[CONTRIBUTION FROM THE LABORATORY OF ORGANIC CHEMISTRY OF THE UNIVERSITY OF NOTRE DAME

The Direct Iodination of Monosubstituted Acetylenes

BY THOMAS H. VAUGHN AND J. A. NIEUWLAND

In a previous communication[1] it has been reported that a solution of iodine in anhydrous liquid ammonia is an effective reagent for the iodination of certain classes of compounds. It was shown that acetylene and monosodium acetylide react with such solutions, giving almost the theoretical yields of pure diiodoacetylene. In an effort to determine whether or not this reaction is general for compounds containing an acetylenic hydrogen, we have treated several mono substituted acetylenes with iodine in ammonia. It has been found that both alkyl and aryl acetylenes are iodinated by such treatment in accordance with the equation

$$RC{\equiv}CH + I_2 + NH_3 \longrightarrow RC{\equiv}CI + NH_4I$$

There is, however, a very marked difference among various acetylenes in the ease of this iodination. Phenyl, tolyl and vinyl acetylenes are completely iodinated in a relatively short time at −34°, while the iodination of alkyl acetylenes is very slow at this temperature, amylacetylene, for example, being iodinated to the extent of only 6% in four days. It was found that alkyl acetylenes could be iodinated more completely by warming the reaction mixture up to room temperature in an autoclave. The yields, however, were only 15–50%. A certain amount of loss was expected due to difficulties in isolating materials from liquid ammonia but such losses as were found to occur could not reasonably be explained in this manner. Suspecting that the low yield was occasioned by a reaction of iodine with ammonia, samples of 0.2–0.3 g. of iodine were dissolved in 100 ml. of ammonia and allowed to stand in an autoclave for ten hours at room temperature. After the addition of water the iodide ion produced was determined by precipitation as silver iodide. In three experiments an average of 98.8% of the iodine used was found in the precipitate. Since a small loss of iodine occurred when the samples were dissolved in the ammonia it appears that the following reaction takes place between iodine and ammonia at 25°.

$$3I_2 + NH_3 \longrightarrow NH_4I + N_2$$

That this reaction does not take place to any marked extent at −34° is evident by the fact that uniformly high yields of phenyl, tolyl and vinyl iodoacetylenes have been obtained at this temperature.

Amylacetylene was also iodinated at room temperature with fair results by iodine dissolved in an ethereal solution of ammonia. There was produced along with the iodoacetylene, however, a large amount of addition

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[1] Vaughn and Nieuwland, THIS JOURNAL, **54**, 787–791 (1932).

products. It is worthy of note that the addition of iodine to the triple bond has never been observed in pure ammonia.

The sodium salts of monosubstituted acetylene iodinate instantly in ammonia. Sodium amyl acetylide prepared from sodium in ammonia and amylacetylene, gave a 68% yield of amyl iodoacetylene.

By direct iodination of the corresponding acetylene, ethyl, butyl, amyl, heptyl, vinyl, phenyl and tolyl iodoacetylenes were prepared. Two of these, amyl[2] and phenyl,[3] have been prepared previously by other methods. All of these compounds are colorless liquids when pure but tend to turn yellow on exposure to heat and light. On long standing at room temperature in clear glass bottles the compounds take on the characteristic color of iodine. All, excepting vinyliodoacetylene, may be kept in the dark in a refrigerator for several months without apparent change. The alkyl iodoacetylenes are very volatile and possess extremely powerful odors. This odor strongly resembles that of diiodoacetylene and grows more pleasant as the molecular weights of the compounds increase.

Vinyliodoacetylene was found to exhibit certain peculiar properties and will be discussed in a later communication.

Experimental Part

Materials.—Ethyl, butyl, amyl and heptyl acetylenes were prepared from the corresponding alkyl bromide and monosodium acetylide in liquid ammonia.[4] Fractions boiling over a range of 1° were used in the iodinations. Phenylacetylene was prepared by the method of Hessler[5] from β-bromostyrene and molten potassium hydroxide. The compound boiled at 140–141° at 745 mm. Tolylacetylene was prepared from *p*-methylacetophenone. The ketone was treated with phosphorus pentachloride, and hydrogen chloride removed from the resulting chloro compounds by alcoholic potassium hydroxide.[6]

