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SULFUR HETEROCYCLES.

12.* REACTIONS OF CYCLIC ANHYDRIDES OF β-SULFINOCARBOXYLIC ACIDS WITH NUCLEOPHILES

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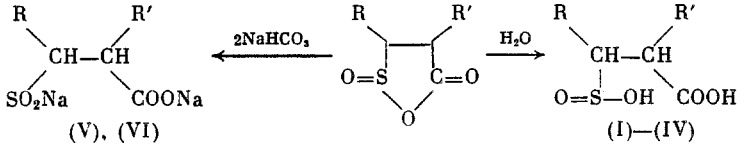
We have recently [2] reported the synthesis of a new class of heterocyclic compounds, namely the internal anhydrides of β-sulfinoalkanoic and o-sulfinobenzoic acids. We here report an examination of the chemical properties of these compounds.

It has been found that both the aliphatic and aromatic mixed anhydrides are hydrolytically unstable, and in air or moist ether they are converted into the sulfinic acids (I)-(IV), which readily disproportionate [3-5]. Treatment of the anhydrides with sodium bicarbonate gives the more stable bis-sodium salts of β-(hydroxysulfinyl)carboxylic acids (V) and (VI).

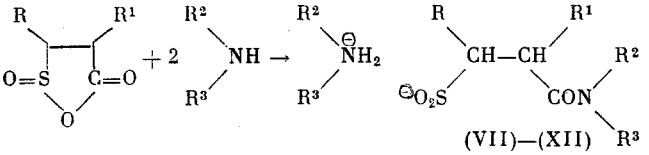


(V), (VI) (I)—(IV)

R = R′ = H(I); R = H, R′ = Me(II), (V); R = Me, R′ = H(III), (VI); RCCR′ = benzo (IV)

These same salts (V) and (VI) have been obtained previously from β-sulfinocarboxylic bis-acid chlorides and sodium bicarbonate, but in admixture with sodium chloride [2].

Aminolysis of the aliphatic anhydrides with primary or secondary amines proceeds exothermically with cleavage of the O-acyl bond to give β-hydroxysulfinylalkanoic acid amides as salts with the amine at the sulfinyl group (Table 1).



(VII)—(XII)

R = R¹ = H, R² = R³ = Et(VII); R = Me, R¹ = H, R² = R³ = Et(VIII); R = R² = H, R¹ = Me, R³ = $PhCH_2$(IX); R = Me, R¹ = R² = H, R³ = $PhCH_2$(X); R = R² = H, R¹ = Me, R³ = Ph(XI); R = Me, R¹ = R² = H, R³ = Ph(XII).

o-Sulfinobenzoic acid reacts with amines in a similar way [6]. The structures of the aminolysis products (VII)-(XII) were confirmed by their IR spectra (Table 2), the $\nu SO_2^{\ominus}$ absorption being seen as two bands at 945-970 (symm) and 980-1030 cm^{-1} (asymm).

Alcoholysis of 1,2-oxathiolan-5-one-2-oxides with equimolar amounts of alcohols also results in O—CO bond fission to give monoesters of β-hydroxysulfinylalkanoic acids at the

*For previous communication, see [1].

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TABLE 1. Physicochemical Properties of (II), (III), (V)-(XIX), and (XXIII)

Compound	Yield, %	Mp, °C, or Bp, °C (p, mm)	n_D (T, °C)	Found/Calculated, %				Empirical formula	Equivalent, found/calculated
				C	H	S	N		
(II)	~100	[a]	–	30,97 / 31,58	5,26 / 5,26	–	–	$C_4H_8O_4S$	–
(III)	~100	[a]	–	–	–	20,67 / 21,04	–	$C_4H_8O_4S$	84 [b] / 76
(V)	73	~340 (temp. decomp.)	–	24,40 / 24,49	2,99 / 3,06	15,69 / 16,32	–	$C_4H_6Na_2O_4S$	99 [c] / 98
(VI)	94	~340 (temp. decomp.)	–	24,09 / 24,49	3,02 / 3,06	16,07 / 16,32	–	$C_4H_6Na_2O_4S$	98 [c] / 98
(VII)	84	a,d	–	–	–	12,20 / 12,03	10,22 / 10,60	$C_{11}H_{26}N_2O_3S$	134 [c] / 133
(VIII)	98	a	–	–	–	10,96 / 11,43	–	$C_{12}H_{28}N_2O_3S$	–
(IX)	82	142–145	–	61,58 / 62,07	6,79 / 6,90	8,72 / 9,19	–	$C_{18}H_{24}N_2O_3S$	–
(X)	82	154	–	–	–	8,75 / 9,19	–	$C_{18}H_{24}N_2O_3S$	–
(XI)	74	170	–	–	–	9,61 / 10,00	–	$C_{16}H_{20}N_2O_3S$	–
(XII)	86	130–133	–	59,50 / 60,00	6,12 / 6,25	10,19 / 10,00	–	$C_{16}H_{20}N_2O_3S$	–

