[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF NOTRE DAME]

Further Studies of Iodination in Liquid Ammonia

BY THOMAS H. VAUGHN AND J. A. NIEUWLAND

We have recently reported that acetylene[1] and phenyl, tolyl[2] and vinyl[2,3] acetylenes react readily with solutions of iodine in liquid ammonia at $-34°$, giving almost the theoretical yields of the corresponding iodoacetylenes. We have also shown that the alkyl acetylenes[2] react very slowly with such solutions at $-34°$ and that while at higher temperatures (25°) iodination takes place more readily the yields are low.

All those acetylenes which iodinate readily possess as a common characteristic a highly unsaturated substituent, the unsaturation of which is conjugated with the triple bond. These may therefore be classed as highly "acid" acetylenes. In order to determine whether or not this ease of iodination was shared by other acetylenes of this class we have subjected xylyl, mesityl, *p*-chlorophenyl, *m*-chlorophenyl, *o*-chlorophenyl, *p*-bromophenyl and α-methylvinyl acetylenes to the action of iodine in ammonia. We have found that all of these acetylenes are rapidly and quantitatively converted to the iodoacetylene at $-34°$. No measurement of rate was made but it was noticed that the halogen substituted phenylacetylenes iodinated much more rapidly than did the alkyl substituted phenylacetylenes.

These iodoacetylenes all exhibit their characteristic instability toward light and heat. They all react with alkaline solutions of mercury cyanide to give the corresponding mercury derivative of the acetylene.[4]

α-Methylvinyliodoacetylene is unstable and polymerizes in the presence of oxygen. This polymerization is similar to but somewhat slower than that of vinyliodoacetylene.[3] As mentioned above the compound gives a mercury derivative but this derivative could not be purified as no suitable solvent for crystallization was found.

In the preparation of xylyl and mesitylacetylenes alcoholic potassium hydroxide was tried for the dehydrohalogenation of the alkyl substituted α-chlorostyrenes but was not as satisfactory as sodamide, giving much lower yields. On the other hand sodamide reacts too vigorously with the halogen substituted α-chlorostyrenes and alcoholic potassium hydroxide is more satisfactory.

Kunckell and Koritzky have reported[5] that mesitylacetylene is a light yellow oil of ethereal odor, b. p. 168–175° at 20 mm., d_{17} 0.8731. We have prepared a compound (I) from mesityl methyl ketone by the following reactions

$$(CH_3)_3C_6H_2COCH_3 + PCl_5 \longrightarrow$$
$$(CH_3)_3C_6H_2CCl{=}CH_2 + NaNH_2 \longrightarrow$$
$$(CH_3)_3C_6H_2{-}C{\equiv}CH \quad (I)$$

which is a colorless liquid, b. p. 100.6–101.5° at 20 mm., m. p. 2.7–3.5°; d_{25} 0.9185; n_D^{25} 1.5429; MR'_D obs. 49.42, calcd. 48.35; γ_{25}, 31.55 dynes/cm., [P] obs. 370.6, calcd. (data of Mumford and Phillips[6] $\sigma = -9.5$), 371.5; mol. wt. obs. 144.5, calcd. 144. Our compound (I) reacts with alkaline mercury cyanide solution giving a derivative whose analysis checks the values calculated for dimesitylethynyl mercury. Its iodo derivative also analyzes as calculated and is converted by mercury solutions into the same derivative as that obtained from the original material. The substance and its iodo derivative have dipole moments which are consistent with those of other similar acetylenes.[7] The analytical data, chemical behavior and physical properties all indicate that the material is mesitylacetylene.

Experimental Part

***sym*-Trimethyl-α-chlorostyrene.**—A mixture of 55 g. of mesityl methyl ketone and 80 g. of phosphorus pentachloride was heated on the steam-bath for four hours, cooled and then poured over ice. The oil which formed was roughly separated and neutralized with 10% sodium hydroxide. The material was extracted with ether and the extract dried over sodium sulfate. The ether was removed and the residue fractionated under reduced pressure. A yield of 48 g. (78% of the theoretical) b. p. 122–124° at 25 mm. was obtained. *Anal.*[8] Calcd. for $C_{11}H_{13}Cl$: Cl, 19.65. Found: Cl, 19.51.

