

5. The qualitative tests and the analyses of the product show that it is chemically the same as that obtained by the older method.

6. The source of the amino-hydroxyphenyl-arsonic acid does not affect the toxicity of the arshenamine obtained from it.

The writer wishes to express his thanks to Dr. Reid Hunt for his interest in the work, his helpful suggestions and his kindness in determining the toxicity of the preparations.

BOSTON, MASS.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF CALIFORNIA.]

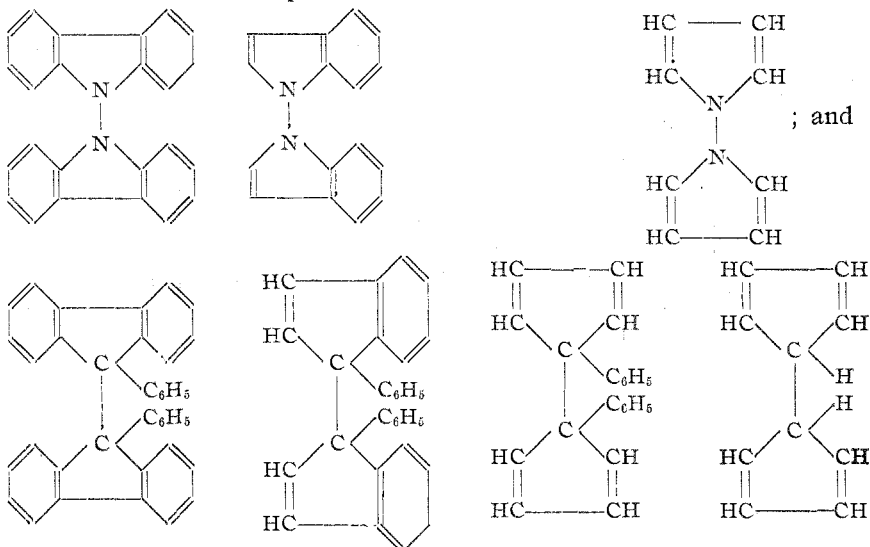
A BIVALENT NITROGEN DERIVATIVE OF CARBAZOLE.

BY GERALD E. K. BRANCH AND JULIAN F. SMITH.

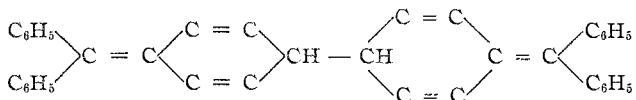
Received September 13, 1920.

Introduction.

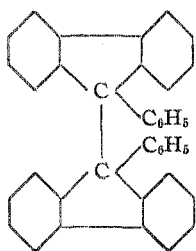
The two series of compounds



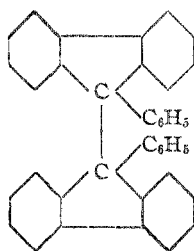
are of interest since they vary by graduated steps from compounds closely allied to the tetra-aryl hydrazines and hexa-arylethanes to purely aliphatic types which are similar in form to the quinoid modifications such as



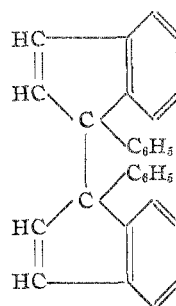
Substances of Type I p. 2406 have been prepared and appear to show some evidence of dissociation, but to a less extent than the corresponding hexa-arylethanes. They do not give colored solutions and no dissociation has been shown by molecular weight determinations, but, on the other hand,



(I).



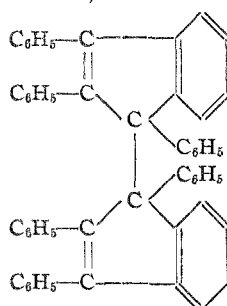
(II).



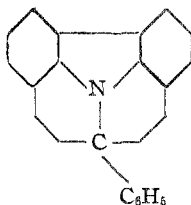
(III).

the γ absorb oxygen to form peroxides.¹ Thus it would appear from the evidence at present in our possession that the change from a compound of the type of hexaphenyl ethane to one of Type II is associated with a decrease in dissociation.

