PREPARATION OF 2-CHLOROSULFENYLCARBOXYLIC ACIDS AND 1,2-DITHIOLAN-3-ONES

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In the present communication we studied the chlorination of the 2-(acetylthio)propionic and 1-chloropropionic acids, and also their esters, amides and acid chlorides, with chlorine and SO_2Cl_2.

Several competing reactions are realized simultaneously when 2-(acetylthio)propionic acid, its ester and its acid chloride (I)-(III) are chlorinated with SO_2Cl_2: chlorination to the corresponding sulfenyl chloride (IV)-(VI), subsequent reaction of the sulfenyl chloride with the starting compound to give the disulfide (VII)-(IX), and conversion of the latter to the same sulfenyl chloride (IV)-(VI). Under identical conditions, the 2-(acetylthio)propionic acid derivatives also react with 2-chlorosulfenylpropionic acid derivatives just as easily as with SO_2Cl_2. The intermediately formed disulfides (VII)-(IX) could be isolated during reaction with 2-(acetylthio)propionic acid (I) and its ester (II), but in the latter case only by reducing the reaction time. The ease with which the CH_3CO-S bond is cleaved by SO_2Cl_2 depends on the electron-acceptor properties of the substituents attached to the carbonyl carbon. The methyl ester (II) reacts most easily, while the reaction of the acid chloride is noticeably more difficult (Table 1).

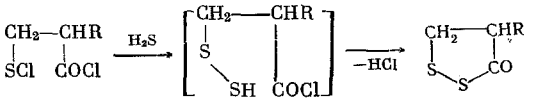
Different results were obtained in the reactions of (I) and (II) with chlorine. In this case the cleavage of the CH_3CO-S bond is accompanied by chlorination in the 2-position even with a 1:1 ratio of the reactants. This is explained by the intermediate formation of the trichloride and its subsequent decomposition in the same manner as was observed previously [4, 5]:

$$CH_3COSCH_2CH_2COX + 2Cl_2 \xrightarrow[-CH_3COCl]{-30^\circ} [Cl_3SCH_2CH_2COX] \xrightarrow[-HCl]{} ClSCH(Cl)CH_2COX$$

In contrast to 2-acetylthiopropionic acid, the presence of chlorine in 2-acetylthio-1-chloropropionic acid (XII) and its derivatives (XIII)-(XV) not only makes the CH_3CO-S bond more stable, but it also noticeably passivates the formed sulfenyl chlorides. At the same time, the effect of changes in the carboxyl group remains the same as in the case of compounds (I)-(III). Thus, dimethylamide (XV) reacts most easily with SO_2Cl_2, while the acid chloride (XIII) reacts with the greatest difficulty (see Table 1). It should be mentioned that dilution slows up the chlorination markedly. In general, the reaction of acid chloride (XIII) with SO_2Cl_2 does not go in a solvent.

On the basis of the obtained results it is possible to compose the following order for the reactivity of 1-chloro-2-(acetylthio)propionic acid derivatives: dimethylamide > ester > acid > acid chloride. As was to be expected, when chlorine, which is a stronger electrophile than SO_2Cl_2, is used the cleavage of (XII)-(XV) proceeds much more easily, with the formation of the same sulfenyl chlorides (see Table 1).

A further study of the acid chlorides of the 2-chlorosulfenylpropionic acids disclosed that their reaction with excess liquid H_2S in an inert gas stream at −78° is accompanied by the formation of intermediate hydrodisulfides, which then spontaneously undergo cyclization with the liberation of HCl. The previously unavailable 1,2-dithiolan-3-ones (XX) and (XXI) were obtained in this manner:



R = Cl (XX); H (XXI)

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TABLE 1. Components of the System: $ClSCHCH_2COX$ (X) – (XI) $\xleftarrow{Cl_2}$ $CH_3COSCH_2CH_2COX$ (I) – (III) $\xrightarrow{SO_2Cl_2}$ $ClSCH_2CH_2COX$ (IV) – (VI) $\xrightarrow{SO_2Cl_2}$ $(-SCH_2CH_2COX)_2$ (VII) – (IX) $\xrightarrow{SO_2Cl_2}$ $CH_3COSCH_2CHClCOX$ (XII) – (XV) $\xrightarrow[Cl_2]{SO_2Cl_2}$ $ClSCH_2CHClCOX$ (XVI) – (XIX)