Mesitylacetylene.—A suspension of 40 g. of sodamide in 250 ml. of mineral oil was prepared by grinding in a ball mill. This suspension was mixed with 171 g. of *sym*-trimethyl-α-chlorostyrene and heated by an oil-bath at 150° for three hours. The mixture was cooled, poured

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(1) Vaughn and Nieuwland, THIS JOURNAL, **54**, 787 (1932).

(2) Vaughn and Nieuwland, *ibid.*, **55**, 2150 (1933).

(3) Vaughn and Nieuwland, *J. Chem. Soc.*, 741 (1933).

(4) Vaughn, THIS JOURNAL, **55**, 3453 (1933).

(5) Kunckell and Koritzky, *Ber.*, **33**, 3263 (1901).

(6) Mumford and Phillips, *J. Chem. Soc.*, 2113 (1929).

(7) Wilson and Wenzke, to be published.

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

over ice, acidified with dilute hydrochloric acid and extracted with ether. The extract was dried over anhydrous sodium sulfate and the ether removed. On fractionation of the residue under reduced pressure 120 g. (71% of the theoretical yield) of mesitylacetylene, b. p. 103–107° at 23 mm. was obtained. *Mol. wt.* (lowering of vapor pressure of ether) calcd. for $C_{11}H_{12}$, 144; obs. 144.5. The physical properties of mesitylacetylene are given earlier in this article. For analysis the compound was converted to the mercury derivative,[4] dimesitylethynyl mercury, m. p. 238.5–239.0°. Calcd. for $C_{22}H_{22}Hg$: Hg, 41.21. Found: Hg, 41.49.

Mesityliodoacetylene.—A solution of 25.4 g. of iodine and 14.4 g. of mesitylacetylene in 500 ml. of liquid ammonia, contained in a 600 ml. Dewar flask, was allowed to stand for twenty-four hours. The solution was treated slowly with 250 ml. of 5% sodium thiosulfate solution, being stirred during the additon to prevent lumping. The precipitate of mesityliodoacetylene was filtered off, washed well with water, and dried. A yield of 26 g. (96% of the theoretical) was obtained. After crystallization from methyl alcohol the substance melted at 91.8–92.2°. Its mercury derivative melted at 239°.

Anal. Calcd. for $C_{11}H_{11}I$: I, 47.0. Found: I, 47.4.

Xylyliodoacetylene.—Xylylacetylene was obtained in the same manner as mesitylacetylene, the yield of chlorostyrene being 82% and that of the acetylene 75%. It gave a mercury derivative melting at 140.0–140.4°. The iodoacetylene was prepared as above in 90% yields and is a brownish liquid, soluble in ether and alcohol, b. p., with slight decomposition, 121–122° at 4 mm., d_{24} 1.556, n^{24}_{D} 1.6394, MR'_D calcd. 58.81, obs. 59.20. These properties check well with those reported by Grignard and Perrichon.[9] The mercury derivative of the iodoacetylene melted at 140.4°.

***p*-Chloro-α-chlorostyrene.**—Five hundred grams of *p*-chloroacetophenone and 690 g. of phosphorus pentachloride gave 337 g. (60% of the theoretical) of the chlorostyrene of b. p. 125–129° at 26 mm. The material was refractionated and the middle portion, b. p. 114.4–116.4° at 20 mm., reserved for characterization. This was again fractionated giving an almost colorless yellow liquid, b. p. 115–116° at 20 mm.; d_{25} 1.247; n^{25}_{D} 1.5735; m. p. −6 to −5°; γ_{25} 37.34 dynes/cm.; MR'_D calcd. 45.87, obs. 45.73; [P] calcd. ($\sigma = -5.2$) 344.8, obs. 342.8. *Anal.* Calcd. for $C_8H_6Cl_2$: Cl, 40.98. Found: Cl, 40.69.

***p* - Chlorophenyliodoacetylene.**—*p* - Chlorophenylacetylene[10] was obtained in 36% yield from the α-chlorostyrene by treatment with 25% alcoholic potassium hydroxide. It is a colorless crystalline substance, m. p. 45.4–46.1°, d_{50} 1.24. *Anal.* Calcd. for C_8H_5Cl: Cl, 26.76. Found: Cl, 26.46. Its mercury derivative melted at 221.5–222.0°. The iodoacetylene was obtained in 98% yields, m. p. 84.7–85.0°. Using ethyl alcohol as a medium crystallization losses run about 20%. *p*-Chlorophenyliodoacetylene gave a mercury derivative melting at 221.5°.

