By treating the 2- and 3-ω-chloroacetylphenanthrenes with piperidine, 2- and 3-ω-piperidinoacetylphenanthrenes, respectively, were obtained. Their structure was proved by direct comparison (melting points and mixed melting points) of their hydrochlorides and picrates, with the corresponding derivatives obtained from the ω-bromoacetylphenanthrenes.

Summary

1. The preparation of 2-, 3- and 9-ω-bromoacetylphenanthrenes is described.

2. The preparation of 2-, 3- and 9-ω-dimethylamino-, -ω-diethylamino- and -ω-piperidinoacetylphenanthrenes is described.

3. The preparation of dimethylaminomethyl-, diethylaminomethyl- and piperidinomethyl-2-, 3- and 9-phenanthryl carbinols, by catalytic reduction of the corresponding ω-amino ketones, is described.

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A New Reaction of 1-Iodoacetylenes and Some New Mercury Acetylides

BY THOMAS H. VAUGHN

It has been pointed out by Johnson and McEwen[1] that the substitution of mercury for an acetylenic hydrogen by means of an alkaline solution of a mercuric salt produces compounds which are readily crystallizable and which possess sharp, definite melting points. They have advocated the use of these mercury derivatives as a general means of identifying and characterizing monosubstituted acetylenes.

We have found that substituted iodoacetylenes react with both Nef's alkaline mercuric iodide solution[2] and the mercuric cyanide reagent of Hofmann and Kirmreuther[3] producing the same compounds as do the acetylenes themselves. The reaction in the case of mercuric cyanide solution may be represented as

$$2RC{\equiv}CI + 2Hg(CN)_2 \longrightarrow (RC{\equiv}C)_2Hg + 2(CN)_2 + HgI_2$$

The reaction is easily carried out and gives a high yield of the mercury derivative. It is obvious that a determination of the melting point of the mercury compound affords a suitable means of identifying iodoacetylenes. The mercuric iodide which precipitates along with the mercury acetylide serves to distinguish between the iodoacetylenes and the acetylenes. The mercuric iodide usually separates as the yellow variety but is occasionally obtained in the red form. There is no apparent reason why the

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[1] Johnson and McEwen, THIS JOURNAL, **48**, 469 (1926).

[2] Nef, *Ann.*, **308**, 299 (1899).

[3] Hofmann and Kirmreuther, *Ber.*, **41**, 314 (1908).

bromo, chloro and perhaps even the cyanoacetylenes will not give an analogous reaction. We hope to investigate these possibilities in the near future.

Johnson and McEwen did not use the same solvent for the crystallization of different mercuric acetylides but treated each case individually. We have found that all types of these acetylides can be conveniently crystallized from methyl alcohol, thus enhancing the value of the method for routine use. In the case of the iodoacetylenes the use of methyl alcohol as a crystallizing medium has a further advantage in that it serves to separate the mixture of mercuric acetylide and mercuric iodide, the iodide remaining in solution after the acetylide has crystallized.

In order that the properties of more compounds of this type might be available a number of new mercury acetylides have been prepared from the corresponding acetylenes. The melting points and analytical results of these compounds are given in Table I. Data on several compounds prepared by Johnson and McEwen are included for purposes of comparison and also for the purpose of bringing together all known members of the di-*n*-alkinyl mercury series. The melting points of acetylides prepared from iodoacetylenes are also given in Table I.

TABLE I

SUBSTITUTED DIETHINYL MERCURYS

Acetylene synonym	Formula	M. p. of compound from acetylene, °C.	M. p. of compound from iodoacetylene	Mercury analyses, % Calcd.	Found
Methyl	$(CH_3C{\equiv}C)_2Hg$	203 –204[a]			
Ethyl	$(C_2H_5C{\equiv}C)_2Hg$	162 –163[a]	161 –163		
Propyl	$(C_3H_7C{\equiv}C)_2Hg$	118.4–118.8	118.3–118.8	59.93	59.92
Butyl	$(C_4H_9C{\equiv}C)_2Hg$	96.2– 96.4	96.0– 96.5	55.30	55.36
Amyl	$(C_5H_{11}C{\equiv}C)_2Hg$	61[a]			
Hexyl	$(C_6H_{13}C{\equiv}C)_2Hg$	80.4– 80.7	80.0– 80.1	47.90	47.98
Heptyl	$(C_7H_{15}C{\equiv}C)_2Hg$	67.8– 68.5		44.89	45.15
Octyl	$(C_8H_{17}C{\equiv}C)_2Hg$	79.5– 80.0 83 – 84[a]	80.0– 80.7		
Nonyl	$(C_9H_{19}C{\equiv}C)_2Hg$	79.0– 79.3		39.87	40.01
Decyl	$(C_{10}H_{21}C{\equiv}C)_2Hg$	84.3– 85.1	84.2– 84.8	37.78	37.70
Vinyl	$(CH_2{=}CH{-}C{\equiv}C)_2Hg$	142.0–142.5[b]	142.0	66.28	66.21[c]
m-Xylyl	$[(CH_3)_2C_6H_3C{\equiv}C]_2Hg$	140.3–140.5		43.73	43.77
Mesityl	$[(CH_3)_3C_6H_2C{\equiv}C]_2Hg$	238 –239[b]		41.21	41.49