TABLE 1 (continued)

Compound	Yield, %	Mp, °C, or Bp, °C (p, mm)	n_D (T, °C)	Found/Calculated, %				Empirical formula	Equivalent, found/calculated
				C	H	S	N		
(XIII)	90	[a]	1,4820 (20)	36,48 / 36,10	5,58 / 6,02	19,96 / 19,28	–	$C_5H_{10}O_4S$	162[b] / 166
(XIV)	87	[a]	1,4810 (20)	35,78 / 36,10	6,26 / 6,20	19,21 / 19,28	–	$C_5H_{10}O_4S$	150[b] / 166
(XV)	89	[a]	1,4795 (20)	–	–	18,35 / 17,77	–	$C_6H_{12}O_4S$	–
(XVI)	40 [e,f]	52–55 (0,02)	1,4608 (16,5)	39,48 / 40,00	6,48 / 6,67	17,72 / 17,77	–	$C_6H_{12}O_4S$	–
(XVII)	44[f]	69–71 (0,01)	1,4541 (16,5)	–	–	14,87 / 15,38	–	$C_8H_{16}O_4S$	–
(XVIII)	58[f]	50–52 (0,01)	1,4585 (20)	39,77 / 40,00	6,68 / 6,67	–	–	$C_6H_{12}O_4S$	–
(XIX)	52[f]	52–54 (0,01)	1,4530 (22,5)	45,70 / 46,15	7,62 / 7,69	–	–	$C_8H_{16}O_4S$	–
(XXIII)	35[f]	78 (0,02)	1,4535 (23)	42,80 / 43,30	6,91 / 7,22	15,82 / 16,49	–	$C_7H_{14}O_4S$	–

[a]Oil, decomposes on distillation in vacuo
[b]Neutralized with NaOH.
[c]Oxidimetric with $KMnO_4$ [2].
[d]Crystallizes in the cold.
[e]Yield of (XVI) in the reaction of 4-methyl-1,2-oxathiolan-5-one-2-oxide with an excess of methanol on heating.
[f]Yield of diester after distillation.

TABLE 2. Some IR Spectral Parameters (ν, cm^{-1}) of (III), (V)-(XIX), and (XXIII)

