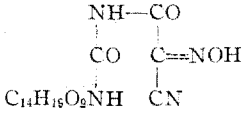
Four grams of tetraacetylglucose-urea, 1 g. of cyanoacetic acid and 2 cc. of acetic anhydride were heated at 100° for ten minutes. On adding water to the cooled solution a crystalline substance separated. After crystallizing several times from dilute alcohol it melted constant at 135°.

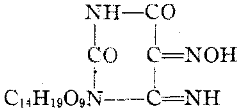
Anal. Calcd. for $C_{18}H_{23}O_{11}N_3$: C, 47.15; H, 5.27; N, 9.17. Found: C, 47.16; H, 5.24; N, 9.12.

Theoretically this substance could be either an acyclic or a cyclic compound (I or II). In order to determine its constitution molecular proportions of the compound and sodium nitrite were warmed in water for several minutes. The solution became yellow in color and on acidifying with acetic acid prismatic, plate-like crystals separated. After recrystallization from boiling water they melted at 179–180°. That we are dealing here with a nitroso derivative of the acyclic compound I as represented by formula IV is supported by the yellow color, and, furthermore, by the fact that cyanoacetic acid itself and sodium nitrite interact in a similar manner.

Anal. Calcd. for $C_{18}H_{22}O_{12}N_4$: C, 44.34; H, 4.75; N, 11.50. Found: C, 44.42; H, 4.74; N, 11.18.



IV



V

If the reaction product resulting from condensation with cyanoacetic acid is to be represented by the cyclic structure II, it should react with ammonia with removal of the acetyl groups and with formation of the stable cyclic glucoside. We found, however, that such treatment yielded smoothly glucose urea, leading to the conclusion that formula I and not II represents the correct constitution of the original condensation product.

Anal. Calcd. for glucose urea: C, 37.82; H, 6.35. For $C_{10}H_{15}O_7N_3$ (from II): C, 41.53; H, 5.22. Found: C, 37.93; H, 6.40; N, 12.36.

Under no conditions did we succeed in converting the ureide I into the pyrimidine II by the action of alkali. We also attempted to effect ring closure of the ureide I by means of catalytic hydrogenation as previously applied successfully by Rupe,[7] and later by Johnson and Bergmann[8] for the preparation of uracil and thymine, respectively. We obtained no evidence of the formation of a uracil-glucoside derivative. An attempt finally was made to condense tetraacetylglucose-urea with malonic acid to obtain a barbituric acid glucoside derivative. Twelve grams of acetic anhydride, 10 g. of acetylglucose-urea and 2.7 g. of malonic acid were heated at 100° for thirty minutes. We obtained a deep orange colored solution. Dilution with water led to the precipitation of a crystalline substance from which we succeeded in separating a product that crystallized from methyl alcohol without coloration after treatment with norite. It melted at 206–207°. The results of analysis indicated that we were not dealing with a barbituric acid derivative, but with the acyclic compound *di-(tetraacetylglucose)-ureide of malonic acid*, $C_{14}H_{19}O_9NH\text{-}CONHCOCH_2CONHCONHC_{14}H_{19}O_9$.

Anal. Calcd. for $C_{33}H_{44}O_{22}N_4$: C, 46.68; H, 5.23; N, 6.60. Found: C, 46.51; H, 5.34; N, 6.86.

When this diureide was allowed to interact with alcoholic ammonia at ordinary temperature, glucose urea was formed.

Summary

1. Methods have been described for preparing 1-arabinose-urea, *sym*-dixylose-urea and heptaacetyllactose isothiocyanate and derivatives.

2. Condensation of cyanoacetic acid with tetraacetylglucose-urea leads to the formation of the ureide $C_{14}H_{19}O_9NHCONHCOCH_2CN$. Attempts to condense this to a pyrimidine construction were unsuccessful.

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(7) Rupe, *Helv. Chim. Acta*, **8**, 850 (1925).

(8) Johnson and Bergmann, THIS JOURNAL, **55**, 1733 (1933).

NEW HAVEN, CONN. RECEIVED APRIL 4, 1938

[CONTRIBUTION FROM THE BUREAU OF CHEMISTRY AND SOILS, U. S. DEPARTMENT OF AGRICULTURE]

Fixation of Active Nitrogen by Organic Compounds

BY LOUIS B. HOWARD[1] AND GUIDO E. HILBERT

The most promising of various possible methods for directly introducing some form of elementary nitrogen into organic substances is the one utilizing active nitrogen[2] which consists essentially of atomic nitrogen. General experience has shown that molecular nitrogen is inert toward organic compounds and no catalyst has yet been discovered which will activate nitrogen to the extent that it will interact with organic materials. In this connection, it is noteworthy that practically all of many assumed reactions between nitrogen and organic molecules proceed with an increase in free energy.[3] In contrast to the ordinary form of nitrogen, atomic nitrogen, in view of its high reactivity, trivalent-like structure, (N<), and relatively long life, would be expected to interact

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(1) Now in the Bureau of Entomology and Plant Quarantine, Whittier, California.

