packed into the narrow tube (2), which was suspended in an air-bath. The liquid bath (3) served as an insulator for the air-bath, and also to bring it up to the required temperature. A thermometer suspended in the liquid bath indicated the approximate temperature of the air-bath, while a sensitive thermocouple (1) inserted directly into the sample showed the exact freezing temperature of the phenothiazine. The liquid bath was heated by means of an electric heater (4) connected to a variable-voltage transformer. The thermocouple was made of 34-gage copper and constantan wires, with the hot junction inserted into a 3-mm. glass tube one end of which was drawn down to about 1 mm. and sealed. A drop of mercury in the constricted portion of this glass tube helped to make thermal contact between the hot junction and the surroundings, thus reducing any lag to a minimum. The mercury droplet did not affect the characteristics of the thermocouple. By means of a precision potentiometer and galvanometer, the voltage produced was read to within 1 microvolt—equivalent to 0.019° at the melting point of phenothiazine. The thermocouple, standard cell, and potentiometer were standardized at the National Bureau of Standards previous to their use in this work.

Procedure for Freezing-point Determinations.—After the sample had been packed into the freezing-point tube and the apparatus assembled as shown in Fig. 1, the temperature was raised until the solid phenothiazine had melted. (The approximate melting temperature could also be determined, but since the heat required for melting the sample had to be drawn from the surrounding air the melting point was not so sharp as the freezing point.) The voltage input to the electric heater was then reduced until the temperature of the liquid bath dropped to 3 or 4° below the freezing point of the phenothiazine, and the molten material was allowed to cool. The molten compound was permitted to supercool to 0.1–0.5° below the freezing point, when crystallization was induced by "scratching" or seeding. The temperature then rose to the freezing point where it remained constant during crystallization. During the period of cooling and freezing the molten pheno-

thiazine was stirred by an up-down movement of the glass tube containing the thermocouple.

Results

The highest freezing point obtained for recrystallized phenothiazine was $184.21 \pm 0.02°$. This freezing point was obtained after three recrystallizations from toluene and butanol. These experiments were replicated four times. One sample of sublimed material followed by two recrystallizations from toluene gave a freezing point of 184.7°.

In seven replications the freezing point determined in our apparatus of sublimed phenothiazine varied between 185.10 and 185.13°. Three replications of melting points gave an average of $185.14 \pm 0.04°$. The freezing point of pure phenothiazine was thus established at $185.11 \pm 0.02°$.

From the results obtained in this investigation it is evident that to obtain phenothiazine of the highest purity the compound must be sublimed under carefully controlled conditions. This is demonstrated by the fact that when phenothiazine is recrystallized after sublimation the product has a significantly lower freezing point, and also that repeated recrystallizations of the original material did not raise the freezing point of the crystals obtained above $184.21 \pm 0.02°$, or approximately 0.9° lower than that of the pure compound.

Summary

The freezing point of pure phenothiazine prepared by sublimation has been found to be $185.11 \pm 0.02°$.

NOTES

The Disproportionation of R_6Pb_2 Compounds

BY GEORGE CALINGAERT, HAROLD SOROOS AND HYMAN SHAPIRO

It was shown in a previous paper from this Laboratory[1] that the different alkyl groups in mixtures of R_4Pb compounds will, under the influence of a suitable catalyst, redistribute themselves at random between all the lead atoms, giving a mixture of all the possible R_4Pb compounds in which the concentration of each of these

compounds can be predicted on the basis of the probability law. R_6Pb_2 compounds, on the other hand, when heated, disproportionate to yield the corresponding R_4Pb compounds and metallic lead, and it has been suggested[2] that this takes place in accordance with the equation

$$2R_6Pb_2 = 3R_4Pb + Pb \qquad (1)$$

The question then arises as to whether the decomposition of a mixture of R_6Pb_2 and R'_6Pb_2 will yield only R_4Pb and R'_4Pb, or whether it will

(1) Calingaert, Beatty and Soroos, THIS JOURNAL, **62**, 1099 (1940).

(2) Calingaert, Chem. Rev., **2**, 43–85 (1925).

yield in addition the three mixed compounds, $R_3R'Pb$, $R_2R'_2Pb$ and RR'_3Pb.

A mixture of Me_6Pb_2 and Et_6Pb_2 without the addition of any catalyst was heated in an atmosphere of nitrogen at 100° for five hours. No appreciable gas evolution was observed, and at the end of that period no R_6Pb_2 was found in the product, which was composed only of R_4Pb and metallic lead. The R_4Pb product was separated from the metallic lead and fractionated.

