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# A NEW METHOD FOR THE PREPARATION OF PERFLUOROCARBOXYLIC ACIDS

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## SUMMARY

The reaction of both primary perfluoroalkyl iodides and bromides containing 3 ~ 12 carbon atoms $[CF_3(CF_2)_nX$, n = 2 ~ 11, X = Br, I$]$ with a Rongalite-$NaHCO_3$ reagent in aqueous dipolar aprotic solvents, such as DMF or DMSO, has been investigated. The reaction gave sodium perfluorocarboxylates $[CF_3(CF_2)_{n-1}CO_2Na$, n = 2 ~ 11$]$ in 51 - 86 % yields, and these were transformed to the respective perfluorocarboxylic acids $[CF_3(CF_2)_{n-1}CO_2H$, n = 2 ~ 11$]$ by treatment with sulfuric acid. This provides a new method for the synthesis of perfluorocarboxylic acids.

## INTRODUCTION

Although the preparation of perfluorocarboxylic acids from perfluoroalkyl iodides has already been reported, all the reactions

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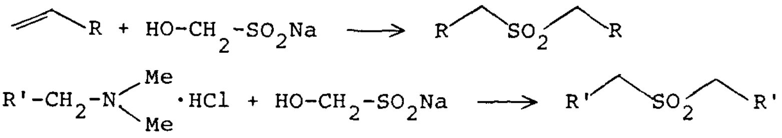
need a strong oxidizing agent such as fuming sulfuric acid [1], chlorosulfonic acid [2], fluorosulfonic acid [3] or a halogen fluorosulfate [4]. It was found that the same conversion can be achieved by stirring perfluoroalkyl iodides with Rongalite, a reducing agent, in the presence of sodium bicarbonate in a polar aprotic solvent-water solution under rather mild conditions. The yields were satisfactory.

Additionally, the reaction has been extended to perfluoroalkyl bromides. Perfluoroalkyl bromides containing 4 ~ 8 carbon atoms were successfully converted to the corresponding sodium perfluorocarboxylates under similar conditions in good yields.

Rongalite, sodium formaldehyde sulfoxylate, is a useful reducing agent in many redox catalyst systems for polymerization [5] and textile dyeing [6], but its application in organic synthesis has hardly been reported. Rongalite reacts for example with olefins [7] or Mannich bases [8] to form symmetrical sulfones (Scheme 1).



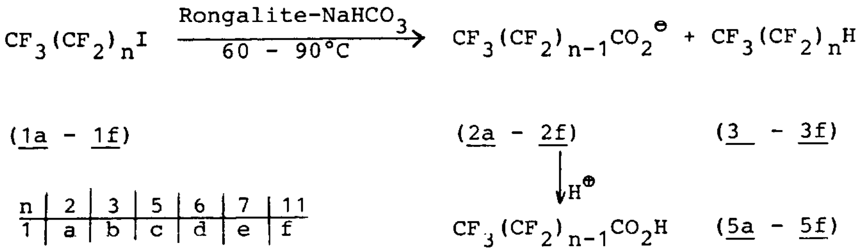
Scheme 1. Some reactions of Rongalite.

The present reactions have not been observed before. It is a new application of Rongalite and is the first example of the 'hydrolysis' of perfluoroalkyl halides under 'reducing' conditions.

## RESULTS AND DISCUSSION

### The reaction of perfluoroalkyl iodides

When perfluoropropyl iodide (1a), perfluorobutyl iodide (1b), perfluorohexyl iodide (1c), perfluoroheptyl iodide (1d), perfluorooctyl iodide (1e) and perfluorododecyl iodide (1f) reacted with Rongalite-$NaHCO_3$ in aqueous DMF or DMSO solution, sodium pentafluoropropanoate (2a), sodium heptafluorobutanoate (2b), sodium nonafluorohexanoate (2c), sodium perfluoroheptanoate (2d), sodium perfluorooctanoate (2e) and sodium perfluorododecanoate (2f) were produced respectively. In the case of 1c, 1d, 1e and 1f 1H-tridecafluorohexane (3c), 1H-pentadecafluoroheptane (3d), 1H-heptadecafluorooctane (3e) and 1H-pentacosafluorododecane (3f), respectively, were detected as the main by-products (see Scheme 2).



$$CF_3(CF_2)_nI \xrightarrow[60 - 90°C]{\text{Rongalite-NaHCO}_3} CF_3(CF_2)_{n-1}CO_2^{\ominus} + CF_3(CF_2)_nH$$

(1a - 1f) (2a - 2f) (3 - 3f)

$$\downarrow H^{\oplus}$$

$$CF_3(CF_2)_{n-1}CO_2H$$ (5a - 5f)

| n | 2 | 3 | 5 | 6 | 7 | 11 |
|---|---|---|---|---|---|---|
| 1 | a | b | c | d | e | f |

Scheme 2. The reaction of perfluoroalkyl iodides with Rongalite.

