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A New Route to Perfluorovinylamines by the Pyrolytic Reaction of an Alkali Metal Salt of Perfluoro(2-dialkylamino-propionic acids)

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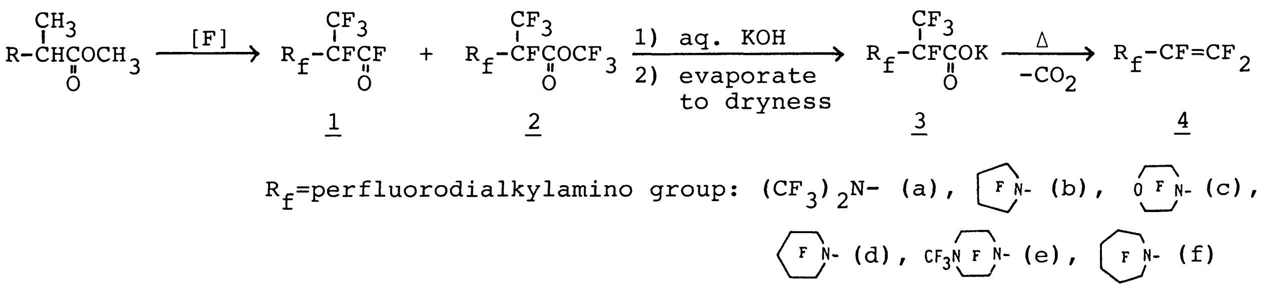
A potentially general route to various kinds of perfluorovinylamines is described involving a pyrolysis of an alkali metal salt of perfluoro(2-dialkylamino-propionic acids)

Much attention has been focused on the preparation of fluoroolefins, because they are one of the most fundamental and important starting materials for organofluorine chemistry as well as fluoropolymers.$^{1)}$ However, as perfluorovinylamines, to our knowledge, only three olefins like perfluoro(N,N-dimethylvinylamine),$^{2)}$ perfluoro(N-vinylpiperidine)$^{3)}$ and perfluoro(N-vinylmorpholine)$^{4)}$ have appeared in the literature, which have been prepared in a long synthetic pathway involving two key reactions methodologically: (1) an addition of perfluorodialkylamino radical to appropriate olefins to form intermediate 1:1 adducts (2) subsequent double bond formation of the intermediate adduct either by a removal of hydrogen halides$^{2)}$ or by a pyrolysis$^{3,4)}$ of it.

On the other hand, it is known that the pyrolysis of an alkali metal salt of perfluorocarboxylic acids is a valuable synthetic method for perfluoroolefins.$^{5)}$ An industrial application of this reaction is a preparation of perfluoro(alkylvinylethers) from an alkali metal salt of perfluoro(2-alkoxy-propionic acids), which are important monomers for perfluoro(alkylvinylether)/tetrafluoroethylene copolymer.$^{1)}$ Our idea was to apply this method to the synthesis of perfluorovinylamines.

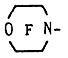
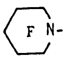
Recently we have shown that various perfluoro(2-dialkylamino-propionyl fluorides)(1) and perfluoro(methyl 2-dialkylamino-propionates)(2), the latter of which being formed in small quantities, if any, could be obtained in moderate yields by the electrochemical fluorination of corresponding methyl 2-dialkylamino-propionates.$^{6)}$



$$\text{R-CH(CH}_3\text{)COCH}_3 \xrightarrow{[F]} \text{R}_f\text{-CF(CF}_3\text{)COF} + \text{R}_f\text{-CF(CF}_3\text{)COCF}_3 \xrightarrow[\text{2) evaporate to dryness}]{\text{1) aq. KOH}} \text{R}_f\text{-CF(CF}_3\text{)COK} \xrightarrow[-\text{CO}_2]{\Delta} \text{R}_f\text{-CF=CF}_2$$

Scheme 1.