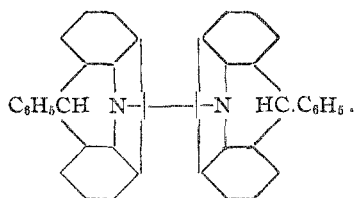
Only one compound of Type III is known, namely IV. This is a colored substance which readily absorbs oxygen, the description of which is very similar to that of hexaphenyl ethane. The molecular weight, however, was not determined.²



(IV).



(V).



(VI).

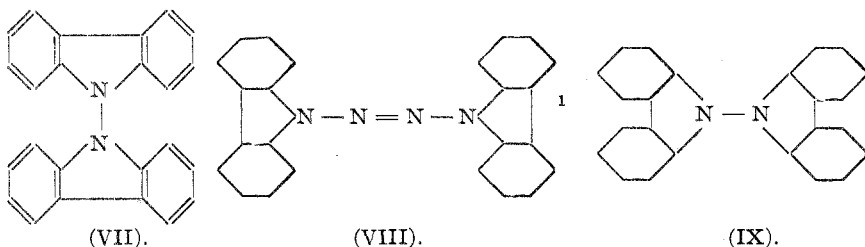
None of the corresponding nitrogen compounds is known, with the possible exception of a substance obtained by Bizzari by the reduction of the compound V which he believed to be the compound VI. He gives little evidence in favor of this view, neither a combustion nor a molecular-weight determination. He based his belief chiefly on the amount of silver solution which it could reduce, assuming that this would give the amount of reduction which the mother substance had undergone. But his figures show too large a variation to be very convincing. Thus he obtained in 2 experiments 2.45 and 1.72 equivalents of silver for a calculated value of 2. He describes the substance as giving a yellow solution and being unstable to the action of mineral acids.³

¹ Gomberg and Cone, *Ber.*, **37**, 3546 (1904); Schmidlin and Garcia-Benus, *ibid.*, **45**, 1344 (1912); Herzenstein, *Dissertation* Zurich 1911.

² Kohler, *Am. Chem. J.*, **40**, 317-333 (1908).

³ Bizzari, *Gazz. chim. ital.*, **20**, 407-17 (1890).

Wieland and his co-workers describe 3 unsuccessful attempts to prepare a compound of the structure VII. First by the oxidation of carbazole



with lead dioxide,² second by the expulsion of nitrogen from a substance corresponding to VIII and third by boiling *N*-nitroso-carbazole in xylene which gave a mixture of carbazole and 3-nitro-carbazole.³

A Di-bi-phenylene Hydrazine.

By oxidizing carbazole with silver oxide we obtained 2 substances, one soluble, the other insoluble in ether. The former we have not as yet investigated any further, but the latter appears to be a poly-carbazyl derivative of the substance IX which dissociated to a great extent in solution.

This substance is an almost white powder, but gives red-brown solutions with blue fluorescence. It melts at 283–287°, with decomposition; stem corrected 292–296. It is very soluble in benzene or any benzene derivative, in chloroform, bromoform, ethylene bromide, carbon disulfide, thiophene and pyridine; slightly soluble in carbon tetrachloride and ethyl acetate, and insoluble in ligroin, ether, alcohol, acetic acid and water. On evaporation of a solution it leaves a brown vitreous mass from which the unchanged substance may be obtained as a white powder on treatment with alcohol. The vitreous mass above described retains the solvent, for if chloroform be used it gives a strong test for halogen even after standing in the air for 2 weeks. This strong affinity for the solvent is also indicated by its high solubility (more than 50 g. in 100 g. of benzene) in spite of its high melting point.⁴ The color is approximately the same in all solvents, but the fluorescence varies considerably. Thus in carbon tetrachloride a saturated solution, though markedly colored, shows no fluorescence, although as judged by color it is noticeable in even more dilute solutions in benzene or ethyl acetate. The fluorescence of a nitrobenzene solution is green instead of blue.