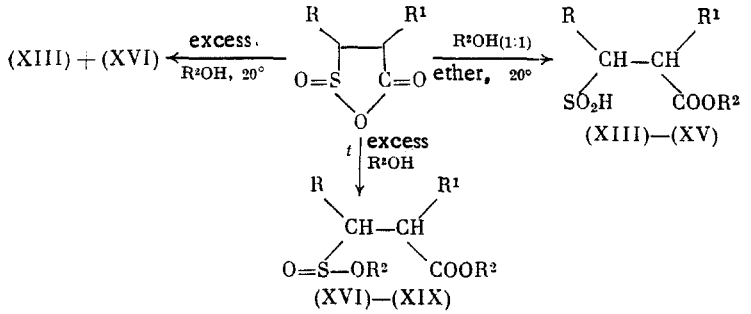
Compound	C=O	S=O	N—H	$^{\oplus}NH_3$ or $^{\oplus}NH_2$	CH_3	Other bands
(III)	1710–1726	1025, 1054	–	–	–	2500–3300 (OH)
(V)	1570–1590, 1415–1435	995–1030	–	–	1380, 2965, 2980	1255 (C–O)
(VI)	1570–1590, 1430	990–1040	–	–	1370, 2952, 2985	1240 (C–O)
(VII)	1617–1638	947–970 (symm) 1015–1030 (asymm)	2985	2400–2800	1385, 2945, 2985	–
(VIII)	1615–1635	955–970 (symm) 1000–1030 (asymm)	2985	2400–2800	1385, 2945, 2985	–
(IX) *	1635, 1550	950–965 (symm) 993–1020 (asymm)	3265	2800–3100	1375, 2950, 2980	1565 (Ar)
(X)	1630–1640, 1552	950–965 (symm) 995–1020 (asymm)	3265	2640–3100	1375, 2930, 2970	1570–1580 (Ar)
(XI)	1655, 1535	945–955 (symm) 980–1000 (asymm)	3300	2500–3000	1385, 2940, 2975	1600 (Ar)
(XII)	1660, 1550	950–970 (symm) 990–1025 (asymm)	2970	2500–2900	1365, 2935, 2970	1600 (Ar)
(XIII)	1730–1740	1050–1080	–	–	–	2890–3050 (OH)
(XIV)	1730–1742	1030–1060	–	–	–	2800–3050 (OH)
(XV)	1730–1745	1030–1040	–	–	–	2900–3050 (OH)
(XVI) **	1730–1742	1135	–	–	1365, 2960, 2990	1175, 1220 (C–O)
(XVII)	1725–1735	1135	–	–	1380, 2945, 2990	1168, 1215 (C–O)
(XVIII)	1730–1740	1130	–	–	1368, 2955, 2985	1170, 1230 (C–O)
(XIX)	1730–1740	1134	–	–	1375, 2945, 2990	1175, 1225 (C–O)
(XXIII)	1730–1740	1130	–	–	1360, 2945, 2985	1170, 1216 (C–O) 1450–1460 (CH_3O+CH_2)

*After keeping for five months, the IR spectrum of (IX) showed, in addition to $RSO_2^{\ominus}$, absorption at 1160-1260 cm^{-1} ($RSO_3^{\ominus}$).

**The PMR spectrum of (XVI) is given in the Experimental section.

carboxyl group. The products (XIII)-(XV) (Table 1), like the bis-acids (I)-(IV), are quite strong acids (pH ~ 1). Varying the conditions of this reaction enables other alcoholysis products to be obtained. For example, reaction of 1,2-oxathiolan-5-one-2-oxides with an excess of the alcohol under mild conditions give a mixture of the mono- (XIII) and diesters (XVI) (in a ratio of 2:1), but on heating the β-sulfinoalkanoic acid diesters (XVI)-(XIX) only are obtained (Table 1).

Since direct esterification of sulfinic acids under these conditions does not normally occur [3], the formation of the diesters (XVI)-(XIX) is apparently due to the possible intramolecular assistance of the $COOR^2$ group. The results of the alcoholysis of the aliphatic anhydrides were confirmed by IR (Table 2) and PMR spectrosopy. As would be expected [5], the νS=O frequency in the sulfinate esters (XVI)-(XIX) is higher (1130-1135 cm^{-1}) than in the acids (absorption at 1025-1080 cm^{-1}). A characteristic difference of the IR spectra of the relatively unstable carboxy- or alkoxycarbonyl-alkanesulfinic acids (I)-(III) or (XIII)-(XV) from those of the more stable sulfinocarboxylic acid bisesters (XVI)-(XIX) is the presence of strong absorption at 1170-1330 cm^{-1}.



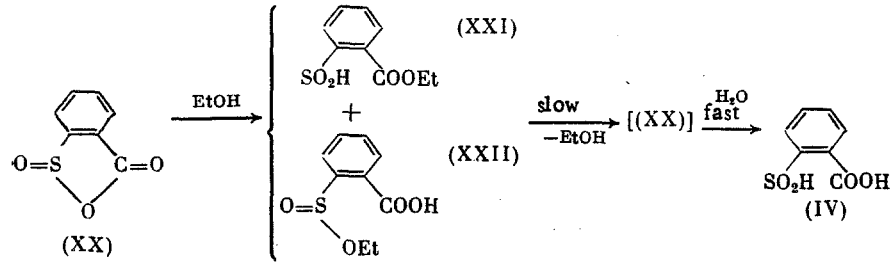
(XIII)—(XV)

(XVI)—(XIX)

R = H, $R^1 = R^2 = Me$(XIII); R = R^2 = Me, R^1 = H(XIV); R = Me, R^1 = H, R^2 = Et (XV); R = H, $R^1 = R^2 = Me$(XVI); R = H, R^1 = Me, R^2 = Et(XVII); R = R^2 = Me, R^1 = H(XVIII); R = Me, R^1 = H, R^2 = Et(XIX).

