TRIFLUOROACETIC ACID IN THE SYNTHESIS OF THIOLCARBAMATES AND S-METHYL ALKANETHIOATES

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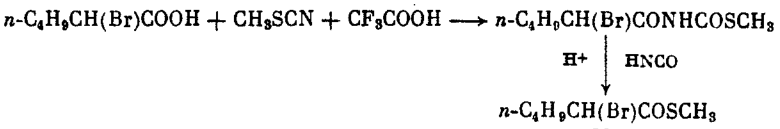
The major products of the reaction of 2-bromohexanoic acid with methyl thiocyanate in trifluoroacetic acid are S-methyl 2-bromohexanethioate (II) (55% yield), S-methyl 2,2,2-trifluoroethanethioate (IV) (31% yield), N-trifluoroacetyltrifluoroacetamide (V) (11% yield), and N-trifluoroacetyl-S-methylthiolcarbamate (III) (29% yield). N-2-Bromohexanoyl-S-methylthiolcarbamate (I), N-2-bromohexanoyltrifluoroacetamide (VI), 2-thiapropioamide(VII), and S-methyl hexanethioate(VIII) are also formed in minor amounts.

The reaction of alkanoic acids with an excess of alkyl thiocyanates incapable of undergoing isomerization in trifluoroacetic acid gives S-alkyl esters of thiolic acids [1], while a dehalogenated transnitrilation product, namely, capronitrile, is formed in the reaction with 2-bromohexanoic acid (BHA). These reactions have not been studied in detail.

Hence, we carried out a detailed study of the reaction of BHA with methyl thiocyanate (MTC) in trifluoroacetic acid (TFA) using IR, NMR, and chromato-mass spectral methods.

BHA was found to react with MTC similarly to an alkanoic acid and is converted mainly through N-2-bromohexanoyl-S-methylthiolcarbamate (I) to S-methyl 2-bromohexanethioate (II) in 55% yield.



$$n\text{-}C_4H_9CH(Br)COOH + CH_3SCN + CF_3COOH \longrightarrow n\text{-}C_4H_9CH(Br)CONHCOSCH_3 \xrightarrow[H^+]{HNCO} n\text{-}C_4H_9CH(Br)COSCH_3$$

(II)

In addition to catalysis of the formation of thiolate esters [1], TFA also reacts directly with MTC to give N-trifluoroacetyl-S-methylthiolcarbamate (III) in 29% yield and its thermolysis product, S-methyl 2,2,2-trifluoroethanethioate (IV) in 31% yield.

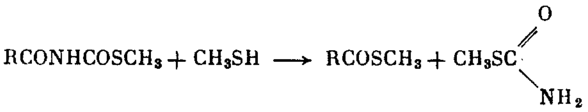
$$CF_3COOH + CH_3SCN \rightarrow \underset{(III)}{CF_3CONHCOSCH_3} \xrightarrow[\Delta]{H^+} \underset{(IV)}{CF_3COSCH_3}$$

In addition to (II) and (III), N-trifluoroacetyltrifluoroacetamide (V) (11%) and 2-bromohexanoyltrifluoroacetamide (VI) (7%) were also detected. Acetamides (V) and (VI) are apparently the products of the transamidation of (I) and (III), respectively [3].

$$(I) + CF_3COOH \rightarrow \underset{(V)}{n\text{-}C_4H_9CH(Br)CONHCOCF_3} + CO_2 + CH_3SH$$

$$(III) + CF_3COOH \rightarrow \underset{(VI)}{CF_3CONHCOCF_3} + CO_2 + CH_3SH$$

Thiapropioamide (VII) (5%) and S-methyl hexanethioate (VIII) (3%) were also detected among the reaction products. Amide (VII) is formed in the presence of moisture [4] in the catalytic hydrolysis of MTC. The thiolysis of thiolcarbamates may serve as an alternative pathway for the formation of (VII).



(VII)

$R = n\text{-}C_4H_9CH(Br), CF_3.$

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A chromato-mass spectral study showed that methanethiol is formed in the reaction mixture.