Found: C, 86.0; H, 4.44; N, 8.22; Ag, 1.4.

Found (corrected for Ag as impurity): C, 87.2; H, 4.50; N, 8.33.

¹ Fussel, *Dissertation*, Univ. Muenchen, 1912.

² Wieland and Gambarjan, *Ber.*, **39**, 1506 (1906).

³ Lecher, *Dissertation*, Univ. Muenchen, 1913.

⁴ Hildebrand, *THIS JOURNAL*, **38**, 1452–73 (1916).

The molecular weight in benzene varies directly with the concentration as shown in Table I.

TABLE I.

Wt. C ₆ H ₆ . G.	Sample. G.	F. p. lowering. ° C.	Apparent mol. wt.	Dissociation. %.	K in mols./1000 g. of solvent.
26.31	0.1192	0.048	472	40	7.5×10^{-3}
26.31	0.4748	0.180	501	31.8	12.9×10^{-3}
26.31	0.9828	0.351	544.5	21.4	13.4×10^{-3}
				Mean	11.3×10^{-3}

The substance adds nitric oxide to give a yellow crystalline substance melting above 270°. It does not give a precipitate with oxygen in a benzene solution, nor does it decolorize iodine. In benzene solution it reacts violently with bromine giving off some hydrogen bromide; and forms a slight precipitate, but the major portion goes to a benzene soluble bromine compound with a very high melting point. In benzene solution with hydrochloric acid it gives a slightly yellow precipitate, soluble in pyridine, which contains no chlorine. In conc. sulfuric acid it dissolves with a brilliant green color, and a green sulfate is obtained on dilution. The base from this sulfate is not, however, the original substance, but is similar to the substance obtained by treating it with hydrochloric acid, being of a high melting point, insoluble in benzene, and soluble in pyridine. Carbazole forms similar sulfates when oxidized in sulfuric acid solution which give bases which are insoluble in benzene, but soluble or insoluble in pyridine according to the methods of oxidation.

Discussion of the Constitution.

The method of preparation and the analysis show that the substance is made up of carbazole nuclei linked together by the removal of hydrogens.

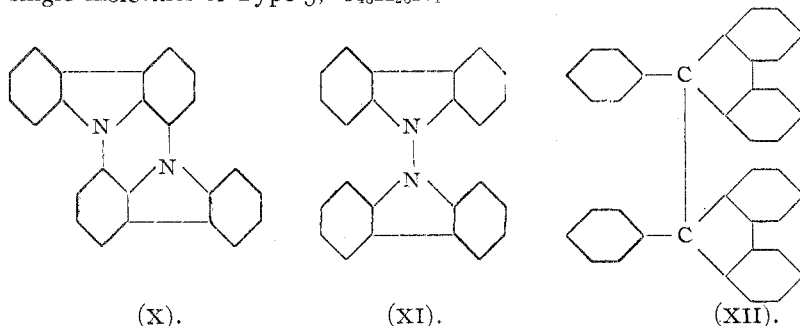
The way the molecular weight varies with dilution shows that the substance dissociates in solution, for, as has been mentioned already, the substance has a strong affinity for the solvent. This would necessitate that variations from the law of dilute solutions would be in the sense of producing a greater lowering of fugacity of the benzene than would be expected from Raoult's law. This would mean that the molecular weight would appear too low. But such an effect must be more marked in the concentrated than in the dilute solutions and would, therefore, produce a lower molecular weight in the former than in the latter, which is just the opposite from what was observed. Error would also be introduced into the molecular weight determination if both solvent and solute crystallized out as a solid solution. This point was tested by freezing out some of the benzene from the solution, filtering it off, and washing rapidly with a little cold benzene and then re-melting. By comparing the color of this solution with the mother liquor it was apparent that the former must be less than one hundredth as concentrated as the latter.¹ We thus see

¹ The solution obtained by melting the crystallized benzene was colorless but had

that the molecular weight determinations are not appreciably in error from the formation of a solid solution.