Iodination of Alkyl Acetylenes at 25°

Amyl Iodoacetylene.—One liter of liquid ammonia was added to 100 g. of iodine in a 1.5-liter beaker[7] and then 39 g. of amylacetylene added. The beaker was placed in an autoclave and allowed to stand overnight. The pressure was released and the contents of the beaker treated with about 750 ml. of water. To avoid violent spattering the water was added in a fine stream which was directed against the side of the beaker. The oil which separated was well washed with water and 5% hydrochloric acid. After drying over calcium chloride the material was fractionated under reduced pressure. Twenty grams of amylacetylene was recovered and 13 g. (30% of the theoretical) of amyl iodoacetylene was obtained. Amyl iodoacetylene has the following properties: b. p. 80.0° at 11.5 mm.; 90.0° at 16.5 mm.; 93.0° at 21 mm.; m. p. −35 to −37°; d^{22} 1.472; $n_D^{9.7}$ 1.5191; $n_D^{26.5}$ 1.5105; *M* calcd. 45.29, obs. 45.35; mol. wt. (ebullioscopic in benzene) 226, calcd.

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

(3) Liebermann and Sachse, *Ber.*, **24**, 4115 (1891); Peratoner. *Gazz. chim. ital.*, [II] **22**, 81, 94 (1892); Nef. *Ann.*, **308**, 293 (1899).

(4) Lebeau and Picon, *Compt. rend.*, **156**, 1077 (1913); Picon, *ibid.*, **158**, 1184 (1914).

(5) Hessler, THIS JOURNAL, **44**, 425 (1922); "Organic Syntheses," Vol. II, pp. 67–69, John Wiley and Sons, Inc., New York, 1922.

(6) Kunckell and Gotsch, *Ber.*, **33**, 2656 (1901).

(7) Vaughn and Nieuwland, THIS JOURNAL, **54**, 788 (1932).

222. A sample of the substance was analyzed by the modified Chablay method.[8] Calcd. for $C_7H_{11}I$: I, 57.16. Found: I, 57.10.

Ethyl Iodoacetylene.—This compound was prepared by the direct iodination of ethylacetylene in ammonia at 25°. The yield was 15% of the theoretical. Ethyl iodoacetylene has the following properties: b. p. 83–5° at 156 mm.; 92–4 at 217 mm.; d^{22} 1.739; n_D^{14} 1.5307, $n_D^{23.7}$ 1.5247; *M* calcd. 31.48, obs. 31.76.

Butyl Iodoacetylene.—This compound was obtained in 14% yield by the direct iodination of butylacetylene in ammonia at 25°. It has the following properties: b. p. 52.5° at 6 mm.; 60.5° at 10 mm.; 75° at 20 mm.; 82.5° at 30 mm.; d_{25} 1.5552; n_D^{10} 1.5230; n_D^{25} 1.51500; *M* calcd. 40.68, obs. 40.32; mol. wt. (ebullioscopic in benzene) 213, calcd. 208.

Anal. Calcd. for C_6H_9I: I, 61.02. Found: I, 60.84.

This compound was also prepared in 50–60% yields by the action of iodine on butylethinylmagnesium bromide in ether.[9] The material obtained by this method was identical with that prepared by direct iodination.

Heptyl Iodoacetylene.—A 45% yield of heptyl iodoacetylene was obtained by direct iodination at 25°. The compound exhibited the following properties: b. p. 105–107° at 4 mm.; d^{22} 1.355; $n_D^{9.5}$ 1.5097, $n_D^{26.5}$ 1.5024; *M*, calcd. 54.50, obs. 54.66; mol. wt. (ebullioscopic in benzene) 240, calcd. 250.

Iodination of Amylacetylene at −34°.—One hundred grams of iodine was added to 1.5 liters of liquid ammonia contained in a 2-liter flask and 39 g. of amylacetylene run in. The flask was closed with a stopper bearing a 61-cm. piece of 3-mm. glass tubing and allowed to stand for ninety-six hours, ammonia being added from time to time to maintain the volume of the solution. At the end of this time water was added to the contents of the flask and the oil which separated washed with sodium thiosulfate solution, water and 5% hydrochloric acid. The oil was dried over calcium chloride and fractionated under reduced pressure. The yield of amyl iodoacetylene was 4 g. (6% of the theoretical).