[a] Value reported by Johnson and McEwen. [b] Preheated bath. [c] Great caution is necessary in analyzing this acetylide as it sometimes explodes violently on contact with cold sulfuric acid.

Divinylethinyl mercury is unstable. When heated the substance darkens and is almost black at 250°, at which temperature it is still solid. If a capillary containing the substance is placed in a bath at 140° and heated at a rate of about 2° per minute the material melts to a clear colorless liquid at 142.0–142.5°. On standing at room temperature the snowwhite substance gradually assumes a dark golden-yellow color and becomes sensitive to heat, deflagrating on warming. Sunlight, either direct or diffuse, markedly accelerates this change. The pure compound may be kept at 0° in the dark for several days without apparent change.

The dialkinyl mercurys react with iodine in potassium iodide solution giving iodoacetylenes and considerable amounts of addition products. With iodine in liquid ammonia substitution occurs but not the slightest trace of addition products can be detected in the reaction mixture. Hydrogen sulfide reacts rapidly with the mercury acetylides either in solution or in the solid condition, giving a black precipitate of mercuric sulfide.

Three new iodoacetylenes, hexyl, octyl, and decyl, were prepared for use in this work and will be described in detail in the experimental part. These three compounds complete the list of known iodoacetylenes as high as iodododecine.

Experimental Part

Acetylenes.—Propyl, butyl, heptyl and nonyl acetylenes were prepared in 50–80% yields from the corresponding alkyl bromide and sodium acetylide in liquid ammonia.[4] Hexyl and octyl acetylenes were obtained in 50–65% yields from the corresponding 2 bromo-1-ene by the removal of the elements of hydrogen bromide with sodamide in mineral oil.[5]

Xylyl[6] and mesityl acetylenes were obtained by the removal of the elements of hydrogen chloride from the chloro compounds produced by the action of phosphorus pentachloride on the corresponding ketones.

Decylacetylene was obtained by the rearrangement of diamylacetylene by means of sodamide in mineral oil. Octylacetylene was also obtained in like manner by the rearrangement of dibutylacetylene. The rearrangement of α- to β-acetylenes has been reported by several observers but so far as we know no shift of such length as that above has been recorded.

Decylacetylene.—Fifty grams of sodamide and 150 ml. of mineral oil were ground in a ball mill to a very fine suspension. This suspension was placed in a 1-liter flask equipped with a mechanical stirrer and heated to 210° on an oil-bath. Sixty grams of diamylacetylene was dropped in and the heating continued for seven hours. The flask was cooled and 250 ml. of ether added. The contents were poured into 300 ml. of water and acidified with hydrochloric acid. The upper layer was separated and the ether removed. The residue was fractionated under reduced pressure. The low boiling material was diluted with 4 volumes of alcohol and dropped into 200 ml. of well-stirred alkaline mercuric cyanide solution. The precipitate was filtered off, washed with 50% alcohol and dried. It weighed 45 g. (34% yield). The crystals were boiled a few minutes in 500 ml. of 15% hydrochloric acid and allowed to stand for ten days. Although the mercury compound was not yet completely hydrolyzed the upper layer of oil was removed and fractionated through a 30-cm. Vigreux column. Seventeen grams of material (83% yield based on mercury compound, 28% on diamylacetylene) boiling at 96--110 at 12 mm. was obtained. On redistillation practically all of this boiled at 95--98° at 12 mm.; n_D^8 1.4426; $n_D^{25.7}$ 1.4351; d_{24} 0.7758; MR_D' calcd., 56.33; found, 56.13.

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(4) Picon, *Compt. rend.*, **158**, 1346 (1914); **169**, 32 (1919).

(5) Lespieau and Bourguel, "Organic Syntheses," John Wiley and Sons, New York, Collective Volume I, 1932, p. 185.

(6) Grignard and Perrichon, *Ann. chim.*, **5**, 5–36 (1926).