The reaction conditions and yields are shown in Table 1.

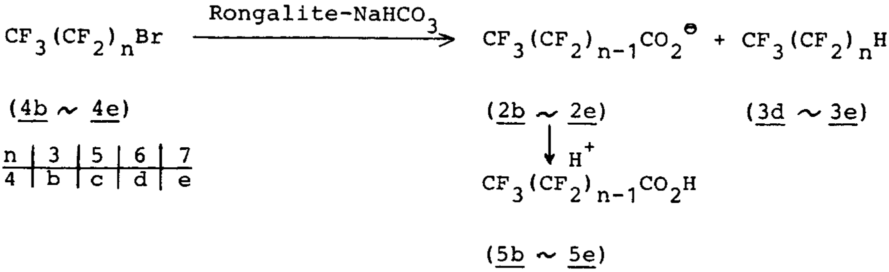
### The reaction of perfluoroalkyl bromides

Perfluoroalkyl bromides are regarded as rather inert species, and as such have found many uses in medicine[9]. Surprisingly, nonafluorobutyl bromide (4b), perfluorohexyl bromide (4c), perfluoro-

Table 1. The reaction of $CF_3(CF_2)_nX$ with Rongalite

| Starting Material | g (mol) | Rongalite g (mol) | $NaHCO_3$ g (mol) | $H_2O$ (ml) | Solvents (ml) | Temp. (°C) | Time (hrs) | Yields (%) |
|---|---|---|---|---|---|---|---|---|
| 1a | 4.5 (0.015) | 4.6 (0.030) | 1.25 ($Na_2CO_3$) (0.0075) | 4 | DMF (20) | reflux | 22 | 74 |
| 1b | 7.0 (0.020) | 7.6 (0.049) | 2.5 (0.030) | 2 | DMF (15) | 80-85 | 15 | 82 |
| | 7.0 (0.020) | 7.6 (0.049) | - | 2 | DMSO (15) | 80-85 | 40 | 58 |
| 1c | 10.0 (0.022) | 6.9 (0.044) | 2.5 (0.030) | 2 | DMF (20) | 80-85 | 17 | 79 |
| | 5.0 (0.011) | 4.0 (0.026) | - | 2 | HOAc (15) | 85-87 | 25 | 32 |
| 1d | 10.0 (0.020) | 7.6 (0.049) | 2.5 (0.030) | 2 | DMF (25) | 90 | 18 | 82 |
| 1e | 12.0 (0.022) | 7.8 (0.051) | 2.8 (0.033) | 3 | DMF (25) | 85 | 31 | 70 |
| 1f | 9.0 (0.012) | 3.7 (0.024) | 1.7 (0.020) | 3 | DMF (20) | 85 | 20 | 51 |
| 4b | 1.5 (0.0050) | 1.4 (0.0091) | 0.4 (0.0048) | 1 | DMF (8) | reflux | 15 | 80 |
| 4c | 2.0 (0.0050) | 1.8 (0.012) | 0.6 (0.0071) | 1 | DMF (10) | 80-85 | 20 | 84 |
| | 2.0 (0.0050) | 1.9 (0.012) | - | 2 | DMSO (10) | 80-85 | 18 | 82 |
| 4d | 2.0 (0.0045) | 1.7 (0.011) | 0.5 (0.0060) | 1 | DMF (10) | 80-85 | 18 | 70 |
| | 10.0 (0.022) | 6.8 (0.044) | - | 3 | DMSO (25) | 80-85 | 25 | 78 |
| 4e | 4.0 (0.0080) | 2.5 (0.016) | 1.0 (0.012) | 2 | DMF (12) | 85 | 20 | 86 |

heptyl bromide (4d) and perfluorooctyl bromide (4e) do react with Rongalite under mild conditions to give sodium perfluorocarboxylates 2b, 2c, 2d and 2e. The results are shown in Scheme 3 and the yields are listed in Table 1.



