for each of them: salt formation (150-220°C), ketonization (290-360°C), and pyrolysis of the salts of the polyketodicarboxylic acids (>350-400°C in relation to the nature of the cation).

CONCLUSIONS

1. Just as in the presence of manganese and cadmium compounds, ketonization of dicarboxylic acids in the presence of zinc compounds occurs by two competing routes (cycloketonization and linear polyketonization). In the case of adipic and pimelic acids, a secondary reaction of crotonic condensation of the resulting ketones also occurs.

2. Zinc oxide catalyzes efficiently the cycloketonization of suberic acid to cycloheptanone, making it possible to obtain it in such a way in the highest yield described in the literature (70%).

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POLYSULFONYLETHYLENES.

COMMUNICATION 1. SYNTHESIS OF TETRAKIS(ALKYL, ARYL) SULFONYLETHENES*

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Tetrasulfonylethylenes (TSE) constitute a class of ethylenes with an electron-deficient C=C bond. The presence of four strong electron-acceptor groups should make the TSE highly active in various nucleophilic processes.

The TSE were unknown before our research, in spite of numerous attempts to prepare them. Thus, the photochemical oxidation of tetra(alkyl,aryl)thioethenes produced a complex mixture whose major components were dithiooxalates and disulfides [2, 3]. Oxidation of tetratolyl-thioethene [4] and 1,1-di(methylsulfonyl)-2,2-di(methylthio)ethene [5] by 30% H_2O_2 in acetic acid produced on heating only ditolyl- and dimethylsulfonylmethane, respectively. Oxidation of more complex tetrathioethenes such as tetrahydrotetrathiofulvalenes by m-chloroperbenzoic acid in CH_2Cl_2 was unsuccessful, and the use of H_2O_2 in acetic acid [4, 5] also resulted in splitting the molecule [6].

In spite of the claims in [7] (see the experimental section), the oxidation of tetrakis-(2 chloroethylthio)ethene (I) by 30% H₂O₂ in acetic acid actually forms di(2-chloroethyl)sulfonylmethane (III) as well and not the tetrasulfone (II):

*For preliminary discussion, see [1].

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We can agree with [5, 6] that the disulfonylmethanes are one of the acid hydrolysis products of TSE formed when (I) is oxidized. Similar fragments are highly characteristic of the reactions of ethylenes activated by certain electron-acceptor groups [8].

We have developed a means of preparing TSE (IIa to IIh) by the oxidation of tetrathioethenes (Ia to Ih) with CF_3CO_3H , a strong oxidizing agent with a relatively small molecule:



The original sulfides (Ia to Ih) were made from tetrachloroethylene by a method which we have developed [9].

An indispensable condition of the oxidation is the simultaneous addition of approximately equal volumes of CF_3CO_3H and CH_2Cl_2 solutions of the sulfides (Ia to Ih) to a cooled reactor in order to keep the temperature from rising above ~ 20 °C. The oxidation is completed by further heating (40-45°C, from 3 min to 1.5 h, as shown in Table 1). Addition of the peracid to the sulfide solution leads to resinification of the original tetrathioethenes and is not recommended.

In view of the marked susceptibility of TSE to acid hydrolysis, the reaction mixture must be carefully washed free of traces of acid to a pH of 7, preventing the formation of the disulfonylmethanes detected earlier [1].

Attempts to perform the oxidation in an anhydrous medium with the use of other peracids such as CH₃CO₃H, permaleic acid, and p-carboxyperbenzoic acid, led to complete mixtures probably consisting of products of different oxidation levels, judging from spectroscopic data.

The structure of the TSE (IIa to IIh) was confirmed by elemental analysis, by a molecular weight determination for (IIb), by hydrogenation to tetrasulfonylethane (IV), and by spectroscopic data. The IR spectra of (IIa to IIh) showed the SO₂ group frequencies; C=C bond absorption was observed only in the Raman spectra as expected from symmetrical molecules; and the C¹³ NMR spectra contained one signal at 165.1 ppm.

Thus, oxidation of tetrathioethylenes by trifluoroperacetic acid (TFPAA) in CH_2Cl_2 can be a convenient method for synthesizing the tetrasulfonylethylenes, which were formerly unknown and unavailable by other methods. This opens up the possibility of detailed research on a new group of electron-deficient ethenes, which may be "sulfur analogs" of tetracyanoethylene.

EXPERIMENTAL

We used absolute solvents. Sulfides (Ia-Ih) and CF_3CO_3H were prepared by methods in [9] and [10], respectively. The IR spectra were taken on a UR-10 instrument with KBr pellets; the Raman spectra were taken on a Romalog-6 spectrometer with 488-nm linear excitation; the C^{13} NMR spectra were taken on a Brucker WP 60 instrument; the PMR spectra were taken on a BS-467 spectrometer (60 MHz). The molecular weight was determined for (IIb) by ebulliometry on a ÉP-68 instrument of the Special Design Bureau of the Institute of Organic Chemistry of the Academy of Sciences of the USSR. A 20% molar excess of the oxidant was used for oxidation. Decolorization of the bright-yellow coloration formed during oxidation served as indicator of the completion of the oxidation. Compound (IIg) was an exception, forming a yellow color unlike the other TSE.

