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

OXIDATION OF CARBAZOLE BY SILVER OXIDE

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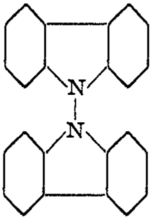
Introduction

By the oxidation of carbazole with silver oxide, Branch and Smith[1] obtained two compounds, one soluble, the other insoluble in ether. Their investigation of the latter shows that it is probably a dicarbazyl derivative of the dibiphenylene hydrazine represented by Formula I, and that it is highly dissociated in dil. benzene solution. The properties, constitution and the mechanism of the formation of the other substance will be discussed in this paper. A third compound of this oxidation of carbazole, whose existence was suspected by Smith at the time of the previous investigation, was also isolated, but was not further studied.



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These three substances are differentiated and separated by their solubilities, the first being soluble in benzene but not in ether nor alcohol; the second is soluble in benzene and ether but not in alcohol; the third is soluble in benzene, ether and alcohol. For the sake of brevity these compounds will be referred to as the B, E and A products, respectively.

Formation

When carbazole, dissolved in benzene or ether, is boiled with silver oxide all three of these substances are formed. Pyridine was also added in the earlier experiments, but it was subsequently found that it had no effect on the course of the reaction. A rough separation can be readily made after distilling the solvent by extracting the residue in turn with alcohol, ether and benzene. The alcoholic extract contains the product A and unchanged carbazole which can be removed by fractional crystallization from toluene, A remaining in the mother liquor. From the ether extract E is obtained, and B from the benzene extract. This gives a rough estimate of the amounts of B, E and A produced. However, E obtained in this way is far from pure, because although B is practically insoluble in ether, it is more soluble in an ethereal solution of E. A more complete

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[1] Branch and Smith, THIS JOURNAL, 42, 2405 (1920).

separation is obtained by making a dilute solution of E in ether and adding petroleum ether as long as B precipitates. The only criterion of the completeness of this purification of E is that it shall remain unchanged by precipitation from ether with petroleum ether no matter how dilute the initial solution. It may be noted here that the process of purifying E from B lowers the melting point. This is due to the formation of solid solutions,[2] as it was found that mixtures of B and E do not give a eutectic but a continuous series of melting points.

Properties

The properties of B have already been described.[1] A is a yellow powder which has not been obtained in sufficient purity to give any definite melting point. It dissolves in alcohol, ether or benzene, and reacts immediately with a solution of bromine in benzene to give an impure-looking substance which in the crude state melts between 85° and 100°.

E is a white powder, very soluble in benzene and ether giving orange-colored solutions with a strong blue fluorescence. It is insoluble in alcohol or petroleum ether. It melts with charring at 189–197° (corr.). Its chemical properties are qualitatively the same as those of B, and may be summed up as follows: it immediately decolorizes bromine in benzene, is isomerized by acids, forms a green sulfate of the isomer, and combines with nitric oxide. However, it reacts in the ratio of one mol. to three mols. of bromine, while B reacts in the ratio of one to one.[3] The melting point of the crude product is 117–125° in the case of E and 225–240° in that of B. In general the derivatives of E melt lower than the corresponding ones of B. The green salt formed by the action of sulfuric acid on E, when treated with sodium hydroxide, gives an isomer, which is soluble in benzene and melts at 250°. The corresponding product from B is insoluble in benzene and melts above 270°. The compounds obtained by the action of nitric oxide are likewise lower-melting and more soluble in the case of E than in that of B. But a still more striking difference is that E gives two nitroso derivatives while B gives only one. These substances are bright yellow solids which decompose at 216–228° and 240–260°: they dissolve in benzene giving yellow solutions, but no fluorescence. They differ from each other in their solubilities in ether.

The Empirical and Structural Formulas

An analysis of E gives for carbon 83.7%, for hydrogen 5.5%, for nitrogen 8.4%, for oxygen 2.39% and no ash. It thus differs from B in

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[2] These are probably glasses rather than mixed crystals, as both substances are amorphous powders.

