[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF ILLINOIS]

THE IDENTIFICATION OF MONOSUBSTITUTED ACETYLENES. DERIVATIVES OF DIETHINYL MERCURY

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The cuprous and silver derivatives of acetylenes of the type $R—C\equiv C—H$ have been used frequently for the detection and identification of compounds of this type and for purposes of purification. The formation of these salts has several disadvantages when applied to the identification and characterization of individual substances. Since these salts cannot be purified easily, and do not melt below the temperature of decomposition or explosion,[1] it is necessary to have recourse to quantitative analysis of each sample, which can establish only an identity of composition and not constitution.

In the course of a study of furyl-acetylene,[2] a suitable means of detecting and identifying this substance was desired, and a search of the literature indicated that the mercuric salt might have the properties of a good derivative. The product of the interaction of monosubstituted acetylenes and mercuric salts varies with the character of the solution. In neutral or acid solution mercuric salts give addition products of varying composition; in alkaline solution, simple mercuric salts are formed which are analogous to the cuprous and silver salts: $2\ R—C\equiv C—H + K_2HgI_4 + 2KOH \longrightarrow (R—C\equiv C—)_2Hg + 4KI + 2H_2O$.

The purpose of the present study was to undertake the preparation of the mercuric salts of a number of monosubstituted acetylenes, in order to determine whether or not the formation of mercuric salts is a general reaction, and whether or not these salts possess properties that render them suitable for purposes of identification.

Acetylene forms in alkaline solution a mercuric salt[3] of the composition C_2Hg, which is extremely explosive. Methyl-acetylene with an aqueous suspension of mercuric oxide, or an alkaline solution of mercuric iodide, gave dipropinyl-mercury.[4] This mercuric salt crystallized in white needles, was quite stable and decomposed only when heated above its melting point.

From phenyl-acetylene and alkaline mercuric iodide, Nef[5] obtained di-

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[1] An exception is the cuprous salt of *tert.*-butyl-acetylene; m. p. 140° with decomp. Favorskii and Morev, *J. Russ. Phys.-Chem. Soc.*, **50**, 571 (1920); *C. A.*, **18**, 2496 (1924).

[2] The investigation of furyl-acetylene and related substances was carried out in the laboratory of Professor Charles Moureu at the College of France, Paris, and will be published elsewhere. A preliminary note has appeared in *Bull. soc. chim.*, [4] **33**, 1241 (1923).

[3] Keiser, *Am. Chem. J.*, **15**, 535 (1893).

[4] Kutscheroff, *Ber.*, **17**, 26 (1883).

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

phenylethinyl-mercury, a white crystalline substance melting at 125°. He had previously prepared this substance by the action of mercury on phenyl-iodo-acetylene.

By the treatment of chloro- and bromo-acetylene with an alkaline solution of mercuric cyanide, or upon heating dichloro- and dibromo-ethylene with this solution, the mercuric salts[6] of monochloro- and monobromo-acetylene have been obtained. Dichloro-ethinyl-mercury formed glittering crystalline plates which melted at 185° and deflagrated at 195°. Dibromo-ethinyl-mercury formed similar crystals which blackened from 153–155° and exploded at a slightly higher temperature. When these salts were heated with aqueous potassium cyanide, chloro- and bromo-acetylene were regenerated in a high state of purity.

For use in this investigation a number of substituted acetylenes, $R-C\equiv C-H$, were prepared in which R was purely aliphatic in character or purely aromatic in character, and in which R contained mixed groups. These were obtained by methods involving the removal of halogen acid from dihalogen compounds or halogenated ethylenes. For the latter, the use of pulverized sodium amide suspended in heavy liquid paraffin was found to be very practical. The acetylene synthesis of Lespieau and Bourguel[7] which consists in treating a Grignard reagent with 2,3-dibromopropene-1 to form a 3-substituted 2-bromopropene-1, followed by treat-

