SULFUR-CONTAINING HETEROCYCLES

7.* NEW METHOD FOR PREPARATION OF 1,2-DITHIOLAN-3-ONES

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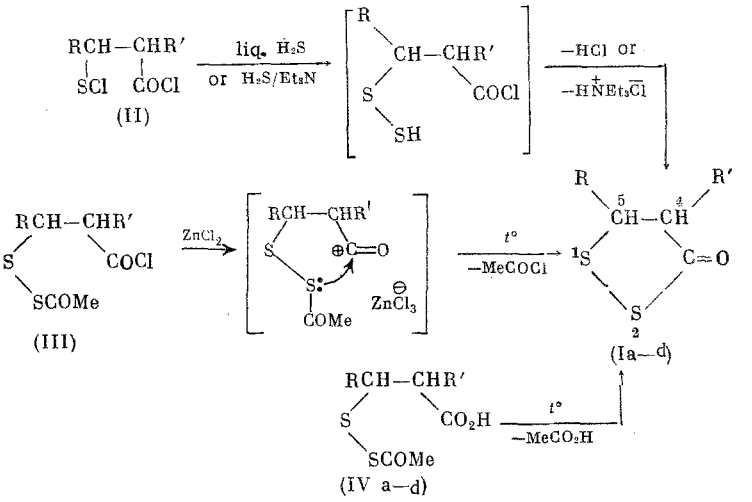
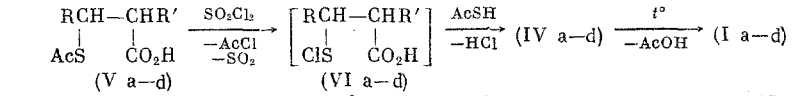
The new heterocyclic compounds, namely 1,2-dithiolan-3-ones (I), were obtained by us previously either by the condensation of the corresponding acid chlorides of β-chlorosulfenylcarboxylic acids (II) with H_2S [2, 3] or by the cyclization of the acid chlorides of β-acetyldithiocarboxylic acids (III) in the presence of catalytic amounts of $ZnCl_2$ [4, 5]. A new synthesis of (Ia-d) by the thermal cyclization of β-acetyldithiocarboxylic acids (IVa-d) is described in the present communication:



R=R'=H (a); R=H, R'=Me (b); R=H, R'=Cl (c); R=Me, R'=H (d).

The previously unknown (IV) acids (with the exception of α-chloro-β-acetyldithiopropionic acid (IVc) [6]) were obtained by us from β-acetylthiocarboxylic acids (Va-d) by chlorination with SO_2Cl_2 and subsequent treatment of the intermediately formed sulfenyl chlorides (VIa-d)† with thiolacetic acid. The (IV) acids were used as such for the cyclization.



R = R' = H (a); R = H, R' = Me (b); R = H, R' = Cl (c); R = Me, R' = H (d).

The analytically pure (IV) and (VI) could not be isolated. The structure of these compounds was confirmed by the IR and PMR spectra (Table 1). The instability of (IV) is explained not only by its tendency to cyclize, but also to symmetrize (see below). The (IV) acids when stored at ~ 20°C, and especially when heated, easily lose HCl, apparently due to intramolecular cyclization to the unstable mixed anhydrides.

* See [1] for Communication 6.

† The chlorination of the unsubstituted acid (Va) gave, besides sulfenyl chloride (VIa), also β, β'-dithiodipropionic acid (VIIa) as a by-product.

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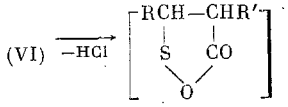
TABLE 1. Infrared and PMR Spectra of Some β-Acetyldithio- (IV) and β-Chlorosulfenylcarboxylic Acids (VI)

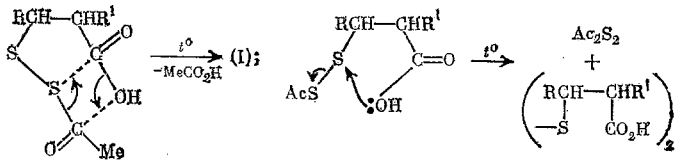
Compound	ν CO, cm^{-1}	δ, ppm, J, Hz			
		CH_2CH_2	Me	MeCOS	CO_2H
(IVa)	1715 (CO_2H) 1732(COS)	2,83–3,61 m	–	2,63 s * 2,7 s	12,3 s
(IVb)	–	$CHCH_2$ 2,81–3,61 m	1,49 d J_{Me-CH}=6	2,63 s * 2,69 s	12,6 s
(IVc)	–	CH_2 2,37–2,9 m CH 2,9–3,8 m	1,6 distorted d J_{Me-CH}=6,6	2,2 s* 2,6 s	12.1 s
(VIa)	1715	2,7–3,6 m	–	–	11.45s
(VIb)	1715	2,45–4,0 m	1,3 d J_{Me-CH}=7	–	12.0 s

*The two MeCOS signals (~ 1:1) belong to the rotational isomers caused by the hindered rotation around the S–S bond [7].