The error introduced into the molecular weight determinations by the presence of the silver depends upon the form in which it appears. The most probable assumption is that it is present as colloidal silver, in which case a deduction of 1.4% from the observed will give the corrected values. In this case the substance can contain only 4 or 5 carbazole nuclei.¹

If the substance contains 4 carbazole nuclei, the possibilities which we have to consider fall into the following 6 types: (1), a double molecule of the simple hydrazine, $C_{12}H_8NNC_{12}H_8$; (2), a double molecule of the corresponding benzidine or semidine, $HNC_{12}H_7.C_{12}H_8NH$; (3) a double molecule in which 2 carbazole nuclei are linked in 2 places such as the substance X; (4) a dicarbazyl hydrazine $C_{12}H_8NC_{12}H_7N.NC_{12}H_7NC_{12}H_8$; (5) the corresponding benzidine or semidine; (6) the dicarbazyl derivative of single molecules of Type 3, $C_{48}H_{28}N_4$.



Types 1 and 2 should give hydrogen = 4.82%. Types 3 and 6 hydrogen = 4.28%; and 4 and 5, hydrogen = 4.56%. The value found was 4.5%. This alone is almost sufficient to show that the substance does not belong to Types 1, 2, 3 or 6.

The addition of nitric oxide is characteristic of dissociating hydrazines, and likewise the instability to acids is a property common to all hydrazines, whereas they are not the reactions we should expect from Types 2, 3, 5 and 6.

If the substance is the hydrazine $C_{12}H_8N.NC_{12}H_8$, and reacted with nitric oxide it would give *N*-nitroso-carbazole, 3-nitroso-carbazole, or 3-nitro-carbazole.² The substance actually formed melted too high to be any of these.

a slight fluorescence. The mother liquor on diluting 120 times was still perceptibly colored and more markedly fluorescent. The trace of solute in the benzene crystals is due more probably to incomplete washing than to the formation of a solid solution.

¹ The assumption made here is that the dissociation is only into 2 molecules.

² As has been mentioned above, *N*-nitroso-carbazole when boiled in xylene will give 3-nitro-carbazole.

There is no reason to believe that compounds of Types 5 or 6 would dissociate, nor that those of Types 1, 2 or 3 would associate in dilute solution.¹

Similarly, if the compound contains 5 carbazole nuclei only a hydrazine formula could explain the properties. The analysis agrees just as well with a tricarbazyl dibiphenylene hydrazine as with the dicarbazyl derivative, although the equilibrium constant of dissociation varies less if calculated on the assumption that it is the latter. However, the experimental error is too great to allow us to reject the possibility of the former, as it is obvious that the error made in the determination of the molecular weight will be greatly exaggerated when the results are calculated as equilibrium constants.

If the silver is present as a benzene soluble salt the effect on the molecular weight determination is greater the smaller the equivalent weight of the acid radical, and assuming this equivalent weight to be zero it can only give a range to the molecular weights from 490 to 575, and although this brings a compound of 6 carbazole nuclei within the range of the molecular weight, the substance cannot be completely dissociated at the lowest concentration and at the same time exist to so appreciable an extent at the higher concentrations. If, on the other hand, we assume that the silver exists as a colloidal salt of silver, the error introduced into the molecular weight determinations is greater the higher the equivalent weight of the acid, but unless we make preposterous assumptions concerning the molecular weight of this imaginary acid we cannot do more than bring a substance containing 3 carbazole nuclei within the range of determined molecular weights, and we should have to assume that the substance is practically undissociated at the highest concentrations but very markedly at the lower. It would thus appear that the substance is almost certainly a dicarbazyl or a tricarbazyl derivative of the substance XI.

Observations.