Since BHA undergoes reductive debromination in decane at 150-200°C to give hexanoic acid [2], we assume that the analogous reaction proceeds at lower temperatures upon acid catalysis.

$$n\text{-}C_4H_9CH(Br)COOH \xrightarrow{H^+} n\text{-}C_5H_{11}COOH \xrightarrow{CH_3SCN} n\text{-}C_5H_{11}COSCH_3$$

We should stress that the transamidation and thermolysis of thiolcarbamates (I) and (III) are catalyzed by TFA. Thus, these processes do not occur upon heating (III) at reflux but take place rapidly in TFA at reflux, leading to the complete transformation of (III) to (IV) and (VI).

Thus, TFA, on one hand, catalyzes the thermolysis of the thiolcarbamate processes and, on the other, reacts with MTC competitively with the carboxylic acid. This results in a decrease in the TFA concentration in the reaction mixture and, consequently, the accumulation of (I), (III), and (V) becomes possible.

EXPERIMENTAL

The PMR and ^{13}C NMR spectra were taken on a Bruker 200 spectrometer at 200 and 50 MHz, respectively, with TMS as the internal standard.

The mass spectra were taken on a KRATOS MS25RF chromato-mass spectrometer with a DS 90 data conversion system. The ionizing electron energy was 70 eV. The temperature of the ion source was 260°C using a 25-m capillary column packed with SE-30. The temperature programming involved an increase from 30 to 150°C at 5°C/min and from 150 to 300°C at 10°C/min.

The IR spectra were taken on a Bruker IF-48 spectrometer neat and in CCl_4 solution.

Reaction of 2-Bromohexanoic Acid (BHA) with Methyl Thiocyanate. A sample of 0.03 mole MTC was added to a solution of 0.01 mole freshly distilled BHA and 0.03 mole CF_3COOH. The reaction mixture was distilled at reflux for 2 h and then fractionated in vacuum. The product yields were determined using gas-liquid chromatography and authentic samples.

Thermolysis of N-(Trifluoroacetyl)-S-methylthiolcarbamate (III) in TFA and Heptane. A sample of 0.01 mole (III) was heated at reflux for 2 h in 20 ml TFA. The reaction mixture was analyzed using gas-liquid chromatography and authentic samples. The thermolysis of (III) in heptane was carried out analogously.

Reaction of TFA and MTC. A mixture of 0.01 mole MTC with 0.01 mole TFA was heated at reflux for 2 h. The precipitate of N-trifluoroacetyl-S-methylthiolcarbamate was decanted and washed with hexane; the yield of (III) was 0.0053 mole. The liquid fraction was analyzed by gas-liquid chromatography. The yield of (IV) was 31%.

S-Methyl 2-Bromohexanethioate (II) was obtained in 55% yield, bp 110°C (10 mm). Found: C, 37.67; H, 5.53%. Calculated for $C_7H_{13}BrOS$: C, 37.34; H, 5.82%. PMR spectrum (δ, ppm): 0.95 t (CH_3), 1.37 m [$(CH_2)_2$], 2.00 m (CH_2), 2.35 s (SCH_3), 4.36 t (CHBr). ^{13}C NMR spectrum (δ, ppm): 12.2 (SCH_3), 13.7 (CH_3), 21.9 (CH_2), 29.2 (CH_2), 34.9 (CH_2), 53.7 (CHBr), 196.3 (CO). IR spectrum (ν, cm^{-1}): 1686 (C=O). Mass spectrum, m/z (I_{rel}, %): $[M]^{+\cdot}$ 224/226 (0.2), $[M-SCH_3]^+$ 177/179 (20), $[M-C_4H_8]^+$ 168/170 (12), $[M-COSCH_3]^+$ 149/151 (10), $[M-Br]^+$ 145 (62), $[COSCH_3]^+$ 75 (70), $[M-COSCH_3-Br]^+$ 69 (100), 55 (90), $[SCH_3]^+$ 47 (45).

N-2-Bromohexanoyl-S-methylthiolcarbamate (I). Mass spectrum, m/z (I_{rel}, %): $[M-COSCH_3NH]^+$ 179/181 (5), $[M-Br-NH]^+$ 173 (30), $[M-CO-Br-NH]^+$ 149 (7), $[COSCH_3]^+$ 75 (5), $[C_5H_9]^+$ 69 (100), $[C_4H_7]^+$ 55 (40), $[SCH_3]^+$ 47 (7).

