Reaction of (IIb) with n-Butanethiol. To a solution of 7.11 g (0.08 mole) of n-butanethiol in 50 ml of chloroform was added 6.97 g (0.07 mole) of Et_3N in 10 ml of chloroform, followed at 0°C by a solution of 7.05 g (0.07 mole) of (IIb) in 20 ml of chloroform. After 3 h at 20°C, the mixture was poured into 200 ml of ice-water, and the organic layer was separated, dried over $MgSO_4$, and fractionated to give 1.4 g of butyl β-mercaptothioloisobutyrate (V). Additionally, 1.1 g of n-butyl 4-thia-2,6-dimethyl-5-oxo-7-mercaptothiolheptanoate (VII) and 1.1 g (12.1%) of what was apparently the trimer $HS[CH_2CH(CH_3)C(O)S]_3Bu$ (n-butyl 4,8-dithia-2,6,10-trimethyl-5,9-dioxo-11-mercaptothiolundecanoate), bp 160-165°C (0.02 mm), n_D^{15} 1.5330 (iodometric mol. wt., found 411. $C_{16}H_{28}O_3S_4$ requires mol. wt. 396) were obtained.

Reaction of β-Methyl-β-thiolactone (IIc) with n-Butanethiol. The reaction of 5.1 g (0.05 mole) of (IIc) with 5.4 g (0.06 mole) of n-BuSH and 5.05 g (0.05 mole) of Et_3N was carried out as for (IIb) to give 2.7 g of n-butyl β-mercaptothiolobutyrate (VI) and 1.6 g of n-butyl 4-thia-3-methyl-5-oxo-7-mercaptothioloctanoate (VIII).

CONCLUSIONS

A method is proposed for the synthesis of β-mercaptothiolcarboxylic acids, by the reaction between β-thiolactones and hydrogen sulfide in the presence of triethylamine.

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SULFUR-CONTAINING CARBOXYLIC ACIDS.

COMMUNICATION 4. β-MERCAPTOTHIOLCARBOXYLIC ACIDS†

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β-Mercaptothiolcarboxylic acids are important key compounds in the synthesis of 1,2-dithiolan-3-ones. Their preparation has, however, received little attention. Thiolcarboxylic acids are usually obtained by the reaction of carbonyl chlorides with H_2S in the presence of $AlCl_3$, chlorine in the α or β position of the acid chlorides not being replaced by SH [2-4]. β-Mercaptothiolcarboxylic acids are known only as the α-acylaminoderivatives, formed in low yields on reaction of 4-isopropylideneoxazolones with H_2S [5, 6].

We have now developed a general method for the preparation of the hitherto unknown β-mercaptothiolcarboxylic acids (Ia-c) from readily available β-halocarbonyl chlorides. Reaction of the latter with H_2S in the presence of triethylamine gives the thiolate anions (II) as intermediates, which then cyclize to the β-thiolactone (III), which is cleaved with H_2S without isolation to give the final products (Ia-c) as the triethylammonium salts. The intermediate β-thiolactones (III) were previously known, being obtained by cyclization of β-halothiolcarboxylic acids [7].

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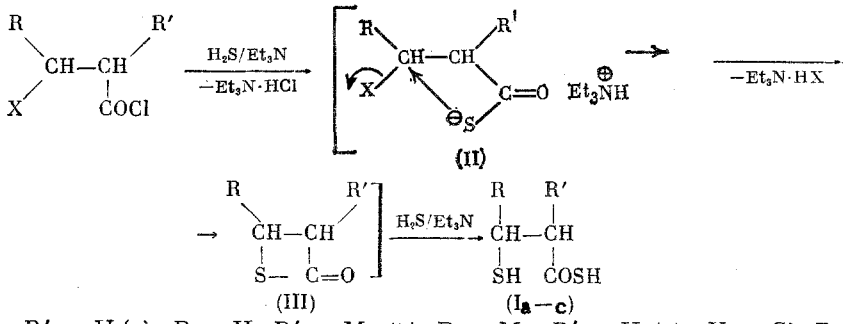
TABLE 1. Some IR and PMR Spectral Parameters and Titration Data for (Ia-c) and (IV)

Compound	PMR spectrum (δ, ppm., J, Hz).	IR spectrum, ν, cm^{-1}		Equivalent, found/calculated	
		C=O	SH	neutralization with NaOH	oxidimetric (I_2)
(Ia)	1,71t (SH, J_{SH-CH_2}=8,0), 2,6–3,2m (CH_2CH_2), 4,69 s (COSH)	1691, 1710	2568	121,9 / 122,0	57 / 61
(Ib)	1,51 d (CH_3, J_{CH_3-CH}=6,7), 1,78 t (SH, J_{SH-CH_2}=8,7), 2,59–3,24 m (CH_2CH), 4,73 s (COSH)	1691, 1708	2570	–	64 / 68
(Ic)	1,47 d (CH_3, J_{CH_3-CH}=6,7), 1,92 d (SH, J_{SH-CH}=6,7), 2,84–3,08 m (CH_2), 3,19–3,69 oct. (CH), 4,8 s (COSH)	1695, 1710	2570	134 / 136	71 / 68
(IV) *	–	1445–1552	2510, 2568	–	112 / 110,5

*The IR spectrum also shows absorption at 2800-3000 cm^{-1} ($\overset{\oplus}{N}H_3$).



