

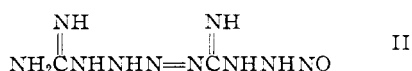
[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF ILLINOIS INSTITUTE OF TECHNOLOGY]

The Structure of Tetracene<sup>1,2</sup>BY SEYMOUR H. PATINKIN,<sup>3</sup> JEROME P. HORWITZ<sup>4</sup> AND EUGENE LIEBER

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The structure of the primary explosive Tetracene, C<sub>2</sub>H<sub>8</sub>N<sub>10</sub>O, has been reinvestigated. The degradative evidence alone fails to establish or exclude the presence of a tetrazole ring in this substance. However, the synthesis of Tetracene from the interaction of aminoguanidinium nitrate with a neutralized solution of tetrazolediazonium chloride at 0° demonstrates that the original structure is in error and that Tetracene is 1-(5'-tetrazolyl)-4-guanyltetrazene hydrate. In addition the product obtained by the interaction of these same coupling reagents in mineral acid is shown to be 1-guanyl-4-(5'-tetrazolyl)-tetrazene nitrate. A mechanism is advanced to explain the formation of Tetracene from the action of sodium nitrite on aminoguanidinium nitrate.

In 1910 Hofmann and co-workers<sup>5</sup> isolated a white crystalline solid of the composition C<sub>2</sub>H<sub>8</sub>N<sub>10</sub>O (I) from treatment of aminoguanidinium nitrate with sodium nitrite in neutral solution. On the basis of the degradative evidence gathered in subsequent studies,<sup>6-8</sup> the structure II 1-guanyl-4-



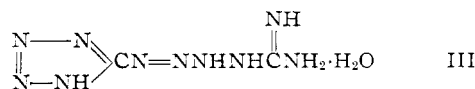
nitrosaminoguanylisotetrazene or simply Tetracene, as it has come to be known,<sup>9</sup> was assigned to the product. Hofmann, *et al.*,<sup>6</sup> originally interpreted the degradative evidence as indicative of the presence of an azide function in place of the β-nitrosohydrazine residue shown in II. In addition one mole of water was assigned to the structure on the basis of the elementary analysis. However, these investigators subsequently found that Tetracene did not lose weight on drying *in vacuo* and furthermore they failed to observe reduction on treatment with hydroiodic acid which would be expected of an azide function. For these reasons they abandoned the postulate of an "azide-hydrate" in favor of structure II.

Our preliminary observations disclosed that Tetracene could be recrystallized from nitric acid without suffering decomposition. This observation is apparently at odds with the behavior found for known nitrosohydrazines. The latter are, in general, stable only at a low temperature and, on treatment with acid or alkali, lose water to yield azides.<sup>10</sup>

The most general procedure for the preparation of 5-aryltetrazoles employs the nitrosation of hydrazidines.<sup>11</sup> It is generally assumed that the mechanism of this synthesis involves the prelimi-

nary formation of an imide azide which subsequently cyclizes to a tetrazole.<sup>11,12</sup> In most cases it is impossible to isolate the intermediate imide azide.

The original workers<sup>6</sup> rejected the possibility of a tetrazole ring being incorporated in I because of the apparent difference in properties between I and 1-(5'-tetrazolyl)-4-guanyltetrazene (III)



the product obtained by coupling tetrazolediazonium chloride and aminoguanidinium nitrate. However, the literature cited above indicates that a structure such as Hofmann's II should be inherently unstable toward dehydration to a tetrazole derivative and that the true structure of Tetracene may, after all, contain a tetrazole ring.

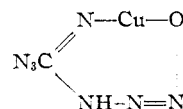
The usefulness of Tetracene as a replacement of other primary explosives such as mercuric fulminate or lead azide, together with the weakness of the evidence which led to the exclusion of a tetrazole ring, provided the impetus to reinvestigate the entire problem.

**Alkaline Degradation.**—The degradation of I with aqueous barium hydroxide afforded a white explosive solid whose infrared spectrum proved to be essentially superimposable with that of 5-azido-tetrazole (IV). No other organic solid could be detected. Repetition of this experiment revealed that one mole of ammonia is liberated within two hours while five hours were required for the liberation of two moles.

Under comparable conditions Hofmann obtained ammonia, cyanamide and β-nitrosoaminoguanyl azide.



This substance could only be isolated in the form of the copper salt and the structure appears to be



based solely on an elementary analysis. According to Hofmann, β-nitrosoaminoguanyl azide, on acidification, is converted to IV which he obtained in the form of a silver salt.