N-Trifluoroacetyl-S-methylthiolcarbamate (III) was obtained in 29% yield, mp 56°C. Found: C, 26.01; N, 7.35%. Calculated for $C_4H_4F_3NO_2S$: C, 25.67; N, 7.49%. PMR spectrum (δ, ppm): 2.36 s (CH_3), 7.0 m (NH). ^{13}C NMR spectrum (δ, ppm): 12.93 (SCH_3), 116.26 (CF_3) (J_{C-F} = 288 Hz), 156.27 ($COCF_3$) (J_{C-F} = 39 Hz), 170.5 ($COSCH_3$). IR spectrum (ν, cm^{-1}): 1747 [C=O(CF_3)], 1653 [C=O(SCH_3)]. Mass spectrum, m/z (I_{rel}, %): $[M]^+$ 187 (3), $[M-SCH_3]^+$ 140 (3), $[M-CF_3H]^+$ 117 (3), $[M-COSCH_3]^+$ 112 (3), $[CF_3CO]^+$ 97 (4), $[COSCH_3]^+$ 75 (8), $[CF_3H]^+$ 70 (100); $[CF_3]^+$ 69 (70); $[SCH_3]^+$ 47 (60).

S-Methyl 2,2,2-Trifluoroethanethioate (IV) was obtained in 31% yield, bp 67°C. The PMR spectrum was analogous to that reported by Wakselman [5]. IR spectrum (ν, cm^{-1}): 1706 (C=O). Mass spectrum, m/z (I_{rel}, %): $[M]^{+\cdot}$ 144 (15), $[CF_3CO]^+$ 97 (3), $[COSCH_3]^+$ 75 (100), $[CF_3]^+$ 69 (60), $[SCH_3]^+$ 47 (33), 45 (25). ^{13}C NMR spectrum (δ, ppm): 15.74 (SCH_3), 115.39 (CF_3, J_{C-F} = 290 Hz), 184 (CO, J_{C-F} = 39 Hz).

N-Trifluoroacetyltrifluoroacetamide (V) was obtained in 11% yield, mp 86°C. Found: C, 22.98; N, 6.70%. Calculated for $C_4HF_6NO_2$: C, 22.68; N, 6.91%. PMR spectrum (δ, ppm): 8.00 m. IR spectrum (ν, cm^{-1}): 1747 [C=O(CF_3)], 3300-3500 (NH). Mass spectrum, m/z (I_{rel}, %):

$[M]^{+\cdot}$ 209 (2), $(M-CF_3]^+$ 140 (11), $[M-CF_3CO]^+$ 112 (8), $[CF_3CO]^+$ 97 (12), $[CF_3]^+$ 69 (90), 59 (23), 57 (17), 51 (23), 45 (100). ^{13}C NMR spectrum (δ, ppm): 117 (J_{C-F} = 287 Hz), 160.36 (J_{C-F} = 37 Hz)

N-α-Bromohexanoyltrifluoroacetamide (VI) was obtained in 7% yield, mp 39°C. Found: C, 32.99; H, 4.07%. Calculated for $C_8H_{11}BrF_3NO_2$: C, 33.12; H, 3.82%. PMR spectrum (δ, ppm): 0.93 t (CH_3), 1.34 m [$(CH_2)_2$], 1.92 m (CH_2), 4.10 t (CHBr), 6.00 m (NH). IR spectrum (ν, cm^{-1}): 1782, 1739 (C=O). Mass spectrum, m/z (I_{rel}, %): $[M]^{+\cdot}$ 289/291 (3), $[M-CO]^{+\cdot}$ 263/265 (7), $[M-SCH_3]^+$ 177/179 (22), $[CF_3CO]^+$ 97 (8), $[CF_3]^+$ 69 (100), $[C_4H_7]$ 55 (85).