(2) For a recent review see Sponer, "Molekülspektren und ihre anwendung auf chemische Probleme," II Text, Verlag von Julius Springer, Berlin, 1936, p. 458, and also Kneser, *Ergeb. exakt. Naturw.*, **8**, 229 (1929).

(3) We are grateful to Dr. R. Wiebe and Dr. R. T. Milner for having made many of these calculations.

with organic compounds. Practically the only work carried out in this direction has been done by Strutt, and by Willey and Rideal,[4] who examined superficially the behavior of a number of compounds toward active nitrogen produced by a condensed discharge. Relatively small amounts of materials[5] were worked with and apart from hydrogen cyanide the production of nitrogenous material of an organic nature[6] was not demonstrated.

In the investigation of the interaction of active nitrogen and organic materials, we were mainly interested in determining whether nitrogen can be fixed to yield a relatively complex product and, if so, what the nature of the product is, since this information is of value in elucidating the mechanism of the reaction. Diphenylacetylene was chosen as the organic partner in the reaction since the aromatic portion of the molecule was expected to confer properties to the nitrogenated material which would make it easy to handle, a matter of considerable importance as small quantities must of necessity be manipulated. Another apparent advantage in favor of diphenylacetylene is the vulnerability of the acetylenic linkage and this was expected *a priori* to be attacked to yield benzonitrile as follows

$$C_6H_5C{\equiv}CC_6H_5 + 2N\!\begin{smallmatrix}/\\-\\\backslash\end{smallmatrix} \text{ or } N_2^* \longrightarrow 2C_6H_5CN$$

In order to gain further information on the mechanism of the reaction the behavior of active nitrogen toward benzonitrile and toward tetrahydronaphthalene also was studied. The active nitrogen used in this investigation was produced by an uncondensed discharge except in two experiments where the nitrogen was activated by a condensed discharge.

Apparatus and Experimental Data

Apparatus.—After preliminary trials the apparatus shown in Fig. 1 was used in the final studies. It consists of three sections: (1) a purification train for removing, as far as possible, oxygen and water from the nitrogen, (2) a discharge tube for activating the nitrogen and (3) a reaction bulb with accessories for introducing the organic material and collecting the reaction products.

Purification of the nitrogen by the following method gave the best results. The nitrogen (Linde water-pumped) was conducted from the tank through tube A, 4 cm. in diameter and 50 cm. long, which was packed with pellets of potassium hydroxide, and then through B, which was heated electrically at 410°.[7] Tube B, 3 cm. in diameter and 100 cm. long, was packed with approximately 500 g. of copper wire, in pieces 0.16 mm. in diameter and 1 cm. long, which was repeatedly oxidized and reduced with air and hydrogen at about 410° to activate the surface. From this furnace the nitrogen was passed through trap C, cooled with liquid air and filled with copper turnings to turbulate the gas and increase the cold surface. The purified gas was then passed through two filed stopcocks into the activation chamber D. In a single run, nitrogen at flow rates up to 8 cc. per second and in volumes as great as 1000 liters could be handled conveniently. After completion of the experiment the copper in the tube B was readily regenerated by passing hydrogen gas through the three way stopcocks at either end.

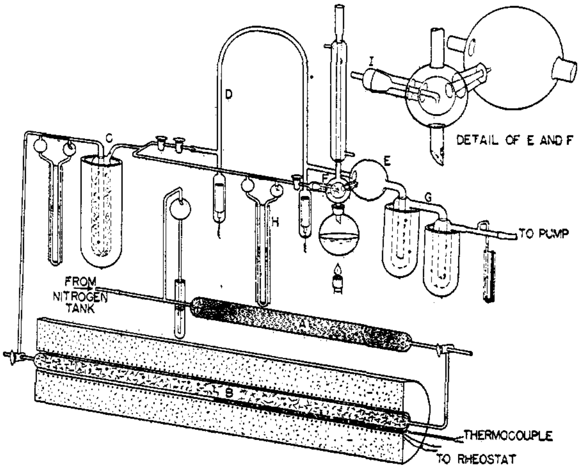

Fig. 1.—Apparatus for the fixation of active nitrogen by organic compounds.

