SYNTHESIS OF TETRAKIS(ALKYL, ARYL) THIOETHYLENES

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By analogy with other tetra derivatives of ethylene, the tetrakisthioethylenes can have interest in organic synthesis. The usual methods for synthesizing these compounds using organometallic compounds are multistep [1-4]. The simplest method for their synthesis is the exchange of chlorine atoms by the SR group under nucleophilic conditions [5]. Complete substitution proceeds with great difficulty when protic solvents are used in this reaction, the components have to be heated for a long time in sealed ampuls, and the yield of the desired products is low [6-8].

In the present paper we report a convenient method for the synthesis of tetrakis(alky1, ary1)thioethylenes from tetrachloroethylene and thiolates in aprotic media (DMF, DMSO, HMPA, etc.), which is based on a substantial acceleration of the corresponding nucleophilic processes.



The reaction of tetrachloroethylene with thiolates (as a suspension in an aprotic solvent) is exothermic at atmospheric pressure and gives tetrakis(alkyl,aryl)thioethylenes (Ia-g) in 60-80% yield (Table 1). The optimum temperature for the reaction of the thiolates of primary aliphatic thiols in DMF solution (80-90°C) can be reached via the exothermic heat of the reaction. Additional heating is required in dilute solutions, and also for the substituted aliphatic or aromatic thiolates. Together with the tetrakisthioethylenes (Ia-g), 10-15% of the tris derivatives (IIa-g) is formed (see Table 1).

Replacing the DMF by stronger aprotic solvents like DMSO and HMPTA fails to increase the yields noticeably, probably because of the possible side reactions of these solvents with the thiolates. Consequently, in our opinion, for preparative purposes it is most convenient to run the reaction in DMF as the medium.

The purity of compounds (Ia-g) and (IIa-g) was checked by TLC. The constants of tetrakisthioethylenes (Ia,e-g) agreed with the literature data [2-4,6,8]. The Raman spectra of (Ia-g) had intense absorption bands in the 1460-1470 cm⁻¹ region, which were assigned to the C=C bond. The analogous frequencies are absent in the IR spectra, which is in agreement with the concept that the tetrakisthioethylenes have a quite high symmetry. Actually, a quite intense absorption of the C=C bond was observed in the same region in the IR spectra of the tristhioethylenes (IIa-g).

EXPERIMENTAL

The IR spectra were taken on a UR-10 spectrometer either as KBr pellets or as a thin layer. The Raman spectra were obtained on a Ramalog-6 laser spectrometer with an excitation line of 5145 Å, either as a thin layer or as a pellet. For the TLC we used Silufol and CCl_4 as the eluant. The tetrachloroethylene was dried and distilled. The sodium thiolates were obtained from the corresponding thiols in either abs. alcohol or abs. toluene solution, and were dried for 3-4 h at 0.02 mm and 20-30°. The experiments were run in a dry nitrogen atmosphere.

General Method for Obtaining Tetrakis(alky1,ary1)thioethylenes. To a suspension of the

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TABLE 1. Yields of Tetrakis- and Tris(alkyl,aryl)thioethylenes $(RS)_2C=C(SR)_2$ (I) and $(RS)_2C=CC1(SR)$ (II) (80-80°)

R	Solvent	Yield, %				Yield, %	
		(I)	(11)	R	Solvent	(I)	(11)
$C_2H_5 *$ $n-C_3H_7 *$ $i-C_3H_7 +$ $C_6H_{13} *$ $C_8H_{17} *$	DMF **	63,7 71,4 55,2 86,5 74,8	12,3 7,4 7,7 10,2 10,0	$C_{6}H_{17} * C_{8}H_{17} * (CH_{2})_{2}OH \ddagger C_{6}H_{5} \ddagger$	DMSO HMPTA DMF "	42,3 68,8 59,2 79,4	27,5 Traces 17,2 ≈1,0

*Without additional heating.

+The reaction mixture was heated for 1.5 h.

tThe reaction mixture was heated for an additional 30-40 min.

TABLE 2. Properties of 1,1,2-Trisalkylthio-2-chloroethylenes (RS)₂C=C(C1)SR (IIa-g)

	bp, *C (p,	Fo	Empirical			
R	mm of Hg)	С	Н	Cl	S	formula
		1				1
C_2H_5	112-112,5(3)	39,80	6,22	14,72	- 39,97	C ₈ H ₁₅ ClS ₃
		39,56	6,42	14,69	39,60	
$n-C_3H_7$	152-153(3)	46,68	7,54	12,27	33,54	C11H21ClS3
		46,37	7,42	12,44	33,75	
i-C3H7	186-187(3)	46,42	7,62	12,38	33,58	C11H31ClS3
	ł	46,37	7,42	12,44	33,75	
C_6H_{13}	45-46 (0,02)	58,80	9,84	8,74	23,69	C20H39ClS3
		58,42	9,56	8,62	23,39	
C_8H_{17}	80-82(0,015)	63,52 .	10,50	7,10	19,38	C ₂₆ H ₅₁ ClS ₃
		63,37	10,37	7,15	19,41	
$(CH_2)_2OH$	160-162(0,02)	32,93	5,14	11,98	32,98	C ₈ H ₁₅ O ₃ ClS ₃
		33,03	5,19	12,18	33,03	l