TABLE I

PROPERTIES OF MERCURIC DERIVATIVES OF VARIOUS ACETYLENES

Substance	Synonym-acetylene	Formula of mercuric salt	M. p. of mercuric salt (uncorr.), °C.
Chloro-ethine	chloro	$(Cl-C\equiv C-)_2Hg$	185 (dec. at 195)
Bromo-ethine	bromo	$(Br-C\equiv C-)_2Hg$	dec. 153–155
Propine-1	methyl	$(CH_3-C\equiv C-)_2Hg$	203–204
Butine-1	ethyl	$(C_2H_5-C\equiv C-)_2Hg$	162–163
3,3-Dimethyl-butine-1	*tert.*-butyl	$(\textit{tert.}\text{-}C_4H_9-C\equiv C-)_2Hg$	91–92
Heptine-1	*n*-amyl	$(n\text{-}C_5H_{11}-C\equiv C-)_2Hg$	61
Decine-1	*n*-octyl	$(n\text{-}C_8H_{17}-C\equiv C-)_2Hg$	83–84
Phenyl-ethine	phenyl	$(C_6H_5-C\equiv C-)_2Hg$	124.5–125
3-Phenyl-propine-1	benzyl	$(C_6H_5-CH_2-C\equiv C-)_2Hg$	106.5–107.5
4-Phenyl-butine-1	phenethyl	$(C_6H_5-CH_2-CH_2-C\equiv C-)_2Hg$	84.5–85
4′-Methylphenyl-ethine	*p*-tolyl	$(p\text{-}CH_3-C_6H_4-C\equiv C-)_2Hg$	199–202 (with previous darkening)
4′-Methoxyphenyl-ethine	*p*-anisyl	$(p\text{-}CH_3O-C_6H_4-C\equiv C-)_2Hg$	207–209 (with previous darkening)
3-Cyclohexyl-propine-1	hexahydrobenzyl	$(C_6H_{11}-CH_2-C\equiv C-)_2Hg$	104
3-Phenoxy-propine-1	phenoxymethyl	$(C_6H_5-O-CH_2-C\equiv C-)_2Hg$	120.5–121
Furyl-(2′-)ethine	furyl	$(C_4H_3O-C\equiv C-)_2Hg$	118–118.5
5′-Bromofuryl-(2′-) ethine	bromofuryl	$(Br-C_4H_2O-C\equiv C-)_2Hg$	175–177
1-Phenyl-propine-1	methylphenyl	no reaction with alkaline mercuric iodide or cyanide	

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[6] Hofmann and Kirmreuther, *Ber.*, **41,** 316 (1908); **42,** 4233 (1909).

[7] Lespieau, *Bull. soc. chim.*, [4] **29,** 528 (1921). Bourguel, *Ann. chim.*, [10] **3,** 191, 325 (1925). The details of the steps in this synthesis have been submitted by Messrs. Lespieau and Bourguel and will appear in "Organic Syntheses" (Wiley) **5,** 49 (1925) and **6** (1926).

ment of the latter with sodium amide, gave excellent results when applied to the synthesis of decine-1 and 4-phenyl-butine-1.

Fourteen different compounds embracing all of the above types were tested and in every case the mercuric salt was obtained readily in good yield and was easily purified. The mercuric salts were white, crystalline solids with sharp melting points that ranged from 61° for di-*n*-heptinylmercury, to 207° for di-*p*-anisylethinyl-mercury. The melting points of the various mercuric salts, including three previously recorded, are given in Table I. It will be noted that in their properties and structure these mercuric salts resemble the true organic mercury compounds, such as the mercury dialkyls and diaryls, rather than ordinary mercuric salts. The term salt is employed by analogy to the cuprous and silver compounds which are commonly referred to as salts.

The procedure used in the preparation of the mercuric salts consisted in adding a dilute solution of the acetylene in alcohol to an excess of the alkaline mercuric iodide reagent,[8] which was prepared by dissolving mercuric chloride in aqueous potassium iodide and adding a solution of sodium hydroxide. A white or grayish-white precipitate formed immediately, which was filtered, washed with dilute alcohol and purified by crystallization. The yields of the crude mercuric salts were usually from 85 to 95%.

The formation of a white crystalline precipitate with this reagent is a delicate test for monosubstituted acetylenes. One cg. of phenyl-acetylene dissolved in 1 g. of alcohol gave a precipitate which was sufficient for the purification and melting-point determination. Ammonia interferes with the test, and aldehydes and ketones cause the precipitation of mercurous salts and metallic mercury, which contaminate the crude product but are readily removed by crystallization from an organic solvent. Disubstituted acetylenes, $R—C\equiv C—R$, of which phenylmethyl-acetylene was used as an example, do not react with the alkaline mercuric iodide reagent.