(12) W. L. Garbrecht and R. M. Herbst, *J. Org. Chem.*, **18**, 1003 (1953).

(1) This work was supported in part by U. S. Naval Ordnance Test Station, Inyokern, China Lake, California, Research Contract No. N123S-61517.

(2) Abstracted in part from a dissertation submitted by Seymour H. Patinkin to the Graduate School of Illinois Institute of Technology in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

(3) Western Cartridge Fellow 1951-1952.

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(5) K. A. Hofmann and R. Roth, *Ber.*, **43**, 682 (1910).

(6) K. A. Hofmann, H. Hock and R. Roth, *ibid.*, **43**, 1087 (1910).

(7) K. A. Hofmann, H. Hock and K. Kirmreuther, *Ann.*, **380**, 131 (1911).

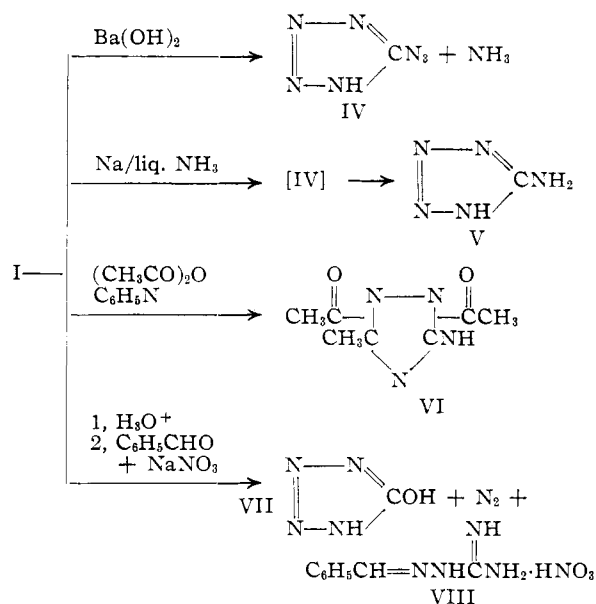
(8) K. A. Hofmann and H. Hock, *Ber.*, **44**, 2946 (1911).

(9) The exact origin of this name has not been ascertained, although it would appear that ordnance investigators shortened the original cumbersome name.

(10) E. Fischer, *Ann.*, **190**, 87 (1877).

(11) F. R. Benson, *Chem. Revs.*, **41**, 1 (1947).

The preceding remarks concerning the stability of nitrosohydrazines suggest that the dehydration of  $\beta$ -nitrosoaminoguanyl azide and cyclization of the resulting carbonimidyl azide would occur prior to the addition of acid. In this connection it is pertinent to point out that the elementary analysis of Hofmann's copper salt also conforms to the requirements of a copper monohydrate salt of 5-azidotetrazole. The interpretation, then, that cyclization occurred during the course of the alkaline degradation would appear more probable than that offered by Hofmann. The alternative, of course, is that Tetracene contains a tetrazole ring.



**Reductive Degradation.**—The addition of excess sodium to a solution of I in liquid ammonia resulted in reductive cleavage as manifested in the isolation of 5-aminotetrazole (V). The previous arguments advanced in connection with the formation of IV appear to be applicable to the present observations. Presumably, IV is the initial product which is subsequently reduced to an amine V.<sup>13</sup>

**Acetylation Studies.**—The interaction of acetic anhydride and I in the presence of a trace of pyridine afforded a mixture of isomeric diacetyl derivatives of 3-methyl-5-amino-1,2,4-triazole (VI). A similar mixture was obtained from the acetylation of both aminoguanidinium nitrate and an authentic sample of 3-methyl-5-amino-1,2,4-triazole.

The acetylation studies represent the first direct evidence for the inclusion of an aminoguanidine residue in I. The incorporation of this same fragment in II appears to be mainly the result of the requirements of elemental analyses.

**Acid Degradation.**—Hofmann observed the evolution of two moles of a gas which he assumed to be pure nitrogen when Tetracene was warmed for a short time with dilute sulfuric acid. Apparently acidic treatment brought about extensive fragmentation as 5-aminotetrazole, urea, hydrazine and cyanogen were also reportedly detected.<sup>5</sup>

(13) 5-Azidotetrazole undergoes a rather facile reduction with a variety of reducing agents, including HI and H<sub>2</sub>S. See E. Lieber and D. R. Levering, *THIS JOURNAL*, **73**, 1313 (1951).

