REACTION OF 1,2-DITHIOLAN- AND 1,2-DITHIOLEN-3-ONES WITH SULFENYL CHLORIDES

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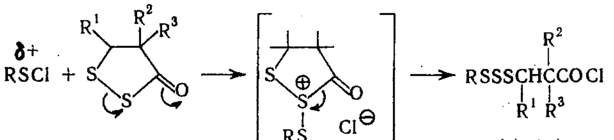
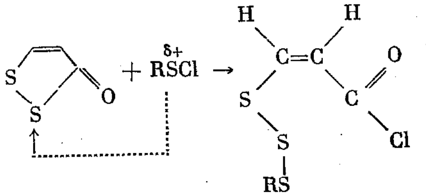
Previously we had reported that the chlorination of the 1,2-dithiolan- and alkyl-substituted 1,2-dithiolen-3-ones with sulfuryl chloride proceeds with an opening of the S—CO bond of the ring [1]. It is known that the sulfenyl chlorides cleave the S—S bond in disulfides [2], and also the S—CO bond in acetyl sulfides [3]. The same as in the reactions of the 1,2-dithiolan-3-ones with SO_2Cl_2, only the S—CO bond is cleaved when the 4- and 5-methyl-1,2-dithiolan-3-ones are reacted with excess sulfenyl chloride (CH_3SCl or C_6H_5SCl) without a solvent at room temperature.



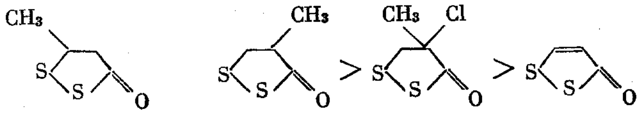
(I)-(V)

4-Chloro-4-methyl-1,2-dithiolan-3-one does not react with C_6H_5SCl at room temperature, and the S—CO bond is cleaved only on heating. Depending on the structure of the 1,2-dithiolan-3-one and the employed sulfenyl chloride, the reaction lasts from one to several days, in which connection CH_3SCl reacts more easily than does PhSCl. 1,2-Dithiolen-3-one is also cleaved by sulfenyl chlorides only at the S—CO bond.



(VI), (VII)

Based on the obtained data the reactivity of the cyclic carbonyl disulfides investigated by us decreases in the following order.



The photochemical, thermal, or catalytic symmetrization of the unsymmetrical disulfides has been widely studied [4]. The unsymmetrical trisulfides are much more difficultly available than the disulfides, and the information on their symmetrization is scanty. The obtained unsymmetrical methyl trisulfides (I), (II), and (VI) are heat stable, and are easily purified by distillation in a high vacuum. Under the same conditions the higher-boiling saturated and unsaturated phenyl trisulfides (III)-(V) and (VII) when distilled in a high vacuum undergo simultaneous symmetrization and ejection of sulfur to give a mixture of unsymmetrical and symmetrical tri- or disulfides (VIII) and (IX).

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TABLE 1. Preparation Conditions and Constants of Acid Chlorides of β-(Methyl(and phenyl)trithio)carboxylic Acids (I)-(VII)

Compound	Formula	Reaction time, h (Temp., °C)	Yield, %	bp, °C (p, mm of Hg)	n_D^{20}	Found, %		Empirical formula	Calculated, %	
						S	Cl* (COCl)		S	Cl* (COCl)
(I)	$CH_3S_3CH(CH_3)CH_2COCl$	24(20)	76	72—74(0,03)	0,5639	43,75	15,87	$C_5H_9OS_3Cl$	44,26	16,39
(II)	$CH_3S_3CH_2C(CH_3)(Cl)COCl$	72(20)	89	75—80(0,01)	1,5701	39,16	14,64	$C_5H_8OS_3Cl_2$	38,32	14,15
(III) †	$PhS_3CH_2CH(CH_3)COCl$	80(20)	60	110(0,02)	—	—	—	—	—	—
(IV) ‡	$PhS_3CH(CH_3)CH_2COCl$	100(20)	75	110(0,02)	—	34,11	11,95	$C_{10}H_{11}OS_3Cl$	34,40	12,71
(V) ‡	$PhS_3CH_2C(CH_3)(Cl)COCl$	13(60)	64	115(0,02)	1,6201	29,72	11,36	$C_{10}H_{10}OS_3Cl$	30,60	12,21
(VI)	$CH_3S_3CH{=}CHCOCl$	192(20)	43	95—98(0,05)	1,6560	46,53	17,28	$C_4H_5OS_3Cl$	47,65	17,30
(VII) ‡	$PhS_3CH{=}CHCOCl$	18(70)	83	125(0,05)	1,6773	35,87	13,23	$C_9H_7OS_3Cl$	36,59	13,50

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*Acidimetric determination.