The discharge tube D was fitted with hollow aluminum[8] electrodes, 2 cm. in diameter and 5 cm. long, mounted on tungsten leads. The path of the discharge between the electrodes was about 1 meter long and the current was produced by a General Electric sign transformer operating on 60 cycles and delivering a secondary current of 30 m. a. at 15,000 v.

From D the active nitrogen was conducted into E, where it mixed with the organic vapor which entered from the vaporizing bulb F. The two liquid air cooled traps G served to condense that portion of the reaction product which was not deposited on the walls of E. The unreacted nitrogen was eliminated from the apparatus by a Megovac pump. Bulb F (shown in detail in Fig. 1) consisted of a small jacketed chamber opening into E through a jet at right angles to the stream of excited nitrogen. The vapor

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[4] Strutt, *Proc. Roy. Soc.*, (London) **A85**, 219 (1911); **88**, 539 (1913); **91**, 303 (1915); and Willey and Rideal, *J. Chem. Soc.*, 669 (1927).

[5] Acetylene, benzene, naphthalene, pentane, heptane, methyl bromide, ethyl chloride and iodide, chloroform, bromoform, 1,1-dichloroethane and ethyl ether were investigated.

[6] In the reaction with benzene there was some indication that benzonitrile was formed. On the walls of the reaction chamber a brown-black solid was produced but no test for the presence of combined nitrogen was made.

[7] Under similar conditions, Stiehler, Chen and Clark, THIS JOURNAL, **55**, 892 (1933), obtained nitrogen containing less than 2.4 $\times 10^{-6}\%$ of oxygen.

[8] Tiede and Hey, *Ber.*, **66**, 85 (1933), tested several metals as electrode materials and found aluminum to give the highest concentration of active nitrogen.

pressure of the organic compound under study was controlled by refluxing a liquid with a suitable boiling point in the external heating system. Passage of the organic material into E was facilitated by a stream of purified nitrogen from C, the pressure of which was regulated by a filed stopcock and recorded by the flowmeter H. In order to recharge F, the glass tube between F and H was cut and the sealed in jet I removed.

Materials.—**Diphenylacetylene** (m. p. 60°) was prepared by the procedure of Schlenk and Bergmann.[9] After several recrystallizations from alcohol it was dried and stored over phosphorus pentoxide *in vacuo*. **Benzonitrile** from the Eastman Kodak Company was purified by triple extraction with dilute sodium hydroxide and dilute sulfuric acid. After drying over potassium carbonate, it was distilled and only the middle fraction collected; b. p. 191°. **Tetrahydronaphthalene** from the Eastman Kodak Company was purified by fractional distillation in which the middle of three fractions was collected; b. p. 208°.

Action of Active Nitrogen Produced by an Uncondensed Discharge on Diphenylacetylene

General Procedure for Carrying out the Reaction.—Diphenylacetylene in bulb F was heated to 100°, the discharge tube put in action, and the system adjusted with regard to pressure and flow rate of nitrogen (see Table II for the different pressures and flow rates used). When a strong lemon-yellow afterglow filled the reaction bulb E and the traps, the stopcock between H and I was opened slightly in order to facilitate the entrance of the organic material into E. Immediately thereafter a violet glow, suggestive of the cyanogen spectrum, filled the reaction bulb and the first liquid-air trap. As the amount of diphenylacetylene introduced was increased, the violet glow in the reaction bulb was quenched and only faintly visible at the point of entrance of the active nitrogen into E; an intense violet glow was, however, exhibited in the first trap. This condition remained constant even though the rate of introduction of the organic material was increased considerably. Generally the rate of flow of gas through F was so regulated that the violet glow in E was just quenched since it was desired to have an excess of diphenylacetylene in the reaction. Shortly after initiation of the experiment a yellowish-brown film was noticeable on E. Eventually E became wholly covered with a relatively thick layer of the brownish-black opaque product and considerable material was deposited in the two traps.