Preparation of Mercury Acetylides from Acetylenes.—A solution of 1.5 ml. of the acetylene in 25 ml. of alcohol was slowly dropped with vigorous stirring into 25 ml. of the alkaline mercuric cyanide reagent of Hofmann and Kirmreuther (100 g. $Hg(CN)_2$ and 46 g. KOH in 400 ml. water). The precipitate was filtered with suction, washed four times with 25-ml. portions of 50% alcohol and dried at the pump. The compound was then almost completely dissolved in boiling absolute methyl alcohol and the hot solution quickly filtered through cotton. The crystals which separated on cooling were washed twice with 5-ml. portions of cold methyl alcohol and dried. As Johnson and McEwen point out, sticky, gummy masses result if the acetylene–alcohol solution is dropped into the mercury solution too rapidly, or without enough stirring. When this occurs the pasty material should be removed and placed under 50 ml. of 95% alcohol, where it is broken up with a pestle. When the solid is well distributed 50 ml. of water is added and the material treated as usual.

Analysis.—The analyses of the mercury acetylides were made by decomposing the compounds according to the method of White[7] and determining mercury volumetrically by the procedure of Rupp.[8]

Iodoacetylenes.—Ethyl, phenyl and vinyl iodoacetylenes were obtained by the direct iodination of the corresponding acetylene in liquid ammonia.[9] Propyl,[10] hexyl, octyl and decyl iodoacetylenes were prepared by the method of Grignard and Perrichon.[6] Butyl iodoacetylene was prepared by the action of iodine on bis hexinyl mercury both in potassium iodide solution and in liquid ammonia.

Surface tensions were measured by the maximum bubble pressure method of Sugden[11] and parachors were calculated by his formula. The theoretical values were calculated by means of the atomic and structural constants of Mumford and Phillips.[12]

Octyl Iodoacetylene.—A solution of ethylmagnesium bromide was prepared from 4.5 g. of magnesium, 19 g. of ethyl bromide and 40 ml. of ether in a 1-liter 3-necked flask equipped with a stirrer, reflux and dropping funnel. To this solution was added over a period of ten minutes a solution of 16.5 g. of octylacetylene in 35 ml. of ether. The mixture was refluxed for thirty minutes and 40 g. of powdered iodine was added slowly through the reflux condenser. The contents of the flask were poured into 200 ml. of water and acidified with acetic acid. The ether layer was separated, washed with 10% of sodium thiosulfate solution and water, and dried over calcium chloride. The ether was removed and the residue fractionated. After two fractionations through a 30-cm. column,[13] 20 g. of octyl iodoacetylene, b. p. 84° at 0.7 mm., was obtained and 3 g. of octylacetylene was recovered; yield 70% on basis of acetylene consumed. Octyl iodoacetylene has the following properties: $n_D^{6.0}$ 1.5069, $n_D^{23.6}$ 1.4987, d_{25} 1.2933; MR_D' calcd., 60.01; obs., 59.87; γ_{25} 31.88 dynes/cm.; [P] calcd., 481.8 cm.; obs., 485.0.

Decyl Iodoacetylene.—Ten and one-half grams of decylacetylene gave 13.5 g. of the iodo derivative, 2.3 g. of the acetylene being recovered (94.5% yield). Its properties are as follows: b. p. 99–102 at 0.3 mm., $n_D^{8.0}$ 1.5016, n_D^{25} 1.49365, d_{25} 1.2370; MR_D' calcd., 69.29; obs., 68.67; γ_{25} 33.25 dynes/cm.; [P] calcd., 561.8; obs., 563.2.

Hexyl Iodoacetylene.—This compound was obtained in an 88% yield and has the following properties: b. p. 95--97 at 7.5 mm.; $n_D^{7.8}$ 1.5148, n_D^{25} 1.50631; d_{25} 1.3830; MR_D' calcd., 50.62; obs., 50.71; γ_{25} 31.34 dynes/cm.; [P] calcd., 401.8; obs., 394.0.

Iodination of Dihexinyl Mercury in Potassium Iodide Solution.—Thirty-five grams

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

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

(9) Vaughn and Nieuwland, THIS JOURNAL, **55**, 2150 (1933).

(10) Vaughn, *ibid.*, **55**, 1293 (1933).

(11) Sugden, *J. Chem. Soc.*, **125**, 27 (1924).

(12) Mumford and Phillips, *ibid.*, **130**, 2113 (1929).

(13) It is very difficult to prevent decomposition of the higher iodoacetylenes during distillation. Very low pressures and absence of strong light are essential for success.

of dihexinyl mercury was added to a solution of 45 g. potassium iodide and 59 g. iodine in 100 ml. of water and allowed to stand two and one-quarter hours with occasional shaking. Sodium thiosulfate solution was added to remove excess iodine and the solution extracted with ether. The ether extract was dried and fractionated. Ten grams (22% yield) of butyl iodoacetylene, b. p. 58–59 at 8 mm., n^{27}_{D} 1.5148, was obtained. A residue of 28.5 g. remained in the flask which even at pressures as low as 0.3 mm. could not be distilled without great decomposition. This material, which had the following properties: n^{28}_{D} 1.695; d_{28} 2.545, was probably impure 1,1,2-triiodohexene-1.