[3] These ratios represent the properties of bromine which immediately reacts with these substances. More of this reagent will combine if either B or E is allowed to stand in contact with excess bromine.

having a little oxygen and being richer in hydrogen. The ratio of carbon to nitrogen is the same as in carbazole, but the percentage of oxygen shows that at least three carbazole nuclei are linked. The combination of three or four molecules of carbazole by an oxidation and the introduction of an atom of oxygen would give $C_{36}H_{23}N_3O$ or $C_{48}H_{30}N_4O$ or compounds with even less hydrogen. These substances would contain 4.5 and 4.4% of hydrogen, which is much lower than the actual value, indicating that the linking up is accompanied by a reduction of the carbazole nuclei. The molecular weight of E in benzene solution measured by the cryoscopic method varies with the concentration, being less in the more dilute solutions. The data are given in Table I and represented graphically in Fig. 1, in which the molecular weight is plotted against the concentration.

TABLE I

CHANGE OF MOLECULAR WEIGHT WITH CONCENTRATION

Concn. G./1000 g. of solv.	F.-p. lowering °C.	Apparent mol. wt.	Dissociation calc. for $C_{36}H_{27}ON_3$ %	$K \times 10^2$ calc. for $C_{36}H_{27}ON_3$ moles/1000 g. of solv.
3.24	0.050	324	59.6	2.20
3.45	.054	320	61.6	2.64
9.71	.132	368	40.5	2.07
14.9	.195	381	35.7	2.28
20.4	.264	386	34.0	2.76
24.0	.309	388	33.2	3.07
31.3	.392	399	29.6	3.02
				Mean 2.58

The type of curve obtained is similar to that for B, and as was shown in the paper on the latter substances proves dissociation.[4] Extrapolation of the curves gives a value of 250–280 for the molecular weight at zero concentration. This corresponds to an average of 1.5 carbazole nuclei per molecule in the products of dissociation. The molecular weight of 1.5 nuclei of carbazole when corrected for the amount of oxygen and hydrogen shown by the analysis is about 260. Therefore, if the dissociation is of the simplest type, that of one molecule into two, then the entire molecule has three carbazole nuclei. As a matter of fact this is the only possibility if the laws of dilute solutions and mass action hold.[5] For if the dissociation constants are calculated from the freezing-point data, assuming various types of reaction and molecular weights, only with the above-

[4] Such physical chemical measurements give us no information as to the nature of the products, which can only be elucidated by the less reliable chemical evidence.

[5] These laws cannot be expected to hold very rigorously. As in the case of B, the dissociation constant appears to increase with the concentration, although this is somewhat hidden owing to the exaggeration of the experimental errors when the data are calculated as equilibrium constants. This is probably not a real increase in the dissociation, but due to variation of the solvent from Raoult's law, as it is in the direction in which such deviation might be expected, as was pointed out in the article on B.

mentioned simple type of dissociation will the values even roughly approximate constancy at assumed molecular weights which are close to integral multiples of 100/92 × 158; but this latter condition is necessary, since the analysis shows that the ratio of carbon to nitrogen is twelve atoms to one and that these elements together represent about 92% of the weight of the molecule; and further with the assumption that one molecule dissociates into two, three is the only such integral multiplier that can be used. We can therefore state with a fair degree of certainty that there are 36 carbon and 3 nitrogen atoms in the molecule. The analysis also shows that the molecule contains one oxygen and 27 to 29 hydrogen atoms. A graphical way of applying the above method is indicated in Fig. 2, in which the common logarithms of the calculated equilibrium constants are plotted against assumed molecular weights expressed in units of 100/92 × 158. For the sake of clarity only a few curves are given, those for three freezing-point determinations being calculated for two types of dissociation. The full line represents the dissociation of one molecule into two, the dotted line a reaction in which one molecule is in equilibrium with three. This case is especially interesting as it gives a good dissociation constant but at an impossible molecular weight.

