The ethereal layer was analyzed by gas-liquid chromatography on column A with temperature programming from 120 to 250°C. The temperature was raised at 25 deg/min. The injector temperature was 250°C. These data indicated that the mixture contained 25% p-$BrC_6H_4NH_2$ and 32% unreacted p-$BrC_6H_4NO_2$. The residue after extraction was treated with dilute hydrochloric acid. The crystalline precipitate was filtered off, washed with hot water and ether, and dried in vacuum to give 0.06 g (40%) bis (4,4'-nitrophenyl) disulfide, mp 180-184°C (mp 181-184°C [9]). Found, %: C 46.62; H 2.50; S 20.45. $C_{12}H_8N_2O_4S_2$. Calculated, %: C 46.74; H 2.60; S 20.78.

Reduction of p-$ClC_6H_4NO_2$ in the Presence of KOH. A mixture of 0.36 g (2 mmoles) p-$ClC_6H_4NO_2$, 0.04 g (2 mmoles) KOH, 15 ml methanol, and 1.5 ml (10 mmoles) H_2S was placed into an autoclave and stirred for 20 min at ~20°C and 0.15 MPa to give 0.07 g (25%) p-$ClC_6H_4NH_2$, mp 69-70°C (mp 70°C [9]). The yield of the product as indicated by gas-liquid chromatography was 29%. Found, %: C 56.38; H 5.29; N 11.1. C_6H_6NCl. Calculated, %: C 56.47; H 4.70; N 11.0.

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SYNTHESIS OF TETRAALKYLAMMONIUM THIOLATES

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547.569.1

A convenient method has been developed for the preparation of tetraalkylammonium thiolates by the reaction of tetraalkylammonium hydroxides with various thiols in benzene.

Pure samples of tetraalkylammonium thiolates are required for the photoinduced catalytic thiylation of aryl halides [1]. A method for the synthesis of $R_4N^+ArS^-$ has been described in the patent literature [2], involving the reaction of a tetraalkylammonium hydroxide (R_4NOH) with thiophene in water, aliphatic alcohols, or ketones. This reaction is complicated by the formation of disulfide or polysulfide side-products.

In an attempt to obtain tetramethylammonium phenylthiolate by the method described using water as the solvent, we obtained a product with the same melting point as indicated in the patent report [2]. However, the IR spectral and elemental analysis data indicated that this sample consists of a mixture of the starting reagent and desired product as well as a series of impurities. The ready oxidation and hygroscopicity of tetraalkylammonium thiolates prevent the use of ordinary methods of purification for separating the desired product from this mixture.

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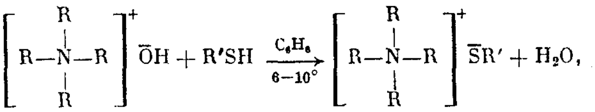
TABLE 1. Physical Indices of Tetraalkylammonium Thiolates R_4NSR'

Compound	R	R'	Mp, °C	Found/Calculated, % C	H	N	S	Empirical formula	Yield, %
(III)	Me	Et	162–165	53,20 53,33	12,36 12,59	9,96 10,37	23,03 23,71	$C_6H_{17}NS$	96
(IV)	Me	Cyclohexyl	157–158	63,44 63,49	12,28 12,17	7,33 7,41	16,79 16,93	$C_{10}H_{23}NS$	100
(V)	Me	Furfuryl	110–115	56,87 56,75	9,10 9,09	7,30 7,48	16,96 17,11	$C_9H_{17}NSO$	98
(VI)	Me	4-Pyridyl	95–98	58,57 58,70	8,93 8,70	14,86 15,21	16,89 17,39	$C_9H_{16}N_2S$	97
(VII)	Et	*n*-Bu	108–110	65,21 65,76	12,98 13,24	6,45 6,39	13,80 14,62	$C_{12}H_{29}NS$	94
(VIII)	Et	*n*-C_8H_{17}	110–115	68,92 69,82	12,98 13,45	4,93 5,09	12,27 11,64	$C_{16}H_{37}NS$	98
(IX)	Et	*n*-$C_{12}H_{25}$	117–122	71,93 72,50	13,48 13,60	3,97 4,20	10,10 9,70	$C_{20}H_{45}NS$	99
(X)	*n*-Bu	*n*-$C_{12}H_{25}$	liq. cryst.	75,08 75,84	13,64 13,77	3,67 3,16	6,95 7,23	$C_{28}H_{61}NS$	93
(XI)	*n*-Bu	Phenyl	86–90	74,85 75,21	11,50 11,68	3,61 3,99	9,40 9,12	$C_{22}H_{41}NS$	97
(XII)	*n*-Bu	*p*- Tolyl	80–85	75,47 75,61	11,50 11,78	3,61 3,84	9,40 8,77	$C_{23}H_{43}NS$	96

We have developed a general method for the preparation of tetraalkylammonium thiolates without these disadvantages [3]. This new method is based on the reaction of R_4NOH with various thiols



$$\left[R-\overset{\displaystyle R}{\underset{\displaystyle R}{N}}-R\right]^+\bar{O}H + R'SH \xrightarrow[6-10^\circ]{C_6H_6} \left[R-\overset{\displaystyle R}{\underset{\displaystyle R}{N}}-R\right]^+\bar{S}R' + H_2O,$$

where R is a C_1–C_4 alkyl group and R' is a C_2–C_{12} alkyl, phenyl, lower alkylphenyl, furfuryl, pyridyl, or cyclohexyl group.