(which increases on storage), as a result of the formation of disproportionation products (thiosulfonates and sulfonic acids).

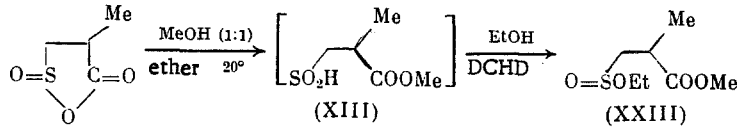
In contrast to the aliphatic anhydrides, which undergo cleavage with alcohols at the O—CO bond only, the o-sulfinobenzoic anhydride (XX) is cleaved by alcohols both at the O—CO and O—SO bonds to give a mixture of the isomeric monoesters (XXI) and (XXII). The latter are much less stable than the aliphatic monoesters (XIII)-(XV), spontaneously losing alcohol, it appears, to give the starting anhydride (XX). In the presence of atmospheric moisture, (XX) is readily hydrolyzed to the bisacid (IV).



(XX) (XXI) (XXII) (IV)

It is noteworthy that the o-sulfinobenzoic acid diester is not formed either under mild hydrolytic conditions, or when (XX) is boiled with an excess of alcohol.

Starting from the aliphatic anhydrides, it is also possible to obtain mixed bisesters of β-sulfinocarboxylic acids such as (XXIII), by initial alcoholysis with one alcohol, then treatment of the resulting monoester (XIII) with another alcohol in the presence of dicyclohexylcarbodiimide (DCHD).



(XIII) (XXIII)

In the absence of dicyclohexylcarbodiimide, treatment of (XIII) with an excess of boiling alcohol results in transesterification with the formation of the bisethyl ester (XVII).

2,1-Benzoxathiol-3-one-1-oxide (XX) reacts readily with triphenylphosphine with opening of the ring to give the oligomeric product (XXIV) containing the sulfinyl grouping o-$(SOC_6H_4 \cdot CO)_n$. Biologically active compounds have been found among the ammonolysis products of cyclic anhydrides [6].

EXPERIMENTAL

PMR spectra were obtained on a Perkin—Elmer R-12 spectrometer (60 MHz) relative to the external or internal standards HMDS or TMS, and IR spectra in liquid films or KBr disks. The constants, elemental anayses, and oxidimetric [2] or acidimetric titrations of the products (II), (III), (V)-(XIX), and (XXIII) are given in Table 1, and the IR spectral data for (III), (V)-(XIX), and (XXIII) in Table 2. Dry solvents and reactants were used in all the experiments. The starting β-sulfinocarboxylic acid anhydrides were obtained as in [2].

β-(Hydroxysulfinyl)propionic Acid (I). A small amount of 1,2-oxathiolan-5-one-2-oxide (mp 49°C) was kept in an open watch glass for 3-7 days, to give (I), mp 77-79°C. No depression of mp was seen on admixture with a sample of (I) obtained as in [4], and the IR spectrum was identical with that given in [4].

β-(Hydroxysulfinyl)isobutyric (II) and -butyric (III) Acids. To a solution of 1.34 g (0.01 mole) of 4- or 3-methyl-1,2-oxathiolan-5-one-2-oxide in 5 ml of ether at −10°C was added with stirring 0.18 g of water in 15 ml of ether. After 1.5 h at 20°C, the solvent was removed under reduced pressure, and the residue dried by driving off traces of water with benzene (20 ml) and kept in vacuo at 30°C (20°C at 2 mm). There were obtained (II) or (III), yield 1.52 g, soluble in water (pH ~ 1) and DMSO, and insoluble in CCl_4 and CH_2Cl_2. On prolonged storage in a vacuum desiccator over P_2O_5, decomposition occurred (acidimetry).

