

fractionation described under "3-Methylpyridine," Section B. The total volume, 200 cc., was converted into the compound $C_7H_9N.HCl.2HgCl_2$ by mixing it with 187 cc. of conc. hydrochloric acid and adding the mixture to a solution of 950 g. of mercuric chloride in 3600 cc. of boiling absolute alcohol. The compound which separated as the solution cooled to 15° was recrystallized four times from 1 liter of boiling alcohol. The melting point of the product was 128° , which remained unaltered by further crystallization. The yield was 80 g.

The base was regenerated by treatment with a concentrated solution of 19 g. of sodium hydroxide. The base containing dissolved water was separated from the precipitate by filtration and was dried over solid sodium hydroxide. Through a dry apparatus the base distilled completely at 157.1° under 760 mm. pressure. The mass of 1 cc. at 25° is 0.9273 g. With water it gives a minimum critical solution temperature of 22.5° . The base was identified as 2,4-dimethylpyridine by oxidation to pyridine-2,4-dicarboxylic acid by the method described in the case of 3-methylpyridine, using double the proportion of potassium permanganate. The product melted sharply at 241° ; vigorous evolution of carbon dioxide commenced at once, indicating a dicarboxylic acid. An aqueous solution of the acid gave a deep red coloration with ferrous sulfate solution, which indicates a methyl group in Position 2 in the original base.

Summary.

Pure samples of pyridine and certain of its homologs have been prepared. Boiling points and densities have been determined and found to be as follows: pyridine, b. p. 115.3° , d_4^{25} 0.9776; 2-methylpyridine, b. p. $128-9^\circ$, d_4^{25} 0.9404; 3-methylpyridine, b. p. 143.8° , d_4^{25} 0.9515; 2,6-dimethylpyridine, b. p. about 137.5° , d_4^{25} 0.9200; 2,4-dimethylpyridine, b. p. 157.1° , d_4^{25} 0.9273.

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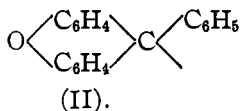
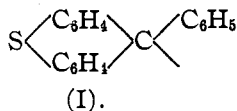
[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF MICHIGAN.]

PHENYL-THIO-XANTHYL.

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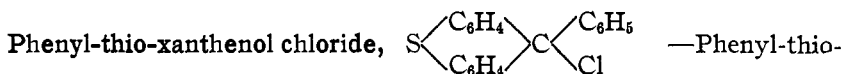
The free radical, phenyl-thio-xanthyl (I), differs structurally from phenyl-xanthyl (II) only in the substitution of a sulfur for an oxygen



atom. The difference in the degree of dissociation of the dimolecular forms of these two radicals, as reported in the literature, is therefore

quite perplexing. Schlenk and Renning¹ found 82% of the latter substance to be monomolecular by determining the molecular weight in a boiling benzene solution of 1.5% concentration, while they report only 14% of the former to be monomolecular in freezing benzene (0.7% solution). A later investigation² showed phenyl-xanthyl to be 70% monomolecular in freezing naphthalene (1.5% solution).

As Schmidlin³ justly observes, molecular-weight determinations of free radicals are of value only when accompanied by the determinations of oxygen absorption. Otherwise unnoticed transformations or isomerizations of the radicals may vitiate the results. The results of Gomberg and Schoepfle on phenyl-xanthyl were checked by parallel oxygen absorptions; it now seemed desirable to repeat the investigation of phenyl-thio-xanthyl, controlling the work by this essential test.



xanthenol was prepared from thio-xanthone and phenyl magnesium bromide,⁴ the thio-xanthone having been made from thiosalicylic acid.⁵ The xanthenol used in this work was recrystallized from hot petroleum ether (100–110°), and had a melting point of 105° or over.

The red additive compound, phenyl-quo-thio-xanthenol chloride-hydrochloride⁶ was made by passing a slow stream of dry hydrogen chloride into a concentrated ethereal solution of the carbinol. It is quite insoluble in this solvent. The red crystals were quickly filtered, washed, and dried in a vacuum desiccator over sulfuric acid.

