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Journal of Fluorine Chemistry 69 (1994) 257–259

JOURNAL OF FLUORINE CHEMISTRY

A one-pot synthesis of (*S*, *S*)-dialkyl-*N*-(perfluoroalkylsulfonyl)carbodithioimidates

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Received 22 August 1993; accepted 8 December 1993

Abstract

An easy synthesis of the title compounds by the condensation of carbon disulfide and perfluoroalkylsulfonamides in the presence of potassium hydroxide with subsequent alkylation is described.

Keywords: Synthesis; Dialkyl *N*-(perfluoroalkylsulfonyl)carbodithioimidates; Condensation reaction; NMR spectroscopy; IR spectroscopy; Mass spectrometry

1. Introduction

Ketene dithioacetals are very versatile and useful intermediates in organic synthesis due to the special ability of sulfur atoms to stabilize both neighbouring positive and negative charges. Functionalized ketene dithioacetals are widely used in the synthesis of heterocyclic compounds [1–4].

The nitrogen-containing counterpart, (*S*,*S*)-dialkyl N-substituted carbodithioimidates, Y–N=C(SR)$_2$, are also important and resourceful sulfur-containing compounds as precursors of nitrogen-containing heterocyclic compounds [5,6].

To the best of our knowledge, there are no reports about the preparation of these compounds. The introduction of the perfluoroalkylanesulfonyl group should make the nitrogen–carbon double bond more active owing to the strong electron-withdrawing ability of the R_fSO_2 group [7]. We have successfully prepared the 1,1-bis(alkylmercapto)-2-perfluoroalkylsulfonyl ethylenes, $R_fSO_2CH{=}C(SR)_2$ [8], and in this paper we wish to report an easy one-pot synthesis of (*S*,*S*)-dialkyl *N*-(perfluoroalkylsulfonyl)carbodithioimidates.

2. Results and discussion

Although the preparation of various ketene dithioacetals has been extensively studied [1], there is only one general procedure for preparing *N*-sulfonylcarbondithioimidates [5]. When we followed this method in an attempt to prepare the fluorine-containing analogues $R_fSO_2N{=}C(SR)_2$ (**4**), however, the yields of **4** were very low and the major products were $R_fSO_2NR_2$ (**3**).

$$\underset{(\mathbf{1})}{R_fSO_2NH_2} \xrightarrow[\text{DMF}]{\text{KOH(aq.)/CS}_2} \xrightarrow{\text{RX}} \underset{(\mathbf{3})}{R_fSO_2NR_2} + \underset{(\mathbf{4})}{R_fSO_2N{=}C(SR)_2}$$

It is clear that in this reaction the perfluoroalkylsulfonyl amide R_fSO_2NHK formed is not sufficiently reactive, being mainly alkylated with RX forming **3** and only giving a small amount of **4**.

It was interesting to find that when solid potassium hydroxide was used instead of its aqueous solution, and the reaction was carried out in $(MeOCH_2)_2$ (MG), the expected compounds were obtained in moderate yield.

$$\mathbf{1} \xrightarrow[\text{MG}]{\text{KOH(s)/CS}_2} R_fSO_2N{=}C(SK)_2 \xrightarrow{\text{RX}} \underset{(\mathbf{4})}{R_fSO_2N{=}C(SR)_2}$$

R_f: CF_3 (**1a**); $Cl(CF_2)_2O(CF_2)_2$ (**1b**); $I(CF_2)_2O(CF_2)_2$ (**1c**); R: $(BrCH_2)_2$ (**2a**); CH_3I (**2b**); $C_6H_5CH_2Br$ (**2c**); $BrCH_2CH{=}CH_2$ (**2d**).

In this case, the nucleophilicity of R_fSO_2NHK was increased owing to the coordinating effect of MG on K^+, and then reacted with CS_2 forming the dianion which was then alkylated to give **4**.

