SULFUR-CONTAINING HETEROCYCLES.

COMMUNICATION 10.\* SYNTHESIS OF MIXED ANHYDRIDES OF SULFONIC AND CARBOXYLIC ACIDS

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In a previous communication without detailed description [2], we reported the synthesis of the first representative of a new class of heterocyclic compounds, 3-methyl-1,2-oxathiolan-5-one-2-oxide by the reaction of the disodium salt of  $\beta$ -(oxysulfinyl) butyric acid with oxalyl chloride. In the present work, the same method was used to obtain new representatives of such anhydrides. The starting disodium salts (I)-(IV) were obtained as mixtures with NaCl by the saponification of the corresponding acid chlorides of  $\beta$ -(chlorosulfinyl)alkanoic acids (V)-(VIII) by NaHCO3

> $\begin{array}{c|cccccccc} R & R^{1} & R & R^{1} \\ \hline CH-CH & 4NaHCO_{3} \\ SOCI & COCI \\ (V)-(VIII) & COCNa \\ (V)-(VIII) & (1)-(IV) \end{array}$  $R = R^{1} = H(I), (V); R = Me, R^{1} = H(II), (VI); R = H, R^{1} = Me$  (III), (VII); RCCR = benzo-(IV) (VIII)

Salt (IV) was obtained both as the bis(acid chloride) (VIII) (as a mixture with NaCl) and in pure form from o-sulfinobenzoic acid and NaHCO3. Removal of the water of crystallization from sodium salts (I)-(IV) was accomplished by prolonged drying in vacuum over  $P_2O_5$ . Disodium salts (I)-(IV) are stable and remain unchanged upon storage. The composition of the mixtures of (I)-(IV) + 2NaCl was monitored by oxidimetric titration and determination of the halide ion content. The IR spectra of all the salts show a strong v(S=0) band as a characteristic triplet at 965-1050  $\text{cm}^{-1}$ .

Sulfinate (I) was converted to bis (acid chloride) (V) by heating with excess  $SOCl_2$  at reflux [3] (but does not react with one equivalent of SOCl<sub>2</sub> in a solvent). We should have expected that the reaction of disodium salts (I)-(IV) with an equimolar amount of a more active chlorinating agent would lead to the formation of a mono(acid chloride) which would readily cyclize to mixed anhydrides (IX)-(XII). However, the difference in the reactivities of the  $SO_2Na$  and  $CO_2Na$  functional groups in (I)-(IV) proved to be slight. Thus, POCl<sub>3</sub> and PCl, give an irresolvable mixture of small quantities of bis(acid chlorides) and anhydrides, for example,

> M П

One of the methods for the preparation of acid chlorides of carboxylic acids is the reaction of RCO<sub>2</sub>Na with oxalyl chloride [4]. Representatives of a new compound class, internal anhydrides of  $\beta$ -sulfinalkanoic acids (IX)-(XI), were obtained only by the reaction of disodium salts (I)-(IV) with one equivalent of oxalyl chloride. The yields and physical constants of these compounds are given in Table 2. \*For Communication 9, see [1]. *†Deceased.* 

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$$e - CHCH_2COONa \xrightarrow{PCl_s} OS \xrightarrow{CO + Me - CHCH_2COC} OS \xrightarrow{O} SO2Na (II) (X), ~~30\% (VI), 10-15\%$$

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Com- pound	Yield, %	Cl ion content, % (found*'/ calculated)	IR spectrum	O xidimetric equi	
			COONa	SCONa	calculated)
(I)	99	21,1/23,8	1575–1615, 1400–1430	985-1050	144/149
(11)	100	21,0/22,7	1570–1590, 1415–1437	998-1040	157/156,5
(III)	95	21,5/22,7	1570–1600, 1410–1435	990-1035	<b>1</b> 55/156, <b>5</b>
(IV)	95	18,3/20,4	1575–1600, 1390–1415	965-1040	175/183

TABLE 1. Characteristics of Mixtures (I)-(III), (VII) + 2NaCl Obtained from Di(Acid Chlorides) (IV)-(VI), (VIII)

\*Volhard procedure.

+Titration with  $KMnO_4$ ; calculation equivalent = (M + 117)/2.