Isolation and Description of Reaction Products.—After all the sample had been introduced, the discharge was discontinued and the pressure brought up to atmospheric. The liquid air containers were removed from the traps and the system swept out for about four hours with purified nitrogen at a rate approximating 20 l. per hour. *Hydrogen cyanide* was collected in a solution of sodium hydroxide and determined by the Liebig method. The reaction bulb and traps were detached from the apparatus and had a distinct mixed odor of *benzonitrile, phenyl isocyanide* and hydrogen cyanide. Much of the *dark brown amorphous solid I*, which is the major product of the reaction, was removed by a combination of scraping and extraction with hexane.[10] Collection of the insoluble product on a filter was followed by thorough pulverization and repeated extraction with warm hexane to remove the last traces of the unreacted acetylene derivative. After drying *in vacuo* at 100° and weighing, it was submitted to elementary analysis. The solid material which could not conveniently be removed from E and G was dissolved in concentrated sulfuric acid and the nitrogen determined by the Kjeldahl method. An aliquot of the combined hexane extracts was likewise analyzed for nitrogen. In order to show the relative amounts of nitrogen obtaining in these fractions the representative results for experiment 3 (see Table II) are given in Table I.

TABLE I

NITROGEN DISTRIBUTION

Fraction	Nitrogen, mg.
Hydrogen cyanide	96
Recovered solid	250
Sulfuric acid solution	98
Hexane extracts	41

The sum of the amounts in the last three fractions is listed in Table II under the column "nitrogen fixed as solid." It is apparent that a relatively unimportant amount is extracted by hexane and this fraction was not further investigated.

The amount of benzonitrile formed in the reaction was so small that it could not be identified by chemical means. An alcoholic extract of some of the slightly pasty solid product formed in an experiment was distilled and the first fraction (one-third) diluted twenty-five times. The absorption bands of this solution were determined by using a quartz spectrograph and a hydrogen discharge tube as a source of light. Spectrographic results although suggestive that benzonitrile was present were not wholly satisfactory as the apparent presence of diphenylacetylene in the unknown tended to confuse the interpretation of the results.

The average of duplicate carbon, hydrogen and nitrogen analyses of (I) prepared under a variety of conditions is recorded in Table II. The percentages of nitrogen listed were determined by the Dumas method and were always from 0.2 to 1.0% higher than the values obtained by the micro Kjeldahl method in which the material was digested for twenty minutes as generally recommended. In a few cases, the percentage of oxygen present in the solid was determined by direct analysis,[11] in order to account for the fact that the sum of the carbon, hydrogen and nitrogen values did not total 100%. The value for oxygen obtained by direct analyses differed by 0.5 to 1.0% from the figure calculated by difference. We believe that the analyses for nitrogen by the Dumas method are low and responsible for this discrepancy. In this connection, it is of interest that certain high melting nitrogenous materials have been found by Milner and Sherman[12] to give low

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[9] Schlenk and Bergmann, *Ann.*, **463**, 76 (1928).

[10] Most of the diphenylacetylene did not react and is to be found in this solution.

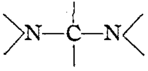
[11] Dr. R. T. Milner kindly carried out these determinations by his unpublished modification and adaptation to the semi-micro scale of the method by ter Meulen, *Rec. trav. chim.*, **43**, 899 (1924); **53**, 118 (1934).

[12] Milner and Sherman, *Ind. Eng. Chem., Anal. Ed.*, **8**, 331 (1936).

nitrogen values when determined by the Dumas method. Re-analysis of specimens prepared in experiments 1, 3 and 6 after they had stood from eighteen months to two years in stoppered containers from which no effort to exclude air was made, indicated that the products had been altered. The new results (see analyses f in Table II) were uniformly lower in carbon and nitrogen and higher in oxygen while hydrogen fluctuated but little.

When heated (I) showed a little shrinkage at 300° but remained unmelted at 320°. Upon much stronger heating it decomposed without melting to give ammonia, a small quantity of colorless oil and a considerable residue of charred material. The oil had a foul, isonitrile-like odor and appeared to be insoluble in dilute hydrochloric acid; the acid extract gave a negative color test for aniline with sodium hypochlorite.

Solubility tests showed (I) to be very slightly soluble in alcohol, ether, hexane, benzene and xylene, partially soluble in nitrobenzene and acetonitrile and readily soluble in benzonitrile, from which it was precipitated by hexane. It dissolved fairly readily in concentrated hydrochloric or glacial acetic acid from which solution it was not precipitated either by chilling or dilution with much water but only by making alkaline. The precipitated product was flocculent and continued washing resulted in an increased tendency of the solid to remain suspended, thus exhibiting a behavior quite similar to the peptization of a colloid. Its elementary analysis differed but slightly from the original; in accordance with a sodium ash of 3% the value for nitrogen was 3% less.