sodium thiolate in an aprotic solvent was added in drops a solution of tetrachloroethylene in the same solvent, at such a rate that the temperature of the reaction mixture was maintained at $80-90^{\circ}$. In case of need the mixture was heated for 0.5-1.5 h at the same temperature (see Table 1). After reaching 20° (when the reaction was run in DMF) most of the DMF was evaporated in vacuo, the residue was extracted with ether, and the extract was washed with water until neutral and then dried over MgSO₄. After evaporating the ether, the residue was treated with a little n-hexane or n-pentane. The crystals of compounds (Ia-g), which were obtained at the temperature of Dry Ice, were filtered and then recrystallized from either n-pentane or n-hexane. The mother liquor, which contained (IIa-g) with a small amount of (Ia-g), was distilled.

When the reaction was run in DMSO or HMPTA the reaction mixture was diluted with a large amount of ether, washed with water, and worked up as described above.

<u>Tetrakis(hexylthio)ethylene (Id).</u> From 4.8 g of tetrachloroethylene and 16.8 g of sodium hexylthiolate in 40 ml of DMF we obtained 12.15 g (86.5%) of (Id), mp 22-23° (from pentane), bp 86-88° (0.02 mm). Found: C 63.39; H 10.86; S 25.72%. $C_{26}H_{52}S_4$. Calculated: C 63.34; H 10.63; S 26.01%.

<u>Tetrakis(n-octylthio)ethylene (Ie)</u>. From 4.1 g of tetrachloroethylene and 17 g of sodium n-octylthiolate in 40 ml of DMF we obtained 11.4 g (74.8%) of (Ie), mp 30-31° (from pentane), bp 80-82° (0.015 mm). Found: C 67.47; H 11.33; S 21.10%. $C_{34}H_{6.8}S_{4}$. Calculated: C 67.49; H 11.32; S 21.19%.

CONCLUSIONS

A convenient method was developed for the synthesis of tetrakis(alkyl,aryl)thioethylenes by reacting tetrachloroethylene with thiolates in aprotic solvents as the medium.

LITERATURE CITED

- 1. A. Fröling and J. F. Arens, Rec. Trav. Chim., 81, 1009 (1962).
- 2. J. Hine, R. P. Bayer, and G. G. Hammer, J. Am. Chem. Soc., 84, 1751 (1962).
- G. A. Wildschut, H. J. T. Bos, L. Brandsma, and J. F. Arens, Monatsh. Chem., <u>98</u>, 1043 (1967).
- 4. D. Seebach, K. H. Geiss, A. K. Beck, B. Graf, and H. Daum, Chem. Ber., 105, 3280 (1972).
- 5. W. E. Truce and R. Kassinger, J. Am. Chem. Soc., 80, 6450 (1958).
- 6. P. Claesson, J. Prakt. Chem., <u>15</u>, 193 (1877).
- 7. W. R. H. Hurtley and S. Smiles, J. Chem. Soc., <u>1926</u>, 2263.

8. U.S. Patent 3,101,377 (1963); Chem. Abstr., 60, 1595f (1964).

PURE DIASTEREOMERS OF L-MENTHYL ESTERS OF α -MERCURATED PHENYLACETIC ACID AND DETERMINATION OF DIASTEREOMERIC PURITY EMPLOYING NMR SPECTROSCOPY

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In connection with studying the stereochemistry of the reaction of the complexes of zerovalent platinum with the mercury derivatives of the L-menthyl esters of phenylacetic acid [1] the need arose of restudying the diastereomers of RHgBr (I) and (II), and R_2Hg (III) and (IV), which were obtained previously in our laboratory [2].

A new method for separating the RHgBr diastereomers is given in the present paper, which makes it possible to obtain the pure (I) diastereomer for the first time. The more soluble low-rotary (II) diastereomer was obtained with a maximum diastereomeric purity of 94%, $[\alpha]_D^{20}$ -18°, and the calculated angle of rotation of the pure (II) is $[\alpha]_D^{20}$ -10°.

The diastereomeric composition of the studied compounds was determined from the PMR spectroscopy data. As an example, in Fig. 1 is given the spectrum of RHgBr, a mixture of (I) + (II) with $[\alpha]_D^{20}$ -53°. The HCHg proton in (I) and (II) respectively gives singlets with δ 3.59 and 3.56 ppm, and $^2J_{H-Hg}$ = 278 and 309 Hz. The configuration of the HČHg center was assigned on the basis of the DOR, as will be described in the complete paper.

The symmetrical R_2 Hg compounds (III) and (IV) were obtained by the symmetrization of RHgBr with ammonia. The diastereomeric composition of the R_2 Hg was estimated by reduction to RHgBr using HgBr₂ in THF under the bimolecular electrophilic substitution conditions of the S_E^2 type, which, as is known, proceeds with a retention of the configuration of the carbon atom [3]. The obtained data are summarized in the following scheme:



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