There are 2 points of interest in this work, the anomalous reaction which has taken place and the high dissociation of the compound obtained. The reaction consists of an alternate oxidation and an isomerization similar to that of the benzidine conversion, but at present we have no evidence as to whether it is a benzidine or semidine shift nor whether it is *ortho* or *para*, though presumably the latter. Such a process might be repeated almost indefinitely and give a class of compounds almost as complicated as the proteins. It is probable that oxidation of carbazole in acid solution would give a similar set of reactions, only in that case isomerization would take place much more readily, and the products obtained would be expected to be benzidines rather than hydrazines. This corresponds

¹ A possible exception to this may be the high molecular weights obtained for $(C_6H_5)_2As.As(C_6H_5)_2$ by Porter and Borgstrom, *THIS JOURNAL*, 41, 2048-51 (1919).

with the work on the oxidation of ditolylamine in conc. sulfuric acid by Kehrman and Micewicz.¹

The fact that this compound is one of the most highly associated hydrazines known² is of exceptional interest because by analogy with the *ortho* linked hexaphenyl ethane, such as the compound XII, we should have expected very little dissociation.

We have no explanation to offer, but we do not think that the high dissociation of the compound can be explained entirely by the complicated nature of the compound, but believe that it indicates a real difference in the play of forces within the pyrrol nucleus from those within the nucleus of cyclo-pentadiene.

Experimental.

A mixture of 36.3 g. of silver oxide and 26.4 g. of carbazole was shaken up with 600 cc. of dry benzene, a little pyridine was added, and the mixture was boiled for 2 days under a reflux condenser protected from the air. The product was nearly a quantitative yield of the 2 substances described in the preceding pages. The purification was effected by filtering off the silver and silver oxide, evaporating the benzene off *in vacuo*, triturating the gummy residue with alcohol till it became granular, filtering and washing with alcohol, and drying. The 2 compounds were then separated by extracting with ether for several hours in a Soxhlet extractor.

An oxidation with ether as solvent was carried out under similar conditions, using 3.97 g. of silver oxide and 2.88 g. of carbazole in 100 cc. of dry ether. A few drops of pyridine were added as a catalyst. In the product the ether-soluble compound predominated.

Analysis.—The compound was analyzed by the combustion methods for carbon, hydrogen and nitrogen. The substance was mixed with finely powdered cupric oxide.

Subs., (I) 0.2673, (II) 0.2644, (III) 0.5634: CO₂ (I) 0.8442, (II) 0.8325; H₂O (I) 0.1045, (II) 0.1063, (III) 0.2243.

Subs., 0.3482, 0.3596: dry N, 24.1 cc. (10° and 749.3 mm.), 25.7 cc. (19° and 747 mm.).

Subs., 0.34: AgCl, 0.0063.

Calc. for C₄₈H₃₀N₄ with 1.4% of silver: C, 85.75; H, 4.50; N, 8.34; Ag, 1.40. Found: C, 86.15, 85.89; H, 4.37, 4.49, 4.45; N, 8.23, 8.21; Ag, 1.4.

Molecular Weight Determination.—Barrett's pure benzene, further purified by recrystallization, was used as a solvent. The amount was 26.31

¹ Kehrman and Micewicz, *Ber.*, **45**, 2641-53 (1912).

² The most highly dissociated hydrazine which the authors found described in the literature is $\left\{ (\text{CH}_3)_2\text{N} \langle \text{C}_6\text{H}_4 \rangle \right\}_2 \text{N}-\text{N} \left\{ \langle \text{C}_6\text{H}_4 \rangle \text{N}(\text{CH}_3)_2 \right\}_2$, which is 21% dissociated in nitrobenzene solution at concentrations between 1×10^{-2} and 1.5×10^{-2} total mols per 1000 g. of solvent. Wieland, *ibid.*, **48**, 1078-95 (1915).

g. The weights of samples added were: I, 0.1192 g.; II, 0.4748 g.; III, 0.9828. The readings were:

Pure benzene.....	5.260	5.260	5.258	5.254	5.257	mean 5.258
Sample I.....	5.213	5.205	5.210	5.215	5.210	mean 5.210
Sample II.....	5.075	5.078	5.079	5.078	...	mean 5.078
Sample III.....	4.909	4.905	4.907	mean 4.907

Molecular weight calculated from I = 472, from II = 501, from III = 544.5. The constant for benzene has been taken as 50° per mol of solute per 100 g. of solvent.