Iodination of Dihexinyl Mercury in Liquid Ammonia.—Ten grams of dihexinyl mercury was placed in 350 ml. of liquid ammonia and 15 g. of iodine added. After standing for five hours 500 ml. of water was added, the precipitate of nitrogen iodide removed by filtration, and washed with water. Six grams of oil (54% of the calcd.) settled out of the filtrate. The value for the index of refraction (n^{24}_{D} 1.5168) showed this oil to be very pure butyl iodoacetylene.

Preparation of Mercury Acetylides from Iodoacetylenes.—One-half milliliter of the iodoacetylene was dissolved in 10 ml. of 95% alcohol in a test-tube. Six milliliters of alkaline mercury cyanide solution was added and the tube shaken. On standing the solution slowly turned yellow and deposited mercuric iodide, cyanogen being given off meanwhile. In one to five minutes the acetylide separated, usually in the form of large crystals which almost completely filled the tube. After standing for ten to fifteen minutes (rarely longer) the crystals were filtered off, washed thrice with 5-ml. portions of 50% alcohol and dried at the pump. The mixture of mercuric iodide and acetylide was dissolved in the least possible amount of boiling absolute methyl alcohol, quickly filtered through cotton and allowed to cool. The crystals which separated were collected, washed sparingly with cold methyl alcohol and dried.

A single crystallization seems to afford these mercury compounds in a high state of purity. Only one exception to this statement has been encountered. Dioctinyl mercury prepared from the acetylene obtained by the removal of the elements of hydrogen bromide from bromooctene required three crystallizations from methyl alcohol before acquiring a constant melting point. The melting point of this same compound made from hexylacetylene prepared in liquid ammonia was constant after one crystallization. In several instances, the melting point of the crude reaction product from iodoacetylenes contaminated with mercuric iodide, was taken. In all cases the value obtained was substantially that of the recrystallized material.

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Summary

1. Substituted iodoacetylenes react with alkaline solutions of mercuric salts giving mercuric iodide and high yields of compounds of the type $(RC{\equiv}C)_2Hg$. This reaction may be used to identify iodoacetylenes, the melting point of the acetylide identifying R, and the mercuric iodide serving to distinguish between iodoacetylenes and the acetylenes themselves.

2. Six new aliphatic acetylides of this type have been prepared from the corresponding acetylenes and their melting points recorded.

3. Dixylyl, dimesityl and divinyl ethinyl mercurys have also been prepared and their properties recorded.

4. Iodine in potassium iodide solution reacts with dihexinyl mercury giving a 22% yield of butyl iodoacetylene and a large quantity of addition products. Iodine in liquid ammonia reacts with the same compound, giving a 54% yield of butyl iodoacetylene without a trace of addition products.
5. The bis alkinyl mercuries either solid or in solution react with hydrogen sulfide giving mercury sulfide.
6. Diamyl and dibutyl acetylenes are rearranged at 210° by sodamide in mineral oil to decyl and octyl acetylenes.
7. Hexyl, octyl, and decyl iodoacetylenes have been prepared and some of their physical properties recorded.

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A Phase Rule Study of Mixed Derivatives of Alcohols

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The determination of the percentage of one alcohol mixed with another has been approximated on the basis of gradation of some physical property of the alcohols as mixed. Mixtures of alcohols have even been oxidized to their respective acids and estimated according to variation of the properties of the mixed acids.[1,2,3] A study of the physical properties of mixtures of other derivatives of alcohols might lead to methods for determination of percentage of one alcohol mixed with another. Melting points of solid alcohol derivatives when mixed might offer possibility of determination of relative proportions of the alcohols. If the solid derivatives are relatively easily prepared in the presence of water, the method might be applied to the determination of proportions of mixed alcohols in water solution. Accordingly a phase rule study has been made upon mixed solid derivatives of alcohols.

Compounds Prepared.—The following alcohol derivatives were made and carefully purified.

	Melting point, °C.
Methyl *p*-nitrobenzoate	96.0– 96.5
Ethyl *p*-nitrobenzoate	57.0– 57.5
Methyl 3,5-dinitrobenzoate	106.5–107.0
Ethyl 3,5-dinitrobenzoate	91.5– 92.0
Butyl 3,5-dinitrobenzoate	63.3– 63.3

The various nitrobenzoates were chosen because of their ease of prepara-

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(1) Werkman and Osburn, *Ind. Eng. Chem.*, **3**, 387 (1931).

(2) Archibald and Beamer, *ibid.*, **4**, 18 (1932).

(3) M. Johnson, *ibid.*, **4**, 20 (1932).