known method[2] for the synthesis of aminoethanols.

Experimental

10-Anilino-1-decanol.—A 1-l. three-necked flask was equipped with a reflux condenser, nitrogen inlet, dropping funnel and a sparkless motor-driven stirrer. The apparatus was protected with calcium chloride tubes. Dry nitrogen was passed (1.5–2 cu. ft./hr.) through the flask during all subsequent operations until final decomposition of the reaction mixture. Dry ether (*ca.* 300 ml.) and powdered lithium aluminum hydride (14.3 g., 0.375 mole) were placed in the flask and stirred for a period of two hours prior to portionwise addition of a suspension of ω-carbomethoxypelargonanilide (36.4 g., 0.125 mole) in dry ether (250 ml.) over a 75-minute period. An insoluble product precipitated. Stirring and gentle refluxing were continued for 2.5 hours more, after which the reaction mixture was allowed to stand overnight under a slow stream of nitrogen (0.2 cu. ft./hr.).

Decomposition of the excess lithium aluminum hydride and the reaction complex was effected by the *cautious* addition first of water (60 ml.) from a dropping funnel and later of a 20% solution of sodium hydroxide (300 ml.). Even the great excess of alkali failed to dissolve the inorganic precipitate; hence, the mass was extracted several times with ether before being subjected to filtration under reduced pressure. The combined ethereal extracts were concentrated in a current of air to give a residue of 25.2 g. This was redissolved in ether and stirred with a slight excess of 5% hydrochloric acid. The precipitate of the amine hydrochloride was filtered after separation of the ethereal layer. From the aqueous filtrate a quantity of the desired free amino alcohol was liberated by the addition of 10% sodium hydroxide. The yield comprised 19.1 g. of the **hydrochloride of 10-anilino-1-decanol**, m.p. 101–104°, and 3 g. of 10-anilino-1-decanol, m.p. 42.5–43.7°, for a total of 63% of theoretical. Recrystallization of the hydrochloride twice from benzene–ethanol–ethyl acetate gave a sample of m.p. 104–105°.

Anal. Calcd. for $C_{16}H_{28}ClNO$: Cl, 12.4; N, 4.9; neut. equiv., 285.8. Found: Cl, 12.3; N, 4.9; neut. equiv., 286.

Two recrystallizations of the amino alcohol from aqueous methanol, then from ether–petroleum ether, gave a sample of m.p. 43–44°.

Anal. Calcd. for $C_{16}H_{27}NO$: C, 77.1; H, 10.9; N, 5.6. Found: C, 77.1; H, 10.7; N, 5.7.

4-Anilino-1-butanol (a) From Tetramethylene Chlorohydrin.—Aniline (93 g., 1 mole), tetramethylene chlorohydrin (54.25 g., 0.5 mole) and benzene (100 ml.) were refluxed for 26 hours in a 500-ml. round-bottom flask equipped with a suitable condenser. At the end of this time the supernatant liquid was decanted from the precipitate of aniline hydrochloride and combined with a little benzene used to rinse this precipitate. After distillation of the benzene at atmospheric pressure and the excess aniline at 3 mm. pressure, there was obtained 20 g. of nearly colorless product; b.p. 139–140° (3 mm.); $n^{20}D$ 1.565; yield 24%. In some runs an intermediate fraction, b.p. 85–100° (3 mm.), possibly N-phenylpyrrolidine, was obtained.

(b) **From Succinanilic Acid.**—Following the procedure described for 10-anilino-1-decanol a 42% yield of crude 4-anilino-1-butanol, distilling between 127–137° (*ca.* 2 mm.), was obtained by the reduction of succinanilic acid, using the following reagents: lithium aluminum hydride (5.9 g., 0.154 mole) in dry ether (100 ml.), and succinanilic acid (9.1 g., 0.047 mole) suspended in dry ether (150 ml.). Decomposition of the reaction mixture was effected as before. An analytical sample of the product distilled at 133° (*ca.* 1 mm.); $n^{20}D$ 1.563.

Anal. Calcd. for $C_{10}H_{15}NO$: N, 8.5. Found: N, 8.3.

4-Anilino-1-butanol formed a bright yellow, granular picrate (crystals pptd. from ether), m.p. 98–99°.

Anal. Calcd. for $C_{16}H_{18}N_4O_8$: C, 48.75; H, 4.6; N, 14.2; neut. equiv. 394.3. Found: C, 48.7; H, 4.6; N, 14.4; neut. equiv. 394.

2-*t*-Butylaminoethanol.—In a 500-ml. three-necked flask equipped with a reflux condenser, stirrer, dropping funnel and thermometer were placed 68.7 g. (0.94 mole) of *t*-butylamine, 200 ml. of water and 110 g. (1.04 moles) of sodium carbonate. By means of an ice-bath the temperature was held at 25–30° while 135 g. (0.945 mole) of β-chloroethylchloroformate was dropped slowly into the stirred reaction mixture (*ca.* one hour). Stirring was continued for about two hours, after which the contents of the flask were allowed to stand at room temperature overnight before the accumulated precipitate of the crude carbamate was collected on a filter and washed with ether. The aqueous filtrate was extracted with ether and the combined ethereal extracts evaporated in a stream of air to give a small additional amount of product.