In the PMR spectrum of (III) in DMSO, the signal for the OH group was seen at 7.43 ppm (br.s).

o-(Hydroxysulfinyl)benzoic Acid (IV) was obtained from 2,1-benzoxathiol-3-one-1-oxide (XX) as for (I). Yield of (IV) 100%, mp 112°C [2]. It gave no depression of melting point with an authentic sample. The IR spectrum was identical with that given in [2]. PMR spectrum in DMSO-d (δ, ppm): 7.16 s (SO_2H + COOH), 7.63-8.21 m (C_6H_4), integral intensity ratio of the signals 1:2.

Disodium Salt of β-(Hydroxysulfinyl)isobutyric Acid (V). To a suspension of 5.4 g (0.06 mole) of $NaHCO_3$ in 10 ml of water was added with stirring 4.3 g (0.03 mole) of 4-methyl-1,2-oxathiolan-5-one-2-oxide. On the following day, the mixture was evaporated to dryness under reduced pressure, and the solid residue washed with alcohol and dried in vacuo to constant weight, to give 4.3 g of (V).

Disodium Salt of β-(Hydroxysulfinyl)butyric Acid (VI). Obtained as for (V), from 3-methyl-1,2-oxathiolan-5-one-2-oxide. The salt (VI) was insoluble in alcohol, acetone, and chloroform, but soluble in water.

General Method of Preparation of Ammonium Salts of β-(Hydroxysulfinyl)alkanoic Acid Amides (VII)-(XII). To a solution of 0.01 mole of the 1,2-oxathiolan-5-one-2-oxide in 15-20 ml of ether was added with stirring a solution of 0.02-0.022 mole of the amine in 10 ml of ether. The reaction was exothermic, an oil separating which crystallized on standing. On the following day, the solid was filtered off, washed with ether, and dried in vacuo. Compound (VII) was obtained in benzene solution at 7°C. The noncrystalline diethylamides (VII) and (VIII) were isolated by evaporating the mixture under reduced pressure at 25°C (10 mm) and 40°C (4 mm). The salts (VII), (VIII), and (X)-(XII) were soluble in water. The benzylamide (IX) was sparingly soluble in water and alcohol, but soluble in aqueous alkali.

General Method of Preparation of Monoalkyl Esters of β-(Hydroxysulfinyl)alkanoic Acids (XIII)-(XV). To a solution of 1.34 g (0.01 mole) of 4- or 3-methyl-1,2-oxathiolan-5-one-2-oxide in 10-15 ml of ether was added 0.015 mole of methanol or ethanol, and on the following day the mixture was evaporated at 25°C at 10 and 3 mm. The monoesters (XIII)-(XV) were readily soluble in water, and gave a strongly acid reaction (pH ~ 1).

Reaction of 4-Methyl-1,2-oxathiolan-5-one-2-oxide with Excess Methanol. To 3.37 g (0.025 mole) of 4-methyl-1,2-oxathiolan-5-one-2-oxide was added slowly with stirring 25 ml of methanol. On the following day, the mixture was treated with a solution of 2.11 g (0.025 mole) of $NaHCO_3$ in 50 ml of water with vigorous stirring, the resulting mixture (pH ~ 8) extracted three times with ether, and the extract dried over $MgSO_4$. The aqueous solution was evaporated under reduced pressure, and the residue dried by removing the water with benzene, and kept in vacuo over P_2O_5 to constant weight, to give 2.7 g of a colorless powder consisting of a mixture* of the mono-salt $(SO_2Na)CH_2CH(CH_3)COOCH_3$ (XXV) and the bis-salt $(SO_2Na)\cdot CH_2CH(CH_3)COONa$ (XXVI) in a ratio of ~1:1.

IR spectrum (ν, cm^{-1}): 995-1060 [SO_2Na for (XXV) and (XXVI)], 1735 [COOMe for (XXV)], 1435-1470, 1575 [COONa for (XXVI)]. PMR spectrum in D_2O (δ, ppm): 1.24 d [CH_3 for (XXV) and (XXVI)], 1.86-3.2 m [CH_2CH for (XXV) and (XXVI)], 3.75 s [OCH_3 for (XXV)]. Integral intensity ratios of the signals for CH_3:CH_2CH:OCH_3 ~ 1:1:0.5 (instead of 1:1:1).