Chemical Reactions.

Nitric Oxide.—A mixture of pure dry nitric oxide and carbon dioxide was passed through a solution of 0.8 g. of the substance in 10 cc. of boiling benzene for one hour. A yellow crystalline precipitate was formed, soluble in pyridine, and melting above 270°.

Hydrogen Chloride.—A current of dry hydrogen chloride was passed through a dilute solution of the substance in benzene for 2 hours at room temperature. A yellowish precipitate was formed which was soluble in pyridine, and which had a high melting point. It contained no chlorine. The filtrate yielded more of the precipitate on standing.

Sulfuric Acid.—Treated with cold conc. sulfuric acid, the substance gives a deep green solution, and on dilution with water a green precipitate which, when shaken with alkali, gives a discolored powder, insoluble in benzene but soluble in pyridine.

Oxygen.—A current of pure dry oxygen was passed through a solution of 0.3 g. of substance in 10 cc. of xylene at room temperature for 7 hours. Traces of a precipitate formed within the first hour, which apparently did not increase after that time.

Iodine.—A solution of the substance in benzene was mixed with a solution of iodine in benzene. The solutions were not decolorized, and only a slight trace of precipitate was formed.

Bromine.—On treatment of a benzene solution of the substance with bromine a vigorous reaction takes place, and some hydrogen bromide was liberated. There was some precipitation, similar to that obtained with hydrogen chloride, but the major portion forms a brown solution, and on evaporating off the benzene a brown residue is left, which, on heating, gives a white powder, giving a strong flame test for halogens. It chars before melting, and dissolves in benzene with a yellow-brown color somewhat less intense than the original substance, and gives no fluorescence.

Colorimetric Measurements.

The colors of many free radicals of the trivalent carbon series have been found to deviate from Beer's law, owing to the dimolecular species being colorless. This proof of dissociation has not so far been demonstrated in

the case of the divalent nitrogen compounds. In this case it was found impossible to match, both for hue and depth, the color of the solutions of different concentrations. However, by three observers taking several readings and averaging all the results, it was found that the color was approximately proportional to the concentration. If this is not due to experimental error, it indicates either that both the dissociated and the undissociated forms are colored, or that the color is largely due to impurity.

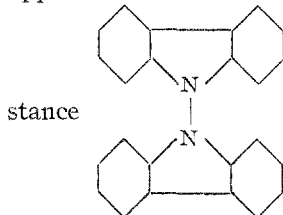
The results are given in Table II, in which the sixth column gives the relative values calculated from the assumption that only the dissociated form is colored, and the dissociation constant is 1.1×10^{-3} mols/1000 g. of solvent, as given by the cryoscopic method.

TABLE II.

Conc. in mols. of $C_{18}H_{10}N_4$ per 1000 g.	No. of readings.	Range of readings.	Average.	Calc. by Beer's law.	Calc. assuming only dissociated molecules colored.
3.62×10^{-2}	35	37-41	39.1	40.2	61.5
2.17×10^{-2}	21	62-70	66.8	67.2	82.6
1.30×10^{-2}	33	107-116	112.0	112.0	112
7.82×10^{-3}	9	170-181	176.8	187.0	155

Summary.

A substance was obtained by oxidizing carbazole with silver oxide which from analysis, molecular weight determinations, and chemical reactions appeared to be either a dicarbazyl or tricarbazyl derivative of the sub-



By the cryoscopic method it was shown that the substance is very highly dissociated into odd molecules, in which the nitrogen is probably divalent.

No verification of this was obtained by the colorimetric method.

It is a pleasant duty to make grateful acknowledgment to H. E. Hudson Branch for assistance in the study of the compound described in these pages. Much of the application of physical methods was carried out with her help.

Thanks are also due to Dr. C. G. Derick and Dr. R. W. Hess of the Research Laboratory of the National Aniline and Chemical Company in Buffalo, New York, for helpful suggestions and material aid in the prosecution of the work. Through their courtesy, a liberal supply of pure carbazole was obtained from the Research Laboratory of the Company.