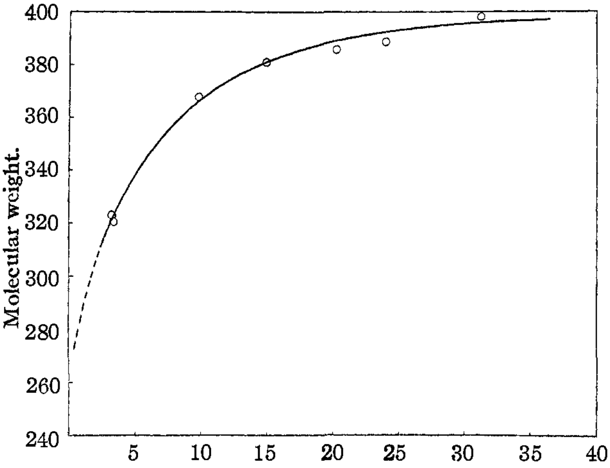

Fig. 1.

The analyses and molecular-weight determinations show that the formula[6] of E is $C_{36}H_{27}ON_3$ or $C_{36}H_{29}ON_3$. The behavior of the substance indicates a very close relationship to B, which is probably a dicarbazyl dibiphenylene hydrazine, and agrees with that of the tetra-aryl hydrazines in general. Therefore E may be considered to be an hydroxy-

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[6] The analysis actually agrees most closely with $C_{36}H_{28}ON_3$, but it seems improbable that this is an odd molecule which dissociates reversibly.

monocarbazyl dibiphenylene hydrazine in which two or three of the carbazole rings have been reduced to diphenylamine nuclei, and which probably dissociates into two dissimilar free radicals. The formation of two derivatives by the action of nitric oxide can be explained by the asymmetry of its dissociation, and the relatively larger amount of bromine rapidly taken up by E than by B, by the presence of the hydroxy group in the former substance. These two observations are of course mere indications of the correctness of the type of structure suggested.

A phenomenon observed during experiments devised to obtain the best conditions for the preparation of E, sheds considerable light on the course of the reaction, and confirms this view of the structure. When carbazole and silver oxide are heated in the presence of ether, the rate of formation of E is at first slow while that of B is rapid, but as the reaction proceeds E is formed more rapidly, while the amount of B approaches a constant value.[7] This shows that B is an intermediate in the preparation of E. However, when B is heated with silver oxide and ether very little E can be isolated, but when B and carbazole and silver oxide and ether are heated together, E is rapidly formed from the start. It would thus appear that E comes from an interaction between B and carbazole in which presumably the former is reduced by the latter. This accounts for the change of the carbazyl into the diphenylamine nuclei in the presence of silver oxide,

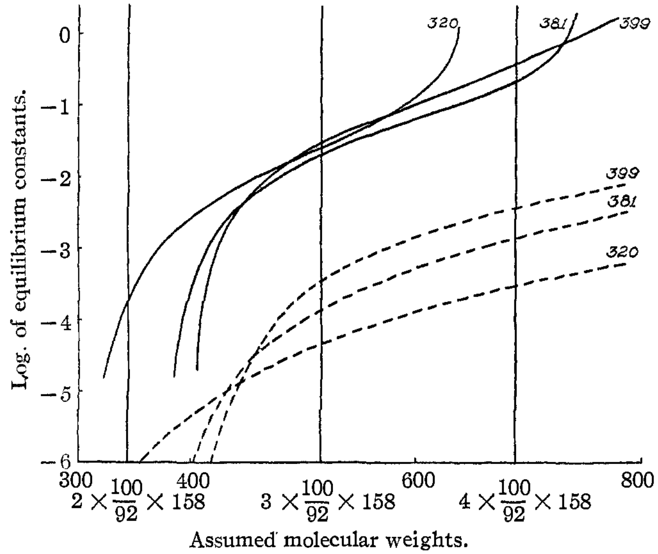

Fig. 2.—Numbers marking curves give experimental values of molecular weight.

