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Synthesis and Properties of the Six Thioxylenol Isomers

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The six dimethylthiophenol isomers were synthesized and oxidized to the corresponding disulfides. The thioxylenols were also condensed with acrylic acid to form solid derivatives.

Commercial mixtures of thiophenol and its methyl homologues are available from caustic washing of gasoline. These can be separated satisfactorily by distillation into thiophenol, mixed thiocresols, and mixed thioxylenols. Analysis of the thiocresol fraction for the three individual isomers is possible by infrared spectroscopy, since pure *ortho-*, *meta-*, and *para-*thiocresols are available as standards. The determination of the isomer distribution in the thioxylenol cut has not hitherto been possible, since none of the six dimethylthiophenols is obtainable from commercial sources and only two of them have been described in the literature.

We have synthesized all six isomers from the corresponding xylidines, and have determined the boiling point and infrared spectrum of each. In addition, each compound was oxidized to the disulfide and also condensed with acrylic acid to form a solid derivative for identification.

EXPERIMENTAL

All melting points are corrected; boiling points were obtained using a calibrated Chromel-Alumel thermocouple. Distillation of the thioxylenols was carried out on a 1.2 cm. × 60 cm. column packed with Heli-Pak.

Starting materials were Eastman Kodak Co. White Label reagents except in the case of 2,3- and 3,4-dimethylanilines, which were Aldrich Chemical Co. research grade products. All were used without preliminary purification. The thioxylenols were synthesized using the method described by Leuckart[1] for the preparation of 2,4-thioxylenol *via* reaction of diazotized xylidines with potassium ethyl xanthate, followed by hydrolysis of the xylyl ethyl xanthate. The acidified hydrolysate was extracted with ether; after drying over Drierite and removal of ether at reduced pressure, the thioxylenol was immediately distilled and a center fraction retained for further work.

In the case of 3,5-thioxylenol, which appears to be especially susceptible to air oxidation, only a small amount of thiol was obtained on distillation. The residue, presumably disulfide, was reduced with hydrogen over Davison 50% MoS_2-on-alumina catalyst (20 weight % catalyst) at 160–170°C; cold hydrogen pressure 1925 p.s.i. Distillation of this reduced material produced 3,5-thioxylenol in a yield comparable to the other isomers.

Thiol titrations were carried out on each of the pure thioxylenols, using the method of Tamele and Ryland,[2] except that methanol was substituted for isopropyl alcohol as solvent.

Reported boiling points for 2,4-thioxylenol at 760 mm. are 207–208°;[3] 212–214°;[1,4] for 2,5-thioxylenol 205–206°,[3] 211–212°;[4] and 204–205°.[5] The use of 3,5-thioxylenol in synthesis is described[6] but no preparation or physical properties given.

TABLE I

PROPERTIES OF THIOXYLENOLS

	Yield,	%	B.P.	Found[a]		
	%	Thiol	(50 mm.)	C	H	S
2,3-Thioxylenol	58	97.8	132.2°C	69.37	7.49	23.1
2,4-	48	99.3	127.0	69.63	7.60	22.7
2,5-	55	99.1	126.3	69.38	7.58	22.4
2,6-	47	99.2	122.0	69.37	7.40	22.6
3,4-	63	99.1	132.5	69.28	7.25	22.9
3,5-	54	99.7	127.5	69.41	7.30	22.8

[a] Calcd. for $C_8H_{10}S$: C, 69.51· H, 7.29; S, 23.20.

The *beta*-(dimethylphenylthio)propionic acids were obtained by refluxing 2.7 g. of pure thioxylenol with 1.44 g. acrylic acid (Eastman Kodak White Label) and 1.2 g. sodium hydroxide in 25 ml. of water for 1 hr. Acidification of the reaction mixtures precipitated oils, solidifying to white solids. These crude acids were purified by repeated crystallizations from hexane.

TABLE II

beta-(DIMETHYLPHENYLTHIO)PROPIONIC ACIDS

		Found[a]		
	M.P., °C	C	H	S
Beta-(2,3-dimethylphenylthio)-propionic acid	94–95	62.58	6.54	15.4
2,4-[b]	81–82	62.82	6.68	15.0
2,5-	101.5–102.5	62.96	6.89	15.3
2,6-	90–91	62.55	6.49	15.4
3,4-	70–71	62.81	6.66	15.6
3,5-	65.5–66.5	62.69	6.39	15.2

[a] Calcd. for $C_{11}H_{14}O_2S$: C, 62.82, H, 6.71; S, 15.25. [b] The reported melting point of *beta*-(2,4-dimethylphenylthio)-propionic acid is 84–85°.[7]

Bis(2,6-dimethylphenyl) disulfide was obtained by extraction of the undistillable pot residue from 2,6-thioxylenol with hot isopropyl alcohol, and purified by a series of recrystallizations from aqueous isopropyl alcohol.