 $R = R^{1} = H$  (IX); R = Me,  $R^{1} = H$  (X); R = H,  $R^{1} - Me$  (XI).

The only cyclic anhydride mixed anhydride differing from (IX)-(XI) by the presence of a double bond in the ring, namely, (XII), was obtained by Walter et al. [5, 6] by the oxidation of 2,1-benzoxathiol-3-one-7-carboxylic acid (XIII). However, this method did not give the unsubstituted anhydride of o-sulfinobenzoic acid (XIV) since only sulfene anhydrides such as (XIII), in which the sulfur atom is coordinated with the carbonyl oxygen atom of the  $CO_2H$  group, are stable [5-7].



Anhydride (XIV) was obtained in crystalline form with mp 82°C by reaction (1). Aliphatic  $\beta$ or  $\alpha$ -methyl-substituted anhydrides (X) and (XI) are liquids which distill invacuum. Unsubstituted anhydride (IX) is an unstable crystalline compound with mp 49-52°C, which is converted to a polymer insoluble in CH<sub>2</sub>Cl<sub>2</sub> upon standing for 1-2 days or attempts to perform vacuum distillation at 0.4 mm.

Chiang et al. [8] have reported that the chlorination of  $\beta$ , $\beta$ '-dithiodipropionic acid by a less than equivalent amount of chlorine gives anhydride (IX) with mp 148-150°C. Later, Kasperek [9] proved that the compound described by Chiang [8] as anhydride (IX) was thiosulfonate (XV) with mp 157-159°C



Compound	Yield,	Mp, °C, bp, °C (p, mm Hg)	Found, calculated, %			Chemical
			C	н	s	tormula
os O (IX)	63	49-52 (CHCl <sub>3</sub> - petr.ether)	30,23 30,00	3,40 3,33	26,21	C₃H <b>₄O₃S</b>
$ \underbrace{OS}_{O}^{Me} CO (X) $	59	54-56 (0,4) $n_D^{21}$ 1,4933	<u>35,59</u> 35,75	<u>4,46</u> 4,48	24,78 23,92	C4H6O3S
$OS \bigcirc CO (XI)$	64	60-64 (0,5) $n_D^{26} 1,4930 *$	35,24 35,75	<u>4,55</u> 4,48	24,04 23,92	C₄H₅O₃S
	70 †	82 (CHCl <sub>3</sub> – petr.ether (or benzene)	49,73 50,00	2,54 2,38	<u>19,16</u> 19,04	C7H4O3S

TABLE 2. Physicochemical Constants and Elemental Analysis Data for Anhydrides (IX)-(XI) and (XIV)

\*Crystallizes upon standing in the cold. †The yield of (XIV) from the pure disodium salt (IV); the yield of (XIV) from the salt obtained through acid chloride (VIII) and containing NaCl was 57%.

In the present work, we obtained the first representative of a homologous series of cyclic mixed anhydrides (IX), homologs (X) and (XI), and the condensed compound (XIV). Sulfinic anhydrides (IX)-(XI) and (XIV), similar to previously reported cyclic mixed anhydrides of  $\beta$ -sulfocarboxylic acids (XVI) [10, 11] and (XVII) [11]



are labile compounds which are readily hydrolyzed by water. Anhydrides (IX)-(XI) and (XIV) may be isolated only in the complete absence of moisture. The corresponding  $\beta$ -sulfinocarboxylic acids are obtained in the presence of moisture.

The IR and PMR spectra and acidimetric titration data for (IX)-(XI) and (XIV) are given in Table 3. The neutralization equivalent (NaOH) and oxidimetric equivalent (with KMnO<sub>4</sub>) of the anhydrides is equal to one-half of the molecular weight.

The IR spectra of aliphatic anhydrides (IX)-(XI) have the v(C=0) band at 1807-1812 cm<sup>-1</sup> while this band is found at 1785 cm<sup>-1</sup> in the spectra of o-sulfinobenzoic acid (XIV). The sulfinic group of anhydrides (IX)-(XI) and (XIV) is seen as two bands at 1105-1130 and 1150-1165 cm<sup>-1</sup>. A comparison of the IR spectra of (IX)-(XI) and (XIV) shows that the C=0 group in (XIV) is conjugated with the benzene ring  $\pi$ -system, in constrast to the S=0 group. This also holds for the case of o-(chlorosulfiny1)benzoic acid (VIII) [3].

