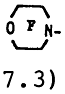
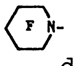
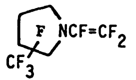
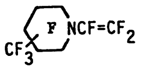
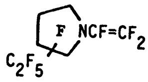
Scheme 2.

We present here an alternative new route for the preparation of perfluorovinylamines (7) using an alkali metal salt of perfluoro(3-dialkylamino-propionic acids)(6) instead of 4, which circumvents the limitation from the previous route, and also has the advantage of brevity, ready availability of starting materials, and high yield. The requisite starting materials can be easily prepared by the electrochemical fluorination of 3-dialkylamino-propionylchloride.HCl. salt$^{7)}$ and/or methyl 3-dialkylamino-propionates.$^{6)}$

A general procedure of the reaction is as follows: dry potassium salt (12.8 g) of perfluoro(3-dimethylamino-propionic acid)(6a) was pyrolyzed in a 200 ml flask, while helium (50 ml/min) was being introduced into it, from 156 °C to 250 °C during 100 min. Reaction took placed apparently at ca. 250 °C as evidensed by the evolution of gases. In a cold trap kept at -78 °C, 6.5 g of fluorocarbon was collected, which was found to be almost pure perfluoro(N,N-dimethyl trifluorovinylamine)(7a). The yield of 7a was 91% based on 5a fed [Run 1 in Table 1]. This product yield was almost comparable to that obtained from the K salt of perfluoro-(2-dimethylamino-propionic acid)(4a). Fig. 1 shows TG curves of 4a and 6a, which reveal that the decomposition temperature (224 °C) of the latter is considerably higher than that (143 °C) of the former. Table 1 shows the results obtained from 6 including those having a perfluoro-dialkylamino group like $(C_2F_5)_2N$- and $(C_3F_7)_2N$-. As shown in Table 1, the yield of 7 depended on the kind of 6 used and perfluoroimines (8) were also formed in many cases as the by-product.

It is considered that perfluoroolefins are formed by the pyrolytic reaction of alkali metal salts both of perfluorocarboxylic acids and perfluorosulfinic acids via perfluorocarbanion intermediate formed by a loss of CO_2, followed by a release of F^- from β-carbon according to ElcB type mechanism. However, when the intermediate perfluorocarbanion contains a heteroatom (O or N) which combines with the β-carbon, the reaction becomes complex, because the anion of the heteroatom bearing a perfluoroalkyl group eliminates competitively with F^- at the β-position as the leaving group. So, considering the similarlity of the molecular structure between 2 and 6, both containing a heteroatom at the same position, it was expected that the pyrolysis of 6 would proceed in a way similar to that occurring with 2 yielding only cleaved products such as tetrafluoroethylene and the compound derived from a perfluoronitranion leaving group (9).

Table 1. Pyrolysis of K salt of perfluoro(3-dialkylamino-propionic acids)(6)

Run	Sample 5 (mmol)	6 (g) a)	Fluorocarbon obtained (g)	Yield/% of 7 b)	Others
1	$R_f = (CF_3)_2N-$ (30.5)	12.8	6.5	91 c)	$CF_3N=CF_2$ (trace), $(CF_3)_2NCF_2CF_2H$ (trace)
2	$R_f = (C_2F_5)_2N-$ (68.2)	32.0	17.5	69	$C_2F_5N=CF(CF_3)$ (3), $(C_2F_5)_2NCF_2CF_2H$ (2)
3	$R_f = (C_3F_7)_2N-$ (39.4)	29.5	17.1	87	$C_3F_7N=CF(C_2F_5)$ (9)
4	R_f =  (36.8)	18.9	8.4	77	
5	R_f =  (37.3)	20.9	10.8	84	 (13)
6	R_f =  (54.0) d)	40.1	16.9	70	 (6),  (21)
7	R_f =  (22.6) d)	10.1	5.7	19	 (32),  (trace)

a) An equal amounts of KF was mixed. b) All products showed spectral data (^{19}F- and ^{1}H-NMR, IR and Mass) in accord with the assigned structures or with the literature values. c) Yields were determined by GLC. d) Starting materials were a mixture of isomers due to the ring isomerization during electrochemical fluorination.