Compound No.	X	Reaction temperature, °C	Reaction time, h	Chlorinating agent/solvent	Yield, %	Bp, °C (p, mm of Hg)	n_D^{20}	Found, %			Empirical formula	Calculated, %		
								C	H	S		C	H	S
V	OCH_3	–30	3/4	SO_2Cl_2	98,0	56 (3)	1,4901	32,16	4,62	21,71	$C_4H_7O_2SCl$	31,19	4,53	20,89
VI	Cl	+30	2 1/2	SO_2Cl_2	81,5	38–39 (2)[1]	1,5230							
VII	OH	+10–0	1/2	SO_2Cl_2 [2]	97,5	Mp 154[3]	—							
VIII	OCH_3	–30	1/4	SO_2Cl_2	56,0[4]	130 (0,02)[5]	1,5045							
X	OH	–30	—	Cl_2/CCl_4	66,0	80–81 (0,01)	1,5325	20,54	2,11	18,65	$C_3H_4O_2SCl_2$	20,59	2,29	18,28
XI[6]	OCH_3	–30	—	Cl_2/CCl_4	78,7	59–60 (3)	1,5089	25,79	3,22	17,76	$C_4H_6O_2SCl_2$	25,51	3,21	17,00
XVI	Cl	80	6	SO_2Cl_2/CCl_4	0									
XVI	Cl	80	5	SO_2Cl_2	76,0	40–41 (3)	1,5341[7]	18,76	1,69	16,96	$C_3H_3OSCl_3$	18,63	1,57	16,58
XVI	Cl	–30	—	Cl_2/CCl_4	70,0		—							
XVII[8]	OH	60	2	SO_2Cl_2/CH_2Cl_2	50,0	78–80 (0,01)	1,5330	20,72	2,34	18,73	$C_3H_4O_2SCl_2$	20,59	2,28	18,28
XVIII[9]	OCH_3	–10	1	SO_2Cl_2	75,0	57–58 (3)	1,5080	26,14	3,39	17,50	$C_4H_6O_2SCl_2$	25,51	3,21	17,00
XIX[10]	$N(CH_3)_2$	–50	1/2	SO_2Cl_2/CH_2Cl_2	100	—	1,5500	30,96	4,77	15,92	$C_5H_9OSCl_2N$	30,48	4,48	15,85

1. Bp 42° (3mm); n_D^{20} 1.5250 [1]. NMR spectrum of (VI), 3.46 ppm (singlet) (CH_2CH_2).
2. 0.05 mole of (I) in 10 ml of CH_2Cl_2.
3. Mp 154 - 155° [2].
4. Together with 23% of (V); prior to distillation the ratio of (V) and (VIII) in the mixture was 46 and 54% (based on the NMR data). The NMR spectra of (V) and (VIII) agree with those given in [3].
5. Bp 118 - 120° (10^{-4} mm) [3].
6. NMR spectrum of (XI) (δ, ppm) : 3.28 (multiplet) (CH_2); 3.77 (singlet) (OCH_3); 5.79 (triplet) with J 6.67 Hz (CH).
7. d_4^{20} 1.6103; found MR 37.39; calculated 37,68. NMR spectrum (δ, ppm) : octet of CH_2 group (AB part of ABX system), δ_A 3.52, δ_B 3.78, J_{AB} 13.35, J_{AX} 3.33, J_{BX} 4.34 Hz; 4.96 (triplet) with J 6.68 Hz (CH).
8. NMR spectrum (δ, ppm) : 3.76 (multiplet) (CH_2); 4.96 (triplet) with J 6.68 Hz (CH).
9. NMR spectrum (δ, ppm) : 3.59 (multiplet) (CH_2); 4.52 (triplet) with J 7.2 Hz (CH); 3.79 (singlet) (OCH_3).
10. NMR spectrum (δ, ppm) : 2.68 (doublet) with J 10.66 Hz ($N(CH_3)_2$); 3.76 (multiplet) (CH_2); 4.41 (multiplet) (CH).