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SSDI 0022-1139(94)03083-C

Compounds **4** are high boiling yellowish liquids. The structure of all these new compounds are fully supported by IR, ^1H and ^{19}F NMR spectroscopy, MS and elemental analysis. The chemistry of these compounds is presently under investigation.

All results obtained are summarized in Table 1.

3. Experimental details

^1H NMR and ^{19}F NMR spectra were recorded on a Varian 360L instrument using Me_4Si and CF_3COOH as internal and external standards, respectively [$\delta_{TFA} = \delta_{CFCl_3} + 76.8$ ppm (positive upfield)] IR spectra were obtained with an IR-440 Shimadzu spectrophotometer. Low-resolution MS spectra were obtained on a Finnigan GC-MS 4021 instrument. Elemental analyses were performed by the Analysis Department of this Institute.

3.1. Preparation of compounds 4 following the literature method [5]

Aqueous potassium hydroxide solution (20 M, 0.66 ml, 13.2 mmol) was added to a solution of **1b** (3.8 g, 11.5 mmol) in DMF (8 ml) at 0 °C. After stirring for 2 h, CS_2 (0.45 ml, 7.4 mmol) was added and after 20 min a second portion of aqueous KOH solution (0.33 ml, 6.6 mmol) and CS_2 (0.23 ml, 3.7 mmol) was added, followed by a third portion of aqueous KOH solution (0.66 ml, 13.2 mmol) and CS_2 (0.23 ml, 3.7 mmol) after an interval of 10 min. The ice bath was removed and the mixture stirred at room temperature for 2 h. A solution of CH_3I (1.50 ml, 23.0 mmol) in 2 ml of DMF was then added dropwise, addition being complete after 10 min. After stirring for 2 h at room temperature, the mixture was poured into 20 ml of water. The oily layer was separated and dried over Na_2SO_4. Vacuum distillation gave **3bb** (3.11 g, 76%) and **4bb** (0.44 g, 4.8%).

Table 1
Compounds **3** and **4**

Reactants	Product	B.p. (°C/mm Hg)	Yield (%)[a]
1b + 2b[b]	**3bb** **4bb**	36–38/2	76 4.8
1b + 2c[b]	**3bc** **4bc**	124–126/2	70 3.5
1a + 2a	**4aa**	82–84/2	69
1b + 2b	**4bb**	42–44/2	65
1b + 2c	**4bc**	134–136/2	59
1c + 2d	**4cd**	77–79/2	64

[a] Isolated yields based on **1**.
[b] According to literature method.

$Cl(CF_2)_2O(CF_2)_2SO_2N(CH_3)_2$ (**3bb**): IR (film) ν(cm^{-1}): 2990 (w), 1470 (w); 1435 (m); 1400 (s); 1360 (m); 1310 (s); 1120–1240 (vs); 985 (s); 780 (m); 760 (m); 715 (s); 590 (m). ^1H NMR δ: 2.70 (s, 2×CH_3) ppm. ^{19}F NMR δ: −2.3 (s, $ClCF_3$); 6.0 (m, OCF_2); 10.6 (m, CF_2O); 40.5 (s, CF_2S) ppm. MS *m/z* (%): 360/362 (M^+H, 4.09/1.51); 344 ($M^+ - CH_3$, 16.52/5.17); 135/137 ($ClCF_2CF_2^+$, 16.77/7.13); 119 ($C_2F_5^+$, 15.70); 108 ($M^+ - R_f$, 27.68); 78 (SO_2N^+, 43.27). Analysis: Calc. for $C_6H_6ClF_8NO_3S$: C, 20.03; H, 1.67; N, 3.89; F, 42.28%. Found: C, 20.04; H, 1.81; N, 4.29; F, 42.64%.