Mass spectrometric analysis<sup>14</sup> of a sample of gas collected on treatment of I with 15% sulfuric acid showed, in agreement with Hofmann's assumption, that the evolved gas was essentially pure nitrogen (99.9 mole per cent.). On the other hand, rate measurements, plotted in Fig. 1, show that only one mole of nitrogen is liberated rather rapidly (20–45 minutes) followed by a slow, continuous evolution over a considerably longer period.

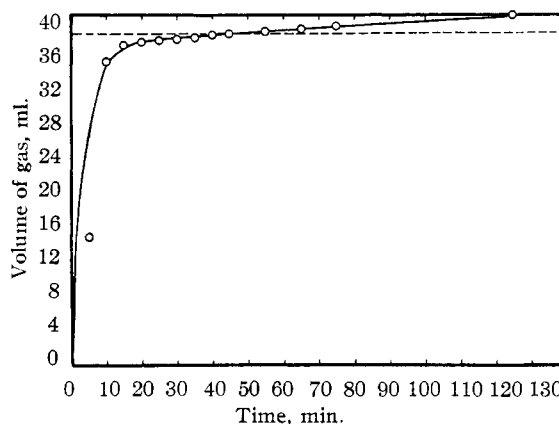
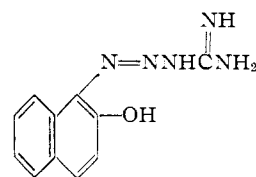


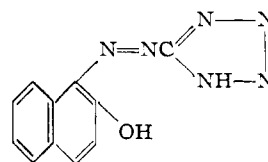
Fig. 1.—Rate measurement for the acid decomposition of tetracene (1.25 mmoles), volume of N<sub>2</sub> vs. time.

Tetracene was next degraded on a somewhat larger scale with 15% sulfuric acid and, following the removal of the excess acid as barium sulfate, the filtrate yielded 5-hydroxytetrazole (VII). It was subsequently found that this same degradation could be accomplished somewhat more expeditiously with dilute hydrochloric acid.

Hofmann noted that an azo dye could be obtained by heating  $\beta$ -naphthol with an acidified suspension of I in water.<sup>5,6</sup> This corroborated for him the existence of a nitrosamine function in II, though he did not investigate the dye. Shreve, Carter and Willis confirmed<sup>15</sup> Hofmann's observation and assigned the structure to the product.



The formation of dyes with I was further investigated by Reilly and co-workers,<sup>16</sup> who clearly established the presence of a tetrazole ring in the azo dye obtained with  $\beta$ -naphthol.



(14) Analysis by Consolidated Engineering Corp., Pasadena, California.

(15) R. N. Shreve, R. P. Carter and I. M. Willis, *Ind. Eng. Chem.*, **36**, 426 (1944).

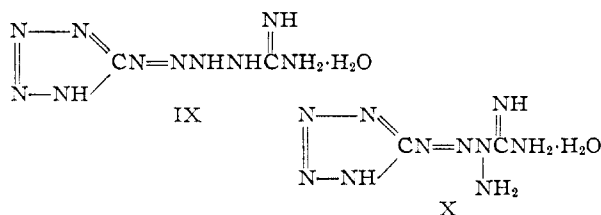
(16) J. Reilly, J. P. Teigan and M. F. Carey, *Sci. Proc. Roy. Dublin Soc.*, **24**, 349 (1948).

However, these workers visualized the occurrence of a prior cyclization reaction as a means of accounting for the formation of tetrazolediazonium hydroxide, followed by the interaction of the coupling components to produce the dye.

On the other hand, the facile conversion of I into VII by aqueous mineral acid, together with the fact that this transformation resulted in a relatively rapid evolution of one mole of nitrogen, pointed strongly to the presence of a 5-tetrazoleazo moiety.<sup>17</sup>

Further verification of the presence of an aminoguanidine fragment in Tetracene was obtained when we found that the addition of a mixture of benzaldehyde and sodium nitrate to the acid hydrolysate of I afforded a 45% yield of benzalaminoguanidinium nitrate (VIII). Significantly, it proved possible to isolate 5-hydroxytetrazole (VII) from the benzaldehyde filtrate.

The first and second mole of ammonia detected in connection with the alkaline degradation of I, as well as the slow continuous evolution of nitrogen noted in the gasometric studies, are observations which are explicable in terms of a secondary degradation involving an incipient aminoguanidine molecule.<sup>18</sup> The fact that all the nitrogen originally contained in I is accounted for simply in the acid degradation products (N<sub>2</sub>, VII, VIII) makes it possible to elaborate our earlier structural hypotheses to two additional plausible structures (IX, X) for I. Of these, however, only IX is consistent with the isolation of an azide IV in the alkaline degradation.