Among other possible methods of preparing suitable derivatives which were considered, was the use of ethinylmagnesium halides, $R—C\equiv C—Mg—X$. Preliminary tests were made on these substances with phenylisocyanate and with benzophenone. The former yields the anilides of the corresponding propiolic acids, and the latter yields diphenylethinyl carbinols. These reactions are now under investigation.

Experimental Part

Preparation of the Mercuric Salts. $(R—C\equiv C—)_2Hg$. **General Procedure.**—Into a cooled, dilute solution of 2 equivalents of alkaline

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[8] The alkaline mercuric cyanide reagent of Hofmann and Kirmreuther may be used to replace the alkaline mercuric iodide reagent. The precipitates obtained are identical in constitution. From a limited number of experiments, the cyanide reagent appeared to yield a precipitate less contaminated with free mercury and other impurities. Since mercuric chloride was more readily available than the cyanide, the former was commonly used.

mercuric iodide[9] was dropped slowly, during mechanical stirring, a solution of 1 equivalent of the acetylene in 20 volumes of 95% alcohol. A white, crystalline precipitate separated at once, and in some cases the reaction mixture became almost solid. In one or two instances where the acetylene was added too rapidly, a gummy solid separated which later became crystalline. The mixture was stirred for two or three minutes, filtered with suction and the precipitate washed with 50% alcohol. The mixture should not be allowed to stand long before filtration or the precipitate becomes gray due to secondary reactions which probably form metallic mercury. The crude products were usually purified by crystallization from alcohol or benzene. In some instances it was advantageous to make the first purification by dissolving in a small amount of benzene or ether and precipitating the mercuric salts by the addition of petroleum ether, in which they are almost insoluble.

Methyl-acetylene.[10]—Fifty-five g. (0.25 mole) of 1,2-dibromopropane was slowly added to a mixture of 56 g. (1 mole) of potassium hydroxide and 56 cc. of 95% alcohol in a flask heated in an oil-bath at 160°. A vigorous reaction occurred and the gas evolved, after passing through an efficient water-cooled reflux condenser and a U-tube condenser cooled to —18°, was collected in 150 cc. of cold alcohol. Heating of the reaction flask was continued for one-half hour after all of the bromide had been added.

DIPROPINYL-MERCURY.—The alcoholic solution of methyl-acetylene gave a grayish-white precipitate weighing 11 g. (16% of the calculated amount based upon the 1,2-dibromopropane). The crude material was extracted in a Soxhlet tube with two 100cc. portions of pure acetone, from which the purified salt crystallized in thin, glistening plates. After a crystallization from methyl alcohol the pure dipropinyl-mercury melted at 203–204° (uncorr.) with slight darkening. Kutscheroff[4] did not report the melting point of this substance.

Anal. Subs., 0.1484, 0.1352, 0.1305: HgS, 0.1245, 0.1136, 0.1094. Calcd. for C_6H_6Hg: Hg, 71.99. Found: 72.34, 72.45, 72.28.

Ethyl-acetylene.[11]—The method described under methyl-acetylene was used for this preparation, except that water at 25° was circulated in the reflux condenser and the ethyl-acetylene, b. p. 18°, collected in the U-tube. From 100 g. of 1,2-dibromobutane, 145 g. of potassium hydroxide and 145 cc. of alcohol, 17 g. of distillate was obtained.

DIBUTINYL-MERCURY.—The crude distillate from the preparation described above gave 26 g. of crude mercuric salt (a 34% yield based upon 1,2-dibromobutane). The dibutinyl-mercury crystallized from 95% alcohol in glistening, white flakes, or long, white needles; m. p., 162–163°.

Anal. Subs., 0.3158, 0.3221: HgS, 0.2403, 0.2452. Calcd. for $C_8H_{10}Hg$: Hg, 65.36. Found: 65.60, 65.61.

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[9] Prepared according to the procedure of Nef, by dissolving 66 g. (0.486 g. equiv.) of mercuric chloride in a solution of 163 g. (0.61 g. equiv.) of potassium iodide in 163 cc. of water and adding 125 cc. of 10% sodium hydroxide solution (0.31 g. equiv.).

[10] Markownikoff, *Bull. soc. chim.*, **1861,** (trans.), 90. Liebermann, *Ann.*, **135,** 267 (1865).