2-Thiapropioamide (VII) was obtained in 5% yield, mp 103-105°C. IR spectrum (ν, cm^{-1}): 1638 (C=O), 3368, 3249 (NH). Mass spectrum, m/z (I_{rel}, %): $[M]^{+\cdot}$ 91 (30), $[M-NH_2]^+$ 75 (3), $[CH_3SH]^+$ 48 (100), $[SCH_3]^+$ 47 (70).

S-Methyl hexanethioate (VIII) was obtained in 3% yield, bp 60-61°C (15 mm). PMR spectrum (δ, ppm): 0.95 t (CH_3), 1.25 m [$(CH_2)_2$], 2.25 t (SCH_3), 2.52 t (CH_2). IR spectrum (ν, cm^{-1}): 1995 [1]. Mass spectrum, m/z (I_{rel}, %): $[M]^{+\cdot}$ 146 (2), $[M-CH_3]^+$ 131 (22), $[M-SCH_3]^+$ 99 (72), $[COSCH_3]^+$ 75 (25), $[C_5H_{11}]^+$ 71 (68), $[C_4H_9]^+$ 57 (10), $[C_4H_7]^+$ 55 (42), $[SCH_3]^+$ 47 (55), $[C_3H_7]^+$ 43 (100), $[C_3H_5]^+$ 41 (65).

LITERATURE CITED

1. V. A. Vinokurov, E. G. Gaevoi, L. Z. Klimova, et al., Zh. Org. Khim., 23, No. 10, 2297 (1987).
2. Yu. N. Polivin, R. A. Karakhanov, V. A. Vinokurov, et al., Izv. Akad. Nauk SSSR, Ser. Khim., No. 7, 1682 (1990).
3. G. R. Jargue, M. M. Calvet, and F. M. Archilla, Anales Royal Soc. Espan. Fis. Quim., 54b, 233 (1958).
4. S. Patai, The Chemistry of Cyanates and Their Thio Derivatives, J. Wiley and Sons, New York (1977), p. 217.
5. T. Nguegen and C. Wakselman, J. Fluor. Chem., 35, No. 3, 523 (1987).

MIXED POLYNITROORTHOCARBONATES

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The reaction of β-nitro- and β-fluoro-β-nitrodichloroformals with β-nitroalcohols in the presence of ferric chloride gave mixed 2:2-polynitroorthocarbonates.

Sitzmann and Gilligan [1-3] have recently reported the synthesis of mixed 1:3- and 1:1:2-orthocarbonates with the formulas $(RO)_3COR'$ and $(RO)_2(R'O)COR''$, where R, R', and R'' are represented by one of the groups: CH_2CF_3, $CH_2CF_2NO_2$, $CH_2CF(NO_2)_2$, $CH_2C(NO_2)_3$, $CH_2C(NO_2)_2CH_3$. These compounds were obtained according to Schemes (1) and (2).

$$(RO)_3CSSCCl_3 \xrightarrow{Cl_2} (RO)_3CCl \xrightarrow{R'OH} (RO)_3COR' \qquad (1)$$

$$(RO)_2C{=}S \xrightarrow{ClSCCl_3,\ R'OH} (RO)_2(R'O)CSSCCl_3 \xrightarrow{Cl_2} (RO)_2(R'O)CCl \xrightarrow{R''OH} (RO)_2(R'O)COR''. \qquad (2)$$

Despite the possibility of obtaining mixed 2:2-orthocarbonates, in principle, using this method, such compounds have not been described in the literature. We have obtained these compounds from nitro- and fluoronitrodichloroformals, whose syntheses were reported in our recent work [4]. This reaction was carried out in dichloroethane at 20-80°C in the presence of ferric chloride over 1-2 h.

$$(RO)_2CCl_2 + 2HOR' \xrightarrow[-2HCl]{FeCl_3;\ DCE} \underset{(I)—(IV)}{(RO)_2C(OR')_2}$$

$R = CH_2CF(NO_2)_2$, $R' = CH_2C(NO_2)_3$ (I), $CH_2C(NO_2)_2CH_3$ (II), $CH_2C(NO_2)_2Cl$ (III), $CH_2CF_2NO_2$ (IV); $R = CH_2C(NO_2)_3$, $R' = CH_2CF(NO_2)_2$ (I).

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