

from the filtrate 1.1 g. of the same substance was obtained. The residue was a black gum.

The product, when treated with norite and crystallized from 80% aqueous alcohol, melted at 215°. Two grams dissolved in 100 cc. of 80% aqueous alcohol and, on cooling the solution, 0.7 g. separated in the form of long, colorless needles. One gram was soluble in 400 cc. of boiling acetone and did not crystallize on cooling. The substance was only slightly soluble in pure alcohol or water. Solutions of the compound quickly turned purple when exposed to the air. This triamino compound was by far the least soluble and the most sensitive to decomposition of any of the amino derivatives studied.

Anal. Calcd. for $C_{19}H_{20}N_6$: N, 25.30. Found: N, 25.10, 25.08.

Summary

1. A new method for the synthesis of nitrotriarylguanidines has been developed. By desulfurization of a mixture of the thiourea and amine through the combined action of iodine and pyridine, *p*-nitrophenyldiphenylguanidine, two di-*p*-nitrophenylphenylguanidines, and tri-*p*-nitrophenylphenylguanidine have been prepared. A di-*m*-nitrophenylphenylguanidine has also been obtained.

2. An instance of guanidine isomerism has been observed in the case of the two di-*p*-nitrophenylphenylguanidines. These substances are interconvertible isomers, which differ widely in melting points and in behavior toward heat, acids and pyridine.

3. Four previously undescribed nitroarylthioureas have been prepared.

4. Four amino derivatives of triphenylguanidine have been obtained, and their pharmacological effect on the tubercle bacillus has been investigated.

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

IODINATION IN LIQUID AMMONIA

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Solutions of iodine in liquid ammonia have been used by several investigators as a nitridizing agent.¹ In these reactions hydrogen has been nitridized off of organic compounds with the subsequent formation of ammonium iodide. A survey of the literature shows that no substitutions of iodine for hydrogen have been reported.

It has been pointed out by Richter² and shown by Datta and Chatterjee³ that iodination generally takes place most readily in the presence of sub-

¹ Shurman and Fernelius, *THIS JOURNAL*, **52**, 2425-30 (1930); Strain, *ibid.*, **51**, 272 (1929); **49**, 1564 (1927); Bergstrom, *J. Phys. Chem.*, **32**, 440 (1928).

² Richter, "Organic Chemistry," translation by Spielmann, Blakiston's Son & Co., Philadelphia, 1919, Vol. I, p. 92.

³ Datta and Chatterjee, *THIS JOURNAL*, **39**, 439 (1917).

stances which combine with the hydrogen iodide produced. From this consideration liquid ammonia would appear to be a suitable medium in which to carry out iodinations since any hydrogen iodide produced would at once react with the ammonia to produce ammonium iodide.

Such has proved to be the case. Iodine in liquid ammonia is capable of replacing various types of labile hydrogen. Substitution occurs in acetylenes, in ketones, in amines, and in compounds containing the $\text{—COCH}_2\text{CO—}$ group. The reaction of iodine and acetylene in liquid ammonia affords a convenient method for the preparation of diiodoacetylene.

Preparation of Diiodoacetylene.—One hundred grams of iodine is placed in a 1.5-liter beaker and the bottom of the beaker cooled by immersion in a shallow dish of liquid ammonia. After standing for a minute or so, 750 ml. of ammonia is added as rapidly as possible.⁴ Acetylene, from a Prestolite cylinder, washed with water and dried by spraying through concentrated sulfuric acid, is bubbled through the solution at a rate of 200 to 500 ml. per minute. The contents of the beaker should be mechanically stirred. In two and one-half to three hours the solution becomes perfectly clear, indicating the end of the reaction. The beaker is covered with a watch glass and placed in a hot water-bath to evaporate the ammonia. When the volume has been reduced to about 150 ml., 500 ml. of water is slowly added to precipitate the diiodoacetylene. The precipitate is filtered by suction and pressed as dry as possible by means of a sheet of rubber. The product should weigh 60–65 g. The moist diiodoacetylene is dissolved in 300 ml. of petroleum ether and treated with 35 g. of calcium chloride. After standing overnight, the solution is decanted from the calcium chloride into a tall beaker which is immersed in liquid ammonia. The diiodoacetylene which crystallizes is filtered off on a cold funnel.⁵ A yield of 30–35 g. (54–63% of the theoretical) of material melting at 78.5–78.9° is obtained. By evaporating the mother liquor and cooling, a further 3–5 g. may be obtained. The moist material may also be dried by desiccation *in vacuo* under sulfuric acid, whereby 50–54 g. (90–97%) of diiodoacetylene can be obtained. This method of drying is not to be recommended, however, as partial decomposition occurs.