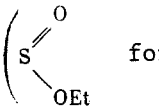
*According to the IR and PMR spectra.

Evaporation of the ether extracts under reduced pressure and distillation of the residue gave 1.44 g (32%) of the diester (XVI). The constants and IR spectrum of (XVI) are given in Tables 1 and 2.

PMR spectrum of (XVI) in CCl_4 (δ, ppm): 1.33 d (CH_3), J_{CH_3-CH} = 7.3 Hz, 2.47-3.35 m (CH_2CH), 3.73 s (OCH_3), integral intensity ratio of signals, 1:1:2.

General Method of Preparation of Diesters of β-(Hydroxysulfinyl)alkanoic Acids (XVI)-(XIX). To 2.68 g (0.02 mole) of 4- or 3-methyl-1,2-oxathiolan-5-one-2-oxide was added slowly 60 ml of methanol or ethanol (the reaction was exothermic). On the following day, the mixture was boiled for 3 h, evaporated under reduced pressure, and fractionated to give the diesters (XVI)-(XIX) as colorless oils, soluble in water and organic solvents.

Reaction of 2,1-Benzoxathiol-3-one-1-oxide (XX) with Ethanol a) Reactant Ratio 1:1. To a solution of 1.43 g (0.008 mole) of (XX) in 10 ml of chloroform was added 0.6 ml (0.01 mole) of ethanol, and after one day the mixture was evaporated under reduced pressure to give 1.65 g (91%) of an oil which solidified on standing, mp 64°C, which gave no depression of melting point with material from experiment b) (see below). The mixture of isomers [the ethyl esters of o-(hydroxysulfinyl)benzoic acid (XXI) and o-(ethoxysulfinyl)benzoic acid (XXII)] was sparingly soluble in water, and gave an acid reaction (pH ~ 1).

IR spectrum (ν_0, cm^{-1}): 1020-1040 s [SO_2H for (XXI)], 1125-1145 s ( for (XXII)), 1710-1725 v.s [COOEt for (XXI)], 1680-1690 s [COOH for (XXII)], 2750-3200 v.s (OH), 1590 med (Ar), 1190, 1240 (C–O), 1240-1275 (CH_2). PMR spectrum in CH_2Cl_2 (δ, ppm): 1.3 t (CH_3, 3H, $J_{CH_3-CH_2}$ = 7.3 Hz), 3.51-4.33 oct (CH_2, 2H), 7.34-8.4 m (C_6H_4, 4H), 9.56 s (OH, 1H).

Found, % [for the mixture of isomers (XXI)-(XXII)]: S 15.18; mol. wt. (acidimetric) 200. $C_9H_{10}O_4S$. Calculated, %: S 14.95, mol. wt. 214.

The freshly-prepared mixture (XXI)-(XXII) on storage (20°C, 14-20 days) was gradually converted into the bisacid (IV), mp 108°C [no depression of melting point with an authentic sample of (IV), IR and PMR spectra identical with those given above for (IV)] as a result of the decomposition of the intermediate anhydride (XX).

b) On Heating with Excess Alcohol. 3.36 g (0.02 mole) of (XX) was dissolved in 30 ml of ethanol, and after 30 min at 20°C the mixture was boiled for 4 h and kept overnight. It was then evaporated under reduced pressure, and the residue dried by driving off traces of water with benzene to give 3.75 g (88%) of a mixture of (XXI) and (XXII) [(XXI) predominating] as an oil which solidified on standing, mp 60°C. The solubility, acidity, and IR spectrum of the mixture were similar to those of the latter; the IR spectrum was complicated by the presence of by-products of disproportionation. PMR spectrum (emulsion in CCl_4) (δ, ppm): 1.25 t (CH_3, 3H, $J_{CH_3-CH_2}$ = 7.3 Hz), 3.81-4.45 oct (CH_2, 2H), 7.59-8.32 m (C_6H_4, 4H), 11.49 s (OH, 1H).