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[7] A similar observation was made with respect to the relationship of E and A, that is, the rate of formation of A increases with the quantity of E, and the quantity of E approaches a constant value.

a phenomenon which is demonstrated by the high percentage of hydrogen unaccompanied by any change in the carbon to nitrogen ratio. It is assumed here that the benzene rings are not reduced. The reduced B radicals and the carbazyl radicals combine, accounting for the presence of the three nitrogen atoms shown by the molecular-weight data. The excess of carbazyl nuclei eventually goes to B, in whose formation they are no doubt intermediate. The hydroxy group may be introduced by oxidation with silver oxide or hydrolysis. As the former is more likely, we favor the formula $C_{36}H_{27}ON_3$ rather than $C_{36}H_{29}ON_3$. This easy reduction of the carbazole ring in B is very peculiar, and probably points to the profound change in the bonds of a molecule possessing an odd number of electrons, as the reverse of this reaction, the change of a diphenyl to a biphenylene derivative, is a well-known phenomenon among free radicals. However, it may also mean that the dissociation of B, and by analogy also that of E, is into a less and a more hydrogenated molecule, just as quinhydrone gives on solution an equilibrium with hydroquinone and quinone. It is even possible that the failure of Gomberg and Sullivan[8] to obtain a check between the measure of dissociation by cryoscopic methods, and the amount of free radical present by absorption of oxygen was due to the existence of both types of dissociation.

Experimental Part

Preparation and Purification.—A mixture of 38 g. of silver oxide, 27.9 g. of carbazole and 1000 cc. of ether was boiled for nine days. The ether was then evaporated, and the residue extracted with alcohol, ether and benzene. On evaporation, these extracts gave 13.5 g., 5.5 g. and 9 g. of solid products, respectively. The residue from the alcoholic extract was recrystallized from the minimum quantity of toluene; the crystals were carbazole, which after another crystallization melted at 225°, and mixed with a known sample of carbazole, melted at 230°. The toluene mother liquor gave on evaporation a sticky mass which, on trituration with water, hardened to about 2 g. of yellow powder described as A in this paper. The residue from the benzene treated with alcohol gave a slightly discolored powder, which after extraction with ether in a Soxhlet apparatus melted at 284–290° (corr.) and was identical with the substance described by Branch and Smith. The residue from the ethereal extract of the reaction mixture was a thick mass, which hardened to a powder on trituration with alcohol. It was then extracted with alcohol in a Soxhlet apparatus. The melting point was raised thus to about 220°. It was dissolved in excess of ether, and successive portions of petroleum ether were added. At first the precipitates formed melted at about 280°, but later additions of petroleum ether gave precipitates melting at about 200°. At this stage the mother liquor was evaporated, and the residue on standing under alcohol gave a white amorphous powder. Repetition of this process caused no further change in the properties. It melts with decomposition at 189–197° (corr.). In later preparations the crude product was mixed with B before extraction with hot alcohol, as in this way the difficulty due to its agglutinating during the treatment was avoided.

Mechanism of the Reaction.—Carbazole, silver oxide and ether were heated to boiling in the proportions 27.9 g. to 38 g. to 1000 cc. for various

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[8] Gomberg and Sullivan, THIS JOURNAL, **44**, 1810 (1922).

lengths of time, and products were separated, after evaporation of the ether, by successive extractions with alcohol, ether and benzene. The results of several experiments are given in Table II expressed as percentages of the weight of carbazole used.

Table II

Rate of Formation of E and B

Time in days	3	6	9	12
% insol. in alc. but sol. in ether	1–2	7–20	20–30	20–25
% insol. in ether but sol. in benzene	15–25	30	30	30

B was heated with silver oxide under ether for five days. It gave very little ether-soluble substance.

A mixture of carbazole and B was heated with silver oxide under ether for five days. About 40% of that portion of the reaction product which was insoluble in alcohol was soluble in ether. E was isolated from the ether solution.

Analyses.—E was analyzed by the combustion method for carbon, hydrogen and nitrogen, the substance being mixed with finely divided cupric oxide.

Subs., 0.1118, 0.2770, 0.1557, 0.1618: CO_2, 0.3405, 0.8557, 0.4791, 0.4959; H_2O, 0.0550, 0.1330, 0.0778, 0.0798.

Subs., 0.2637, 0.3251, 0.2518: moist N, 19.8 cc. (16°, 759 mm.), 22.9 cc. (13°, 759 mm.), 18.1 cc. (13°, 748 mm.).

Calc. for $C_{36}H_{29}ON_3$: C, 83.2; H, 5.63; O, 3.08; N, 8.09. Calc. for $C_{36}H_{27}ON_3$: C, 83.5; H, 5.25; O, 3.09; N, 8.13. Found: C, 83.05, 84.25, 83.92, 83.59; H, 5.51, 5.37, 5.59, 5.52; N, 8.6, 8.3, 8.3. Av. C, 83.7; H, 5.5; O, 2.4; N, 8.4. Ash, nil.