Some qualitative information on the mode of attachment of nitrogen in the molecule was secured by the following experiments. Emich's test[13] for the  $>N-\overset{|}{\underset{|}{C}}-N<$ grouping by fusion of (I) with calcium oxide and subsequent formation of the characteristic yellow silver salt of cyanamide was positive. That some of the nitrogen can be removed as ammonia was shown by the following experiment. Weighed samples of about 0.05 g. each were heated for different lengths of time in Kjeldahl flasks with 2 *N* sodium hydroxide and the liberated ammonia collected in standard acid. The amount of nitrogen given off as ammonia after one, three and four hours of digestion was 2.60, 3.37 and 3.83%, respectively, of the weight of the sample. An attempt to hydrolyze the solid by heating 0.2 g. with 25 cc. of concentrated hydrochloric acid in a sealed tube at 180° for three hours was unsuccessful. No ammonium chloride or other crystalline material could be isolated from the acid solution. The insoluble material apparently differed from the original only in being much less soluble in cold concentrated sulfuric acid. Treatment with hot glacial acetic acid and zinc dust affected (I) only slightly. A brown flocculent solid was recovered and melted at 215–235° (dec.). In appearance and solubility it resembled the original product.

Oxidation with nitric acid yielded crystalline material, whereas chromic oxide in acetic acid and potassium permanganate in acetone did not give tractable products. Two grams of (I) was treated with a solution of 50 cc. of concentrated nitric acid and 75 cc. of water. A reaction occurred immediately with evolution of oxides of nitrogen and after twenty minutes of refluxing the solid was largely dissolved, giving a dark orange colored solution. After heating for two hours, the reaction mixture was cooled and the liquid fraction decanted from the insoluble tarry material. The acid solution was made alkaline and then slightly acidified with hydrochloric acid. *A buff colored solid (II)* (0.32 g.) separated and was collected on a filter, washed with cold water and dried. It was practically insoluble in benzene, slightly soluble in ether and partially soluble in alcohol. Extraction with benzene in a Soxhlet apparatus for one day left a residue of 0.12 g. (*Anal.* Found: C, 58.7; H, 3.2; N, 9.7, 9.6; ash, 4.8.) Evaporation of the benzene extract left only an intractable tar. The weakly acidic filtrate from (II) was extracted repeatedly with ether, and the extracts combined, filtered and evaporated to dryness *in vacuo*. The solid residue was subjected to fractional sublimation under diminished pressure at 100°; from the sublimed material there was obtained 0.15 g. of recrystallized *benzoic acid;* m. p. 122°. Continued sublimation at 135° yielded 0.1 g. of a light yellow crystalline material; m. p. 175–185°. Crystallization from water gave a nearly colorless product; m. p. 215–220° in a closed capillary.

Anal. Calcd. for $(C_{10}H_7NO_5)_x$: C, 54.3; H, 3.2; N, 6.3; O, 36.2. Found: C, 54.8, 55.1; H, 3.4, 3.6; N, 6.5; O (by difference), 35.3, 34.8. *Neutral equivalent.* Sub., 3.27 mg.: 2.54 cc. of 0.01 *N* NaOH. Found: 129.

Increased purification of the nitrogen used in the nitrogenation affected the composition of the solid reaction product and influenced the behavior of the discharge. Nevertheless, the reaction appeared to proceed in the same manner and the properties of (I) were not changed appreciably although the percentage of oxygen was lowered markedly. As the oxygen content of the nitrogen was diminished the discharge persisted at higher pressures. For example, when tank nitrogen without purification was used a pressure greater than 10 mm. extinguished the discharge, whereas when rigorously purified nitrogen was used pressures up to 25 mm. were attainable before the discharge failed. For comparison, the data from one of the experiments (No. 1) performed by using nitrogen containing an appreciable amount of oxygen have been included in Table II. In this case the nitrogen was passed over heated copper gauze and then through a liquid air trap. In all other recorded work (Table II) nitrogen purified by the scheme outlined earlier was used.

Variation in Stray Discharge.—In order to demonstrate the unimportance of stray discharge, which unavoidably leaks from the discharge tube to the reaction bulb, a sheath of copper foil cooled by an air blast was wrapped about the tube joining D and E and grounded to a water line. Although this did not completely eliminate the stray discharge it did materially lessen the amount reaching E. This was applied in experiment 4 which otherwise differed in no way from 3. Inspection of Table II shows that the yield of fixed nitrogen did not fall off.