$$CF_3(CF_2)_nBr \xrightarrow{\text{Rongalite-NaHCO}_3} CF_3(CF_2)_{n-1}CO_2^{\ominus} + CF_3(CF_2)_nH$$

(4b ~ 4e) (2b ~ 2e) (3d ~ 3e)

$$\downarrow H^+$$

$$CF_3(CF_2)_{n-1}CO_2H$$

(5b ~ 5e)

| n | 3 | 5 | 6 | 7 |
|---|---|---|---|---|
| 4 | b | c | d | e |

Scheme 3. The reaction of perfluoroalkyl bromides with Rongalite.

It was observed that fewer by-products, 3d ~ 3e, were isolated, probably because the C-Br bond is much stronger than the C-I bond.

The reaction between perfluoroalkyl halides and Rongalite is exothermic, so at the beginning heating must be carefully controlled, in order to avoid overheating. The optimal reaction temperature range is 60 - 90°C in DMF or DMSO-$H_2O$ solution.

At a temperature below 50°C the reaction rate was very slow, while the amount of side-products, for example $R_fCF_2H$, increased significantly at a too high reaction temperature, say, above 100°C.

No reaction took place when the reaction was carried out in water, in which perfluoroalkyl halides have only very poor solubility. Many polar organic solvents, such as DMF, DMSO, acetic acid, acetonitrile, formaldehyde, and morpholine, were tested. It was found whatever the solvent, that when DMF or DMSO was added, a reaction occurred immediately and gave the best results. The same products were formed in aqueous acetic acid solution but in low yield and no reaction was detected in aqueous acetonitrile or formaldehyde solution. $\omega\underline{H}$-perfluoroalkanes were formed as the main products in morpholine-$H_2O$ systems.

Without sodium bicarbonate the pH of the reaction mixture increased considerably and the Rongalite decomposed rapidly. The yield can be improved either by adding Rongalite in two or more doses or by using $NaHCO_3$ or $Na_2CO_3$ to keep the reaction system basic. $NaHCO_3$ is better owing to its mild basicity.
The reaction mechanism is under investigation.

## SPECTROSCOPIC DATA

The structural determinations of the products were achieved by $^1H$-, $^{19}F$-NMR and IR. All the infrared spectra of perfluorocarboxylates 2a ~ 2f showed a typical strong peak at 1670 - 1700 $cm^{-1}$, demonstrating the presence of carboxylate groups. $^{19}F$-NMR spectra indicated that during the reaction the perfluoroalkyl iodides or bromides, 1a ~ 1f and 4b ~ 4e lost two fluorine atoms and the peaks of the $CF_2CO_2Na$ groups in the products appeared at -111.2 (2f) ~ -120.4 (2a) ppm. To check our structural designation for 2a - 2f, they were transformed into their free acids 5a ~ 5f, showing in their IR spectra a moderate to strong peak at 1715 ~ 1805 cm$^{-1}$ and having the literature boiling points or/and melting points. $^{19}$F-NMR and IR data are listed in Tables 2 and 3.