$Cl(CF_2)_2O(CF_2)_2SO_2N(CH_2C_6H_5)_2$ (**3bc**): IR ν-(cm^{-1}): 3065 (w); 2970 (w); 1500 (m); 1460 (m); 1400 (s); 1355 (m); 1310 (s); 1120–1220 (vs); 1065 (m); 1000 (m); 980 (s); 940 (m); 900 (m); 800 (w); 755 (s); 705 (s). ^1H NMR δ: 4.54 (s, 4H); 7.70 (m, 10ArH) ppm. ^{19}F NMR δ: −2.0 (s, $ClCF_2$); 5.8 (m, OCF_2); 10.9 (m, CF_2O); 39.9 (s, CF_2S) ppm. MS *m/z* (%): 512 (M^+H, 1.37/0.51); 420 ($M^+ - CH_2C_6H_5$, 12.63/4.58); 260 ($^+SO_2N(CH_2C_6H_5)_2$, 8.45); 135/137 ($ClCF_2CF_2^+$, 19.67/6.92); 91 ($^+CH_2C_6H_5$, 100.00); 77 ($C_6H_5^+$, 15.77). Analysis: Calc. for $C_{18}H_{14}ClF_8NO_3S$: C, 42.27; H, 2.74; N, 2.74; F, 29.75%. Found: C, 42.34; H, 2.81; N, 2.96; F, 29.96%.

3.2. Preparation of (S,S)-dialkyl N-(perfluoroalkylsulfonyl)carbodithioimidates (4): general procedure

A solution consisting of **1a** (1.5 g, 10 mmol), aqueous KOH (0.66 g, 10 mmol) and 15 ml of MG was stirred for 4 h at room temperature. Then CS_2 (0.80 ml, 13 mmol) was added dropwise to the solution and the whole stirred for another 4 h before a second portion of aqueous KOH (0.66 g, 10 mmol) was added. A solution of $Br(CH_2)_2Br$ (1.88 g, 10 mmol) in 5 ml of MG was then added dropwise at 0 °C. Addition was complete within 10 min. After stirring for 2 h at room temperature, the mixture was poured into 5 ml of ice water, the oily layer separated and dried over Na_2SO_4. Vacuum distillation gave **4aa** (1.7 g, 69%).

$CF_3SO_2N{=}\overline{CS(CH_2)_2S}$ (**4aa**): IR ν(cm^{-1}): 3000 (w), 2935 (m); 1615 (m); 1570 (m); 1520 (s); 1490 (s); 1475 (s); 1470 (s); 1350 (s); 1210 (s); 1125 (s); 1070 (m); 950 (m); 850 (s); 640 (s); 610 (m). ^1H NMR (CD_3CN) δ: 3.72 (s, 2×CH_3) ppm. ^{19}F NMR δ: 1.0 (s, CF_3) ppm. MS *m/z* (%): 252 (M+H, 1.67); 251 (M^+, 21.35); 182 ($M^+ - CF_3$, 100.00); 168 ($M^+ - CF_3 - CH_2$, 49.45); 136 ($M^+ - CF_3 - SCH_2$, 18.45); 118 ($M^+ - CF_3SO_2$, 8.41); 92 ($(SCH_2)_2^+$, 12.60); 76 (CS_2^+, 8.69); 69 (CF_3^+, 52.54); 60 ($SC_2H_4^+$, 45.47). Analysis: Calc. for $C_4H_4F_3NO_2S_3$: C, 19.12; H, 1.59; N, 5.58; F, 22.71%. Found: C, 19.37; H, 1.70; N, 5.77; F, 22.40%.

Compounds **4bb, 4bc, 4cd** were prepared similarly.