It should be mentioned that the cyclization of the β-(acetyldithio)carboxylic acids (IV) is always accompanied by a secondary symmetrization reaction, with the formation of diacetyl disulfide and the disulfide of the corresponding β-mercaptocarboxylic acid (VII). When isolation is by distillation the latter remains in the still, while the mixture of the diacetyl disulfide and (I) products is then separated by fractional distillation.

Either photochemical, thermal, or catalytic symmetrization has been widely studied for the unsymmetrical dialkyl disulfides [8-10]. Alkyl(acyl) disulfides are much more stable toward symmetrization [11, 12]. The 2-(acetamidoethyl)acetyl and benzoyl disulfides undergo partial disproportion only under drastic conditions [12]. Symmetrization was not observed for the esters [6] and acid chlorides [6, 8] of β-(acetyldithio)carboxylic acids. For the β-(acetyldithio)carboxylic acids (IV) themselves both the cyclization to (I) and symmetrization are apparently facilitated by the coaction of the CO_2H group and the possibility of forming five-membered rings.



(IV) (IV) (VII)

It is known that the easy symmetrization of o-(phenyldithio)benzoic acid, and especially of its Na salt, is caused by the anchimeric involvement of the CO_2H group [9]. The yields of the cyclization products (I) are much higher than of the symmetrization products (Ac_2S_2, Table 2). We did not run special studies on the symmetrization, although from the results given in [9] it follows that the symmetrization of (IV) can be suppressed by varying the reaction conditions, which naturally would permit obtaining the 1,2-dithiolan-3-ones (I) in higher yields.

EXPERIMENTAL

The PMR spectra were taken on a Perkin–Elmer R-12 spectrometer (60 MHz) in CCl_4 solution using HMDS as the external standard. The chlorination of the β-(acetylthio)carboxylic acids (Va-d), treatment of the reaction mixture with thiolacetic acid, and the cyclization to (Ia-d) are best run during the same day and using absolute solvents.

TABLE 2. Properties of 1,2-Dithiolan-3-ones (I)* and Yield of Diacetyl Disulfide during Cyclization of (IV)

Compound	R	R′	yield, %	mp, °C (p, mm Hg)	$n^{20}D$	ν, cm^{-1}		Yield of $(MeCOS)_2$, %
						CO	S—S	
(Ia)	H	H	45	60(1)	1.5961	1710	578,610	35
(Ib)	H	Me	67	75(5)	1.5741	1715	565.600	20
(Ic)	H	Cl	63	84(4)	1.6180	1710	550, 600	27
(Id)†	Me	H	78	75(7)	1.5778	1720	535,595	17

* Cf. [5] for (Ia-d).

† Found: C 36.13; H 4.43; S 46.80%. $C_4H_6OS_2$. Calculated: C 35.82; H 4.47; S 47.50%.

General Procedure for Obtaining 1,2-Dithiolan-3-ones (Ib-d). To 0.4 mole of the β-(acetylthio)carboxylic acid (Vb, c*, d) in 80 ml of CCl_4 at 20° was added 0.45 mole of SO_2Cl_2; after 1.5 h the solvent and acetyl chloride were removed in vacuo (20-30° at 10 mm). To the residue [sulfenyl chlorides (VIb-d)] at 0° was added 0.5 mole of thiolacetic acid, and after 1 h the excess AcSH was removed in vacuo (40° at 2 mm). The residue in the still, namely the β-(acetyldithio)carboxylic acid (IVb-d), was heated at 140-200° (in the bath) in a vacuum of 2 mm. The collected distillate was carefully fractionally distilled. The yields of (Ib-d) and Ac_2S_2, and the constants and IR spectral data for (Ib-d) are given in Table 2. The IR and PMR spectral data for (IVb, d) and (VIb) are given in Table 1.