Table 2. $^{19}$F-NMR spectral data of products

| Products | Solvent | Chemical Shifts (ppm) |
|---|---|---|
| $C_2F_5CO_2Na$ (2a) | Acetone | -120.4 (m, 2F), -83.1 (m, 3F) |
| $C_3F_7CO_2Na$ (2b) | EtOAc | -118.9 (m, 2F), -84.2 (m, 3F), -126.4 (m, 2F) |
| $C_5F_{11}CO_2Na$ (2c) | EtOAc | -118.0 (m, 2F), -82.2 (m, 3F), -127.4 (m, 2F), -123.6 (m, 4F) |
| $C_6F_{13}CO_2Na$ (2d) | EtOAc | -117.6 (m, 2F), -82.3 (m, 3F), -127.1 (m, 2F), -123.4 (m, 6F) |
| $C_7F_{15}CO_2Na$ (2e) | EtOAc | -117.5 (m, 2F), -82.1 (m, 3F), -127.1 (m, 2F), -123.2 (m, 8F) |
| $C_{11}F_{23}CO_2Na$ (2f) | Acetone | -111.8 (m, 2F), -76.5 (m, 3F), -121.6 (m, 2F), -117.1 (m, 16F) |
| $C_2F_5CO_2H$ (5a) | Ether | -125.0 (m, 2F), -85.6 (m, 3F) |
| $C_3F_7CO_2H$ (5b) | Ether | -122.0 (m, 2F), -83.6 (m, 3F), -127.5 (m, 2F) |
| $C_5F_{11}CO_2H$ (5c) | Ether | -120.0 (m, 2F), -82.2 (m, 3F), -127.4 (m, 2F), 123.7 (m, 4F) |
| $C_6F_{13}CO_2H$ (5d) | Ether | -120.3 (m, 2F), -82.6 (m, 3F), -127.4 (m, 2F), -123.7 (m, 6F) |
| $C_7F_{15}CO_2H$ (5e) | Ether | -118.2 (m, 2F), -82.8 (m, 3F), -127.7 (m, 2F), -123.5 (m, 8F) |
| $C_{11}F_{23}CO_2H$ (5f) | Ether | -114.0 (m, 2F), -76.3 (m, 3F), -121.5 (m, 2F), -117.5 (m, 16F) |
| $C_6F_{13}H$ (3c) | Ether | -139.5 (d, 2F) $^1J_{HF}$ = 55 Hz, -82.4 (m, 3F), -130.5 (m, 2F), -127.3 (m, 2F), -124.0 (m, 4F) |

(Continued)

Table 2 (<u>cont</u>.)

| Products | Solvent | Chemical Shifts (ppm) |
|---|---|---|
| $C_7F_{15}H$ (<u>3d</u>) | Ether | -140.6 (d, 2F) $^1J_{HF}$ = 52 Hz, -83.2 (m, 3F), -131.4 (m, 2F), -126.4 (m, 2F), -124.7 (m, 6F) |
| $C_8F_{17}H$ (<u>3e</u>) | Ether | -139.9 (d, 2F) $^1J_{HF}$ = 52 Hz, -83.3 (m, 3F), -130.7 (m, 2F), -127.5 (m, 2F), -123.5 (m, 8F) |
| $C_{12}F_{25}H$ (<u>3f</u>) | Acetone | -133.9 (d, 2F), $^1J_{HF}$ = 49 Hz, -76.4 (m, 3F), -124.7 (m, 2F), -121.5 (m, 2F), -118.6 (m, 2F), -118.0 (m, 2F), -117.0 (m, 12F) |
| $C_4F_9Br$ (<u>4b</u>) | - | -65.4 (m, 2F), -83.5 (m, 3F), -127.1 (m, 2F), -119.8 (m, 2F) |
| $C_6F_{13}Br$ (<u>4c</u>) | - | -66.1 (m, 2F), -82.8 (m, 3F), -127.5 (m, 2F), -123.9 (m, 2F), -122.3 (m, 2F), -118.6 (m, 2F) |
| $C_7F_{15}Br$ (<u>4d</u>) | - | -64.6 (m, 2F), -82.6 (m, 3F), -127.1 (m, 2F), -122.1 (m, 6F), -118.1 (m, 2F) |

Table 3. IR spectra of products

| Compounds | Sample form | Bands ($cm^{-1}$) |
|---|---|---|
| <u>2a</u> | Pellet | 3400 (br), 1670 (vs), 1405 (m), 1325 (m), 1250 ~ 1100 (vs), 1025 (s), 815 (m), 730 (m) |
| <u>2b</u> | Pellet | 3340 (br), 1675 (vs), 1400 (m), 1335 (m), 1250 ~ 1050 (vs), 960 (s), 932 (s), 810 (s), 720 (m), 640 (m), 585 (m) |
| <u>2c</u> | Pellet | 3415 (br), 1688 (vs), 1400 (m), 1350 (m), 1265 ~ 1000 (vs), 950 (m), 864 (m), 810 (m), 745 (m), 730 (m), 712 (m), 654 (m) |

Table 3. (cont.)