***m* - Chlorophenyliodoacetylene.**—*m* - Chlorophenylacetylene[10] prepared by Dr. M. M. Otto of this Laboratory was iodinated as above. After treating the reaction product with water the mixture was extracted with ether and the extract, after washing with dilute acid, dried over calcium chloride. The ether was removed at a pressure of 25 mm. and the residue left at this pressure at 35–40° for four hours in an attempt to remove the last traces of solvent. The residue represented a 91% yield of the iodoacetylene and had the following properties: m. p. 11.1°, n^{25}_{D} 1.6638, d_{25} 1.818, MR'_D calcd. 52.48, obs. 53.66. *Anal.* Calcd. for C_8H_4ICl: total halogen, 61.9. Found: total halogen, 59.6. The analysis indicates that the material is not quite pure, probably being contaminated by a small amount of ether. *m*-Chlorophenyliodoacetylene gives a mercury derivative melting at 137.9–138.4°. That from the acetylene melts at 138.0–138.5°.

***o*-Chlorophenyliodoacetylene.**—This substance was obtained in 95% yield from *o*-chlorophenylacetylene[11] which was prepared by Dr. Otto. After crystallization from methanol it melted at 37.7–38.0°. *Anal.* Calcd. for C_8H_4ICl: total halogen, 61.9. Found: total halogen, 62.4. It gave a mercury derivative which melted at 212–213°, checking the melting point of the compound obtained from the acetylene.

***p*-Bromophenyliodoacetylene.**—*p*-Bromophenyl acetylene prepared by the method of Dufraisse and Dequesnes[12] gave a mercury derivative melting at 256.0–256.5°.[10] Upon iodination the acetylene gave a 98% yield of *p*-bromophenyliodoacetylene, m. p. 93.8–94.0°. The mercury derivative prepared from the iodoacetylene melted at 256.5–257.0°.

Methylvinyliodoacetylene.—Methylvinylacetylene, prepared by the method of Carothers and Coffman,[13] reacted with alkaline solutions of mercury giving precipitates but these precipitates were incapable of crystallization from the ordinary solvents. Methylvinyliodoacetylene was obtained from the acetylene in 90% yield. On distillation of the crude material through a 25-cm. column practically all came over at 72° at 47 mm. If the heating was continued, the last few drops in the flask always exploded with great violence. The purified material is almost colorless and has the following physical properties: b. p. 80.8–81.0° at 72 mm.; d_{30} 1.7127; n^{30}_{D} 1.5656; γ_{25} 32.77 dynes/cm.; MR'_D calcd. 36.14, obs. 36.55; [P] calcd. ($\sigma = -3$) 267, obs. 268.2. *Anal.* Calcd. for C_5H_5I: I, 66.1. Found: I, 66.3.

On standing in the presence of oxygen the material darkens and becomes more viscous, finally setting to a black solid. This change is much slower than in the case of vinylacetylene. Methylvinyliodoacetylene gives a mercury derivative which like that from the acetylene could not be recrystallized.

Summary

1. Two new substituted α-chlorostyrenes and six new iodoacetylenes have been described.

2. The properties of mesitylacetylene have been reported.

3. In all cases which have so far been examined any monosubstituted acetylene containing an unsaturated substituent whose unsaturation is

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

[10] Otto, to be published.

[11] Bergmann and Bondi, *Ber.*, **66**, 278 (1933).

[12] Dufraisse and Dequesnes, *Bull. soc. chim.*, **49**, 1880 (1931).

[13] Carothers and Coffman, THIS JOURNAL, **54**, 4074 (1932).

conjugated with the triple bond is readily and completely iodinated by a solution of iodine in ammonia at its boiling point. For such acetylenes iodination in liquid ammonia offers the best method for the preparation of the iodoacetylene.

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[CONTRIBUTION FROM THE KENT AND JONES CHEMICAL LABORATORIES, UNIVERSITY OF CHICAGO]

The Resolution of *dl*-Erythronic Acid[1]

BY J. W. E. GLATTFELD AND LOUIS R. FORBRICH

One of the by-products in the preparation of 2,3-dihydroxybutyric acid is a lactone which we have called 3-hydroxyisocrotonic lactone.[2] The yield of this by-product in the process employed is fairly high (about 23%). It has proved possible to convert this lactone with excellent yield into *dl*-erythronic lactone[3] and a good supply of the latter is now on hand. Experiments are being conducted with the object of reducing the erythronic lactone to erythrose and, in order to obtain the active erythroses, it is necessary to have the corresponding active erythronic lactones. The work reported below was carried out for the purpose of supplying these necessary active lactones.

