ties of material and 2.70 g. (0.02 mole) of trichlorosilane in 10 ml. of ether was added dropwise. After stirring for ten minutes, the mixture was poured into dilute acid and worked up as described in (b). Crystallization from ethyl acetate gave 4.3 g. (40%) of the pure silane, m. p. 216–217° (cor.), which gave no depression of melting point when mixed with the material from (a) and (b), respectively.

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## Secondary Amine Salts of Some Thiophenols

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In some recent studies in this Laboratory involving the condensation of formaldehyde and secondary amines with thiophenols, it was noted that if the secondary amine was first mixed with the thiophenol, an appreciable amount of heat was generated and a crystalline precipitate was formed. It was decided to investigate these precipitates on the supposition that they were salts.

TABLE I

SALTS OF SECONDARY AMINES AND SOME THIOPHENOLS

| Salts of *p*-thiocresol | Solvent used in prep. | Solvent used in recryst. | Yield, % | Color of crystals | M. p., °C. | Formula | S Analyses, % Calcd. | S Analyses, % Found | | Specific conductivity × 10⁴ Aqueous sol. | Specific conductivity × 10⁴ 95% alcohol sol. |
|---|---|---|---|---|---|---|---|---|---|---|---|
| Diethylamine[a] | Dioxane | Benzene | 72 | Colorless | 51–52 | $C_{11}H_{19}SN$ | 16.24 | 15.63 | 15.52 | 5.99 | |
| Piperidine | Ethyl alc. | Ethyl alc. | 89.5 | Colorless | 137–138 | $C_{12}H_{19}SN$ | 15.31 | 15.42 | 15.59 | 6.75 | 1.14 |
| Morpholine | [b] | | 94 | Colorless | 71.5 | $C_{11}H_{17}OSN$ | 15.17 | 15.27 | 15.30 | 5.43[g] | |
| Salts of 2-thionaphthol | | | | | | | | | | | |
| Diethylamine[c] | Dioxane | Dioxane | 89 | Yellow | 107 | $C_{14}H_{19}SN$ | 13.73 | 13.92 | 13.71 | 4.74 | |
| Piperidine | Dioxane (40 ml.) | Dioxane | 91 | Yellow | 139–140 | $C_{15}H_{19}SN$ | 13.47 | 13.24 | 13.03 | 6.05 | 1.74 |
| Morpholine | Dioxane | [d] | 28.5 | Yellow | 86–87 | $C_{14}H_{17}OSN$ | 12.96 | 13.18 | 12.85 | 3.29[g] | |
| Salts of 1-thionaphthol[e] | | | | | | | | | | | |
| Diethylamine | Dioxane | Dioxane | 93.5 | Cream | 99–102 | $C_{14}H_{19}SN$ | 13.73 | 13.84 | 13.88 | 5.50 | |
| Piperidine | Ethyl alc. (50 ml.) | Ethyl alc. | 68 | Cream | 145–149 | $C_{15}H_{19}SN$ | 13.47 | 13.41 | 13.13 | 4.74[f] | 1.61 |
| Morpholine | Dioxane | Dioxane | 47 | Cream | 95–96 | $C_{14}H_{17}OSN$ | 12.96 | 12.90 | 12.83 | 3.23[g] | |

[a] This salt appears to sublime at about 127°. [b] This salt was prepared by the direct union of morpholine and *p*-thiocresol. [c] This salt appears to sublime at about 101°. [d] This salt was not recrystallized. Melting point of crude salt did not change on recrystallization. [e] It has been shown in this laboratory that the 1-thionaphthol from the source used also contained some 2-thionaphthol. This may explain why the melting points of these salts were not too sharp. See Grillot, Levin, Green and Bashford, THIS JOURNAL, 72, 1863 (1950). [f] An 0.008 *M* solution was used. [g] A saturated solution was employed.

Previously, Kraus and White[1] dissolved thiophenol in liquid ammonia and obtained a white crystalline precipitate, which they assumed was the ammonium salt of thiophenol. It was insoluble in petroleum ether and gradually decomposed on standing in the air with the evolution of ammonia. Gordy and Stanford[2] observed that white crystalline solids are formed when piperidine, cyclohexylamine and triamylamine are mixed with thiophenol. These were believed to be salts but were not further studied.

From the results of our investigation, we feel that there is sufficient evidence to indicate that the products of the interaction of the thiophenols and the secondary amines are true salts. The compounds obtained, with the exception of the morpholine salts, are insoluble in ether. All are appreciably soluble in water, but their aqueous solution soon becomes cloudy due to hydrolysis.

### Experimental

The 1-thionaphthol was obtained from a sample of a rubber peptizing agent RPA No. 4 that contained about 30% by weight of this thiophenol and which was kindly furnished us by Mr. M. A. Youker of E. I. du Pont de Nemours and Company. The fraction distilling at 145–147° at 13 mm. pressure was collected as the desired material. All the other chemicals used in this investigation were of the practical grade and were obtained from the Eastman Kodak Company, Rochester, N.Y.

Five grams of the thiophenolic compound was dissolved in 20–25 ml. of the appropriate solvent (see Table I). An equivalent amount of the amine was then added to this solution and the resulting mixture was cooled to 15–20° in an ice-bath. After crystallization was complete, the salt was removed by filtration, was washed with small portions of ether and was then dried in a vacuum desiccator. These salts were recrystallized from ether, benzene, 95% ethyl alcohol or dioxane, as is indicated in Table I.

One hundredth molar aqueous solutions of the salts were prepared and their conductivities were determined. If the salts were not soluble to this extent, saturated solutions were employed. The equivalent conductivity of the aqueous solutions of the diethylamine and the piperidine salts of *p*-thiocresol agreed closely with the conductivity of the aqueous solutions of the free amines. (We found specific conductivity of diethylamine to be 6.08 × $10^{-4}$ and piperidine to be 6.86 × $10^{-4}$.) Saturated aqueous solutions of the thiols gave no measurable conductivity in the conductivity apparatus used by us. From these results we have concluded that these salts are rapidly and nearly completely hydrolyzed in an aqueous solution.

The conductivities of the piperidine-thiol compounds were then determined in a 95% ethyl alcohol solution. Such a solution has a sufficiently large dielectric constant that the salts should ionize, while hydrolysis in this solvent should be slower than in water. A measurable conductivity of these salts in the alcohol solution was obtained, whereas solutions of the thiols and the amines in this solvent gave no measurable conductivity in our apparatus.

Analyses, physical properties and conductivity data are summarized in Table I.

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(1) Kraus and White, THIS JOURNAL, 45, 768 (1923).

(2) Gordy and Stanford, *ibid.*, 62, 497 (1940).