| Compounds | Sample form | Band ($cm^{-1}$) |
|---|---|---|
| 2d | Pellet | 3450 (br), 1695 (vs), 1424 (m), 1360 (m), 1235 ~ 1100 (vs), 830 (m), 743 (m), 727 (m), 660 (m), 545 (m), 525 (m) |
| 2e | Pellet | 3420 (br), 1685 (vs), 1398 (m), 1360 (m), 1260 ~ 1100 (vs), 1013 (m), 808 (m), 745 (m), 735 (m), 721 (m), 660 (m), 555 (m), 528 (m) |
| 2f | Pellet | 3520 (br), 1700 (vs), 1428 (m), 1320 ~ 1150 (vs), 845 (m), 685 (m), 604 (m), 574 (m) |
| 5a | Film | 3500 (br), 1770 (s), 1300 ~ 1200 (vs), 1032 (s), 790 (m), 715 (m) |
| 5b | Film | 3200 (br), 1790 (s), 1450 (m), 1370 (m), 1270 1100 (vs), 990 (s), 950 (s), 725 (m) |
| 5c | Pellet | 3450 (br), 1770 (s), 1638 (m), 1405 (m), 1260 ~ 1100 (vs), 869 (m), 820 (m), 750 (m), 730 (m), 655 (m) |
| 5d | Pellet | 3450 (br), 1715 (s), 1380 (m), 1290 ~ 1050 (vs), 820 (s), 754 (m), 675 (m), 580 (m), 550 (m) |
| 5e | Pellet | 3420 (br), 1710 (s), 1465 (m), 1346 (m), 1260 ~ 1100 (vs), 1020 (m), 796 (m), 731 (m), 666 (m), 642 (m), 560 (m), 530 (m) |
| 5f | Pellet | 3520 (br), 1805 (m), 1665 (m), 1300 ~ 1150 (vs), 685 (m), 600 (m), 570 (m) |

## EXPERIMENTAL

IR spectra were recorded on either a Perkin-Elmer 398 spectrophotometer or a Bruker IFS-85 FT-IR spectrometer. Liquids were measured as capillary films between KBr plates. Solid samples were prepared by grinding the sample with spectral quality KBr powder and preparing a pellet. Weak bands and shoulders are not reported.

$^1$H, $^{19}$F-spectra were obtained on either a Bruker WM 250 PFT-spectrometer or a Bruker HX 60-spectrometer with chemical shifts relative to TMS ($^1$H) or $CFCl_3$ ($^{19}$F).

Starting materials: Commercially available perfluoroalkyl iodides (1a ~ 1f) and bromide 4e were purified by washing with $NaHSO_3/H_2O$, dilute hydrochloric acid and water, respectively, drying with $MgSO_4$, all this followed by distillation before use.

Perfluoroalkyl bromides, 4b ~ 4d, were prepared via photobromination of the corresponding iodides [10] in over 95% yields.

Rongalite, sodium formaldehyde sulfoxylate (Fluka AG) was used directly without further purification.

## Reaction of perfluoroalkyl iodides or bromides with Rongalite-$NaHCO_3$ in aqueous DMF solution

In a typical reaction, a mixture of 10.0 g (0.020 mole) 1d, 7.6 g (0.049 mole) Rongalite, 2.5 g (0.030 mole) $NaHCO_3$, 25 ml DMF and 2 ml water was stirred vigorously in a three-neck flask equipped with a stirrer and a condenser at ca. 90°C for 18 hrs. The solvents were removed under reduced pressure using a vacuum line. The liquid collected in the receiver separated into two phases; the heavy layer was washed with water and distilled to give a colorless liquid (b.p. 95 - 96°C) [13], which was identified by $^1$H, $^{19}$F-NMR spectra to be 1H-pentadecafluoroheptane (3d) ($^1$H-NMR: $\delta = 6.04$, t-t, $^1J_{HF} = 52$ Hz, $^3J_{HF} = 5.3$ Hz).

The dry solid left in the flask was extracted by hot ethyl acetate (3 x 25 ml). The ester solution was evaporated to dryness and the solid left was washed with $CH_2Cl_2$ (3 x 2.5 ml) to give a solid product from which pure 2d, as colorless crystals, was obtained by recrystallization from water (6.45 g, 83 %). 2d was identified by $^{19}F$-NMR, IR spectra (Tables 2 and 3).

## Reaction of perfluoroalkyl iodides or bromides with Rongalite in aqueous DMSO solution

In a typical procedure, a mixture of 10.0 g (0.022 mole) 4d, 6.8 g (0.044 mole) Rongalite, 25 ml DMSO and 3 ml $H_2O$ was stirred at 80 - 85°C for 10 hrs, then 2.0 g (0.013 mole) more Rongalite were added into the reaction system. After another 15 hrs stirring, $NaHCO_3$ solution was added until no more bubbles formed. Working up as above gave 6.7 g 2d (78 %).