The crude β-chloroethyl-N-*t*-butylcarbamate (150 g., 90% yield) was then placed in a 2-l. flask, cyclized, hydrolyzed and decarboxylated in one operation by the cautious addition of potassium hydroxide (224 g., 4 moles) in methanol (900 ml.). This step was somewhat exothermic. Refluxing for two hours completed the reaction after which the inorganic precipitate was filtered. Excess dry potassium carbonate was added to the filtrate, allowed to remain for two hours, then filtered. The alcohol was then evaporated and the product was distilled under reduced pressure into a receiver attached directly to the large-bore arm of a Claisen type head. The 2-*t*-butylaminoethanol was collected as long, hygroscopic white needles; over-all yield: 48.7 g., 44%, b.p. 72° (14 mm.) and 84° (20 mm.), m.p. 43–45°.

Anal. Calcd. for $C_6H_{15}NO$: N, 11.9; neut. equiv., 117.2. Found: N, 12.2; neut. equiv., 117.

This compound gave a bright yellow picrate; crystals from methanol, m.p. 156–157°.

Anal. Calcd. for $C_{12}H_{18}N_4O_8$: C, 41.7; H, 5.2; N, 16.2. Found: C, 41.7; H, 5.2; N, 16.0.

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[2] Roger Adams and J. B. Segur, THIS JOURNAL, **45**, 785 (1923); J. B. Pierce with Roger Adams, *ibid.*, **45**, 790 (1923).

On the Melting Point, Oxidation, and Vapor Pressure of Lead Bromide

BY J. L. HYDE

Disagreement in the literature regarding the m.p. of lead bromide, as recently reviewed by Knowles,[1] clearly indicates some difficulty in the preparation of the pure compound. The present investigation reports some factors affecting the purity of $PbBr_2$, which is now known to melt at 370°,[1,2] and indicates errors in most of the available thermodynamic data, arising from the use of impure samples reported to melt at 488°.

In this work, Mallinckrodt lead bromide (No. 0469) was used as a starting material. It gave lead and bromine analyses corresponding to less than 2 mole % of a basic bromide (calculated as $PbO_{1/2}Br$). It also gave an X-ray powder pattern closely corresponding to that obtained for $PbBr_2$ by Calingaert, Lamb and Meyer,[2] but differing considerably from the earlier pattern given by Hanawalt, Rinn and Frevel.[3]

Attempted recrystallization from distilled water gave a solution of approximately *p*H 3 and an undissolved residue due to hydrolysis. Analysis of a typical residue corresponded to about 78 mole % $PbO_{1/2}Br$.

Recrystallization of the Mallinckrodt lead bromide was successfully carried out in 0.001 *N* hydro-

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[1] Knowles, THIS JOURNAL, **72**, 4817 (1950).

[2] Calingaert, Lamb and Meyer, *ibid.*, **71**, 3709 (1949).

[3] Hanawalt, Rinn and Frevel, *Ind. Eng. Chem., Anal. Ed.*, **10**, 457 (1938).

bromic acid, which effectively prevented hydrolysis. The first crop of crystals was obtained by allowing the solution to crystallize at 70°, filtering while hot, washing the product once by stirring with acetone, and air-drying at room temperature. The purity of this crop was just equal to that of the starting material, indicating that the practical limit of purity had been reached. This 70° crop had a slightly stressed crystal lattice as shown by extra peaks in the X-ray diffraction pattern. Subsequent crops of crystals obtained at lower temperatures yielded products of equal purity, but having considerably increased stresses in the lattice. These stresses could be relieved by heating for a few hours in an oven at about 140° or in an evacuated sealed tube (to prevent oxidation) at temperatures up to 350°. These heat treatments produced patterns which duplicated the pattern of the starting material.

Melting points were conveniently determined on a hot stage apparatus, measuring temperatures with a 400° thermometer or a thermocouple, calibrated *in situ* at one temperature (m.p. of $K_2Cr_2O_7$). By causing samples to melt within about one second, oxidation effects were minimized. The pure samples all melted at 369–370°, and the residues produced by hydrolysis generally showed partial melting at approximately 480–490°, depending on the content of lead oxybromide. Since, according to Baroni,[4] $PbBr_2{\cdot}PbO(s)$ decomposes into $PbBr_2(l)$ and $PbBr_2{\cdot}2PbO(s)$ at 480°, the observed melting points (or solidus points) of the hydrolyzed samples may be explained on this basis. The transition which, according to Knowles,[1] occurs at 497° probably corresponds to this decomposition. It is possible that some of the earlier investigators worked with lead bromide containing $PbBr_2{\cdot}PbO$, thus obtaining "melting points" which were much too high.