Proof of Identity of Diiodoacetylene.—Since diiodoethylene might also be formed by the action of iodine on acetylene, it was felt necessary to prove that the compound obtained was actually diiodoacetylene. An analysis would be of little value as the difference between the two compounds amounts to but two hydrogen atoms in a total molecular weight of 280. The melting point could not be used to identify the compound since values for this constant of the ethylenic and acetylenic compounds have been variously reported from 73–76° and 74–82°, respectively.

To prove its structure a portion of the substance was chlorinated by the procedure of Howell and Noyes.⁶ A good yield of hexachloroethane, m. p. 185°, was obtained and no hydrogen chloride was produced. This proves the absence of hydrogen in the original compound.

To 15 g. of the compound in 100 ml. of benzene, 13.7 g. of iodine was added and the

⁴ Ammonia has been added in this manner to as much as 200 g. of iodine a number of times without the occurrence of a single explosion. Although a violent reaction takes place and a small amount of iodine vapor is lost, the procedure appears to be perfectly safe.

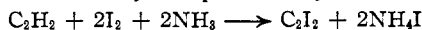
⁵ A convenient cold funnel can be made by inserting a 15-cm. funnel into a 25-cm. funnel, closing the annular opening by rubber tubing, and filling the space between the two funnels with liquid ammonia.

⁶ Howell and Noyes, *THIS JOURNAL*, **42**, 991–1010 (1920).

mixture refluxed for one hour. The solution was allowed to stand overnight and deposited a crop of lemon yellow crystals of tetraiodoethylene, m. p. 188–9°.

Diiodoacetylene was prepared by the method of Dehn⁷ and was found to melt at 78°. The melting point of a mixture of this material and that from the liquid ammonia synthesis was also 78°. The substance also gave a brown precipitate with ammoniacal cuprous chloride solution. Thus it is clearly shown that the substance obtained was actually diiodoacetylene.

To elucidate the mechanism of the reactions occurring in the iodination of acetylene, weighed samples of 0.5 to 1.0 g. of iodine were dissolved in ammonia and treated with acetylene. After completion of the reaction and evaporation of the ammonia, the amount of iodide ion produced was determined by titration with standard silver nitrate solution by the method of Fajans. It was found that exactly 50% of the iodine used was converted to iodide. Since the remaining 50% of iodine was obtained in the form of diiodoacetylene, the reaction may be represented by



Iodination of Sodium Acetylide.—An attempt was made to prepare monoiodoacetylene by treating 1 mole of sodium acetylide in liquid ammonia with 1 mole of iodine. On adding water to the reaction mixture approximately 50% of the acetylene present as acetylide was liberated and a precipitate of diiodoacetylene was obtained. This is in accord with the work of Moissan,⁸ who obtained tetraiodoethylene by the action of iodine on sodium acetylide in benzene and at variance with that of Skosarewski,⁹ who reported the formation of triiodoethylene under similar circumstances. Since the reaction between iodine and sodium acetylide in ammonia is almost instantaneous it is recommended for the rapid preparation of diiodoacetylene.

Decomposition of Diiodoacetylene.—There are several references in the literature to the decomposition of diiodoacetylene. According to Baeyer,¹⁰ on heating at 100° for some time, the compound explodes. Nef¹¹ states that violent explosions are caused by heating the substance in sealed or open tubes at 81–100° for two to twenty minutes. The products of these violent reactions are carbon and iodine. Meyer and Pemsel¹² and Schenk and Litzendorff¹³ have shown that the decomposition can be controlled in solution to give tetraiodoethylene and carbon.

Since the material was at hand, the decomposition points of samples of eighteen different preparations of diiodoacetylene were measured. The decomposition point was determined by placing a small amount of the substance in a capillary tube, attaching to a thermometer, and heating in a Thiele melting point apparatus. As the decomposition point was reached the substance exploded with a sharp report and iodine vapor filled the tube. Of the eighteen preparations (two samples of each) the average decomposition point was 125°, the lowest being 121° and the highest 128°. On one occasion, however, a few grams in a test-tube exploded at 84°. At another time, during an attempted distillation *in vacuo*, 15 g. of the substance exploded at 98° and 4 mm. of pressure with sufficient violence to wreck the apparatus.

It has also been found that the substance can be set off by friction. Small amounts were placed in a mortar and struck a sharp blow with a pestle. An explosion of considerable violence, resembling that of nitrogen iodide in nature, took place in all cases.

⁷ Dehn, *THIS JOURNAL*, **33**, 1598–1601 (1911).

⁸ Moissan, *Compt. rend.*, **127**, 914 (1898).

⁹ Skosarewski, *J. Russ. Phys.-Chem. Soc.*, 863–872 (1904).

¹⁰ Baeyer, *Ber.*, **18**, 2275 (1885).

¹¹ Nef, *Ann.*, **298**, 347 (1897).

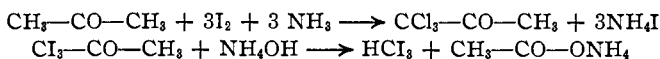
¹² Meyer and Pemsel, *Ber.*, **29**, 1411–1412 (1896).