			Found/(Calculated, 7	10		Heating time,	IP spectrum	Raman spec-
H.	Yield, 70	mp, °C (solvent)	υ	Ħ	SS SS	Empincai formula	min (40-45°C)	$(\nu, \text{ cm}^{-1}) \text{ of SO}_2$	trum of $C=C$ (ω , cm^{-1})
	-								
CH3	67	230 (with decomposition)	21,04	3,62	37,32	$C_6H_{12}O_8S_4$	90	1160, 1335	1535
C_2H_5	84	203-204 (CH _o Cl _o :ether)	30,38	5,30	32,22	$C_{10}II_{20}O_8S_4$	20 - 30	1150, 1330	1535
n-C ₃ H ₇	71	234-235 /hengene.ether)	37,10 37,10	6,12	228,33 28,33	$C_{14}H_{28}O_8S_4$	15-20	1150, 1330	1530
n-C4H3	75	(Denzene ; curci) 173–174 (CH ₂ Cl ₂ ; ether)	21,14 42,54 79 54	7,01	25,13	$C_{18}H_{36}O_8S_4$	15 - 20	1148, 1332	1532
n-C6H13	81	$(CH_2Cl_2; pentene)$	50,33 50,33	8,23	20,71	C26H52O8S1	ي 1-5 2-5	1150, 1348	1530
n-C ₈ H ₁₇	17	101,5-102 (ether · pentane)	55,55 55,55 55,80	9,18 0,18	17,53	$C_{14}H_{38}O_8S_4$	3-5	1150, 1348	1530
C ₆ H ₅	67	213,5-214 (CH ₃ Cl ₂ : ether)	53,20 53,06	3,45 3,45 3,40	21,60 21,60	$C_{26}H_{20}O_8S_4$	120150	1580 (C=C) (Ph) 1162, 1332	1498
(CH ₂) ₂ Cl [†]	20	202–204 * (with decomposition)	22,53 22,48	2,97 3,02	23,87	$C_{10}II_{16}Cl_4O_sS_4$	60	1160, 1315	1560
						~	-		_

SO₂R

 RSO_{3}

TABLE 1. Properties and Yields of Tetrakis(alkyl,aryl)sulfonylethenes (IIa-IIh)

*In view of the low solubility of the sulfone, it was washed with CH2Cl2 and ether and analyzed without crystallization. *Cl found for sulfone, 26.41%; calculated, 26.54%.

<u>Tetrakisethylsulfonylethene (IIb).</u> Add to 5 ml CH_2Cl_2 with stirring at 20-25°C (cooling) simultaneously at about the same rate 8.76 g of (Ib) in 90 ml CH_2Cl_2 and a solution of CF_3CO_3H prepared from 10 ml 97% H_2O_2 and 60 g (CF_3CO_2O in 50 ml CH_2Cl_2 .

Heat the yellow solution that is formed at $40-45^{\circ}$ C until it is decolorized, dilute with CH₂Cl₂, wash with NaHCO₃ solution until weakly basic and then wash with H₂O to pH 7, dry with MgSO₄, and evaporate off the solvent. We obtained 10.82 g (83.5%) of (IIb), mp 203-204°C (CH₂Cl₂: ether 1:1); mol. wt. found 391.8, calculated **396.5**.

Sulfones (IIa to IIh) were prepared by an analogous procedure; the properties of the compounds and the reaction conditions are given in Table 1.

Because it is insoluble in CH_2Cl_2 , sulfide (Ih) was sprinkled in as a powder simultaneously with the addition of the oxidizing agent. Sulfones (IIa) and (IIh) were precipitated during the oxidation and therefore the reaction mixture was cooled to 5-10°C, the precipitate of (IIa) or (IIh) was filtered off and washed several times with CH_2Cl_2 , then with ether.

Di(2-chloroethylsulfonyl)methane (III). Add with stirring 1 ml 30% H₂O₂ to 0.3 g sulfide (Th) in 6 ml glacial acetic acid at 50°C, heat 2 h at 70-80°C until decolorized, evaporate off the major part of the acid, dissolve the residue in CH₂Cl₂, wash with NaHCO₃ solution, then with water, and dry with MgSO₄. After evaporation of the solvent, we obtained 0.15 g (78.9%) of (III), mp 113-114°C (CH₂Cl₂:ether).* IR spectrum (ν , cm⁻¹): 1120, 1330 (SO₂ group); PMR spectrum (δ , ppm (CD₃)₂CO): 3.96-4.05 m (2 Cl(CH₂)₂SO₂), 5.13 s (CH₂(SO₂)₂). Percentage composition found: C 22.21, H 3.81, Cl 26.56, S 23.70. Percentage calculated for C₅H₁₀Cl₂O₄S₂: C 22.30, H 3.74, Cl 26.34, S 23.82. The sulfone (III) showed no melting-point depression and was identified by IR and PMR spectra with a well-characterized sample of di-(2-chloroethylsulfonyl)methane synthesized by a procedure in [9] from CH₂Cl₂ and HS(CH₂)₂OH with successive chlorination with the aid of SOCl₂ and oxidation by CF₃CO₃H of the di(2-hydroxyethylthio)methane that is formed.

<u>Tetrakisethylsulfonylethane (IV)</u>. Hydrogenate 0.2 g of (IIb) in 20 ml benzene over Pd β/γ -Al₂O₃ at 20°C for 20 min. The theoretical amount of H₂ was absorbed. The catalyst was filtered off and washed with benzene and acetone and the solvent was evaporated from the filtrate. We obtained 0.13 g (68%) of (IV), mp 131-132°C (ether:pentane). Percentage composition found: C 29.80, H 5.39, S 32.10. Percentage calculated for C₁₀H₁₂O₈S₄: C 30.14, H 5.30, S 32.18. IR spectrum (v, cm⁻¹): 1330, 1145 (SO₂).

CONCLUSIONS

We have developed a preparative method for the synthesis of the formerly unknown tetrakis(alkyl,aryl)sulfonylethenes, including the oxidation of tetrakis(alkyl,aryl)thioethenes by trifluoroperacetic acid.

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^{*}This mp was quoted for the tetrasulfone (IIh) in [7], but it actually has a mp of 202-204°C (see Table 1).