The temperature range of the reaction (6-10°C) is dictated because benzene freezes at lower temperatures, while the yield of the desired product is reduced at higher temperatures due to formation of the corresponding disulfide. The subsequent distillation of benzene was carried out in vacuum at a temperature not exceeding 50-55°C since decomposition of the product occurs at higher temperatures. Tetraalkylammonium thiolates are obtained under these conditions in almost quantitative yield (see Table 1).

The sample of tetramethylammonium phenylthiolate prepared by this procedure virtually does not display IR bands for the OH group (3300-3600 cm^{-1}) and its melting point was 20°C higher than that reported in the indicated patent report [2]. The structure of the phenylthiolate was supported by ^1H and ^{13}C NMR spectroscopy.

The ready oxidizability and hygroscopicity of tetraalkylammonium thiolates also complicates their analysis and determination of their physical indices. Thus, the melting point determinations for these compounds must be carried out in evacuated, sealed capillaries, while the elemental analyses must be performed immediately upon their preparation with storage in an inert atmosphere. These circumstances may account for the discrepancies in the elemental analysis data in some cases.

We have considerably expanded the range of tetraalkylammonium thiolates by using aliphatic and heteroaromatic thiols in the reaction with R_4NOH in addition to aromatic thiols. The properties of these compounds have not been studied extensively. Tetraalkylammonium phenylthiolates may be used as intermediates in the synthesis of tetraalkylammonium aluminum hydrides employed as reducing agents [2] and as initiators for the quantitative polymerization of acrylates to give polymers with narrow molecular weight distribution [4].

Testing of these tetraalkylammonium thiolates for biological activity at the All-Union Scientific Research Institute of Chemical Agents for the Protection of Plants (VNIIKhSZR) and the All-Union Scientific Research Institute of Disinfection and Sterilization (VIIDiS).

EXPERIMENTAL

The melting points were obtained on a Koeffler block. The IR spectra were taken for vaseline mulls on a UR-20 spectrometer. The ^{1}H NMR spectra were measured relative to TMS on a Bruker WM-250 spectrometer at 250 MHz. The ^{13}C NMR spectra were measured relative to TMS on the same spectrometer at 62.89 MHz.

General Procedure. A sample of 0.015 mole R_4NOH was mixed with 10 ml benzene under argon. The mixture was cooled to 6°C. A sample of 0.015 mole thiol was added dropwise with stirring. The temperature of the reaction mixture was maintained $\leq$10°C. After 1 h, this mixture was evaporated on a rotary evaporator at 10 mm Hg. The crystalline residue was dried for 12 h at 0.01-0.001 mm Hg and 50-55°C.

Tetramethylammonium Phenylthiolate (I). a. A sample of 1.36 g (0.015 mole) Me_4NOH was mixed with 1.7 g (0.015 mole) thiophenol in 10 ml benzene at 10°C to give 2.69 g (97.8%) (I), mp 161-164°C (in a sealed, evacuated capillary) (mp 141-144°C [2]). Found, %: C 65.27; H 9.25; N 7.38; S 17.44. $C_{10}H_{17}NS$. C 65.58; H 9.29; N 7.65; S 17.44. There are no bands in the IR spectrum at 2600 (SH) and 3300-3600 cm^{-1} (OH). ^{1}H NMR spectrum in CD_3OD (δ, ppm): 7.33 d (2H, o-CH, J 7.9 Hz), 6.91 t (2H, m-CH, J 7.5 Hz), 6.74 t (1H, p-CH, J 7.3 Hz), 2.98 s (12H, $N(CH_3)_4$. ^{13}C NMR spectrum in CD_3OD (δ, ppm): 121.29 (p-C), 128.58 (o-C), 134.49 (m-C), 150.78 (S–C), 55.97 (NMe_4).

b. Experiment for comparison under the conditions of the indicated patent [2]. A sample of 10% aqueous Me_4NOH (0.033 mole) was added to 3.6 g (0.033 mole) thiophenol under argon until thiophenol was completely dissolved. A small amount of diphenyl disulfide was separated by filtration under argon. The filtrate was evaporated on a rotary evaporator at 45°C. The product was then dried for 24 h at 70°C and 0.001 mm Hg to give 5.7 g (94.2%) (I), mp 143-146°C (in a capillary). IR spectrum (ν, cm^{-1}): 3300 (OH). Found, %: C 59.98; H 10.16; N 7.82; S 12.09. Calculated, %: C 65.59; H 9.29; N 7.65; S 17.48.

Tetramethylammonium Dodecylthioate (II). In accord with the general procedure, 1.36 g (0.015 mole) Me_4NOH and 3 g (0.015 mole) dodecanethiol in benzene gave 4.05 g (98.8%) (II), mp 146-148°C (in a capillary). The IR spectrum lacks bands at 2600 (SH) and 3300-3600 cm^{-1} (OH). Found, %: C 68.48; H 13.96; N 4.93; S 11.92. $C_{16}H_{37}NS$. Calculated, %: C 69.82; H 13.45; N 5.09; S 11.64.

The physical indices of the other tetraalkylammonium thiolates obtained, (III)-(XII) are given in Table 1.

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