[Contribution from the Department of Chemistry, University of Notre Dame]

Melting Point Curves of Some Alkyl and Acetylenic Mercury Derivatives

By Thomas H. Vaughn with R. J. Spahr and J. A. Nieuwland

In recent communications the preparation and properties of a number of compounds belonging to the series of normal dialkynylmercurys[1] and normal bisalkylmercury acetylides[2] have been reported. When the melting points of the members of these series were plotted against the number of carbons in the alkyl group it was noticed that there appeared to be an almost constant difference of approximately 30° between the two curves.

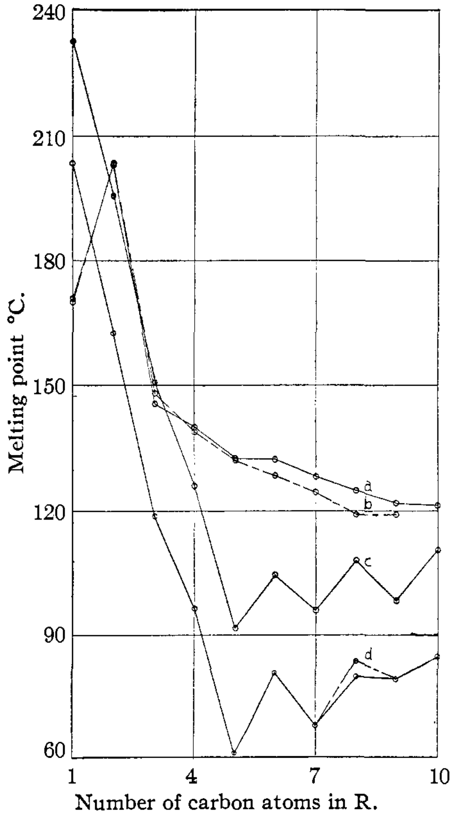

Fig. 1.—Melting point curves. Curves a and b have been elevated 10° in order to minimize overlapping.

That such a constant difference existed seemed rather unusual and interesting particularly in view of the character of the central groups. In order to have more complete data for comparison we have completed the bisalkylmercury acetylide series up to the decyl member. The melting point curves for both series as high as the decyl derivative are shown in Fig. 1. Although the difference is not constant the curves show a remarkable similarity.

In the reported preparation of the lower members of this series[2] the corresponding alkyl mercury halide was dissolved in 10% aqueous potassium hydroxide and the solution treated with acetylene. With the higher members it was not practical to use aqueous solutions or even 10% alcoholic potassium hydroxide because of the low solubility of the substituted mercury halides. Accordingly very dilute alcoholic solutions of caustic were used, care being taken, however, that an excess of the amount of potassium hydroxide necessary to convert the

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(1) Vaughn, This Journal, **55**, 3453 (1933).

(2) Spahr, Vogt and Nieuwland, *ibid.*, **55**, 2465 (1933).

alkyl mercury halide to the hydroxide was present.[3] The yields from the modified procedure are uniformly high.

Since the use of a common medium for crystallization would considerably enhance the value of these derivatives in identifying alkyl mercury halides,[2] *n*-propanol was tried on a number of bisalkylmercury acetylides and was satisfactory for the methyl, ethyl, propyl, hexyl, heptyl, octyl, nonyl, decyl, phenyl and *p*-tolyl derivatives.

Heptyl, octyl[4] and nonyl[5] mercury bromides were prepared for use in this work and it was found that after repeated crystallizations from alcohol melting point values 3 to 6° higher than those reported in the literature were obtained. The melting point data in the literature for the entire series were then plotted against molecular weights (Curve b, Fig. 1).[6] It was found that the regular alternation usually found in such curves was absent. The entire series as high as decyl was then prepared and purified in these laboratories and the melting point data obtained are tabulated in Table I along with the data from the literature.

TABLE I

ALKYL MERCURY BROMIDES

Alkyl mercury bromide	Crystn.	M. p. in literature, °C.	M. p. observed, °C.
Methyl	2	160[a]	160.8–161.3
Ethyl	6	193.5[b]	193.0
Propyl	4	138[b]	135.4
Butyl	4	129[c]	129.9–130.0
Amyl	3	122[b]	122.2–122.4
Hexyl	2	118.5[b]	122.0–122.2
Heptyl	3	114.5[b]	117.8–118.4
Octyl	3	109[b]	114.8–115.0
Nonyl	4	109[d]	111.6–112.0
Decyl	3	...	111.0–111.4

[a] Crymble, *J. Chem. Soc.*, **105**, 668 (1914).