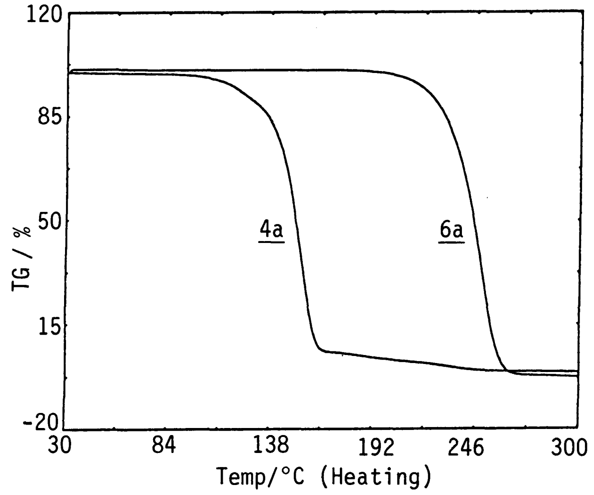
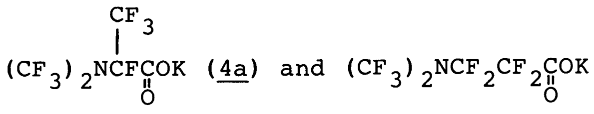
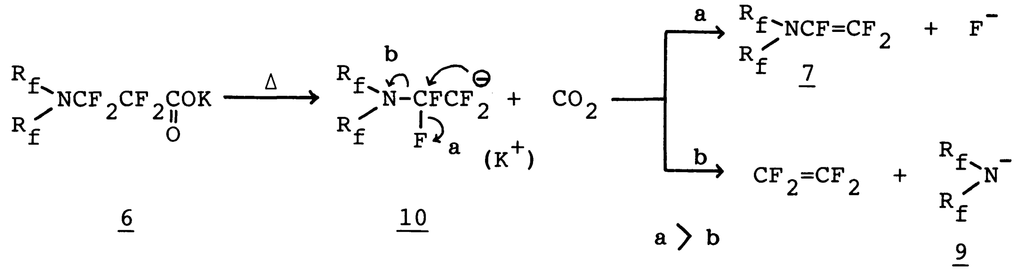


Fig. 1.

Thermogravimetric analysis of 
$(CF_3)_2NCF(CF_3)C(=O)OK$ (4a) and $(CF_3)_2NCF_2CF_2C(=O)OK$ (6a) in N_2, heating rate 20 °C/min.



Scheme 3.

However, contrary to our expectation, 6 afforded 7 as the main product together with small quantities of perfluoroimines (8). The imine (8) is considered to be formed from 9 by a successive elimination of F^-. This result demonstrated clearly the differnece in the mode of pyrolytic reaction between 2 and 6, which depends on the strength of the leaving group (R_fO^- from 3 and $(R_f)_2N^-$ from 10, respectively) compared with that of F^- from the intermediate perfluorocarbanion (3 from 2 and 10 from 6, respectively). In the case of 10, the reaction pathway prefers a to b because the F^- is more facile to release than $(R_f)_2N^-$ in terms of the easiness as the leaving group [Scheme 3]. This point is considered to be the key which makes this reaction an alternative valuable one for the preparation of 7.

Thus, the drawback of the previous method is now supplemented by using an alkali metal salt of perfluoro(3-dialkylamino-propionic acids), which has made it possible to synthesize a whole series of 7 having various kinds of perfluorodialkylamino group. We believe that the simplicity of the reaction and the method for the preparation of perfluorovinylamines (7) based on the pyrolysis of an alkali metal salt of either 2- or 3-(perfluorodialkylamino)-substituted perfluoropropionic acids make this approach industrially attractive.

Further studies on the preparation of other series of N-containing perfluoroolefins are now in progress.

References

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