The oxidation of lead bromide is predictable from thermodynamic calculations. Using the most recent data from the literature,[5–9] we have calculated the free energy equation for the reaction

$$PbBr_2(s) + {}^1/_2O_2(g) = PbO(s,\ yel.) + Br_2(g)$$

$$\Delta F^0,\ \text{cal./mole} = 14{,}385 + 3.14T\ln T + 4.63 \times 10^{-3}T^2 + 85.64T^{1/2} - 35.69T$$

This leads to a value for the equilibrium constant $K = [Br_2]/[O_2]^{1/2} = 6.3 \times 10^{-4}$ at 327°C., indicating that with a large excess of air substantial oxidation should occur. This might be suspected from the behavior of lead iodide, which is very easily oxidized on heating in air.[10]

In deriving the equation for the free energy of sublimation of lead bromide, Kelley[11] used a m.p. of 488° in connection with the corresponding heat capacity, heat of fusion and vapor pressure data, which are probably open to question. At the present writing, no newer experimental data of this type have been located with the exception of the vapor pressure data of Niwa, Sato and Yosiyama,[12] who did not give the m.p. of their lead bromide. Due to the effusion method used by these authors their values may be inherently a little too high.

On the basis of existing information, Kelley's equation for the free energy of sublimation[11] has been rederived on the basis of a m.p. of 370°, assuming that the specific heat equation for the liquid and the heat of fusion which he used were valid at this temperature. The result

$$\Delta F^0,\ \text{subl., cal./mole} = 42{,}570 + 4.13T\ln T + 1.55 \times 10^{-3}T^2 - 71.20T$$

is believed to represent the best available experimental data.

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[4] Baroni, *Atti accad. Lincei*, **20**, 384 (1935).

[5] National Bureau of Standards, "Tables of Selected Values of Chemical Thermodynamic Properties," 1949.

[6] Thompson, "The Total and Free Energies of Formation of the Oxides of Thirty-two Metals," The Electrochemical Society, New York, N. Y., 1942, p. 44.

[7] Spencer and Spicer, THIS JOURNAL, **64**, 617 (1942).

[8] Bichowsky and Rossini, "The Thermochemistry of the Chemical Substances," Reinhold Publishing Corp., New York, N. Y., 1936.

[9] Kelley, Bur. Mines Bulletin 434 (1941).

[10] Van Klooster and Stearns, THIS JOURNAL, **55**, 4121 (1933).

[11] Kelley, Bur. Mines Bulletin 383 (1935).

[12] Niwa, Sato and Yosiyama, *J. Chem. Soc. Japan*, **60**, 918 (1939).

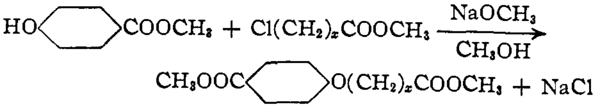
Esters of *p*-Carboxyphenoxyalkanoic Acids

BY E. F. IZARD AND STEPHANIE L. KWOLEK

In the course of research on condensation polymers, a group of dimethyl esters of quite regular structure but of varying chain length and belonging to a homologous series with the general formula, ROOCO(CH$_2$)$_n$COOR, was prepared. Included in this group are methyl *p*-carbomethoxyphenoxyacetate, methyl *p*-carbomethoxyphenoxybutyrate, methyl *p*-carbomethoxyphenoxyvalerate, methyl *p*-carbomethoxyphenoxycaproate, methyl *p*-carbomethoxyphenoxyheptanoate and methyl *p*-carbomethoxyphenoxyundecanoate.

With the exception of methyl *p*-carbomethoxyphenoxyacetate, none of these esters is recorded in the literature. Christiansen[1] reported having obtained the former in a 74% yield and melting at 92–92.7° from *p*-carboxyphenoxyacetic acid. This melting point has a slightly lower value than that recorded in this paper.

The procedure employed for the preparation of this series of compounds is outlined in the general reaction



$$HO\langle\ \rangle COOCH_3 + Cl(CH_2)_xCOOCH_3 \xrightarrow[CH_3OH]{NaOCH_3} CH_3OOC\langle\ \rangle O(CH_2)_xCOOCH_3 + NaCl$$

Experimental

Because of similarity in the preparation of the six dimethyl esters previously named, only the procedure for the synthesis of methyl *p*-carbomethoxyphenoxyvalerate will be given in detail.

Methyl *p*-Carbomethoxyphenoxyvalerate.—The synthesis of this compound required a preliminary preparation of methyl δ-chlorovalerate by a modified Adams and Thal procedure,[2] whereby a refluxing methyl alcohol solution of δ-chlorovaleronitrile was saturated with dry hydrogen chloride; yield 85.1%; b.p. 106–107° at 38 mm. Dry hydrogen chloride was used in place of sulfuric acid which might cause replacement of the chlorine atom.

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[1] W. G. Christiansen, THIS JOURNAL, **48**, 463 (1926).

[2] R. Adams and A. F. Thal, "Organic Syntheses," Coll. Vol. 1, John Wiley and Sons, Inc., New York, N. Y., 1941, p. 270.