[11] Dupont, *Compt. rend.*, **148,** 1523 (1909).

tert.-**Butyl-acetylene.**—This hydrocarbon was prepared from pinacolone[12] and the fraction boiling at 37–39° was used in the following preparation.

DI(3,3-DIMETHYLBUTINYL)-MERCURY.—This salt was obtained in 94% yield on following the usual procedure. Repeated crystallization from 95% alcohol gave the pure salt; m. p., 91–92°.

Anal. Subs., 0.2048, 0.2007: HgS, 0.1322, 0.1292. Calcd. for $C_{12}H_{18}Hg$: Hg, 55.25. Found: 55.65, 55.50.

n-**Amyl-acetylene.**[13]—Thirty-nine g. (0.29 mole) of 1-chloroheptene-1 was allowed to drop slowly into a well-stirred suspension of 29 g. (0.74 mole) of pulverized sodium amide in 200 cc. of Nujol. The latter was contained in a 1-liter flask which was heated in an oil-bath to 150–155°, before the addition of the halide was started. The heating was continued for two hours after all of the halide had been added and, after cooling, 300 cc. of ether was added. The thick paste was poured onto cracked ice and acidified with hydrochloric acid. The ether layer was separated, dried with calcium chloride and distilled at atmospheric pressure to remove the ether. The residual Nujol solution of the reaction products, subjected to vacuum distillation, yielded crude heptine-1; b. p., 30–36° (20 mm.). Redistillation at 745 mm. gave 15 g.; b. p., 98.5–101.5°; yield, 54%.

DI-*n*-HEPTINYL-MERCURY.—The crude product from 5 g. of heptine, b. p. 98.5–101.5°, weighed 16 g.; yield, 80%. After two crystallizations from methyl alcohol, the di-*n*-heptinyl-mercury was obtained as white needles; m. p., 61°.

Anal. Subs., 0.2538, 0.3247: HgS, 0.1519, 0.1938. Calcd. for $C_{14}H_{22}Hg$: Hg, 51.33. Found: 51.60, 51.46.

n-**Octyl-acetylene.**—Decine-1 has been prepared by isomerization[14] of methyl-heptyl-acetylene by means of metallic sodium, and by treatment of the monosodium salt of acetylene, in liquid ammonia, with *n*-octyl iodide.[15] It may be prepared more conveniently from *n*-heptyl bromide through bromodecene.

2-BROMODECENE-1.—A solution of *n*-heptylmagnesium bromide was prepared from 179 g. (1 mole) of heptyl bromide and 24 g. (1 mole) of magnesium with 500 cc. of ether. The yield as shown by titration was 85%. This solution was added slowly to a well-stirred solution of 200 g. (1 mole) of 2,3-dibromopropene-1 in 200 cc. of ether. A vigorous reaction occurred and the reaction mixture separated into two layers. After all of the solution had been added the mixture was refluxed for two hours, cooled and poured into 400 cc. of *N* hydrochloric acid and 600 g. of ice. The ether layer, after separation and drying with calcium chloride, was distilled from a steam-bath, and the residue fractionated under reduced pressure. A small amount of dibromopropene was recovered and the crude 2-bromodecene was collected at 90–130° (22 mm.). On redistillation, the latter distilled almost completely at 78–84° (4 mm.) and weighed 114 g.; yield 60%. For determination of physical constants and analysis a sample was twice redistilled. Pure 2-bromodecene-1 is a colorless liquid with a pleasant odor; b. p., 115–116° (22 mm.); 76–77° (3 mm.); d_0^0, 1.1044; d_{20}^{20}, 1.0864; d_4^{20}, 1.0844; n_{C}^{20}, 1.46015; n_{D}^{20}, 1.46290; n_{F}^{20}, 1.47011; MR_{D} (obs.), 55.630; MR_{D} (calcd.), 55.628.

Anal. Subs., 0.1768, 0.1784: 8.07 cc., 8.18 cc. of 0.1 *N* $AgNO_3$. Calcd. for $C_{10}H_{19}Br$: Br, 36.48. Found: 36.48, 36.65.

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[12] Ivitsky, *Bull. soc. chim.*, [4] **35**, 357 (1924). Gray with Marvel, THIS JOURNAL, **47**, 2801 (1925).