$Cl(CF_2)_2O(CF_2)_2SO_2N{=}C(SCH_3)_2$ (**4bb**): IR ν(cm^{-1}): 2940 (2); 1685 (m); 1460 (w); 1425 (m); 1390 (s); 1350 (m); 1305 (m); 1295 (m); 1100–1240 (vs); 1050 (m); 975 (s); 780 (w); 720 (m); 580 (s). ^{1}H NMR δ: 2.78 (s, 2×CH_3) ppm. ^{19}F NMR δ: −2.3 (s, $ClCF_2$); 5.9 (m, OCF_2); 10.3 (m, CF_2O); 39.1 (s, CF_2S) ppm. MS *m/z* (%): 433/435 (M^+-2, 0.96/0.34); 403/405 (M^+-S, 7.26/2.46); 377/379 ($M^+H-CSCH_3$, 13.19/4.58); 360/362 ($M^+-O-CSCH_3$, 14.17/4.68); 324 ($M^+-Cl-CS_2$, 9.04); 109 ($M^+H-R_f-CS_2$, 100.00); 94 ($(^+SCH_3)_2$, 12.66). Analysis: Calc. for $C_7H_6ClF_8NO_3S_3$: C, 19.29; H, 1.39; N, 3.21; F, 34.94%. Found: C, 18.96; H, 1.55; N, 3.61; F, 35.10%.

$Cl(CF_2)_2O(CF_2)_2SO_2N{=}C(SCH_2C_6H_5)_2$ (**4bc**): IR ν(cm^{-1}): 3060 (w); 2965 (w); 1650 (m); 1500 (m); 1400 (s); 1310 (s); 1100–1220 (vs); 1065 (m); 980 (s); 760 (s); 705 (s). ^{1}H NMR δ: 4.61 (s, 4H); 7.73 (m, 10ArH) ppm. ^{19}F NMR δ: −1.7 (s, $ClCF_2$); 6.0 (m, OCF_2); 10.9 (m, CF_2O); 39.4 (s, CF_2S) ppm. MS *m/z* (%): 556/558 (M^+H-S, 1.14/0.54); 524/526 (M^+H-SO_2, 5.88/2.56); 511/513 ($M^+H-C_6H_5$, 6.42/2.08); 246 ($(^+SCH_2C_6H_5)_2$, 12.06); 214 ($(C_6H_5CH_2)_2S^+$, 34.70); 135/137 ($ClCF_2CF_2^+$, 15.17/4.74); 123 ($^+SCH_2C_6H_5$, 11.77); 92 ($(SCH_2)_2^+$, 100.00); 77 ($C_6H_5^+$, 10.67). Analysis: Calc. for $C_{19}H_{14}ClF_8NO_3S_3$: C, 38.84; H, 2.39; N, 2.39; F, 25.89%. Found: C, 38.90; H, 2.51; N, 2.55; F, 25.67%).

$I(CF_2)_2O(CF_2)_2SO_2N{=}C(SCH_2CH{=}CH_2)_2$ (**4cd**): IR ν(cm^{-1}): 3100 (w); 2990 (m); 1665 (m); 1640 (w); 1420 (m); 1300 (s); 1100–1225 (vs); 930 (s); 700 (s); 540 (m). ^{1}H NMR δ: 3.78 (d, 2H); 5.00 (1H); 5.19 (m, 1H); 5.83 (m, 1H) ppm. ^{19}F NMR δ: 4.9 (m, OCF_2); 12.3 (m, CF_2O); 40.2 (s, CF_2S) ppm. MS *m/z* (%): 579 (M^+, 8.21); 564 (M^+-CH_3, 7.97); 551 ($M^+-C_2H_4$, 11.63); 538 ($M^+-CH_2CH{=}CH_2$, 17.76); 236 (M^+-R_f, 6.33); 227 ($ICF_2CF_2^+$, 12.47); 146 ($(^+SCH_2CH{=}CH_2)_2$, 35.84); 101 ($HCF_2CF_2^+$, 13.59); 73 ($^+SCH_2CH{=}CH_2$, 27.65). Analysis: Calc. for $C_{11}H_{10}F_8INO_3S_3$: C, 22.80; H, 1.73; N, 2.42; F, 26.25%. Found: C, 22.94; H, 1.80; N, 2.69; F, 26.36%.

Acknowledgements

The authors wish to thank the Shanghai Natural Science and Technology Foundation and the National Natural Science Foundation of China for financial support.

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