While the evidence presented in the previous sections would appear to debilitate the arguments favoring the presence of a nitrosohydrazine function in Tetracene, it is evident that the degradative evidence, *per se*, does not conclusively exclude this function. However, it was found that the addition of a solution of aminoguanidinium nitrate to a neutralized solution of tetrazolediazonium chloride at 0° afforded a white solid whose infrared spectrum proved to be essentially superimposable with that of Tetracene. This observation represents strong evidence for the inclusion of a tetrazole ring in the structure IX of Tetracene. There exists, however, the remote possibility that the new IX and old II structures for Tetracene may both be valid in the sense that they are interconvertible in respect to the reaction environment.<sup>19</sup> On the other hand, there is an abundance of evidence

(17) The derivatives of the unsymmetrical tetrazene HN=NNH-NH<sub>2</sub> are converted on treatment with acid into a diazonium compound and a hydrazine or further decomposition products of these. T. W. J. Taylor and W. Baker, "Sidgwick's Organic Chemistry of Nitrogen," Oxford University Press, London, 1949, p. 466.

(18) E. Lieber and G. B. L. Smith, *THIS JOURNAL*, **59**, 2283 (1937).

(19) The authors are indebted to one of the referees for this suggestion.

against the occurrence of such a phenomenon. Thus, the isomerization of 1-substituted 5-amino-tetrazoles to 5-substituted aminotetrazoles, which involves the intermediate formation of a guanyl azide derivative, occurs only at elevated temperatures (180–200°).<sup>20</sup> Similarly, the acid-catalyzed disruption of tetrazoles requires a comparable temperature range.<sup>21</sup> Therefore, unless the tetrazole ring in Tetracene should be unique among known tetrazoles, structure IX must be accepted.

The problem of demonstrating the presence of water of hydration presented some difficulty because of the inherent thermal instability of Tetracene. The elements of one mole of water are required by the elementary analysis. Confirmation of the presence of loosely bound water was subsequently obtained by titration with Karl Fischer reagent.

The degradative evidence together with the unequivocal synthesis clearly defines the structure of Tetracene as IX, which is, however, identical with III, the structure proposed by Hofmann for the product obtained by coupling tetrazolediazonium chloride with aminoguanidinium nitrate. In his original procedure for the preparation of III, Hofmann<sup>5,6</sup> reported the use of an equivalent amount of sodium acetate in the neutralization of the diazonium salt. The term "an equivalent amount of sodium acetate" is ambiguous since it was noted that the diazotization of 5-aminotetrazole requires the use of excess mineral acid. In the first attempt to duplicate Hofmann's findings an acidic solution of tetrazolediazonium chloride was treated with three molar proportions of sodium acetate. The addition of a solution of aminoguanidinium nitrate afforded a white solid whose infrared spectrum showed the prominent vibrations (2140, 2180 cm.<sup>-1</sup>) indicative of an azide function. It was observed in a separate experiment that this substance gradually disappeared on prolonged contact with its mother liquor, leaving a small amount of an amorphous solid which was identified from infrared measurements as Tetracene.

Hofmann reported an explosion point of 142° for his coupling product while the product obtained in this Laboratory exploded at 140°. However, our product failed to yield an analysis consistent with III. Pure Tetracene exhibits an explosion point of 135–145°, the exact temperature of the explosion being a function of the rate of heating. The evidence as a whole would suggest that Hofmann had inadvertently obtained a mixture of tetrazenes whose analysis fortuitously approached that of III.

When the amount of sodium acetate was reduced to one equivalent, the product no longer exhibited the azide absorption band, and an analysis was consistent with the empirical formula C<sub>9</sub>H<sub>7</sub>N<sub>11</sub>O<sub>3</sub> (XI), which is significantly different from the requirements of the structure III. The degradation of XI with aqueous barium hydroxide gave 5-aminotetrazole (XII) in 74% yield. In contrast to this observation Hofmann reported that the alkaline degradation of his coupling product pro-

(20) R. A. Henry, W. G. Finnegan and E. Lieber, *THIS JOURNAL*, **76**, 88 (1954).