Action of Active Nitrogen Produced by an Uncondensed Discharge on Benzonitrile.—The general procedure was similar to that already described in the experiments on diphenylacetylene. In this case owing to its high vapor pressure at room temperature it was not necessary to heat the benzonitrile. When the stopcock at I was closed, an in-

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[13] Emich, *Monatsh.*, **10**, 321 (1889).

tense violet glow of excited cyanogen filled E. This was extinguished completely when the stopcock was opened slightly. Although some of the reaction product was deposited on the walls of E, the major portion, consisting essentially of a very dark brown solid partially dissolved in unchanged benzonitrile, collected in the traps. The hydrogen cyanide was swept out, collected and determined as in the diphenylacetylene experiments. The contents of the traps were filtered, and the solid thoroughly extracted with hexane. A current of nitrogen was continually swept over the product during these manipulations. The material was desiccated at 100° *in vacuo* for about three hours and immediately submitted to analysis (see expt. 7 in Table II). The filtrate from the solid was diluted with a large quantity of hexane and the flocculent material, which separated, reprecipitated from benzonitrile with hexane. It was dried and analyzed and appears to be identical with the first fraction. *Anal.* Found: C, 65.64; H, 3.73; N, 26.08. The hexane filtrates were combined and concentrated on the water-bath, giving an oil which by fractional distillation was found to consist almost wholly of unreacted benzonitrile; b. p. 190.5; $n^{25}\text{D}$ 1.5257.

The solid matter remaining in the traps was not taken up in concentrated sulfuric acid and determined for total nitrogen, since in this case such a value is not a measurement of the total nitrogen fixed. In one experiment, 9, the total yield of solid product was determined. The material that was easily separated was combined with the residue recovered from the acetonitrile, which was used to clean out E and G; weight 0.85 g.

Action of Active Nitrogen Produced by an Uncondensed Discharge on Tetrahydronaphthalene.—This run was carried out in exactly the same manner as that described for diphenylacetylene and in its general appearance differed only in that the cyanogen glow was much weaker and the trap contents at the end of the experiment were almost entirely liquid. After the hydrogen cyanide was swept out, the liquid in the traps was poured directly into hexane and the tar-like solid which precipitated triturated with hexane until a dark brown amorphous solid was obtained. It was collected on a filter in an atmosphere of nitrogen, dried *in vacuo* at 76° for one hour and immediately analyzed. The residues in the traps and from the hexane washings were dissolved in concentrated sulfuric acid and the nitrogen determined by the Kjeldahl method. The results are recorded in Table II.

Action of Active Nitrogen Produced by a Condensed Discharge on Diphenylacetylene.—Modification of the apparatus used in the previous experiments was effected by introducing three Leyden jars across the transformer and by connecting a spark gap in series with the discharge tube, the gap being quenched by a blast of air. Instead of being orange-yellow, the color of the discharge was more reddish-blue. Although unchanged with respect to color the after glow was markedly stronger. In Table II are tabulated results secured in two experiments, namely, 5 and 6. The formation of the solid on the walls of the reaction vessel appeared to take place more rapidly than in the corresponding experiments in which the uncondensed discharge was used. The properties and composition of the solid, however, were about the same.

Discussion

From the results shown in Table II it is concluded that active nitrogen reacts with diphenylacetylene, benzonitrile or tetrahydronaphthalene and initiates the formation of the organic nitrogenous material isolated. All other possible reactions which can account for the products seem to have been eliminated. For example, the early experiments in which the nitrogen used contained an appreciable amount of oxygen—one of these, 1, is recorded in Table II—gave products containing as much as 10% oxygen and were open to the criticism that nitrogen oxides instead of active nitrogen might have interacted with diphenylacetylene. That nitrogen oxides are not involved to any great extent in the later work is shown by experiments 2–4, where rigorously