Various procedures were investigated in order to arrive at the most satisfactory method for removing the extra molecule of hydrochloric acid. The simplest procedure proved to be the best. Ten g. of chloride-hydrochloride was suspended in 100 cc. of dry benzene in a distilling flask which carried an extra side arm sealed into the bulb. Through a glass tube inserted in this side arm there bubbled through the liquid a stream of air, dried by passing through conc. sulfuric acid and phosphorus pentoxide. The flask was heated in a glycerine bath to 90°, the solid gradually went into solution and the deep red color lightened considerably. The solvent was completely distilled in the course of 1½ hours, the last portion being removed under reduced pressure to avoid superheating. On cooling, the deep red oil became a mass of lighter colored crystals, from which after recrystallization from a large quantity of dry ether in the absence of moist air, colorless crystals of chloride were obtained. They turned reddish when dried in a stream of air, in spite of most efficient drying systems. Once dry, the crystals could be preserved in a vacuum desiccator for a long time with little change. Yield 60 to 70%.

Analysis. Calc. for $\text{C}_{19}\text{H}_{18}\text{ClS}$: Cl, 11.50. Found: 11.30.

¹ Schlenk and Renning, *Ann.*, **394**, 188 (1912).

² Gomberg and Schoepfle, *THIS JOURNAL*, **39**, 1671 (1917).

³ Schmidlin, "Das Triphenylmethyl," **1914**, p. 159.

⁴ Gomberg and Cone, *Ann.*, **376**, 201 (1910).

⁵ Davis and Smiles, *J. Chem. Soc.*, **97**, 1296 (1910).

⁶ Gomberg and Cone, *Ann.*, **376**, 202 (1910).

In this preparation, heating for too long a period gives a deep red gum which will not crystallize, or else crystallizes as an impure product, and in lower yield.

Oxygen Absorptions.—The preparation of the free radical is difficult because of the sensitivity of the chloride to traces of water, with which it forms carbinol and hydrochloric acid, retaining the latter as the additive salt. The presence of free acid has been shown repeatedly to be harmful to the existence of a free radical. The instability of this free radical, as indicated by the following data, may be due to the influence of acid, although it is also possible that the radical spontaneously polymerizes because of other influences, *e. g.*, light, heat. The nature of the solvent is clearly an important factor, so far as the speed of the change is concerned.

All measurements were made by sealing chloride, molecular silver, and the solvent in a glass tube, shaking at room temperature for the specified time, and measuring the absorption of oxygen in the usual apparatus.⁷

Wt. of Chloride. G.	Time of Shaking.		Oxygen Absorbed.	
	Hours.		Cc. (N. T. P.)	% of Calc.
0.5630	0.5	Using Bromobenzene as solvent.	21.3	104.4
0.4536	0.5		18.0	109.1
0.7535	1.0		27.2	99.3
0.6840	5.25		25.3	102.0
0.6080	18.0		19.5	88.2
0.5953	41.0		14.6	67.6
0.3971	<i>a</i>		14.0	97.2
		Using Benzene as solvent.		
0.8600	0.5		20.8	95.5
0.5800	0.5		20.2	95.7
0.5399	0.5		15.5	79.1
0.5480	0.5		15.5	77.9
0.5725	0.5		17.1	82.2
0.8425	0.5		25.9	84.6
0.7976	1.0		23.5	81.0
0.8940	3.0		24.7	76.0
0.8200	3.0		18.5	62.1
0.4848	6.0		7.5	42.6
0.4777	14.5		4.6	26.6

(*a*) Shaken with solvent and silver in absorption apparatus.

This record of the progressive disappearance of the free radical in solution, as time elapses, makes its instability most apparent and indicates the improbability of isolating it in the solid state.

Attempts to Isolate the Free Radical.—Preliminary trials with chloride and silver, shaken in ether, acetone or ethyl acetate, showed the latter two to be undesirable, since the brown-red solutions changed to a straw yellow in 24 hours. The free radical in solution possesses high tinctorial power; no difference in shade or depth of color can be noted between benzene or bromobenzene solutions giving either high or low values for

⁷ Gomberg and Schoepfle, *THIS JOURNAL*, **39**, 1661 (1917).

oxygen absorption, so that the qualitative test of decolorization with oxygen is misleading unless accompanied by the quantitative measure of absorption.