All three varieties of erythronic acid—*dl*, *d* and *l*—are known in the form of their 1,4 lactones.[4,5,6] The resolution of the *dl*-acid has been twice attempted but neither attempt was entirely successful.[7] This paper reports the complete resolution of the *dl*-acid by the use of brucine and quinine and gives the constants of the two pure optically active lactones.

Experimental Part

The *dl*-Erythronic Lactone.—The *dl*-lactone used in this work was prepared in 61% yield according to the method of Braun by the oxidation of 3-hydroxyisocrotonic lactone with silver chlorate. It was recrystallized from ethyl acetate and then melted at 91–92° and was shown, by titration, to be perfectly pure.

The Resolution.—Preliminary experiments showed that either brucine or quinine could be used as the resolving agent. Recrystallization of the brucine salts from water gave the pure brucine salt of the levorotatory component and recrystallization of the quinine salts from 95% alcohol gave the pure dextrorotatory component. The yields of pure lactone obtained when a single alkaloid was used, however, were not good and the two pure lactones were obtained in larger quantities by the alternate use of brucine and quinine. This procedure is made possible by the fact that of the two brucine salts it is the *d*-(−)-form that is the less soluble and of the two quinine salts the *l*-(+)-form that is the less soluble.

The procedure used was to convert the lactone into its brucine or quinine salt by the usual methods. In the case of the brucine salt, the water solution was then concentrated *in vacuo* at 60° until the ratio of water to salt was 2 to 1, cooled, and stored in the ice box for twenty-four to forty-eight hours. The crop of crystals (Crop 1) was removed by suction filtration but not washed. The mother liquor from Crop 1 was concentrated until the ratio of water to salt was again 2 to 1 and a second crop of crystals (Crop 2) obtained. Crops 1 and 2 were now united and recrystallized from 2 parts of water; Crop B1A was thus obtained. The mother liquor from Crop B1A was added to that from Crop 2. The lactone was set free from Crop B1A and found to be fairly pure *d*-(−)-lactone (see table below).

The combined mother liquors were now hydrolyzed and the lactone obtained was converted into the quinine salt. Again two crops of salts were obtained as in the case of the brucine salt except that 5 parts of 95% alcohol were used. The two crops were united and recrystallized from 5 parts of 95% alcohol and thus yielded Crop Q2A. The mother liquor from Crop Q2A was added to the mother liquor from quinine salt Crop 2. The lactone was set free from Crop Q2A and found to be fairly pure *l*-(+)-lactone (see table below).

The lactone was set free from the quinine salts in the combined mother liquors and converted back into the brucine salt and the process outlined above repeated; two crops of brucine salt obtained and recrystallized from two parts of water gave Crop B3A. The mother liquors gave a lactone that was converted into the quinine salt; this yielded two crops which were combined and recrystallized and gave Crop Q4A. This cycle was again repeated and Crops B5A and Q6A obtained. Crops B3A and B5A were now united as were also Crops Q4A and Q6A and the lactones set free.

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(1) The material in this article is taken partly from a dissertation presented by Louis R. Forbrich in partial fulfilment of the requirements for the degree of Master of Science in the University of Chicago.

(2) Glattfeld, Leavell, Spieth and Hutton, THIS JOURNAL, **53**, 3164 (1931).

(3) Braun, *ibid.*, **51**, 235 (1929).

(4) Lamparter, *Ann.*, **134**, 260 (1865); Sell, *Z. Chem.*, **8**, 12 (1865); Neuberg, *Chem. Centr.*, I, 1229 (1910); Nef, *Ann.*, **357**, 247 (1909); Anderson, *Am. Chem. J.*, **42**, 402 (1909); Lespieau, *Bull. soc. chim.*, [iv] I, 1117 (1907); Cohen, Abstracts of Theses, University of Chicago, Sciences Series, VI, 125 (1927–28); Braun, *loc. cit.*

(5) Ruff, *Ber.*, **32**, 3672 (1899); Glattfeld, *Am. Chem. J.*, **50**, 148 (1913); Jensen and Upson, THIS JOURNAL, **47**, 3021 (1925).

(6) Ruff, *Ber.*, **34**, 1368 (1901).

(7) Lespieau, *loc. cit.*; Anderson, *loc. cit.*