Preparation of Unsubstituted 1,2-Dithiolan-3-one. A solution of 0.1 mole of (Va) in 40 ml of CH_2Cl_2 was added to 0.1 mole of SO_2Cl_2 at 35-40°, and here disulfide (VIIa) was obtained as a white precipitate. After 0.5 h the (VIIa) was filtered and washed with CH_2Cl_2. β, β'-Dithiodipropionic acid (VIIa) is soluble in alcohol or acetone, and also in hot water or ethyl acetate. The yield of (VIIa) was 32%, mp 156-157° (cf. [13]). Infrared spectrum (KBr, ν, cm^{-1}): 530 (S—S), 1700 (CO_2H), 2500-3100 (OH). PMR spectrum (in acetone, δ, ppm): 2.7-3.4 m (CH_2CH_2), 4.91 s (CO_2H). Found: C 34.28; H 4.92; S 31.55%; neutralization equiv. (NaOH) 106; mol. wt. 220 (ebullioscopically in alcohol). $C_6H_{10}O_4S_2$. Calculated: C 34.30; H 4.77; S 30.55%; neutralization equiv. 105, mol. wt. 210.

If a temperature of 10-20° is used and the reactants are mixed in the reverse order the yield of by-product (VIIa) can reach ~ 90%.

The filtrate from (VIIa) was evaporated at 40° (10 mm), and the residue [sulfenyl chloride (VIa)] was treated at 0° with 0.1 mole of thiolacetic acid. Acid (IVa) was obtained as a syrup, n_D^{20} 1.5500, and neutralization equiv. 170 (calcd. 180). The cyclization of (IVa) was run the same as described above for (IVb-d). The yields of (Ia) and Ac_2S_2, and the constants of IR spectral data for (Ia) are given in Table 2. See Table 1 for the IR and PMR spectra of (IVa) and (VIa).

For diacetyl disulfide, bp 70° (3 mm), n_D^{20} 1.5390; ν CO 1750 cm^{-1}; δ, ppm: 2.5 s (Me).

CONCLUSIONS

1. A new method was found for the preparation of 1,2-dithiolan-3-ones by the cyclization of β-(acetyldithio)carboxylic acids.

2. β-(Acetyldithio)carboxylic acids when heated undergo disproportionation to give symmetrical disulfides.

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* Compound (VIc) was obtained by heating (Vc) with SO_2Cl_2 (1:1, 24 h at 60°) in the minimum amount of CCl_4 and subsequent distillation [2].

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BECKMANN – CHAPMAN REARRANGEMENT OF 2,2,6,6-TETRAMETHYL-4-OXIMINOPIPERIDINE-1-OXYL TO 2,2,7,7-TETRAMETHYL-5-OXOHEXAHYDRO-1,4-DIAZEPINE-1-OXYL

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The potential paramagnetic monomer 2,2,7,7-tetramethyl-5-oxohexahydro-1,4-diazepine-1-oxyl (I) is a structural analog of caprolactam. The first attempts to obtain (I) [1-3] encountered a number of difficulties, associated with low yields and a nonreproducibility of the results.

In recent years the problem of synthesizing (I) became even more important in connection with developing a commercial method for the production of triacetoneamine from acetone and ammonia [4]. Apparently, it can be assumed that the most convenient method for converting triacetoneamine to (I) is the Beckmann–Chapman [6] rearrangement of 2,2,6,6-tetramethyl-4-oxopiperidine-1-oxyl oxime [5].

While studying this reaction we found that the stable nitroxyl radical (II), which represents the p-toluenesulfonyl ester of the oxime, is spontaneously converted in the presence of Al_2O_3 to the stable (I) radical even at ~20°C.

In our opinion, the rearrangement of radical (II) includes the intermediate formation of the paramagnetic tosylamide (IV), since the latter is formed from tosylate oxime (II) when it is chromatographed on silica gel. In addition, compound (I) is gradually transformed to tosylamide (IV) even when it is stored at ~20°. In contrast to its diamagnetic analog (VI) and its salt (VII), radical (IV) is comparatively stable in alkaline medium.

The tosylation of triacetoneamine gives the ditosyl derivative (III), which in refluxing methanol is rearranged to tosylamide p-toluenesulfonate (VII): In contrast to the paramagnetic analog (IV), compound (VII) is easily hydrolyzed by aqueous $NaHCO_3$ solution to the corresponding diamagnetic caprolactam analog (V). The same compound can be easily obtained from (VI) by hydrolysis on Al_2O_3.

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