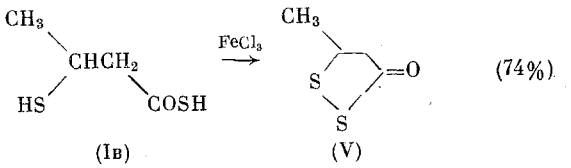
R = R′ = H (a); R = H, R′ = Me (b); R = Me, R′ = H (c); X = Cl, Br.

When β-bromocarbonyl chlorides were used, the yields of β-mercaptothiolcarboxylic acids (Ia-c) were the same as when the β-chloro compounds were used (∿30-50%). Better results were obtained by adding triethylamine (in two portions) to the solution of the acid chloride in chloroform. When the inverse order of mixing of the reactants was used (addition of the acid chloride to triethylamine in a stream of H_2S), the yields of (I) were decreased by a factor of 3-4; i.e., the direct exchange of both halogen atoms by mercapto, avoiding the cyclization stage, gives unsatisfactory results.

The structures of the β-mercaptothiolcarboxylic acids (Ia-c) were confirmed by, in addition to their IR and PMR spectra, iodometric and acidimetric titration (Table 1). As would be expected, the signal for the COSH group in the PMR spectrum is seen as a singlet at lower field (4.7-4.8 ppm) than that for the SH group (a doublet or triplet at 1.7-1.9 ppm). In the IR spectra of (IIa-c), both SH groups are seen in a single narrow range (2568-2570 cm^{-1}).

Thiolcarboxylic acids are known to be cleaved by bases at the S–acyl bond. It is therefore not surprising that on treatment with aqueous alkali ($NaHCO_3$), the β-mercaptocarboxylic acids (I) are converted into β-mercaptocarboxylic acids. However, on treatment with amines (cyclohexylamine or triethylamine) under mild conditions (in an organic solvent at low temperatures), the corresponding thiolcarboxylate salts were obtained [for example, the cyclohexylammonium salt $HSCH_2CH_2COS^{\ominus}$ $\langle\bigcirc\rangle$–$\overset{\oplus}{N}H_3$ (IV)], from which the β-mercaptothiolcarboxylic acids can be recovered by acidification.

Unlike normal mercaptans, mercaptothiolcarboxylic acids (Ia-c) are fairly stable to atmospheric oxygen, although they are readily oxidized by iodine or $FeCl_3$. This method was used to obtain 5-methyl-1,2-dithiolan-3-one (V) in high yield.



(IB) (V)

The IR spectrum of (V) shows absorption for the disulfide bond (533 and 590 cm^{-1}) which is not present in the original acid (Ic).

EXPERIMENTAL

PMR spectra were obtained on a Perkin–Elmer R-12 spectrometer (60 MHz) in CCl_4, from TMS as external standard, and IR spectra in liquid films or KBr disks. IR and PMR spectral data and titration figures for (Ia-c) and (IV) are given in Table 1.

β-Mercaptothiolpropionic Acid (Ia). Into a solution of 25.4 g (0.2 mole) of β-chloropropionyl chloride in 600 ml of dry chloroform at −20°C was passed a rapid stream of H_2S for 1 h, then 40.4 g (0.4 mole) of triethylamine in 100 ml of dry ether was added with stirring. The cooling bath was replaced by a condenser cooled with dry ice–acetone, and H_2S passed in for 0.5 h, then a further 20.2 g (0.2 mole) of triethylamine in 50 ml of chloroform was added in a stream of H_2S. Passage of H_2S was continued at the same temperature of the reaction mixture (−30 to −10°C) for 6 h with stirring. The temperature was then brought to 20°C, the precipitated triethylamine hydrochloride filtered off, and the mother liquors extracted thoroughly with water (3 × 100 ml). The aqueous extract was acidified with 10% hydrochloric acid to pH ∿ 1-2, and the oil which separated was extracted with chloroform (3 × 100 ml) and dried over $CaCl_2$. The solvent was removed under reduced pressure (under nitrogen), and the residue distilled to give 12.2 g (50%) of the thioacid (Ia), mp 60°C (4 mm), n_D^{22} 1.5545. Found: C 30.31; H 5.02; S 52.25%. $C_3H_6OS_2$. Calculated: C 29.51; H 4.92; S 52.46%.

β-Mercaptothiolisobutyric Acid (Ib). From 28.2 g (0.2 mole) of β-chloroisobutyryl chloride there was obtained similarly 8.16 g (30%) of (Ib), bp 58°C (3 mm), n_D^{20} 1.5365. Found: C 36.04; H 5.55; S 47.05%. $C_4H_8OS_2$. Calculated: C 35.29; H 5.88; S 47.06%.