TABLE II

EXPERIMENTAL DATA AND RESULTS

Expt.	Organic material	g.	Pressure in system, mm.	Duration of run, hours	Rate of nitrogen flow, g./hr	Total nitrogen used, g.	Nitrogen fixed as HCN, mg.	Nitrogen fixed as "solid," mg.	Analyses of solid product, % C		H		N		O Detd.	O Differ.
1	Diphenylacetylene	10	8–9	29	. . .	. . .[d]	139	255	71.2	69.8[f]	5.0	4.7	15.3	15.0		8.5
															9.3	10.5
2[a]	Diphenylacetylene	10	4	33	9	286[e]	12	57	71.9		4.5		18.1			5.5
3[a]	Diphenylacetylene	10	9	16	29	455[e]	96	389	76.9	75.2[f]	4.9	4.7	15.6	14.8		2.6
4[a,c]	Diphenylacetylene	10	9	15	29	442[e]	92	432	77.2		4.7		16.3		1.0	1.8
5[b]	Diphenylacetylene	5	9	14	29	403[e]	110	513	72.9		4.7		18.2			4.2
6[b]	Diphenylacetylene	5	9	8	29	228[e]	58	243	74.5	74.0[f]	4.3	4.6	15.4	15.0		5.8
7[a]	Benzonitrile	10	9	39	29	1109[e]	293[g]	. . .	64.7		3.9		25.5			5.9
8[a]	Benzonitrile	10	9	31	29	897[e]	292[g]	. . .	64.1		4.2		26.5			5.2
9[a]	Benzonitrile	5	9	17	29	498[e]	118[g]	238[g] (yield 0.85 g.)	64.0		4.2		28.0			3.8
10[a]	Tetralin	10	9	28	29	811[e]	175	400	74.1		6.5		16.7			2.7

[a] Uncondensed discharge. [b] Condensed discharge. [c] Stray discharge reduced considerably. [d] The nitrogen contained appreciably more oxygen than that used in the other experiments. [e] Purity of nitrogen was highest attained in this work. [f] Data obtained from reanalyses made eighteen to twenty-four months later. [g] This cannot be considered as representing only the nitrogen fixed in the reaction since the starting material contained 13.6% of nitrogen.

purified nitrogen was employed. The oxygen content of the products was lowered markedly (in 4 to 1%) without decreasing appreciably the amount of fixed nitrogen. Our experience indicates that it is a very difficult matter to prepare these nitrogenous products entirely free from oxygen, particularly for large scale experiments where the quantities of nitrogen required make impractical production of oxygen-free nitrogen from a chemical source. The contribution to the nitrogenous products by a reaction, between molecular nitrogen and the organic matter, induced by stray discharge is negligible. In no. 4 stray discharge was reduced considerably below that obtaining in no. 3 without affecting the yield of fixed nitrogen and in no. 2 the decrease in the pressure of the system diminished the yield of products, although in so far as stray discharge alone is concerned lowering the pressure in this range conduces to increased stray discharge.

Interaction of the aromatic compounds and active nitrogen yields essentially a polymerized nitrogenous solid and hydrogen cyanide. The yield of solid was greatly influenced by a change in the pressure of the system, thus increasing the pressure from 4 to 9 mm., increased the yield sevenfold. The ratio of nitrogen fixed by diphenylacetylene as hydrogen cyanide to nitrogen fixed as solid for the uncondensed discharge experiments 2–4 varies from 1:4 to 1:5. Experiments 5 and 6 in which a condensed discharge was employed also gave ratios varying from 1:4 to 1:5 and approximately the same yields of products. Averaging numerous determinations of carbon, hydrogen and nitrogen on specimens obtained under different conditions gives ratios of C:H:N that fluctuate from 4.4:3.3:1 (expt. 2) to 5.4:4.2:1 (expt. 7). Under the same conditions as obtained in the diphenylacetylene experiment, benzonitrile yields a solid similar in appearance and physical properties to the acetylene derivative but differing by containing 7% more nitrogen. In this case the yield of hydrogen cyanide is threefold greater. The action of active nitrogen on tetrahydronaphthalene was studied with the object of determining the mole ratio between the combined nitrogen and the original material in the reaction product and of determining the fate of the aliphatic hydrogen. The yield of hydrogen cyanide in this reaction is double that given by diphenylacetylene. Naphthalene is not formed and the solid product although physically similar has a much higher hydrogen content and an empirical formula close to $(C_{10}H_{10}N_2)_x$. It is to be noted that although the ratios of nitrogen to organic material in the reaction product obtained in the different experiments agree among themselves moderately well for a particular reactant, the ratio changes markedly from compound to compound. Thus, for every two molecules of the original aromatic compound,[14] the nitrogenated solid from the diphenylacetylene experiment contains about six atoms of nitrogen, that from the tetrahydronaphthalene experiment about four atoms of nitrogen and that from the benzonitrile experiment about three atoms of nitrogen. This change in the ratio is perhaps not surprising when it is considered that a decrease in this ratio was accompanied by an increase in the ratio of nitrogen fixed as hydrogen cyanide to nitrogen fixed as solid.

For comparative purposes, an exploratory experiment was performed to investigate the behavior of an aliphatic compound, isoprene, toward active nitrogen. A strikingly different result was secured. Practically no solid matter is formed and instead a nitrogenous low-boiling liquid in good yield and generating ammonia on hydrolysis is produced. In view of the apparent simplicity of this product, further studies with unsaturated aliphatic compounds, which are not being contemplated by us, would be expected to yield fruitful information.