[13] Bourguel, *Ann. chim.*, [10] **3**, 191, 325 (1925). Lewinsohn, *Perfumery Essent. Oil Record*, **14**, 291 (1923). Guest, THIS JOURNAL, **47**, 862 (1925).

[14] Noerdlinger, *Kleine Mitteil. chem. Fabrik Florscheim*, **37**, Nov., 1911. *Chem. Centr.*, **1912**, I, 210.

[15] Picon, *Compt. rend.*, **169**, 32 (1919).

DECINE-1.—The reaction between 2-bromodecene and sodium amide was carried out as described under heptine-1. From 140 g. of crude bromodecene and 63 g. of sodium amide in 300 cc. of Nujol, there was obtained on the first distillation 61 g. of decine, (68% yield) which boiled completely at 80–82° (22 mm.).

DI-*n*-DECINYL-MERCURY.—From 5 g. of decine-1 there was obtained by the usual procedure, 12 g. of the mercuric salt; yield, 70%. The product after two crystallizations from benzene formed white needles; m. p., 83–84°.

Anal. Subs., 0.4953, 0.6377: HgS, 0.2440, 0.3141. Calcd. for $C_{20}H_{34}Hg$: Hg, 42.24. Found: 42.47, 42.46.

Phenyl-acetylene. DIPHENYLETHINYL-MERCURY.[16]—Phenyl-acetylene, b. p. 39–40° (14 mm.), gave a 90% yield of the crude mercuric salt. The pure salt crystallized from 95% alcohol in glittering white leaflets; m. p., 124.5–125°. It is moderately soluble in cold ether and alcohol, and readily soluble in chloroform, benzene and hot alcohol.

PHENYLPROPIOLIC-ANILIDE.—A mixture of 12.5 g. (0.12 mole) of pure phenylacetylene with 55 cc. of a 2 *N* solution of ethylmagnesium bromide was refluxed gently for two hours. The reaction mixture, which had separated into two layers, was cooled and diluted with 200 cc. of ether. A solution of 12 g. (0.10 mole) of phenylisocyanate in 100 cc. of ether was dropped in slowly during stirring. A vigorous reaction took place with separation of a yellow solid. At the end of the reaction the solid was filtered off, washed once with ether and thoroughly triturated in a mortar with dil. hydrochloric acid. The resulting pale yellow anilide, after being washed with water and dried, amounted to 20 g.; yield, 90%. After several crystallizations from methyl alcohol, the phenylpropiolic-anilide separated in small, colorless prisms; m. p.,[17] 126–127°.

Benzyl-acetylene.—The yield of 40% obtained by Lespieau[18] was raised to 52% by the addition of the tribromopropene to the phenylmagnesium bromide, instead of the reverse; 119 g. (0.427 mole) of 1,2,3-tribromopropene was dropped slowly into a stirred ethereal solution of 2 moles of phenylmagnesium bromide. After the addition of the tribromopropene, which required about two hours, the mixture was refluxed for two hours, cooled, and poured into a mixture of 100 cc. of concd. hydrochloric acid and cracked ice. The ether layer was separated, washed with water and dried with calcium chloride. Fractionation gave 26 g. of phenylpropine; b. p., 48–58° (5 mm.); yield, 52.5%.

DIPHENYLPROPINYL-MERCURY.—This salt was prepared in the usual way and was purified by solution in a small amount of hot benzene and addition of a large volume of petroleum ether; b. p., 50–60°. The purified salt separated in white needles, which were filtered off, washed with petroleum ether and crystallized from a small amount of hot absolute alcohol; m. p., 106.5–107.5°.

Anal. Subs., 0.2645, 0.3667: HgS, 0.1436, 0.1993. Calcd. for $C_{18}H_{14}Hg$: Hg, 46.57. Found: 46.80, 46.86.

Phenylmethyl-acetylene, ($C_6H_5—C\equiv C—CH_3$).—This substance did not form a mercuric salt when treated with the alkaline mercuric iodide reagent. For identification, the oil recovered by steam distillation after treatment with the mercuric iodide reagent was converted to the tetrabromide, by adding four atomic equivalents of bromine dissolved in carbon disulfide. After repeated crystallizations, the 1-phenyl-1,1,2,2-tetrabromopropane formed white crystals; m. p.,[19] 78–79°.