Table 1. Pyrolysis of K salt of perfluoro(2-dialkylamino-propionic acids)(3)

Run	Sample (1 and 2) (mmol)	3[a)] (g)	Fluorocarbon obtained (g)	Yield/% of 4[b)]	Others
1	$R_f=(CF_3)_2N-$ 1a (48.3)		9.5	75[c)]	$(CF_3)_2NCHFCF_3$ (5.2)
2	$R_f=$  1b (31.2) 2b (1.8)	14.0	9.4	74	 (2.0)
3	$R_f=$  1c (37.5) 2c (2.2)	18.4	10.8	88	
4	$R_f=$  1d (28.3)	11.1	6.6	68	 (trace)

a) An equal molar amount of KF was mixed. b) All products showed spectral data (^{19}F- and ^1H-NMR, IR, and Mass) in accord with the assigned structures or with the literature value. c) Yields were determined by GLC.

In this communication is disclosed a new efficient method for the synthesis of several kinds of perfluorovinylamines (4) which is based on the pyrolysis of an alkali metal salt of these perfluoro(2-dialkylamino-propionic acids).

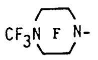
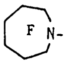
A general procedure of the reaction is as follows: dry potassium salt (14.0 g) of perfluoro(2-pyrrolidino-propionic acid)(3b) was pyrolyzed in a 200 ml flask under reduced pressure (40 mmHg) from 100 °C to 200 °C during 45 min. In a cold trap kept at -78 °C, 9.4 g of fluorocarbons was collected, which consisted mostly of perfluoro(N-vinylpyrrolidine)(4b) and small quantity of N-(1H-tetrafluoroethyl)octafluoropyrrolidine. The yields of 4b was 74% based on 1b and 2b fed [Run 2 in Table 1].

In order to make this method more simple by avoiding the working-up of 3, direct and continuous pyrolysis of 1 and 2 in a reactor contained a fluidized bed of Na_2CO_3 or K_2CO_3 was successfully conducted and the results are summarized in Table 2.

Figure 1 shows TG curves of K salts of perfluoro[2-(N,N-dimethylamino)propionic acids](3a) and perfluoro(2-propoxy-propionic acid)(5) comparatively. It was found that the decomposition temperature of the former (143 °C) was considerably lower than that (217 °C) of the latter.

As in the case of 5 and alkali metal salts of other perfluorocarboxylic acids pyrolytic decomposition of 3 which leads to the formation of 4 is considered to proceed via perfluorocarbanion intermediate formed by a loss of CO_2 as the first step, followed by a release of F^- from β-carbon according to E1cB type mechanism (Route A in Scheme 2). Although other Routes(B,C, and D), which involves an elimination of such anions as CF_3^-, $(R_f')_2N^-$, and F^- from α-carbon respectively, are also possible, these routes will be excluded because the expected compounds such as dimerized compounds arising from carbens were not found in the product.

Table 2. Pyrolysis of 1 and 2 by a continuous-flow method[a)]

Run	Sample (1 and 2) (mmol)	S.V. min^{-1}	Fillers	Temp °C	Conv %	Yield/% of 4[b)]	Bp/°C of 4
1	1a (6.8)	0.02	Na_2CO_3	220	100	95[c)]	13.0[d)]
2	1a (18.0)	0.11	Na_2CO_3	220	97	98	
3	1a (20.8)	0.07	K_2CO_3	200	100	83	
4	1a (14.5)	0.11	K_2CO_3	200	100	84	
5	1b (10.1) 2b (0.9)	0.03	K_2CO_3	200	100	84	56.5-57.5
6	1c (4.2) 2c (0.5)	0.03	K_2CO_3	200	100	94	64.5-65.5[e)]
7	1d (8.4)	0.03	K_2CO_3	200	100	97	78.0-78.5[f)]
8	R_f=  1e (7.3) 2e (0.4)	0.02	K_2CO_3	200	100	86	95.0-95.5
9	R_f=  1f (4.5)	0.01	K_2CO_3	200	100	88	102.0-103.0

a) Pyrolysis was conducted by introducing a calculated amount of 1 and 2 by use of a micro-pump [Shimadzu SPC-100] into a stainless reactor [2.5(id) X 48 cm (long)] contained a fluidized bed of Na_2CO_3 or K_2CO_3 together with a diluent gas (He; ≈100 ml/min). b) All products showed spectral data (^{19}F-NMR, IR, and Mass) in accord with the assigned structures or with the literature values. c) yields were determined by GLC. d) Extraporated from the equation $\log P_{torr}=7.88-1423/T$ (ΔHv= 6.56 kcal/mol. ΔSv=22.9 cal/deg.mol); Lit., bp 17-26 °C (Ref. 2a), bp 11.1 °C (Ref. 2b). e) Lit., bp 63.5 °C (Ref. 4). f) Lit., bp 77.4 °C (Ref. 3).