†Acid chloride (III) gave an uncrystallizable oil with aniline.

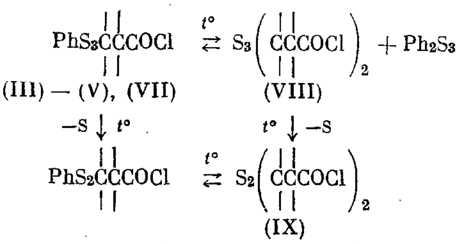
††The compound was analyzed after removal of the excess PhSCl from the reaction mixture (without distillation).

TABLE 2. NMR and IR Spectra of Acid Chlorides of β-(Methyl(and phenyl)trithio)carboxylic Acids (I)-(VII)

Compound	Formula	Chemical shift, δ, ppm (J, Hz)						ν_{CO}, cm^{-1}
		CHS	CHC	CH_2	CH_3C	CH_3S	C_6H_5S M	
(I)*	$CH_3S_3CH(CH_3)CH_2COCl$	3,40—3,60m	—	2,89—3,39m	1,38 d (5,0) 1,50 d (5,0)	2,46 s 2,59 s	—	1800
(II)	$CH_3S_3CH_2C(CH_3)(Cl)COCl$	—	—	3,55	1,83	2,49 s	—	1780
(III)	$PhS_3CH_2CH(CH_3)COCl$	—	2,58—3,63 complex multiplet		1,49 d (6,7)	—	7,16—7,84	1787
(IV)†	$PhS_3CH(CH_3)CH_2COCl$	—	—	—	—	—	—	1787
(V)	$PhS_3CH_2C(CH_3)(Cl)COCl$	—	—	3,62	1,96 s	—	7,23—7,66	1780
(VI)*	$CH_3S_3CH{=}CHCOCl$	8,25 d (6,0)	6,55 d (6,0)	—	—	2,37 s 2,74 s	—	—
(VII)	$PhS_3CH{=}CHCOCl$	7,89 d (6,0)	6,34 d (6,0)	—	—	—	7,07—7,62	—

*The two singlets, corresponding to the CH_3S group (as well as the two CH_3C doublets), are associated with the existence of two rotational isomers due to the restricted rotation around the S—S bond [7].

†The NMR spectrum was not taken due to the poor solubility in CCl_4.



Due to the symmetrization of (III)-(V) and (VII), in the NMR spectra of the first fractions of the distillate, which contain Ph_2S_3, the integral ratio of the C_6H_5S protons to the other protons (CH_2, CH) is greater, and, in reverse, in the last fractions it is lower than the theoretical value. The conversion of symmetrical trisulfides of the (VIII) type to symmetrical disulfides of the (IX) type was described previously [5].

EXPERIMENTAL METHOD

The NMR spectra were taken on a Perkin—Elmer R-12 instrument (60 MHz), using CCl_4 as the solvent and HMDS as the internal standard.

The 1,2-dithiolan-3-ones and 1,2-dithiolen-3-one were obtained from β-(acetyldithio)-carboxylic chlorides as described in [6].

General Procedure for Preparation of Acid Chlorides of β-(Methyl(or phenyl)trithio)-carboxylic Acids (I)-(VII). In the absence of moisture and solvent, in a N_2 stream, 2 moles of the freshly distilled sulfenyl chloride (CH_3SCl or PhSCl) was mixed with 1 mole of the 1,2-dithiolan- or 1,2-dithiolen-3-one; the mixture was then fractionally distilled in a high vacuum. The formation of the β-(methyl(or phenyl)trithio carboxylic chlorides (I)-(V) was confirmed via the IR spectra by the decrease in the ν_{CO} absorption at 1710-1720 cm^{-1}, which is characteristic for a cyclic carbonyl group [6], and by the increase in the acid chloride absorption ν_{CO} 1780-1800 cm^{-1}. The shift of the pair of doublets at 6.58 and 8.43 ppm (J = 6 Hz) of 1,2-dithiolen-3-one [6] indicates the formation of the β-methyl(or phenyl)trithio)acryloyl chlorides (VI) and (VII) with a cis-configuration ($J_{CH=CH}$ = 6 Hz). The temperature, reaction time, yields, and the constants of the obtained compounds are given in Table 1, while the IR and NMR spectra are given in Table 2.

CONCLUSIONS

The 1,2-dithiolan- and 1,2-dithiolen-3-ones are cleaved by CH_3SCl and C_6H_5SCl at the S—CO bond to respectively give the saturated and unsaturated acid chlorides of β-alkyl-(aryl)trithiocarboxylic acids.

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