Amounts of reactants, reaction conditions and yields are given in Table 1.

## The preparation of perfluorocarboxylic acids

In a typical process, a mixture of 6.45 g (0.017 mole) 2d, and 15 ml concentrated sulfuric acid was heated at 120°C under reduced pressure; 5.6 g of a viscous liquid 5d (b.p. 175 - 177°C) (94 %) developed, this solidified in the receiver and was recrystallized from $CCl_4$ to form shiny colorless crystals (m.p. 31 ~ 36°C). Its $^{19}F$-NMR and IR data are shown in Tables 2 and 3.

Amounts of reactants, yields and the physical properties of products are shown in Table 4.

Table 4. The preparation of perfluorocarboxylic acid

| Starting Material | g (mol) | $H_2SO_4$ (ml) | Products (g) | Yields (%) | Boiling Points |  | Melting Points |  |
|---|---|---|---|---|---|---|---|---|
|  |  |  |  |  | Found | Literature | Found | Literature |
| 2a | 2.1 (0.011) | 10 | 5a (1.8) | 97 | 94-96 | 95.5-95.7 [11] | - | - |
| 2b | 2.5 (0.012) | 6 | 5b (2.0) | 92 | 120-122 | 120/735 [12] | - | - |
| 2c | 4.0 (0.012) | 20 | 5c (3.5) | 94 | 155-157 | 157/742 [14] | 12-14 | 11.2-13.4 [12] |
| 2d | 6.45 (0.017) | 15 | 5d (5.6) | 92 | 175-177 | 175/742 [14] | 31-36 | - |
| 2e | 5.0 (0.011) | 10 | 5e (3.8) | 84 | 187-189 | 189/736 [14] | 53-54 | 54.9~55.6 [12] |
| 2f | 3.0 (0.0047) | 5 | 5f (2.5) | 86 | - | - | 112-114 | 112.6~114.7 [12] |

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## REFERENCES

1 H. C. Fielding, in R.E. Banks (ed.), Organofluorine Chemicals and Their Industrial Applications, Ellis Horwood, London, 1979, p. 220.

2 M. Hauptschein, M. Braid, J. Am. Chem. Soc., 83 (1961) 2500.

3 M. Hauptschein, M. Braid, J. Am. Chem. Soc., 83 (1961) 2505.

4 C. J. Shack, K. O. Christe, J. Fluorine Chem., 16 (1980) 63.

5a) G. Dimov, V. Shopov, I. Markova, M. Dimitrova, D. Dobreva, G. Kostov, Khim. Ind. (Sofia) (1983) 104. Also see Chem. Abstr. 99/89506 j; b) T.G. Balyberdina, N. M. Mironova, see Chem. Abstr. 101/92872 r. Deposited Doc., 1982 SPSTL 1320 Khp-D82.

6a) B. M. Kuznetsov, A. Z. Chernomordik, Z. N. Panina, Tekst. Prom-st, (Moscow) (1982) 56. Also see Chem. Abstr. 96/124395 j; b) D. Goerrig, Fr. 1, 563, 437 (1967).

7a) R. Kerber, J. Starnick, Chem. Ber., 104 (1971) 2035;
b) R. Kerber, W. Gestrich, ibid., 106 (1973) 798;
c) B. Jollès-Bergeret, Eur. J. Biochem., 42 (1974) 349.

8 P. Messinger, H. Greve, Synthesis (1977) 259.

9 D. M. Long, C. B. Higgins, R. F. Mattrey, R. M. Mitten, F.K. Multer, C.M. Sharts, D.F. Shellhamer, in R.E. Banks (Editor), Preparations, Properties and Industrial Applications of Organo-fluorine Compounds, Ellis Horwood, Chichester, 1981, pp. 139-156.

10 B. N. Huang, W. Y. Huang, Acta Chimica Sinica 42 (1984) 1106.

11 R. N. Haszeldine, K. Leedham, J. Chem. Soc., (1953) 1548.

12 E. F. Hare, E. G. Shafrin, W. A. Zisman, J. Phys. Chem., 58 (1954) 236.

13 The boiling point of 3d found in literature is 96°C (see R. N. Haszeldine, J. Chem. Soc., (1953) 3761).

14 E. A. Kauck, A. R. Diesslin, Ind. Eng. Chem., 43 (1951) 2332.