SULFUR-CONTAINING HETEROCYCLES

6.* ATTEMPTS TO SYNTHESIZE 5-HALO-SUBSTITUTED 1,2-DITHIOLAN-3-ONES

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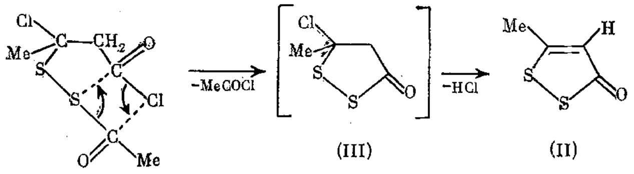
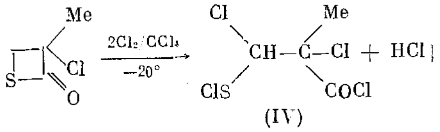
A method was developed for the synthesis of various 5-substituted 1,2-dithiolan-3-one derivatives by the nucleophilic replacement of chlorine in the previously unknown 5-chloro-1,2-dithiolan-3-ones. Two methods for the synthesis of 1,2-dithiolan-3-ones have been described up to now: the condensation of the acid chlorides of β-(chlorosulfenyl)carboxylic acids with H_2S in the presence of a base [3] and the cyclization of the acid chlorides of β-(acetyldithio)carboxylic acids in the presence of a catalyst. However, only the unsaturated 5-methyl-1,2-dithiolen-3-one (II) is formed in high yield from the β-chloro-substituted acid chloride of β-(acetyldithio)butyric acid (I) in the presence of $ZnCl_2$ [1]. It could be assumed that the dehydrochlorination is caused by the presence of the catalyst. In order to synthesize the 5-chloro-1,2-dithiolan-3-ones we studied the possibility of cyclizing acid chloride (I) in the absence of a catalyst. According to the IR spectrum, in the reaction mixture, even at 20°C, along with the starting (I), are present 5-chloro-5-methyl-1,2-dithiolan-3-one (III) and its dehydrochlorination product (II). Only (II) can be isolated after vacuum-distillation. Consequently, in order to synthesize 5-chloro-substituted 1,2-dithiolan-3-ones the starting compounds must be devoid of protons in the α-position.



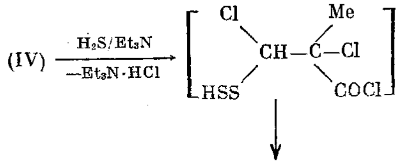
(I) (III) (II)

We were able to obtain the acid chloride of α,β-dichloro-β-(chlorosulfenyl)isobutyric acid (IV) in high yield by the chlorination of α-chloro-α-methyl-β-propiothiolactone under strictly controlled conditions:



(IV)

However, even here, along with (IV), are formed the acid chloride $ClSCH_2C(Me)(Cl)COCl$ (V) [4] and the products of its further chain chlorination. The condensation of (IV) with H_2S in the presence of Et_3N leads to a mixture of 4,5-dichloro-4-methyl-1,2-dithiolan-3-one (VI) and 4-methyl-1,2-dithiolen-3-one (VII) in a 4.4:1 ratio and a yield of at least 20%. The undistillable residue apparently contains mainly trisulfides (VIII). The formation of trisulfides from the esters of β-(chlorosulfenyl)carboxylic acids and H_2S was observed in [5].



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* See [1, 2] for Communications 1-5.

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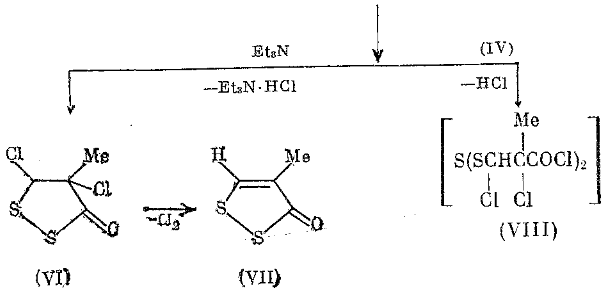
TABLE 1. Constants and Spectra of Obtained Compounds

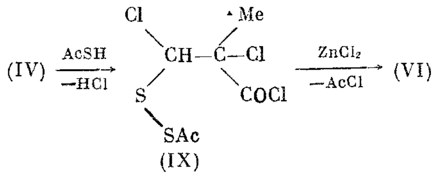
Compound	Yield, %	mp, °C (p, mm Hg)	$n_D(t°, C)$	d_4^{20}
(IV)	91	80–85 (3)	1,5340 (20)	–
(VI)	74	65 (2)	1,6015 (23)	1,5710
(IX)	48	105–110 (0,3)	1,5600 (20)	1,4830

Compound	ν, cm^{-1}		δ, ppm		
	CO	S—S	Me	MeCO	CH
(IV)	1790	–	2,16 s 2,25 s	–	5,97 s 6,03 s
(VI)	1715	485	1,79 s 1,85 s*	–	5,19 s 5,45 s*
(IX)	1745, 1790	485	1.9 s 2,11 s	2,63 s	5,55 (distorted t) J=2,7 Hz

* Mixture of cis- and trans-isomers (ratio) = $^1/_3$–$^1/_4$: $^2/_3$–$^3/_4$).