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[16] Nef, *Ann.*, **308,** 264 (1899).

[17] Stockhausen and Gattermann [*Ber.*, **25,** 3538 (1892)] reported 125–126° for the melting point of the product of the action of aniline on the acid chloride of phenylpropiolic acid.

[18] Lespieau, *Bull. soc. chim.*, [4] **29,** 528 (1921).

[19] Körner [*Ber.*, **21,** 276 (1887)] reported a melting point of 75°.

Phenethyl-acetylene.—4-Phenylbutine-1 has been prepared from phenylbutene by addition of bromine and removal of two molecules of hydrogen bromide by means of alcoholic potassium hydroxide solution.[20] It may be prepared more conveniently from benzyl chloride, through phenylbromobutene.

4-PHENYL-2-BROMOBUTENE-1.—Purified benzyl chloride, b. p. 71–72° (15 mm.), was converted into benzylmagnesium chloride, and the latter was added to an ethereal solution of 2,3-dibromopropene-1, as described for 2-bromodecene-1. From 360 g. (1.8 moles) of dibromopropene, and the magnesium compound from 252 g. (2 moles) of benzyl chloride, there was obtained 166.5 g. of crude phenylbromobutene; b. p., 106–119° (21 mm.); yield, 44%. Pure 4-phenyl-2-bromobutene-1 was obtained as a colorless oil with a pleasant odor; b. p., 117–118° (21 mm.); 77–78° (5 mm.); d_0^0, 1.3102; d_{20}^{20}, 1.2924; d_4^{20}, 1.2901; n_D^{20}, 1.5450; MR_D (obs.), 51.73; MR_D (calcd.), 52.03.

Anal. Subs., 0.1336, 0.1287: 6.46 cc., 6.10 cc. of 0.1 N $AgNO_3$. Calcd. for $C_{10}H_{11}Br$: Br, 37.88. Found: 37.80, 37.88.

4-PHENYLBUTINE-1.—The reaction with sodium amide was carried out as described under heptine-1. From 185 g. (0.88 mole) of crude 4-phenyl-2-bromobutene and 90 g. (2.25 moles) of sodium amide suspended in 400 cc. of Nujol, there was obtained 72 g. of crude 4-phenylbutine-1; b. p., 99–109° (24 mm.); yield, 63%. On redistillation the material passed almost completely at 95–99° (17 mm.).

DIPHENYLBUTINYL-MERCURY.—From 6 g. of phenylbutine there was obtained by the usual procedure, 10 g. of the mercuric salt; yield, 95%. A solution of the crude product in 75 cc. of warm benzene was filtered and treated with 300 cc. of petroleum ether, b. p. 50–60°, which precipitated the pure mercuric salt in small white crystals; m. p., 83.5–84.5°.

Anal. Subs., 0.4603, 0.9647: HgS, 0.2348, 0.4923. Calcd. for $C_{20}H_{18}Hg$: Hg, 43.73. Found: 43.98, 44.00.

***p*-Tolyl-acetylene.**—*p*-Tolyl-acetylene has been prepared from *p*-methyl-chloro-acetophenone through *p*-tolyl-dichloro-ethylene,[21] and by heating *p*-tolylpropiolic acid.[22] This acetylene may conveniently be obtained from *p*-methyl-acetophenone by a procedure analogous to the preparation of phenyl-acetylene from acetophenone; 67 g. (0.5 mole) of *p*-methyl-acetophenone was treated with 110 g. (0.5 mole) of phosphorus pentachloride and the resulting crude *p*-tolyl-chloro-ethylene, after being washed with dil. sodium hydroxide solution, was added to the warm mixture of 84 cc. of absolute alcohol and 84 g. of powdered potassium hydroxide and refluxed on a steam-bath for four hours. After cooling, the mass was poured into cold, dil. sulfuric acid and extracted with ether. Fractionation yielded 17 g. of crude *p*-tolyl-acetylene; b. p., 103–113° (100 mm.). On redistillation this gave 14 g. of pure *p*-tolyl-acetylene; b. p., 63° (20 mm.); yield, 25%. The yield could be improved by subjecting the residues to a second treatment with alcoholic potassium hydroxide.