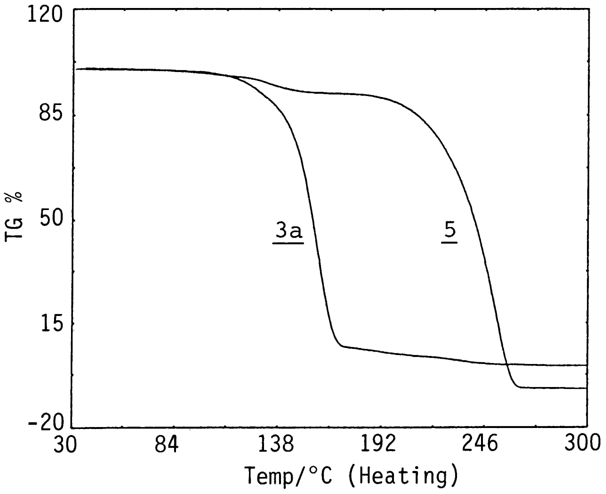
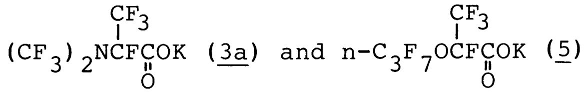
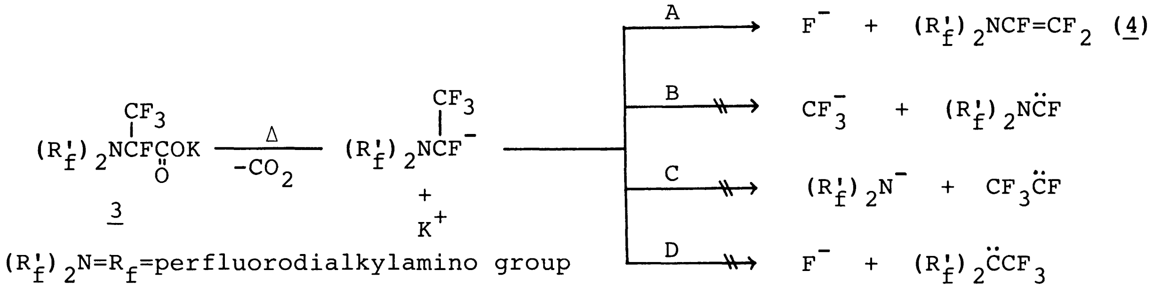


Fig. 1.
Thermogravimetric analysis of



$(CF_3)_2N\overset{CF_3}{\overset{|}{C}}F\underset{\overset{\|}{O}}{C}OK$ (3a) and $n\text{-}C_3F_7O\overset{CF_3}{\overset{|}{C}}F\underset{\overset{\|}{O}}{C}OK$ (5)

in N_2, heating rate: 20 °C/min.



Scheme 2.

Thus, the major advantage of this method is the simplicity of the synthesis and the ease of scaling-up even to an industrial scale. Since, a variety of perfluorovinylamines(4) can be easily prepared by this method, it is expected that the versatility of 4 will be expand in organofluorine chemistry. Unfortunately, the present method can not be applied for the preparation of 4 containing higher homologues of aliphatic perfluorodialkylamino group, because the starting 1 [$(C_nF_{2n+1})_2NCF(CF_3)C(O)F$; $n>1$] could be obtained only in small yields due to the side reaction (cyclization) during the fluorination of corresponding methyl 2-dialkylamino-propionates.$^{6)}$

Further investigation of the preparation of N-containing perfluoroolefins based on the pyrolysis of perfluorocarboxylic acids is being carried out

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