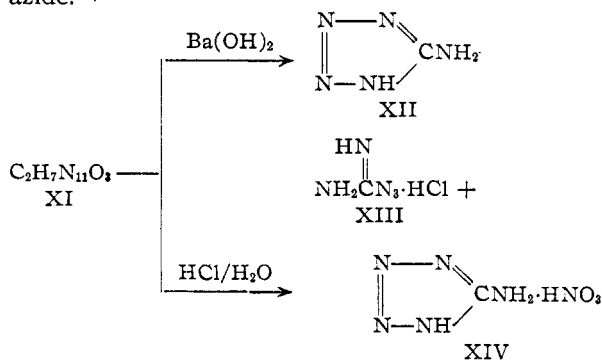
(21) P. A. S. Smith, *ibid.*, **76**, 436 (1954).

duced 5-azidotetrazole (IV), the product which we detected in the corresponding degradation of Tetracene. This discrepancy supports the hypothesis that Hofmann had mistakenly examined a mixture of tetrazenes.

The degradation of XI with aqueous hydrochloric acid failed to produce the copious evolution of nitrogen which occurs with I. However, guanyl azide hydrochloride XIII and 5-aminotetrazole nitrate (XIV) could be isolated. The isolation of a nitrate salt on treatment of XI with hydrochloric acid obviously implies that XI must also be a nitrate salt.

The fact that all the nitrogen originally present in XI is accounted for in the products (XIII, XIV) of the acid degradation suggests that the accompanying slow evolution of gas results from a secondary decomposition or a minor side reaction.

When XI was suspended in water at room temperature, it slowly dissolved; evaporation of the clear solution gave 5-aminotetrazole (XII) in 45% yield. The higher yield (74%) of XII reported in the alkaline degradation probably results from a contribution made by the cyclization of guanyl azide.<sup>22,23</sup>



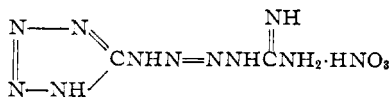
Hofmann obtained an azo dye from  $\beta$ -naphthol and the acid hydrolysate of the compound he assumed to be III. However, he did not say if this dye differed from the azo dye obtained from Tetracene. Our inability to obtain a dye with XI and  $\beta$ -naphthol is construed as additional evidence against a diazoamino structure for this material, and appears to corroborate the hypothesis that Hofmann was working with a mixture of tetrazenes.

The failure to form an azo dye, combined with the degradative evidence, defines the structure 1-guanyl-4(5'-tetrazolyl)-tetrazene nitrate (XV) for XI.<sup>24</sup>

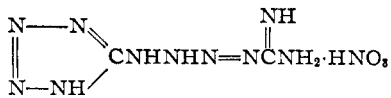
(22) J. Thiele, *Ann.*, **270**, 1 (1892).

(23) E. Lieber and G. B. L. Smith, *Chem. Revs.*, **25**, 233 (1941).

(24) The isomeric structure



is not excluded by the present evidence though it is considered to be very much less probable. The 2-tetrazene is conjugated neither with the tetrazole ring nor the guanidine system and there seems to be little reason to expect it to be the more stable isomer.



XV

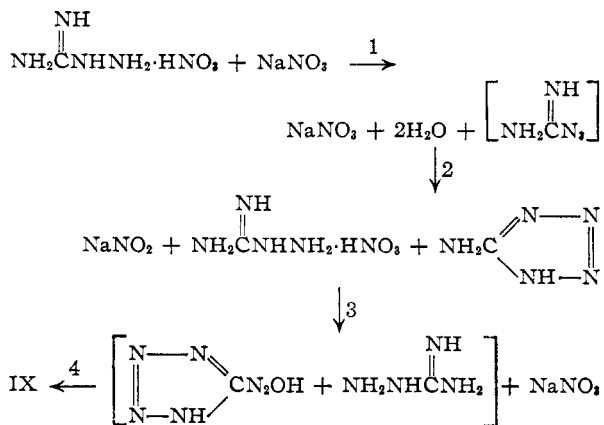
In the presence of mineral acid the coupling of phenylhydrazine with benzenediazonium chloride produces an unstable 1,4-disubstituted tetrazene which immediately breaks up to yield an azide and an amine. If the benzene rings of the two coupling components contain different substituents, two azides and two amines are formed; in other words, the tetrazene appears to be tautomeric.<sup>25-27</sup> Contradistinctly, Tetracene and the nitrate salt XV are examples of relatively stable 1,4-disubstituted tetrazenes, each affording a single azide and amine in the appropriate degradation. Attempts to interconvert these two tetrazenes have been unsuccessful.

The synthesis of Tetracene from tetrazolediazonium chloride and aminoguanidine suggested the possibility of the transient existence of the same coupling components in the formation of Tetracene by the original procedure. It appeared of interest then, as the final phase of this study, to attempt to elucidate the mechanism of this reaction which is still the most satisfactory preparative method (88% yield).