Using ether as solvent, chloride and silver were shaken one hour. On working up in the usual manner, a dark oil was obtained which changed to light red crystals in the course of a day. These crystals could not be redissolved in a large quantity of ether, showing that the original soluble product was no longer present. Redissolved in benzene and treated with petroleum ether, they formed a light pink precipitate without crystalline structure. This material did not absorb oxygen, did not contain chlorine, and did not melt under 240° .

Since bromobenzene solutions appeared to be relatively stable, these were used with a 30-minute shaking period. To avoid the high temperature otherwise necessary to distil the solvent, distillation was dispensed with altogether. A large amount of petroleum ether was added to the solution precipitating a red-brown amorphous mass, which when washed with ether, became light pink. The test for oxygen absorption was made on the final dry product within 5 hours from the beginning of the experiment, but no oxygen was absorbed.

The procedure of Schlenk and Renning¹ was next duplicated. Copper bronze ("Naturkupfer C," which they also had used) was washed with alcohol and with ether, and dried in a stream of hydrogen at 250° for 3 hours. Its efficiency was demonstrated by preparing triphenylmethyl in boiling benzene solution under exactly the same conditions used later for phenylthio-xanthyl. 4.4 g. of pure phenyl-thio-xanthenol chloride and 20 g. of copper bronze were placed in a flask and protected by an atmosphere of carbon dioxide. Sixty cc. of dry thiophene-free benzene was admitted and heated to the boiling temperature in a glycerine bath. A stream of dry carbon dioxide was passed through the apparatus during the whole time of heating. Ten minutes was required to bring the benzene to boiling, heating was continued for 45 minutes and the red-brown solution was filtered into the free radical apparatus, together with 15 cc. of warm benzene. The solvent was evaporated under reduced pressure to $\frac{1}{3}$ its volume and cooled. Since no precipitate appeared, petroleum ether was added and cooling continued overnight. Only a slight deposit of dark red-brown crystals had formed by the next morning, so a large quantity of petroleum ether was used, which threw down a pink amorphous solid. The mother liquor was removed and the product dried at room temperature in a stream of carbon dioxide. Yield, 3.0 g.

Oxygen absorption: 0.5763 g. of substance in xylene solution absorbed 1.3 cc. (N. T. P.) of oxygen, which is 5.5% of the calculated absorption for pure free radical.

The experiment was repeated with the precipitation of the product with petroleum ether immediately after partial evaporation of the solvent, so

that the oxygen absorption was measured 4 hours from the beginning of the operation. The product did not absorb oxygen.

The material obtained in this manner is soluble in benzene, xylene, chloroform and carbon disulfide, giving rich wine-red solutions; it is slightly soluble in warm acetone and is insoluble in ether, petroleum ether and gasoline. Several reprecipitations from benzene solution by petroleum ether gave a colorless amorphous solid, which decomposed at 300° to 302° . It is apparently identical with the products obtained under the other procedures. In no case could any peroxide be isolated.

As a final check upon the possibility of making the free radical by this last method, oxygen absorptions were taken on benzene solutions of chloride which had been boiled with copper bronze. At the end of the heating period the tubes containing the solutions were filled with benzene, cooled to room temperature and sealed. During the entire operation the solutions were under an atmosphere of dry hydrogen. The following measurements were made.

1.0169 g. of chloride, boiled for one hour, absorbed 25.2 cc. (N. T. P.) of oxygen, or 68.3% of the calculated quantity.

0.6516 g. of chloride, boiled for one hour, then allowed to stand for two hours at room temperature, absorbed 15.7 cc. (N. T. P.) of oxygen, or 66.5%.

0.7475 g. of chloride, boiled for three hours, absorbed 12.8 cc. (N. T. P.) oxygen, or 47.2%.

From these experiments we are inclined to conclude that the material obtained by Schlenk and Renning was not the free radical, phenyl-thio-xanthyl; and we believe that their values for the molecular weight and degree of dissociation of this radical should be rejected.

This investigation was made with the assistance of The National Aniline and Chemical Company Fellowship. We wish to express our obligations for the aid we have thus received.

Summary.

The preparation of pure phenyl-thio-xantheno! chloride has been described. The free radical, phenyl-thio-xanthyl, has been prepared in solution and found to be very unstable, the rate of decomposition varying with the nature of the solvent. The radical could not be isolated in the solid state. It has been shown that the values obtained by Schlenk and Renning for the molecular weight of this substance were made on material which was in all probability not the free radical.