The sulfinyl group has a pyramidal configuration. Thus, many sulfinic acid derivatives exist in an optically active form [12]. PMR spectroscopy indicates that 4-methyl-1,2-oxa-thiolan-5-one-2-oxide (XI) is a mixture of trans-(XIa) and cis-(XIb) stereoisomers in 6.4:1 ratio.

The downfield methyl group doublet at 1.74 ppm with the greater coupling constant J = 7.3 Hz was assigned to isomer (XIb), in which the methyl group is close to the positively polarized SO group oxygen atom. In 3-methyl-1,2-oxathiolan-5-one-2-oxide (X), the even greater approximation of these groups makes the cis-isomer energetically unfavorable and this compound apparently exists only in the trans form with  $\delta$  Me 1.43 ppm (d), J<sub>Me-CH</sub> = 6.7 Hz.

TABLE 3. Some Parameters of the IR ( $\nu$ , cm<sup>-1</sup>), PMR ( $\nu$ , ppm, J, Hz), and Mass Spectra and NaOH or KMnO<sub>4</sub> Titration Data for Anhydrides (IX)-(XI) and (XIV)

Com-		IR spectrum		Equivalent, found/calculated	
pound	PMR spectrum	<b>C=</b> 0	S=0	NaOH neutra- lization	Oxidimetric titration with KMnO <sub>4</sub>
(IX) a	1,92–2,33 <sub>m</sub> (CH <sub>2</sub> C), 2,57–3,12 m (CH <sub>2</sub> S)	1812 b	1105b 1165b	<u>-61</u> 60	<u>62</u> 60
(X)	1,43 d(Me), J <sub>CH3-CH</sub> =6.7, 2,39-4,08 m (CHCH <sub>2</sub> )	1812	1110. 1163	<u>68</u> 67	<u>-70</u> 67
(XI)	1,54 d(Me), J <sub>CII,−CH</sub> =6,7 (84%) <sup>C</sup> , 1.74d (CH <sub>3</sub> ), J <sub>CII,−CH</sub> =7,3 (16%) <sup>c</sup> 2.89−3,93 m (CHCH <sub>2</sub> )	1807	1130 1157	<u>68.4</u> 67	-
(XIV)	in DMSO 7.65-8.2 $m(C_6H_4)$	1785	1125. 1150	<u>-84.6</u> 84,0	<u>-77</u> 
a <sub>Mass</sub>	$\frac{1}{120}$	+ 60%	10/1		e1 +

<sup>A</sup>Mass-spectrum: 120(M ' [C<sub>3</sub>H<sub>4</sub>O<sub>3</sub>S] ', 68%), 104([C<sub>3</sub>H<sub>4</sub>O<sub>2</sub>S] ', 32.9%), 76([C<sub>2</sub>H<sub>4</sub>OS] +, 2.1%), 64([O<sub>2</sub>S] +, 11%), 56([C<sub>2</sub>H<sub>4</sub>CO] +, 53.9%), 48([OS] +, 6.6%); 44([CO<sub>2</sub>] ?, 6.6%), 28([C<sub>2</sub>H<sub>4</sub>] +, [CO] +, 100%). <sup>b</sup>In CH<sub>2</sub>Cl<sub>2</sub>.

<sup>C</sup>Mixture of stereoisomers.



 $\delta CH_3$  1,54 a  $J_{CH_3-CH} = 6,7$  Hz (XIa),  $\delta CH_3$  1,74 d,  $J_{CH_3-CH} = 7,3$  Hz) (XIb)

The electron-impact fragmentation of 1,2-oxathiolan-5-one-2-oxide (IX) occurs largely with breakage of the 0- CO bond

 $OS \xrightarrow{} CO \begin{bmatrix} \bullet \\ \bullet \end{bmatrix} \xrightarrow{} OS \xrightarrow{} O \begin{bmatrix} \bullet \\ \bullet \end{bmatrix} \xrightarrow{} OS \xrightarrow{} OS$ 

We are continuing the study of the properties of internal anhydrides (IX)-(XII).