As in preparation a), the monoesters (XXI) and (XXII) gradually lost ethanol on storage and after ~20 days they were completely converted into the bisacid (IV), mp 100-110°C (followed by IR and PMR).

Methyl β-(Ethoxysulfinyl)isobutyrate (XXIII). To a solution of 2 g (0.015 mole) of 4-methyl-1,2-oxathiolan-5-one-2-oxide in 15 ml of ether was added 0.48 g (0.015 mole) of methanol, and on the following day the mixture was treated with stirring with 0.69 g (0.015 mole) of ethanol, followed by 2.76 g (0.013 mole) of dicyclohexylcarbodiimide. After a few hours at 20°C, the solid was filtered off, and the neutral ether solution evaporated under reduced pressure to give 2.6 g (100%) of an oil, which from its IR and PMR spectra was the diester (XXIII); distillation (considerable resinification) gave 0.9 g of (XXIII).

Reaction of 2,1-Benzoxathiol-3-one-1-oxide (XX) with Triphenylphosphine. To 1.65 g (0.01 mole) of (XX) in 35 ml of CCl_4 was added with stirring 2.62 g (0.01 mole) of triphenylphosphine (exothermic reaction). On the following day, the solid polymer (1.2 g, mp 80°C, νS=O 1130 cm^{-1}, νC=O 1700 cm^{-1}) was filtered off, the solution evaporated to dryness, and the residue washed with ether to give 2 g (72%) of Ph_3PO, mp 130°C. Evaporation of the ether solution gave 0.32 g of (XXIV) as a colorless oil, sparingly soluble in water (pH ~ 3) and hot alkali, which did not contain the sulfenic anhydride group (negative KI test).

IR spectrum of (XXIV) (ν, cm^{-1}): 1130 s (S=O), 1730 s (C=O).

CONCLUSIONS

1. 1,2-Oxathiolan-5-one-2-oxides are readily cleaved by nucleophiles (H_2O, ROH, HNR_2) under mild conditions at the O—CO bond only, with the formation of the β-(hydroxysulfinyl)-alkanoic acid derivatives.

2. 2,1-Benzoxathiol-3-one-1-oxide is cleaved by alcohols at both the O—CO and the O—SO bonds to give the unstable monoesters at the carboxyl and sulfinyl groups.

3. Unlike 2,1-benzoxathiol-3-one-1-oxide, 1,2-oxathiolan-5-one-2-oxides on boiling with excess alcohols give β-(hydroxysulfinyl)alkanoic acid bisesters.

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SYNTHESIS OF 2,2,6,6-TETRAMETHYL-4-AMINO-N-(ALKYLAMINODICHLOROTRIAZINE)-1-OXYLPIPERIDINES

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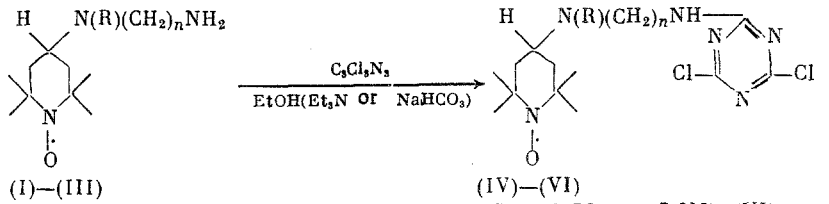
Continuing work on spin labels with varying lengths of the hydrocarbon chain between the nitroxyl and a group capable of binding to macromolecules [1, 2], we here report the synthesis of some dichlorotriazine derivatives of 2,2,6,6-tetramethyl-4-diaminoalkyl-1-oxylpiperidines.

One dichlorotriazine spin label has previously been reported, namely 2,2,6,6-tetramethyl-4-amino-N-(3,5-dichlorotriazine)-1-oxylpiperidine [3], the synthesis of which has been modified [4]. This spin label, tagged with ^{14}C in the triazine ring, has been employed in studies on immunoglobulins [6].

The required compounds were obtained as follows:



(I)—(III) (IV)—(VI)

R = H, $n = 2$(I), (IV); R = MeCO, $n = 4$(II), (V); R = MeCO, $n = 7$(III), (VI).

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