The formation of guanyl azide from the action of nitrous acid on aminoguanidine and the cyclization of the incipient azide in neutral solution are well-known reactions.<sup>22,23</sup> These reactions have been included in a scheme to explain the formation of 1,3-bis-5-tetrazolyltriazenes from the action of sodium nitrite on aminoguanidinium nitrate in the presence of acetic acid.<sup>23</sup> Therefore, it seems reasonable to assume that reactions 1 and 2 are part of a progression of successive reactions terminating with the formation of Tetracene.

It was noted that the preparation of IX by the reaction of aminoguanidinium nitrate with sodium nitrite occurs in a medium which remains neutral during the time required for the reaction to reach completion. This observation is consistent with the requirements of each of the reactions outlined for this process. Furthermore, "step 3" was carried out independently. Precipitation began almost immediately after the reagents were mixed, whereas the normal procedure requires several hours before the inception of precipitation.

The coupling reaction (eq. 4) also appears to be a relatively rapid reaction as observed in connection



(25) P. Griess, *Ber.*, **9**, 1659 (1876).

(26) T. Curtius, *ibid.*, **26**, 1263 (1893).

(27) Cf. ref. 17, p. 382.

with the unequivocal synthesis of IX. On the other hand, the conversion of aminoguanidine into guanyl azide (eq. 1) would be expected to be the slow or rate-determining step. If this were not the case complete conversion to guanyl azide might be anticipated and step 3 would never occur. This hypothesis was substantiated with the observation that the interaction of two moles of aminoguanidinium nitrate and one mole of sodium nitrite increased the yield of IX to 94%.

On the basis of these observations it would appear that the reactions represent a reasonable path for the formation of Tetracene from the interaction of aminoguanidine and sodium nitrite in the absence of acid.

### Experimental<sup>28</sup>

**Tetracene (IX).** (a) **Modification of Original Procedure.**—To a cold solution of 10 g. of aminoguanidinium nitrate (0.07 mole) in 90 cc. of water was added portion-wise with external cooling 7.0 g. of sodium nitrite (0.08 mole). After approximately six hours at room temperature a solid began to be deposited which was collected at the end of 40 hours, washed with water, ethanol and water to give 6.1 g. (88% yield) of Tetracene, explosion point 135°.

*Anal.* Calcd. for  $C_8H_6N_{10}H_2O$ : C, 12.76; H, 4.28; N, 74.46. Found: C, 12.67; H, 4.98; N, 74.31.

The water of hydration was determined by suspending approximately 1.0-g. samples of Tetracene in anhydrous methanol and titrating with Karl Fischer reagent.<sup>29</sup> The average of several determinations showed 0.94 mole of water per mole of Tetracene.

(b) **Coupling Reaction.**—A mixture of 2.06 g. of 5-aminotetrazole hydrate (0.02 mole), 5.5 cc. of concentrated hydrochloric acid (d. 1.18), 40 cc. of water and *ca.* 20 g. of ice was surrounded by an ice-bath and stirred mechanically while a solution of 1.52 g. of sodium nitrite (0.022 mole) in 10 cc. of water was introduced from a dropping funnel. The diazonium solution was stirred for an additional 1.5 hours and the excess nitrous acid destroyed by the dropwise addition of a saturated solution of potassium permanganate. The pH of the reaction mixture was adjusted to 7 (Hydriion paper) by the careful addition of 20% sodium hydroxide (*ca.* 100 cc.) and the neutral mixture then added to a solution of 2.74 g. of aminoguanidinium nitrate (0.02 mole) in 25 cc. of water. A yellow solid appeared almost immediately and, after stirring for an additional 1.5 hours, the product was collected, then washed with water, alcohol and ether, wt. 1.30 g. (35% yield<sup>30</sup>), explosion point 135°. The infrared spectrum of this product was essentially superimposable with that of an authentic sample of IX. Principal maxima (Nujol) in both cases occurred at 1150, 1440, 1615 and 1690  $cm^{-1}$ . Five grams of the product obtained by this procedure was purified for analysis by first dissolving in 33 cc. of cold (0–5°), concentrated nitric acid and reprecipitating the solid by dilution with 660 cc. of water. The solid was collected, washed with water, alcohol and ether, wt. 3.85 g., explosion point 135°.

*Anal.* Found: C, 13.08; H, 4.04; N, 74.45.