DI-*p*-TOLYLETHINYL-MERCURY.—By the usual procedure, from 5 g. of *p*-tolyl-acetylene an almost quantitative yield of crude mercuric salt was obtained. This was purified by solution in 250 cc. of boiling toluene, filtration and addition of 250 cc. of petroleum ether, b. p. 50–60°, to the warm solution. The purified di-*p*-tolylethinyl-mercury separated in long, white needles; m. p., 199–202°; yield, 7.0 g., or 75%. This mercuric salt is moderately soluble in warm benzene or toluene, slightly soluble cold, sparingly soluble in ether or boiling alcohol and almost insoluble in cold alcohol.

Anal. Subs., 0.2008, 0.2372: HgS, 0.1087, 0.1289. Calcd. for $C_{18}H_{14}Hg$: Hg, 46.57. Found: 46.85, 46.67.

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[20] André, *Ann. chim. phys.*, [8] **29**, 550 (1913).

[21] *Ber.*, **33**, 2656 (1900).

[22] *Ann.*, **347**, 359 (1906).

p-Anisyl-acetylene.—A slight modification of the method of Manchot,[23] was used to prepare this substance. *p*-Anisylacrylic acid, from anisalacetone,[24] was treated in ethereal suspension with 1 molecular equivalent of bromine. The ether was evaporated at 25° and the residual crude *p*-anisyl-2,3-dibromopropionic acid was warmed with sodium carbonate solution to give *p*-anisyl-bromo-ethylene, which without purification was converted by the usual procedure to *p*-anisyl-acetylene; b. p., 96–97° (10 mm.) or 61° (3 mm.).

DI-*p*-ANISYLETHINYL-MERCURY.—When treated in the usual way *p*-anisyl-acetylene gave a 95% yield of the crude mercuric salt. This was purified by two crystallizations from toluene, and formed small white crystals, m. p. 207–209°, when rapidly heated. When heated slowly this salt turns brown before the melting point is reached.

Anal. Subs., 0.1930, 0.1667: HgS, 0.0989, 0.0853. Calcd. for $C_{18}H_{14}OHg$: Hg, 43.35. Found: 44.18, 44.12.

Hexahydrobenzyl-acetylene. DICYCLOHEXYLPROPINYL-MERCURY.—From 10 g. of 3-cyclohexylpropine-1, b. p. 55–58° (15 mm.), there was obtained 28.3 g. of the mercuric salt (a yield of 78%) which crystallized from 95% alcohol in long, white needles; m. p., 104°.

Anal. Subs., 0.2925, 0.2202: HgS, 0.1535, 0.1159. Calcd. for $C_{18}H_{26}Hg$: 45.25. Found: 45.24, 45.38.

A sample of the mercuric salt was prepared using the alkaline mercuric cyanide reagent, and after purification the resulting white needles were found to be identical in all respects with those obtained above. The melting points of the two samples were not altered by mixture.

Phenoxymethyl-acetylene. DIPHENOXYPROPINYL-MERCURY.—When treated in the usual way, 3-phenoxy-propine-1, b. p. 87° (20 mm.), gave an 84% yield of the crude mercuric salt. After two crystallizations from alcohol or benzene, it formed long, white needles; m. p., 120.5–121°.

Anal. Subs., 0.3052, 0.3548: HgS, 0.1543, 0.1794. Calcd. for $C_{18}H_{14}OHg$: Hg, 43.35. Found: 43.59, 43.60.

Summary

Simple mercuric salts of the formula $(R—C\equiv C—)_2Hg$ have been formed by treatment of monosubstituted acetylenes with an alkaline solution of mercuric iodide or cyanide. This has been found to be a general reaction for substances of the type, $R—C\equiv C—H$; compounds of the type $R—C\equiv C—R$ do not form mercuric salts under these conditions.

The mercuric salts of 14 monosubstituted acetylenes have been prepared and described, in which the substituted radicals were aliphatic, aromatic and mixed aromatic-aliphatic groups.

These salts were found to possess properties that rendered them suitable for the identification and characterization of the corresponding acetylenes.

The methods of preparation of several monosubstituted acetylenes have been improved. Two new intermediate halogen derivatives, 2-bromodecene-1 and 4-phenyl-2-bromobutene-1 were prepared and described.

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[23] Manchot, *Ann.*, **387**, 281 (1912).

[24] Einhorn and Grabfeld, *Ann.*, **243**, 264 (1888).