β-Mercaptothiolobutyric Acid (Ic). 1). From $ClCHMeCH_2COCl$. From 28.2 g (0.2 mole) of β-chlorobutyryl chloride there was obtained as for (Ia) 8.2 g (30%) of (Ic), mp 61°C (7 mm), $n_D^{21.5}$ 1.5335. Found: C 35.40; H 5.85; S 47.84%. $C_4H_8OS_2$. Calculated: C 35.29; H 5.88; S 47.06%.

2) From $BrCHMeCH_2COCl$. From 37.1 g (0.2 mole) of β-bromobutyryl chloride there was obtained similarly 7.89 g (29%) of (Ic), mp 50-53°C (3 mm), n_D^{20} 1.5350. IR and PMR spectra identical with those of the compound obtained in 1). The acids (IIa-c) gave a crimson coloration with sodium nitroprusside in alkaline solution.

Cyclohexylammonium β-Mercaptothiolpropionate (IV). To a solution of 3.66 g (0.03 mole) of the acid (Ia) in 15 ml of dry ether was added at 0°C under nitrogen 3.27 g (0.33 mole) of cyclohexylamine in 15 ml of dry ether. After 3 h at 20°C, the solid which had separated was filtered off, washed with ether, and dried in a vacuum desiccator over P_2O_5. Yield of (IV) 6.7 g (100%), mp 56°C (in a sealed capillary). Found: S 29.22; N 6.37%. $C_9H_{19}NOS_2$. Calculated: S 29.00; N 6.33%. The salt (IV) was soluble in water and alcohol, but insoluble in acetone and ether.

5-Methyl-1,2-dithiolan-3-one (V). To a solution of 2.72 g (0.02 mole) of the thiol acid (Ic) in 40 ml of methanol was added gradually with stirring and ice-cooling ∿0.5 liter of 0.05 M aqueous $FeCl_3 \cdot 6H_2O$. After 1.5 h at 20°C, the mixture was extracted with ethyl acetate (3 × 50 ml), and the extracts dried over Na_2SO_4. The residue after removal of the solvent was distilled to give 2 g (74%) of (V), bp 83°C (10 mm), n_D^{25} 1.5730 (cf. [8]). The PMR spectrum of (V) coincided with that given in [9]. IR spectrum (ν, cm^{-1}): 1710 (CO), 533, 590 (S–S). With sodium nitroprusside in alkaline solution, (V) gave a blue coloration.

CONCLUSIONS

1. Reaction of β-halocarbonyl chlorides with hydrogen sulfide in the presence of excess triethylamine gives in one step the previously unknown β-mercaptothiolalkanoic acids.

2. Oxidation of β-mercaptothiolbutyric acid gives the cyclic disulfide 5-methyl-1,2-dithiolan-3-one.

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REACTION OF VICINAL DIHALOPOLYFLUOROALKANES WITH SODIUM AZIDE

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Vicinal dihalopolyfluoroalkanes react readily with nucleophilic reagents to form the products of the replacement of one halogen by a nucleophilic residue. These reactions have been studied with F^- anion [1] and C-, O-, and S-nucleophiles [2-5] as examples.

The present work studies the analogous reaction with the azide anion. When vicinal dibromopolyfluoroalkanes and related compounds react with NaN_3 in DMF, N-methylpyrrolidone, or hexametapol, halogen is replaced by an azide group, and β-halopolyfluoroalkyl azides (II) form:

$$RR'C(Br)-CF_2Br \xrightarrow{NaN_3} RR'C(Br)-CF_2N_3$$
(I) (II)

R = F, R′ = Cl (a); R = F, R′ = CF_3 (b); R = F, R′ = COOEt (c); R = CF_3, R′ = COOEt (d).

Analogously, 1,2-diiodotetrafluoroethane (III) yields β-iodotetrafluoroethyl azide (IV). The reaction rate depends to a significant extent on the nature of the leaving halogen. Thus, perfluoromethacrylic ester dibromide (Id) is easily converted to azide IId even at −10°. In the case of perfluoroacrylic ester dibromide (Ic) the reaction is slow, and conversion is complete after several hours at 20°, while the dibromopolyfluoroalkanes Ia, b react with NaN_3 at an appreciable rate only at 70-80°. In this case, along with the β-bromoazides appreciable amounts of the product of the reduction of the second bromine, viz., the α-bromoazides $RCFHCF_2N_3$ (R = Cl, CF_3), are formed; this sharply reduces the yield of azides IIa, b.

Diiodide III is more reactive than dibromides Ia, b and is smoothly converted to iodoazide IV when heated for a short time with NaN_3. In a study of the effect of solvent on the rate of this reaction it was established that III forms a stable crystalline 1:1 adduct with hexametapol that is apparently a donor–acceptor complex. Similar adducts have previously been obtained from III or 1,4-diiodoperfluorobutane and tertiary amines [6].

The reaction of vicinal dibromopolyfluoroalkanes with NaN_3, like the other nucleophilic reactions of these compounds [1, 5], apparently takes place by an ionic chain mechanism. This consists of dehalogenation of the vicinal dibromide [under the influence of N_3^- at the initiation stage, and the intermediate carbanion (B) at the chain-transfer stage], followed

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