## EXPERIMENTAL

The PMR spectra were taken on a Perkin-Elmer R-12 spectrometer at 60 MHz in  $CH_2Cl_2$  (if another solvent is not specifically indicated) relative to internal or external HMDS. The IR spectra were taken either neat or in KBr pellets. The mass spectra were taken on a Varian CH-8 spectrometer. All the reactions were carried out in absolute solvents.

Oxidimetric titration of the sulfinic compounds was carried out as follows. An excess ( $\sim$  30 ml) of 0.1 N KMnO<sub>4</sub> was added to a weighed sample (50-100 mg) of salt (I)-(IV) in water or anhydride (IX)-(XII) neutralized with alkali. After 5-10 min, the mixture was acidified with 10 ml 5 N H<sub>2</sub>SO<sub>4</sub> and 10 ml 10% aqueous KI was added. The I<sub>2</sub> liberated was titrated with 0.1 N Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub>.

Synthesis of the Disodium Salts of  $\beta$ -(Oxysulfinyl)alkanoic Acids (I)-(III). A sample of 0.22 mole bis(acid chloride) (V)-(VII) [3] was added with stirring to a suspension of 73.9 g (0.88 mole) NaHCO<sub>3</sub> in 140 ml water. At the completion of the reaction (pH  $\ge$  7), the suspended traces of NaHCO<sub>3</sub> were filtered off. The aqueous solution was evaporated in vacuum. The residue was dried twice by distillation with benzene and then in a vacuum dessicator over P<sub>2</sub>O<sub>5</sub> or alkali to constant weight (attained in 2-7 days).

The yields of (I)-(III) (in mixtures with double equivalent amount of NaCl), chloride ion content, KMnO<sub>4</sub> oxidimetric titration data, and the IR spectra are given in Table 1. Salts (I)-(III) are soluble in water and insoluble in ethanol. The disodium salt of o-(oxysulfinyl)benzoic acid (IV) was obtained: a) from bis(acid chloride) (VIII) similarly to (I)-(III) or b) from o-(oxysulfinyl)benzoic acid prepared according to Price and Smiles [13] [mp114°C, IR spectrum ( $\nu$ , cm<sup>-1</sup>): 1695 (C=0) 1030, 1125 (S=0), 2500-3200 (OH)] and NaHCO<sub>3</sub>. The yield of (IV) was 91%. The IR spectral data are identical to those given in Table 1.

Attempts to Obtain Cyclic Anhydrides (IX) and (X). a) A mixture of 0.061 mole salt (I) (containing a double equivalent amount of NaCl) and 0.1 mole SOCl<sub>2</sub> in 15 ml benzene was heated at reflux for 2 h. Upon cooling, 0.061 mole of starting (I) (containing a double equivalent amount of NaCl) was filtered off.

b) A sample of 0.0225 mole POCl, was added to a suspension of 0.045 mole sale (II) (containing a double equivalent amount of NaCl) in 40 ml benzene and the mixture as heated at reflux for 1.5 h. After filtration of the precipitate, the mother liquor was evaporated and the residue was distilled in vacuum (0.4 mm). The distillate obtained a mixture of anhydride (X) in 30% yield and di(acid chloride) (VI) in 10% yield as indicated by IR and PMR spectroscopy and analysis for chloride in the sample.

c) Analogously, 0.0455 mole (II) (containing a double equivalent amount of NaCl) and 0.0455 mole PCl<sub>5</sub> in 50 ml CH<sub>2</sub>Cl<sub>2</sub> were maintained for 2 h at 20°C to give a distillate which contained a mixture of (X) in 30% yield and (VI) in 15% yield as indicated by IR and PMR spectroscopy and analysis for chloride in the sample.

<u>General Method for the Preparation of 1,2-Oxathiolan-5-one-2-oxides (IX)-(XI)</u>. A sample of 0.050 mole of thoroughly ground disodium salt (I)-(III) containing 5.85 g (0.1 mole) NaCl was added in small portions to a vigorously stirred solution of 6.35 g (0.050 mole) freshly distilled oxalyl chloride in 40-60 ml benzene. Vigorous evolution of CO and CO<sub>2</sub> was noted. At the end of the exothermal reaction, the mixture was heated at reflux with periodic stirring for 1-1.5 h and then cooled to 20°C. The precipitate (11.7 g) which was a mixture of 0.2 mole NaCl and unreacted starting (I)-(III) was rapidly filtered. The mother liquor was evaporated in vacuum. The residue gave a negative test for halide. NaOH and KMnO<sub>4</sub> titration, mp and  $n_D^{20}$  data, and IR and PMR spectroscopy indicated that the residue is rather pure anhydride (IX)-(XI) in 65-80% yield. Then, the residue was distilled in vacuum or crystallized. The yields of (IX)-(XI) after purification, elemental analysis, and physicochemical constants are given in Table 2. The IR and PMR spectral data and NaOH and KMnO<sub>4</sub> titration results are given in Table 3.