Iodination of Amylacetylene in Ether–Ammonia Solutions.—Liquid ammonia was poured into a solution of iodine in 150 g. of anhydrous ether until 20 g. had been taken up. Nineteen grams of amylacetylene was added and the solution allowed to stand overnight. Water was added and the ether layer washed with sodium thiosulfate, water, and 5% hydrochloric acid and dried over calcium chloride. On fractionation 8 g. (21% of the theoretical) of amyl iodoacetylene was obtained. Five grams of amylacetylene was recovered and 18 g. of a residue, presumably iodo addition products of amylacetylene and amyl iodoacetylene, remained in the flask.

Iodination of Sodium Amyalcetylide.—Amylacetylene was added to a solution of 5 g. of sodium in 500 ml. of liquid ammonia until the blue color was discharged. Forty grams of iodine was then slowly dropped into the solution. A violent reaction took place, the iodine being consumed almost instantly. Water was added and the oil which separated was washed, dried and distilled in the usual manner. The yield of amyl iodoacetylene was 17 g. (68% of the theoretical), 10 g. of amylacetylene being recovered.

Iodination of Phenylacetylene at −34°.—Twenty-nine grams of phenylacetylene was added to 62 g. of iodine dissolved in 1.5 liters of ammonia and the mixture allowed to stand overnight. Water was added and the oil which came down quickly separated to avoid reaction with the ammonium hydroxide.[10] The oil was washed with sodium thiosulfate solution and water and dried over calcium chloride. Sixty grams of material (92% of the theoretical) was obtained which had the following properties: d^{25} 1.7508;

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(8) Vaughn and Nieuwland, *Ind. Eng. Chem., Anal. Ed.*, **3**, 274 (1931).

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

(10) Nef, *Ann.*, **308**, 293 (1899).

n_D^{25} 1.6591; *M* calcd. 47.31, obs. 48.02. On distillation the substance behaved as reported by Peratoner,[11] liberating iodine and forming a solid compound.

Tolyl Iodoacetylene.—Eight grams of tolylacetylene was iodinated in the same manner as was phenylacetylene. The dry oil weighed 16.5 g. (99%). Considerable decomposition took place when the material was distilled. The fraction boiling at 135–141° at 16 mm. had the following properties: d^{27} 1.810; n_D^{27} 1.6870; *M* calcd., 52.02, obs. 51.01. The material was apparently impure tolyl iodoacetylene.

Summary

1. Iodine in liquid ammonia has been found to be an effective reagent for the direct iodination of monosubstituted acetylenes.

2. Phenyl, tolyl and vinyl acetylenes react with iodine in ammonia at −34° giving almost theoretical yields of the corresponding iodoacetylene.

3. Ethyl, butyl, amyl and heptyl acetylenes react slowly with ammonia solutions of iodine at −34°. At 25° 15–45% yields of the iodoacetylenes are obtained.

4. At 25° iodine has been found to react completely with liquid ammonia giving ammonium iodide.

5. Amyl iodoacetylene is produced in 28% yield by the action of iodine in ammonia–ether solution on amylacetylene.

6. Sodium amylacetylide is very rapidly iodinated by the action of iodine in ammonia, giving 68% yields of amyl iodoacetylene.

[11] Peratoner, *Gazz. chim. ital.*, [II] **22**, 96 (1892).

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Narcotine and Hydrastine. A Study of the Mechanism of their Conversion into Narceine, Methylhydrasteine and their Derivatives[1]

BY C. R. ADDINALL AND RANDOLPH T. MAJOR

The transformation of quaternary narcotine halides into the pseudonarceine studied by Roser[1a] was firmly established when Freund and Frankforter[2] proved the identity of pseudonarceine with opium narceine and demonstrated the close structural relationship of narcotine and narceine. Rabe and McMillian,[3] who regarded narcotine and the closely related hydrastine as the inner esters of 1,2-hydramines, showed that two reactions were involved in the hydrolysis of these alkaloids and that in addition to decomposition by cleavage of the C–C linkage, rearrangement took place. On the contrary the quarternary ammonium compounds of nar-

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[1] Presented at the New Orleans meeting of the American Chemical Society, March 29, 1932.

[1a] Roser, *Ann.*, **247**, 167 (1888).

[2] Freund and Frankforter, *ibid.*, **277**, 20 (1893).

[3] Rabe and McMillian, *ibid.*, **377**, 223 (1910).