(c) **From Two Moles of Aminoguanidinium Nitrate (eq. 1).**—To an ice cold solution of 5 g. of aminoguanidinium nitrate (0.036 mole) in 45 cc. of water was added 1.25 g. of sodium nitrite (0.018 mole) while the mixture was cooled externally with an ice-bath. After 40 hours, 1.62 g. of Tetracene, explosion point 135°, was obtained which corresponds to a 94% yield based on the quantity of sodium nitrite employed.

(d) **From Aminoguanidinium Nitrate and 5-Aminotetrazole (eq. 3).**—To a solution of 2.06 g. of 5-aminotetrazole

hydrate (0.02 mole) and 2.74 g. of aminoguanidinium nitrate (0.02 mole) in 100 cc. of water was added 1.60 g. of sodium nitrite (0.022 mole). The solution immediately turned yellow and precipitation began within a few minutes. After three hours 1.4 g. of Tetracene, explosion point 135°, was isolated.

**Acid Decomposition of IX.** (a) **5-Hydroxytetrazole (VII).**—A suspension of 5 g. of Tetracene (0.027 mole) in 250 cc. of 15% aqueous sulfuric acid was refluxed for 20 minutes. The hot, clear solution was treated with a pre-heated solution of 9.0 g. of barium chloride dihydrate (0.37 mole) and the barium sulfate removed by filtration. The filtrate was then evaporated to dryness and the white residue dried *in vacuo*. The dry solid was next refluxed with acetone in a Soxhlet apparatus and the extract evaporated to dryness. Recrystallization of the white residue from water gave 0.78 g. (29% yield<sup>31</sup>) of product, m.p. 240–245°. A second recrystallization from water raised the melting point to 253–254° (lit.<sup>32</sup> 254°). A mixed melting point with an authentic sample of 5-hydroxytetrazole failed to show any depression.

(b) **Benzalaminoguanidinium Nitrate (VIII).**—A suspension of 5.0 g. of Tetracene (0.026 mole) in a mixture of 15 cc. of concentrated hydrochloric acid and 238 cc. of water was refluxed for 30 minutes. The clear solution was cooled to room temperature and 2.7 g. of benzaldehyde (0.026 mole) was introduced followed by the addition of 5.5 g. of sodium nitrate (0.065 mole). A white solid was deposited from the vigorously agitated mixture which was then refrigerated for 18 hours. Filtration yielded 2.6 g. (45% yield) of VIII, m.p. 163–165° (lit.<sup>33</sup> 161°). A sample recrystallized from water melted at 164–164.5° alone and when mixed with an authentic sample of VIII.

*Anal.* Calcd. for  $C_8H_{11}N_5O_3$ : C, 42.66; H, 4.89; N, 31.11. Found: C, 42.74; H, 4.97; N, 30.88.

The aqueous filtrate from the isolation of VIII was evaporated to dryness on a steam-bath in a stream of air and the residue refluxed with acetone in a Soxhlet apparatus. The acetone extract was next evaporated to dryness and the solid recrystallized from water to give 0.4 g. of an off-white solid, m.p. 244–251°. A second recrystallization from water gave white needles, m.p. 253–254° alone or with a genuine sample of 5-hydroxytetrazole (VII).

(c) **Rate Measurements.**—The apparatus used in the rate study was essentially that described by Siggia and Lohr.<sup>34</sup> Approximately one-millimole samples of Tetracene were weighed out to the nearest milligram and transferred to a 100-ml. round-bottomed flask along with 20 ml. of water. The flask was then attached to the system and the apparatus flushed with carbon dioxide until micro-bubbles were observed in the gas buret containing 50% potassium hydroxide (*ca.* one hour was required). The flow of carbon dioxide was interrupted to introduce 20 ml. of 30% aqueous sulfuric acid from a dropping funnel connected to the system by means of a glass seal. The mixture was heated to reflux and volume measurements were recorded at five-minute intervals (*cf.* Fig. 1).

A sample of gas for mass spectrometric analysis was obtained by attaching a glass bulb to the top of the gas buret. One-half of the sample in the gas buret was used to flush out the bulb, the remainder being collected and submitted for analysis.