The amount of metallic lead recovered was only 5% greater than that called for by eq. 1. This is striking proof of how small a quantity of alkyl group is lost through side reactions, in spite of the rather profound change in structure which has taken place, and shows that the over-all disproportionation of R_6Pb_2 compounds is correctly represented by eq. 1.

The composition of the R_4Pb product is given in Table I and shows that it contained not only tetramethyllead and tetraethyllead, which obviously would have been expected, but in addition the other three possible lead alkyls, namely, trimethylethyllead, dimethyldiethyllead and methyltriethyllead. Since it is known[1] that tetraalkyllead compounds do not undergo redistribution in the absence of a catalyst, this indicates that the interchange of alkyl radicals in the present experiment took place either before or during, but not after, the decomposition of the R_6Pb_2 compounds.

TABLE I

COMPOSITION OF THE R_4Pb PRODUCT OBTAINED BY THERMAL DECOMPOSITION OF A MIXTURE OF Me_6Pb_2 AND Et_6Pb_2

Compound	Mole per cent.[a]
Me_4Pb	18
Me_3EtPb	15
Me_2Et_2Pb	23
$MeEt_3Pb$	31
Et_4Pb	13

[a] Determined from the distillation curve.[3]

Experimental

Preparation of Hexamethyldilead and Hexaethyldilead. —Hexaethyldilead was prepared by the method of Hein and Klein,[4] and hexamethyldilead by the method of Calingaert and Soroos.[5] Anal. Calcd. for Me_6Pb_2: Pb, 82.1. Found: Pb, 81.8. Calcd. for Et_6Pb_2: Pb, 70.4. Found: Pb, 70.2.

Decomposition of Hexamethyldilead and Hexaethyldilead.—The decomposition of the mixture of R_6Pb_2 compounds was carried out in two runs; 0.070 mole each of hexamethyldilead and hexaethyldilead was used in the

first, and 0.080 mole of each in the second. The materials were introduced into a 100-cc. 3-neck round-bottomed flask equipped with a nitrogen inlet, thermometer, and reflux condenser to which was connected, in series, a dry-ice trap and mercury bubbler. Each mixture was maintained at $100 \pm 5°$ for five hours while maintaining a nitrogen atmosphere within the system. Decomposition with the deposition of metallic lead and without any noticeable evolution of gas set in immediately and proceeded smoothly; there was also a noticeable evolution of heat.

After cooling to room temperature, the reaction products were filtered, and the metallic lead residues were extracted with several portions of ether. The ether solutions and the lead alkyl products from the two runs were combined and analyzed by distillation.[3] Table I gives the composition of the R_4Pb product. The metallic lead residues were dissolved in nitric acid and analyzed for lead. Found: total Pb, 32.5 g. (0.157 mole).

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ETHYL GASOLINE CORPORATION
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The Preparation of 4(5)-Hydroxymethylimidazole

BY WILLIAM J. DARBY,[1] HOWARD B. LEWIS AND JOHN R. TOTTER

4(5)-Hydroxymethylimidazole is a valuable intermediate for the synthesis of histidine, histamine, and related imidazole derivatives. Pyman's method[2] has been widely used for the preparation of this compound, but it is complicated and gives poor yields. Parrod[3] reported the formation of 4(5)-hydroxymethylimidazole during the prolonged aerobic oxidation of fructose or dihydroxyacetone in ammoniacal copper solution, but made no attempt to develop a preparative method. The procedure of Weidenhagen and Herrmann[4] affords good yields, but the dihydroxyacetone employed as starting material is difficult to secure in quantity. Weidenhagen, et al.,[5] later reported that 4(5)-hydroxymethylimidazole could be obtained from fructose in a yield of 38% of theoretical. Some difficulty was experienced in inducing crystallization of the free base. No analysis was recorded; identification rested solely on the melting point of the picrate. Akabori, et al.,[6] were unable to duplicate the yields reported by Weidenhagen and co-workers.

(1) This work was completed during current appointment as a Fellow in the Medical Sciences of the National Research Council, Department of Biochemistry, College of Physicians and Surgeons, Columbia University, New York, N. Y.

(2) Pyman, J. Chem. Soc., 99, 668 (1911).

(3) Parrod, Bull. soc. chim. (Mem.), 51, 1424 (1932).

(4) Weidenhagen and Herrmann, Ber., 68, 1953 (1935).

(5) Weidenhagen, Herrmann and Wegner, ibid., 70, 570 (1937).

(6) Akabori, Ose and Kanedo. Proc. Imp. Acad. (Tokyo), 16, 191 (1940).

(3) Calingaert, Beatty and Neal, THIS JOURNAL, 61, 2755 (1939).

(4) Hein and Klein, Ber., 71B, 2381 (1938).

(5) Calingaert and Soroos, J. Org. Chem., 3, 535 (1938).