A more efficient synthesis of (VI) proved to be the cyclization of the acid chloride of α,β-dichloro-β-(acetyldithio)isobutyric acid (IX), which was obtained by treating (IV) with thiolacetic acid. In contrast to the alkyl-substituted analogs and the monochloro derivative (I), dichloride (IX) is stable and can be vacuum-distilled without cyclization. The first 1,2-dithiolan-3-one with an electron-acceptor substituent in the 5 position, namely dithiolane (VI), was obtained by us in high yield by the cyclization of (IX) in the presence of $ZnCl_2$ catalyst only under drastic conditions (at 140-150°, in contrast to 80-100° [1]).



The cyclization is accompanied by the dechlorination of (VI) to (VII) when either the temperature or amount of catalyst is increased.

The constants and spectra of the obtained compounds are given in Table 1.

EXPERIMENTAL

The PMR spectra were taken on a Perkin–Elmer R-12 spectrometer (60 MHz) in CCl_4 solution and using HMDS at the external standard.

5-Methyl-1,2-dithiolen-3-one (II). The reaction of β-chloro-β-(chlorosulfenyl)butyroyl chloride with thiolacetic acid as described in [1], followed by evacuation of the mixture at 20° (10 mm) gives an oil that contains (II) (ν, cm^{-1}): 1670 (CO), 1575 (C=C) and (III) [1710 (CO)], along with the main product, namely acid chloride (I) [1735 (COS), 1800 (COCl)]. Distillation led to the isolation of (II) in 34-50% yield, bp 55-56° (0.1 mm), n_D^{20} 1.6335. The PMR spectrum of (II) resembles that described in [1]. The test for halogen was negative.

α,β-Dichloro-β-(chlorosulfenyl)isobutyroyl Chloride (IV). In a flask, fitted with a sparger and a condenser, cooled with a dry ice−acetone mixture, was placed 50 g (0.3 mole) of α-chloro-α-methyl-β-thiolactone in 50 ml of CCl_4. Into the solution at −20° was slowly passed 53 g (0.745 mole) of Cl_2. After 2-4 h the temperature was brought up to ~ 20°, the solvent was removed in vacuo, and the residue was distilled. Based on the iodometric titration, the amount of sulfenyl chloride (IV) in the distillate is 91%. The constants and spectra of (IV) are given in Table 1. Besides (IV), in the first fractions of the distillate was detected sulfenyl chloride (V), whose constants are the same as those described in [4]: PMR spectrum of (V), δ, ppm 2.16 s (Me), 3.55 and 4.3 q (CH_2, $J_{AB} = 15.3$ Hz).

Reaction of Sulfenyl Chloride (IV) with Hydrogen Sulfide. Into a solution of 12 g (0.05 mole) of (IV) in 300 ml of CH_2Cl_2 was passed an H_2S stream for 1 h at −50°, and then 10.1 g (0.1 mole) of Et_3N in 50 ml of ether was added. The temperature was brought up to ~ 20°, 400 ml of ether was added, the $Et_3N \cdot HCl$ precipitate (12 g, 88%) was filtered, and the mother liquor was evaporated and distilled to give 2 g (20%) of a liquid with bp 56-60° (0.3 mm) n_D^{22} 1.6070, which contained 81% of (VI) (see Table 1 for IR and PMR spectra) and 19% of (VII) (the IR and PMR spectra coincide with those described in [1]). The still residue is probably acid chloride (VIII) [1780 cm^{-1} (COCl)].

α,β-Dichloro-β-(acetyldithio)isobutyroyl Chloride (IX). To 70 g (0.29 mole) of (IV) in 200 ml of CCl_4 at 0-10° was added 30 ml (0.425 mole) of thiolacetic acid, and after 1 h the mixture was distilled. The constants and spectra of (IX) are given in Table 1. Found: S 23.60; Cl 36.62%; MR_D 61.02. $C_6H_7O_2S_2Cl_3$. Calculated: S 22.80; Cl 37.78%; MR_D 58.74.

4,5-Dichloro-4-methyl-1,2-dithiolan-3-one (VI). Acetyl disulfide (IX) (30 g) was placed in a still and heated for 1 h at 140-150° in the presence of a catalytic amount of ground anhydrous $ZnCl_2$. In the receiver was collected 5.5 ml of MeCOCl. Fractional distillation of the mixture gave 16 g of (VI), whose constants and spectra are given in Table 1. Found: C 23.50; H 2.00; S 31.56; Cl 34.00%; MR_D 44.30. $C_4H_4OS_2Cl_2$. Calculated: C 23.54; H 1.97; S 31.52; Cl 34.95%; MR_D 44.43.

CONCLUSIONS

1. 5-Halo-1,2-dithiolan-3-ones, which contain a proton in the 4 position, are unstable and under ordinary conditions undergo dehydrohalogenation to 1,2-dithiolen-3-ones.

2. A 5-halo-substituted 1,2-dithiolan-3-one, and specifically 4,5-dichloro-4-methyl-1,2-dithiolan-3-one, was obtained for the first time.

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