[b] Marvel, Gauerke and Hill, THIS JOURNAL, **47**, 3009 (1925).

[c] Marvel and Gould, *ibid.*, **44**, 153 (1922).

[d] Hill, *ibid.*, **50**, 167 (1928).

When these new values are plotted (Curve a,[6] Fig. 1) a small but regular alternation is apparent.

The melting point and analytical data for the new bisalkylmercury acetylides are tabulated in Table II.

Experimental Part

Alkyl Alcohols.—Hexanol, heptanol, octanol, nonanol and decanol were obtained by the action of ethylene oxide on the proper Grignard reagent. The procedure em-

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[3] Spahr, Vogt and Nieuwland, THIS JOURNAL, **55**, 3728 (1933).

[4] Marvel, Gauerke and Hill, *ibid.*, **47**, 3009 (1925).

[5] Hill, *ibid.*, **50**, 167 (1928).

[6] In plotting this curve and Curve a, 10° was added to the actual melting point values in order to minimize overlapping.

TABLE II

BISALKYLMERCURY ACETYLIDES

Acetylide	Formula	M. p., °C.	Hg analyses, % Calcd.	Hg analyses, % Found
Bisheptylmercury	$C_7H_{15}Hg—C\equiv C—HgC_7H_{15}$	95.8- 96.0	64.37	64.05
Bisoctylmercury	$C_8H_{17}Hg—C\equiv C—HgC_8H_{17}$	108.0	61.58	61.35
Bisnonylmercury	$C_9H_{19}Hg—C\equiv C—HgC_9H_{19}$	98.0- 98.8	59.04	59.31
Bisdecylmercury	$C_{10}H_{21}Hg—C\equiv C—HgC_{10}H_{21}$	110.4-111.0	56.70	56.51

ployed was based on that of Dreger[7] but was modified in the manner of adding the ethylene oxide and in the method of working up the reaction products. These two modifications shorten the time of preparation by approximately eight to ten hours.

Preparation of Octanol.—A solution of 330 g. of hexyl bromide in 700 ml. of ether was added in the usual manner to 48 g. of magnesium turnings contained in a 2-liter 3-necked flask fitted with dropping funnel, mercury-sealed Bennings stirrer[8] and reflux condenser. As soon as the reaction was completed (thirty to forty-five minutes) the flask was placed in an ice-salt bath and the reflux condenser replaced by a liquid ammonia cooled spiral condenser.[9] The dropping funnel was replaced by an inlet tube reaching almost to the surface of the liquid and 95 g. of ethylene oxide added as rapidly (forty-five to sixty minutes) as the vigorous refluxing permitted. The cooling bath was removed and after refluxing ceased 250 to 275 ml. of ether was removed by distillation from a water-bath. Three hundred and thirty milliliters of dry benzene was added and the distillation continued without interruption of stirring until the temperature of the effluent vapor reached 65°. The mixture was then refluxed for one hour and hydrolyzed with ice cold 10% sulfuric acid. The benzene layer was separated and washed twice with 10% sodium hydroxide solution. The benzene was removed by distillation and the residue fractionated under reduced pressure. The yield was 185 g. (71% of the theoretical) of material boiling at 105° at 15 mm. The same procedure was followed in preparing other alcohols. The following yields were obtained: hexanol, 59%; heptanol, 58%; nonanol, 55%; decanol, 52%.

Alkyl Bromides.—The bromides were prepared by the action of phosphorus tribromide on the corresponding alcohols. Yields of 60 to 80% were obtained.

Alkyl Mercury Bromides.—These compounds were prepared in tenth molar quantities by the action of an excess of mercuric bromide on the corresponding alkylmagnesium bromide.[4] In the preparation of methyl mercury bromide the methyl bromide was prepared by dropping phosphorus tribromide into methyl alcohol. The gas was led through a water-cooled reflux condenser and sprayed through concentrated sulfuric acid to remove alcohol. After passing over soda lime the gas was led directly into the reaction flask which was equipped with a liquid ammonia cooled spiral reflux condenser.[9] The reaction was easily controlled by regulating the dropping of the phosphorus tribromide.