Molecular-Weight Determinations.—The molecular weight of E was determined at various concentrations by the cryoscopic method, using purified benzene as the solvent.

Chemical Reactions.—1.6164 g. of E dissolved in benzene was titrated with a solution of bromine in benzene until the color was not immediately discharged; 1.53 g. of bromine was needed, or a ratio of 1 mole of E to 3.05 moles of bromine. Hydrobromic

Table III

Molecular Weights

Wt. of benzene in g.	Wt. of E in g.	Number of f. p.'s taken	Average deviation from mean in °C.	F.-p. lowering in °C.	Mol. wt.[a]
		Series I			
32.33	0	5	0.001	0	...
32.35	0.1047	4	.001	.050	324
32.35	.3141	4	.001	.132	368
32.35	.6587	4	.001	.264	386
32.35	1.011	3	.001	.392	399
		Series II			
32.86	0	5	.001	0	...
32.86	.4885	3	.002	.195	381
32.86	.7882	3	.001	.309	388
		Series III			
32.22	0	4	.001	0	...
32.22	.1113	4	.001	.054	320

[a] Constant for benzene: 50° per mole per 100 g.

acid was formed in the reaction. When the benzene was evaporated and the residue washed with alcohol a gray powder was obtained that was soluble in benzene, insoluble in alcohol, and melted at 117–125°. In a similar experiment with B, 0.41 g. of bromine was needed for 1.5253 g., a ratio of 1 mole of B to 1.1 moles of bromine. The resulting derivative in the crude state melted at 230–245° (corr.).

E was dissolved in cold concd. sulfuric acid, giving a green solution. This was poured into ice and water and a green powder was precipitated, which on treatment with aqueous sodium hydroxide gave a white powder soluble in benzene and melting at 250°. B under similar treatment gave a product insoluble in benzene and melting above 270°.

About 1 g. of E was dissolved in a little benzene in a flask fitted with a reflux condenser and protected from the air by a mercury trap. The flask was fitted to a nitric oxide generator and the air swept out of the whole system with carbon dioxide. The benzene was then heated to boiling. Nitric oxide was generated and washed with concd. sulfuric acid and sodium hydroxide solution and passed through the benzene solution of E. The latter soon lost its fluorescence. After treatment with the gas for about an hour most of the benzene was distilled in a vacuum, the rest being allowed to evaporate in an open vessel. The residue was a bright yellow powder giving a yellow solution in benzene, but without fluorescence. It was sparingly soluble in ether, and sufficiently soluble in petroleum ether to give a slight yellow color to the solvent. It was dissolved in 150 cc. of ether, then evaporated to about $^1/_3$–$^1/_4$ of its volume. It gave a somewhat brownish-yellow powder which slowly charred between 240° and 260°. The mother liquor gave a bright yellow powder on evaporation, which decomposed into a gas and a char between 216° and 228°.[9]

Summary

A study has been made of the ether-soluble but alcohol-insoluble product, whose formation during the oxidation of carbazole by silver oxide was described by Branch and Smith.

The molecular weight investigated by the cryoscopic method was found to vary with the concentration, this variation and the analytical data uniquely agreeing with the assumption of a molecule containing three carbazole nuclei reversibly dissociating into two substances.

The high percentage of hydrogen in the substance showed that partial reduction of the carbazole nuclei had taken place. An atom of oxygen had also been introduced into the molecule.

The properties, dissociation, isomerization with acid, ready addition of nitric oxide, and high reactivity to bromine indicated that the substance was a tetra-aryl hydrazine.

The formation was found to depend on the presence of both dicarbazyl diphenylene hydrazine and carbazole, which points to a reduction of the former by the latter to give a diphenylamine instead of a carbazole derivative, this being a reaction of the reverse type to that by which a biphenylene derivative and a triphenylmethane are formed from a hexaphenylethane.

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[9] We are indebted to Mr. L. H. Rankin, who performed the experiment on the action of nitric oxide on E.