¹³ Schenk and Litzendorff, *ibid.*, **37**, 3453–3464 (1904).

Miscellaneous Iodinations

Ketones.—When acetone was added to a solution of iodine in ammonia a slow reaction took place. After the disappearance of the color the solution was evaporated and water added, which precipitated 8 to 12% yields of iodoform, m. p. 119°. The precipitate was filtered off and the iodide content of the filtrate determined by the method of Fajans. Values of 87 to 90% of the iodine used were obtained.

Since it has been shown by Étard¹⁴ that tribromoacetone is decomposed by ammonium hydroxide to give bromoform and ammonium acetate, it seems likely that the reactions which occur are as follows



These equations, however, fail to account for the large amount of iodide ion which is found in the filtrate.

Dawson and Leslie¹⁵ have shown that in aqueous and non-aqueous solutions the rate of reaction of iodine with acetone is proportional to the hydrogen-ion concentration. In liquid ammonia the ammonium ion plays the same role as the hydrogen ion does in water. Reaction mixtures of iodine and acetone in ammonia to which ammonium nitrate had been added were found to clear up much more rapidly than similar uncatalyzed mixtures. No exact measurements of rate were made.

Methyl ethyl ketone also reacts with iodine in ammonia giving 92 to 96% of iodide and 2 to 5% of iodoform.

Amines.—Mono- and dibutylamines react slowly with iodine in ammonia. On treatment with water, heavy, red, insoluble oils were obtained which could not be crystallized and which on heating decomposed with the evolution of iodine vapor. No definite compounds were isolated.

Compounds of the Structure —CO—CH₂—CO—.—Malonic ester reacts with iodine in ammonia almost instantaneously and gives a red, viscous oil which is insoluble in water, and which decomposes on heating with the liberation of iodine vapor. Acetoacetic ester also immediately decolorizes ammonia solutions of iodine. The products of this reaction were not investigated.

No Reaction.—Benzene, ethylene, trimethylethylene, propylene, pentane and triphenylmethane did not react with iodine in ammonia at the boiling point of the solution at atmospheric pressure.

Conclusions

1. Liquid ammonia has been found to be an excellent medium in which to carry out certain iodinations.

2. Iodine in ammonia reacts with acetylene and with sodium acetylide to give diiodoacetylene in good yield. A method of preparation has been based on this reaction.

3. The decomposition point of diiodoacetylene has been determined and found to be 125 ± 4°. It has also been found that diiodoacetylene can be detonated by a sharp blow.

4. Acetone reacts with iodine in ammonia and gives 8 to 12% yields of iodoform. Methyl ethyl ketone also reacts, giving smaller yields of the same material.

¹⁴ Étard, *Compt. rend.*, **114**, 754 (1892).

¹⁵ Dawson and Leslie, *J. Chem. Soc.*, **95**, 1863 (1909).

5. Mono- and dibutylamines, malonic ester, and acetoacetic ester react with ammonia solutions of iodine. No definite compounds were isolated from the reaction products.

6. Benzene, ethylene, trimethylethylene, propylene, pentane, and triphenylmethane do not react with iodine under the conditions studied.

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EFFECT OF ULTRASONIC RADIATION ON INDICATORS

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In a study on oxidations promoted by ultrasonic radiation, Schmitt, Johnson and Olson¹ found that when a dilute aqueous solution of brom thymol blue (to which sufficient sodium hydroxide was added to produce a blue-green color) was radiated, the solution became yellow in a very short time. Since the addition of alkali caused a prompt return of the blue color they concluded that comparatively few of the dye molecules were destroyed but they were "altered by the radiation and give rise to hydrogen ions." This seems to us a very significant finding, and we have repeated and extended their experiments. Unfortunately our results do not confirm theirs.

Experimental

The oscillating current was generated by two 75-watt tubes (UX852) connected in a modified Hartley circuit. The quartz plate (about 47×50 mm.) lay between two brass electrodes, the distance between which could be adjusted. The vibrating part was placed in a dielectric liquid, xylene or benzene. The quartz plate vibrated at the rate of 1.3×10^6 times per second. On the upper electrode was placed a cooling coil of glass tubing through which cold water circulated.

Indicators used in this investigation were: thymol blue, brom phenol blue, brom cresol green, chlor phenol red, brom cresol purple, brom thymol blue, phenol red, congo red, methyl red, litmus, alizarin red and methyl violet.

About 15 cc. of dilute aqueous solution of each indicator (3 drops of 0.04% indicator solution in 15 cc.) was placed in a small, thin test-tube 15 mm. in diameter. The tube was held so that its bottom was just buried in the mount of the vibrating dielectric. After exposing for ten minutes, the tube was taken out and its color compared with that of the unexposed control. The temperature of the indicator solutions never rose above 35°.

¹ Schmitt, Johnson and Olson, *THIS JOURNAL*, **51**, 370 (1929).