Anhydrides (IX)-(XI) are insoluble in hexane and cyclohexane, have low solubility in CCl<sub>4</sub>, but are highly soluble in  $CH_2Cl_2$ , chloroform, benzene, and ether. These products react with water with dissolution (pH  $\sim$  1).

 $\frac{2,1-\text{Benzoxathiol-3-one-1-oxide (XIV).}{\text{ This product was obtained analogously from either a sample of 14.77 g (0.064 mole) pure sulfinate (IV) or a sulfinate sample containing NaCl in 40 ml benzene and 8.18 g (0.064 mole) oxalyl chloride. The yield of (XIV) was 7.6 g (70%). The product was obtained after crystallization from benzene with mp 76°C. After reprecipitation by petroleum ether and crystallization from chloroform solution, a sample was obtained with mp 82°C. The elemental analysis and spectral data for (XIV) are given in Tables 2 and 3.$ 

## CONCLUSIONS

A general method was developed for the preparation of previously unreported anhydrides of  $\beta$ -sulfinocarboxylic acids, namely, 1,2-oxathiolan-5-one-2-oxides and 2,1-benzoxathiol-3one-1-oxide (XIV) by the action of disodium salts of  $\beta$ -oxysulfinylcarboxylic acids with oxalyl chloride.

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SALT FORMATION BY REACTION OF FLUORINE-CONTAINING **B-DIKETONES WITH AMINES** 

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On heating unsymmetrical polyfluorinated  $\beta$ -diketones with NH<sub>3</sub> and with amines condensation occurs on one of the carbonyl groups with the formation of  $\beta$ -aminovinylketones [1, 2]. In [3, 4] in the condensation of  $\beta$ -diketones with N-nucleophiles the recorded condensation intermediates derived from PMR were the geminal hydroxyamines (II), (III).

Fluoroalkyl substituents stabilize geminal adducts of carbonyl compounds with nucleophiles [5]. For that reason we undertook the task of isolating adducts of polyfluorinated B-diketones (Ia-g) with ammonia and with amines. However, it appears that  $\beta$ -diketones (Ia-g) with NH3, methylamine, and dimethylamine at 10-20°C do not form adducts (II) or (III) but salts (IV) (see Table 1). We verified this by chemical methods and by PMR spectra

> $R_{\mathbf{F}} = HCF_{2}^{\circ}(\mathbf{a}); C_{2}F_{5}(\mathbf{b}); H(CF_{2})_{2}(\mathbf{c}-\mathbf{e}, \mathbf{g}); H(CF_{2})_{4}(\mathbf{f}); R^{1} = Me(\mathbf{a}-\mathbf{c}, \mathbf{f}); Bu(\mathbf{d});$ t - Bu (e);  $H(CF_2)_2$  (g).

The condition for the formation of stable salts (IV) is an adequate difference between the acid-base properties of the  $\beta$ -diketone and the amine. Thus acetylacetone (pK<sub>a</sub> = 9.05 ± 0.04 [6]) does not form a stable ammonium salt. The same thing was observed in the reaction between aniline and unsymmetrical polyfluorinated  $\beta$ -diketones (Ia-f) (pK<sub>a</sub> = 6.61-4.70 [6]), although for the symmetrical  $\beta$ -diketone (Ig) (pKa = 2.43 ± 0.073 [6]) we obtained a stable salt (IVk).

The reactions of compounds (IVa-k) with copper (II) acetate at  $\sim$  20°C yield the Cu(II)  $\beta$ -diketone salts. With dry HCl the corresponding  $\beta$ -diketones and amine hydrochlorides are formed in quantitative yields



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