The general mechanism of the reaction appears to involve a number of consecutive processes, (1) the interaction of atomic nitrogen and the aromatic compound to form an active intermediate, (2) stabilization of the intermediate to form the solid on the wall and (3) bombardment and further reaction of the solid with active nitrogen. In the collision between the organic molecule and active nitrogen it is not unlikely that a fragment is ejected. The structure of this fragment probably depends on the point of attack of the active nitrogen on the organic molecule and this view accounts, in part at least, for the formation of the simpler materials, hydrogen cyanide, excited cyanogen, (CN*), benzonitrile, etc. That a nitrogen-free, organic particle of relatively high molecular weight is not split off is suggested by the absence of this type of material in the products of the reaction. The most reasonable explanation

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[14] We are, of course, assuming that the empirical formula of the original organic material has not suffered any great change on reacting with active nitrogen to form the solid.

for the high nitrogen content of the solid is that a considerable quantity of nitrogen is introduced by the reaction of active nitrogen with the solid on the walls of the vessel. The similar results secured by the employment of either a condensed or uncondensed discharge for the activation of nitrogen are in accord with the present concept that active nitrogen consists principally of atomic nitrogen, which most probably is the form taking part in the above reaction.

Comparison of the results of this work with those obtained by Kroepelin and Vogel[15] in the study of the action of atomic hydrogen on oleic acid and paraffin oil reveals a striking similarity in the course of the two reactions. (1) In both cases the initial reaction involves combination with the active element and the probable simultaneous formation of free radicals. (2) The active intermediates formed are subsequently stabilized and yield, to a certain extent, brown polymerization products. (3) The introduction of oxygen into the products can be avoided only by using an atmosphere absolutely free from oxygen.

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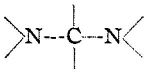
Summary

Nitrogen activated by a condensed or uncondensed discharge reacts with diphenylacetylene to form a brown nitrogenous high-melting solid, hydrogen cyanide, excited cyanogen (CN*) and probably traces of benzonitrile and an isonitrile. From its physical and chemical properties, the brown solid, which is the major product of the reaction, appears to be a complex material of high molecular weight. It contains about 16–18% nitrogen, is resistant to acid hydrolysis, liberates ammonia on alkaline hydrolysis, yields benzoic acid and an unidentified, crystalline acid possessing nitrogen on nitric acid oxidation and seems to contain  $>N-\overset{|}{\underset{|}{C}}-N<$ group. Tetrahydronaphthalene and benzonitrile also react with atomic nitrogen to form amorphous solids having physical properties similar to the product from the acetylene derivative. The ratios of fixed nitrogen to organic material in the solid products from the three compounds decrease in the order diphenylacetylene, tetrahydronaphthalene, benzonitrile. In accordance with this, the ratios of nitrogen fixed as hydrogen cyanide to nitrogen fixed as solid decrease in the reverse order. In contrast to the behavior of the aromatic compounds, isoprene with active nitrogen gives instead of a polymerized solid a low-boiling nitrogenous liquid. The results are discussed with reference to the general mechanism of the reaction.

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[15] Kroepelin and Vogel, *Ber.*, **68**, 684 (1935); see also v. Bogdandy, Polanyi and Veszi, *Z. angew. Chem.*, **46**, 15 (1933).

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Condensations by Sodium. XIV. The Phthalic Acids and Some Factors Influencing Yields of Butyl- and Dimethylmalonic Acids

BY AVERY A. MORTON AND FRANKLIN FALLWELL, JR.

This paper describes the formation of all the phthalic acids in these reactions employing sodium and shows that they arise from two distinct sources. When phenylsodium, prepared by refluxing benzene with amylsodium, is carbonated, a third to a fifth of the total acids formed is a mixture of iso- and terephthalic acids, the remainder being benzoic acid. On the other hand preparing the same reagent, phenylsodium, in the presence of sodium benzoate, refluxing and treating the product with carbon dioxide gives the ortho isomer as the sole phthalic acid present. These results demonstrate clearly that there are two types of organosodium intermediates present. According to our common conventions one would be a *m*- or *p*-phenylenedisodium compound and the other sodium *o*-sodiobenzoate. The non-identity of their carbonation products provides a sharp distinction, the lack of which made tracking to the possible sources of butylmalonic acid[1] very difficult.

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[1] Morton, Fallwell and Palmer, THIS JOURNAL, **60**, 1426 (1938).