The alkyl mercury bromides were purified by recrystallizations from alcohol until no further change in the melting point was observed. The number of crystallizations required by the several bromides is given in Table I. All melting points were taken by the capillary tube method in a bath whose temperature was rising 1.5° per minute at the fusion point, using standardized partial immersion thermometers graduated in tenths of a degree.

Alkyl Mercury Acetylides.—These were prepared by a modification of the method of Spahr, Vogt and Nieuwland.[2]

Bis Decylmercury Acetylide.—Two grams of decyl mercury bromide and 2 g. of potassium hydroxide were dissolved in 250 ml. of alcohol at room temperature. The

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(7) Dreger, "Organic Syntheses," Coll. Vol. I, 1932, pp. 299–301.

(8) Bennings, *Proc. Ind. Acad. Sci.*, **37**, 263 (1927).

(9) Vaughn and Pozzi, *J. Chem. Educ.*, **8**, 2433 (1931).

solution was filtered and treated with dry acetylene under a pressure of 10 cm. of mercury.[10] The precipitate of acetylide was collected on a fluted filter and after washing three times with 10 ml. of alcohol crystallized twice from *n*-propanol. The filtrate from the reaction mixture on standing lost acetylene and, due to the decomposition of the monoalkylmercuri acetylide, deposited more of the bis compound.

Analysis of Compounds.—Decyl mercury bromide was analyzed according to the method of White.[11] Calcd. for $C_{10}H_{21}HgBr$: Hg, 47.56. Found: Hg, 47.40. The acetylides were decomposed by White's process[11] and the mercury determined by the volumetric procedure of Rupp.[12] Results are listed in Table I.

Summary

1. Decyl mercury bromide and four new bisalkylmercury acetylides have been prepared and their melting points reported.
2. *n*-Propanol has been found to be a suitable medium from which to crystallize members of the bisalkylmercury acetylide series.
3. The melting point curves of the dialkynyl mercurys and the bisalkylmercury acetylides are very similar and lie approximately 29° apart.
4. The values for the melting points of the alkyl mercury bromides as high as the decyl member have been determined on pure samples. The melting point curve shows a small but regular alternation.
5. A simplified procedure for the preparation of straight chain alcohols has been reported.

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(10) Vaughn, *ibid.*, **9**, 528 (1932).

(11) White, THIS JOURNAL, **42**, 2359 (1920).

(12) Rupp, *Chem.-Ztg.*, **32**, 1077 (1908).

NOTRE DAME, INDIANA

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Preparation of *tert*-Butylacetic Acid and its Derivatives

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V. H. WALLINGFORD

This study was undertaken because of our interest in compounds containing the neopentyl group.[2]

No significant information is available on the preparation, properties or derivatives of *tert*-butylacetic acid. Although it has been reported[3] several

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(1) Mallinckrodt Research Fellow.

(2) Whitmore and co-workers, THIS JOURNAL, 1932–1933.

(3) (a) Delacre [*Bull. sci. acad. roy. Belg.*, 7–41 (1906); *Chem. Zentr.*, I, 1233 (1906); *J. Chem. Soc.*, **90** [I], 476 (1906)] by oxidation of 3,3-dimethylbutanol-1; (b) Ozanne and Marvel [THIS JOURNAL, **52**, 5270 (1930)], by ozonolysis of 2-bromo-4,4-dimethylpentene-1; (c) McCubbin and Adkins, [*ibid.*, **52**, 2549 (1930)] by oxidation of 4,4-dimethylpentanone-2. (d) McCubbin [*ibid.*, **53**, 357 (1931)] by oxidation of dineopentyl ketone. (e) Whitmore and Church, [*ibid.*, **54**, 3710 (1932)] by ozonolysis of 2,4,4-trimethylpentene-1; (f) Favorsky and Opel [*J. Russ. Phys.-Chem. Soc.*, **50**, 34–80 (1918); *Chem. Abstracts*, **18**, 2498 (1924)] by oxidation of *tert*-butylallene; (g) Favorsky and Morew [*J. Russ. Phys.-Chem. Soc.*, **50**, 571–581 (1918); *Chem. Abstracts*, **18**, 2496 (1924); *Chem. Zentr.*, III, 998 (1923)] by oxidation of *tert*-butylacetylene.