EXPERIMENTAL

All of the experiments were run in a nitrogen atmosphere using absolute solvents. The NMR spectra were taken on a Perkin–Elmer R-12 instrument (60 MHz), using HMDS as the internal standard.

Acid Chloride of 1-Chloro-2-(acetylthio)propionic Acid (XIII). To 22.65 g of 1-chloro-2-(acetylthio)-propionic acid (XII) was added 25.90 g of PCl_5 in small portions. Fractional distillation gave 19.85 g (81%) of (XIII), bp 78° (2 mm); n_D^{20} 1.5105; d_4^{20} 1.413. NMR spectrum (δ, ppm): 2.41 (singlet) ($COCH_3$); 3.46 (doublet) with J 7.1 Hz ($(CH_2)_2$); 4.55 (triplet) with J 7.1 Hz (CH). Found: C 30.55; H 3.14; S 16.36; Cl 35.40%; MR 42.60. $C_5H_6O_2SCl_2$. Calculated: C 29.90; H 2.99; S 15.99; Cl 35.29%; MR 43.01.

Acid Chloride of 2-(Acetylthio)propionic Acid (III). In a similar manner, (III) was obtained in 70% yield from PCl_5 and 2-(acetylthio)propionic acid (I), bp 61-62° (2 mm); n_D^{20} 1.4984; d_4^{20} 1.264. NMR spectrum: 2.36 (singlet) ($COCH_3$); 3.19 ppm (multiplet) (CH_2CH_2). Found: C 36.08; H 4.04; S 19.17; Cl 21.21%; MR 36.36. $C_5H_7O_2SCl$. Calculated: C 36.21; H 4.24; S 19.20; Cl 21.32%; MR 38.15.

The chlorination was run with an equimolar ratio of the reactants in a solvent (CCl_4, CH_2Cl_2), or without a solvent. At the end of reaction the solvent was distilled off, and the residue was fractionally distilled (see Table 1).

4-Chloro-1,2-dithiolan-3-one (XX). To 3 ml of liquid H_2S at −78° was added in drops a solution of 4.48 g of the acid chloride of 1-chloro-2-chlorosulfenylpropionic acid (XVI) in 50 ml of CH_2Cl_2, cooled to −60°. The orange color disappeared. The temperature of the mixture was brought up to room temperature and then the mixture was fractionally distilled. We obtained 1.6 g (45%) of (XX), bp 78° (3 mm); n_D^{20} 1.6343; ν_{CO} 1710 cm^{-1}. NMR spectrum: 3.50 (multiplet) (CH_2) and 4.65 ppm (multiplet) (CH). Found: C 23.41; H 2.01; S 39.98; Cl 22.72%. $C_3H_3OS_2Cl$. Calculated: C 23.28; H 1.94; S 41.38; Cl 22.99%.

1,1-Dithiolan-3-one (XXI). In a similar manner, from the acid chloride of 2-chlorosulfenylpropionic acid (VI) was obtained (XXI) as a yellow oily substance, which readily polymerized when stored or distilled: ν_{CO} 1720 cm^{-1}. NMR spectrum: multiplet of AA'BB' system with $\delta_1(CH_2)$ 2.83 ppm, $\delta_2(CH_2)$ 3.33 ppm, and $J_{1,2}$ 6 Hz. Found: C 29.58; H 3.32; S 51.96%. $C_3H_4OS_2$. Calculated: C 29.97; H 3.35; S 53.35%.

CONCLUSIONS

1. A new method was found for the preparation of 2-chlorosulfenylcarboxylic acids by the chlorination of 2-(acetylthio)carboxylic acids and their derivatives.

2. The stability of the S-acetyl bond is determined by the electron-acceptor effect of the substituents.

3. 1,2-Dithiolan-3-one and 4-chloro-1,2-thiolan-3-one were obtained.

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