The other disulfides were obtained by bubbling air through a mixture of one gram thioxylenol in 25 ml. ammonium hydroxide. The precipitated disulfide was extracted with ether, washed with 10% sodium hydroxide, and recrystallized from aqueous isopropyl alcohol. Crystals were obtained except in the case of bis(2,4-dimethylphenyl) disulfide and bis(3,5-dimethylphenyl) disulfide, which were light amber oils and not further characterized.

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(1) R. Leuckart, *J. prakt. Chem.*, (2) **41**, 192 (1890).

(2) M. W. Tamele and L. B. Ryland, *Ind. Eng. Chem., Anal. Ed.*, **8**, 16 (1936).

(3) L. Gatterman, *Ber.*, **32**, 1147 (1899).

(4) S. Ruhemann, *Ber.*, **46**, 3389 (1913).

(5) F. Taboury, *Ann. Chim. (Paris)*, (8), **15**, 15 (1908).

(6) K. v. Auwers and W. Thies, *Ber.*, **53**, 2297 (1920).

(7) F. Krollpfeiffer and H. Schultze, *Ber.*, **56B**, 1819–24 (1923).

TABLE III
SYMMETRICAL BIS(DIMETHYLPHENYL) DISULFIDES

	M.P., °C	Found[a]		
		C	H	S
Bis(2,3-dimethylphenyl)disulfide	99.0–99.5	69.86	6.46	23.4
2,4-	Oil	70.18	6.74	22.7
2,5-	46.5–48.0[b]	69.74	6.39	23.3
2,6-	102.5–104.0	70.05	6.66	23.6
3,4-	50–51	69.45	6.60	23.3
3,5-	Oil	69.80	6.84	23.1

[a] Calcd. for $C_{16}H_{18}S_2$: C, 70.02; H, 6.61; S, 23.37. [b] Bis-(2,5-dimethylphenyl) disulfide is reported to melt at 46–47°.[5]

DISCUSSION

Although thiophenols are generally believed to show little intermolecular hydrogen bonding,[8] it is evident from an examination of the boiling points in Table I that this phenomenon must exist to a certain extent. The lowest-boiling compound, 2,6-thioxylenol, has a normal boiling point more than four degrees below that of any of the other isomers due to steric interference by the two ortho methyl groups with intermolecular bonding. This behavior is analogous to, although less pronounced than, that of 2,6-xylenol, which boils some 10 degrees below any of the other dimethylphenols.

Infrared spectra of the six thioxylenols were obtained and compared with the spectra of the same compounds in dilute cyclohexane solutions. No clear evidence for or against intermolecular hydrogen bonding could be secured by this method, due to the weak absorption of the SH bond.

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[8] L. J. Bellamy, *The Infrared Spectra of Complex Molecules*, London, Methuen, 1954, p. 289.

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Some Unusual Water Solubility Properties of Alkyl Tetraalkylphosphorodiamidates

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A number of alkyl tetraalkylphosphorodiamidates have been prepared; some of these have been found to possess unusual water solubility characteristics. A number of other miscellaneous types of phosphorus compounds are described.

During an investigation of the physical properties of a variety of classes of organic phosphorus compounds, the unusual inverse water solubility of the alkyl tetraalkylphosphorodiamidates, $ROP(O)(NR'_2)_2$, prompted us to further investigate these compounds.

Little has appeared concerning the preparation and properties of the phosphorodiamidates, where all substituents are aliphatic,[1] since Michaelis[2] first prepared four of these compounds in 1903.

The compounds of this type which we have prepared are listed in Table I. Except where otherwise indicated in the EXPERIMENTAL, yields were 85% or better.

Most of these compounds were prepared by reacting the appropriate alcohol with phosphoryl chloride to give the alkyl phosphorodichloridate, which was then reacted with excess amine. Under the experimental conditions used, there was never any indication of diester formation. When the amine was readily available, excess amine was used as the acid acceptor. When the amine was of limited availability, triethylamine or pyridine was used. The diamidates prepared from dimethylamine were obtained in higher yield when aqueous rather than anhydrous dimethylamine was used. With all other amines, however, aqueous solutions gave lower or negligible yields. Consequently, except for the preparation of the diamidates of dimethylamine all reactions were carried out under anhydrous conditions.

Compound XVI could not be prepared by this procedure. The reaction of phosphoryl chloride with 2-ethylmercaptoethanol gave only polymeric products, so an inverse synthesis was used for this compound. Phosphoryl chloride was treated with a large excess of diethylamine, and the phosphorodiamidic chloride which was isolated was then allowed to react with the sodium salt of 2-ethylmercaptoethanol to give the desired product.

All attempts to prepare derivatives of diisopropylamine were unsuccessful.

The intermediate acid chlorides were all fuming, lachrymatory liquids; the diamidates were all liquids. The low molecular weight diamidates had pepper-like odors; the higher molecular weight diamidates generally had camphor-like odors.

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[1] G. M. Kosolapoff, *Organophosphorus Compounds*, John Wiley and Sons, New York, 1950.

[2] A. Michaelis, *Ann.*, **326**, 129 (1903).