**Alkaline Degradation of IX.** (a) **5-Azidotetrazole (IV).**—A mixture of 1.88 g. of Tetracene (0.01 mole) in 300 cc. of 0.4 *M* barium hydroxide was refluxed for two hours. A small amount of solid (0.27 g.) was deposited on cooling which was identified as barium carbonate. The filtrate was then neutralized with dilute sulfuric acid, the mixture digested and the barium sulfate removed by filtration. Evaporation of the filtrate to near dryness on a steam-bath in a stream of air left a thick sirupy mass which solidified on cooling. The solid residue was then triturated with five 25-cc. portions of hot benzene. The slow evaporation

(28) All melting points are uncorrected. Explosion points were determined with a Dennis bar apparatus (L. M. Dennis and R. S. Shelton, *This Journal*, **52**, 3128 (1930)). Analyses are by the Micro-Tech Laboratories, Skokie, Illinois. Infrared absorption measurements were obtained with a Perkin-Elmer recording spectrophotometer, Model 21.

(29) K. Fischer, *Angew. Chem.*, **48**, 394 (1935).

(30) Yields as high as 56% were obtained by adding three equivalents of sodium hydroxide in the neutralization procedure.

(31) A recent study in this Laboratory (K. Hattori, E. Lieber and J. P. Horwitz, unpublished work) has indicated that the optimum temperature for the conversion of tetrazolediazonium chloride into 5-hydroxytetrazole (VII) is 5–10°. Under these conditions the yield of VII is 52%. It seems reasonable, then, to attribute the relatively low yield of VII in the present study to the elevated temperature to which the transient diazonium salt has been subjected.

(32) R. Stollé, *Ber.*, **62**, 1118 (1929).

(33) J. Thiele and K. Heidenreich, *ibid.*, **26**, 2599 (1893).

(34) S. Siggia and L. J. Lohr, *Anal. Chem.*, **21**, 1201 (1949).

of the combined, dried, benzene extracts gave 0.37 g. of a white solid, m.p. 70–74°. Recrystallization from benzene gave long white needles, m.p. 77–79° (Fisher–Johns apparatus), lit.<sup>13</sup> 72–73° (Dennis bar). The infrared spectrum of this material proved to be essentially superimposable with an authentic sample of 5-azidotetrazole with principal maxima occurring in both cases at 1050, 1070, 1100 and 2125  $\text{cm}^{-1}$ .

(b) **Measurement of Evolved Ammonia.**—An apparatus was set up similar to that described above for the nitrogen measurements. To an accurately weighed sample of Tetracene (0.4–1.0 mmole) was added 30 ml. of 0.2 *N* barium hydroxide. The flask was immediately connected to the apparatus and nitrogen passed through the system for ten minutes. The reaction mixture was heated to reflux and the evolved ammonia swept by the carrier gas into a series of two saturators containing standard hydrochloric acid. The acid traps were back-titrated with standard sodium hydroxide at the conclusion of each run. The results are provided in Table I.

TABLE I  
MEASUREMENT OF AMMONIA EVOLVED IN THE ALKALINE  
DEGRADATION OF TETRACENE

Sample of tetracene, mmoles	Time of reflux, hr.	Ammonia, mmoles	$\text{NH}_3$ Tetracene
1.02	0.5	0.95	0.93
1.02	2.0	1.14	1.12
0.93	2.0	0.97	1.04
.481	5.0	.82	1.70
.487	5.0	.86	1.57

**Acetylation Studies (VI).** (a) **Tetracene.**—A suspension of 6.0 g. of Tetracene (0.032 mole) in 300 cc. of acetic anhydride containing 0.5 cc. of pyridine was stirred mechanically while the mixture was heated just to reflux. The light-brown solution was cooled to room temperature and excess acetic anhydride removed under reduced pressure, the last traces being removed in a vacuum desiccator. Recrystallization of the residue from absolute ethanol with Norite gave 2.2 g. of a colorless product, m.p. 196–201°. Three additional recrystallizations from absolute ethanol afforded an analytical sample, m.p. 203–205°.

*Anal.* Calcd. for  $\text{C}_7\text{H}_{10}\text{N}_4\text{O}_2$ : C, 46.15; H, 5.50; N, 30.77. Found: C, 46.09; H, 5.52; N, 31.13.

Recrystallization of this same sample from acetone raised the melting point to 204–207°, yet failed to cause any significant change in the analysis. Under a microscope it was noted that two species were present, the major component representing about 95% of the total. Both solids were observed to sublime and melt at the same temperature.

(b) **Aminoguanidinium Nitrate.**—A mixture of 6.0 g. of aminoguanidinium nitrate (0.044 mole) and 100 cc. of acetic anhydride containing 0.5 cc. of pyridine was heated just to reflux. The same purification procedure described above afforded 0.5 g. of a white crystalline solid, m.p. 202°. Microscopic studies again indicated a mixture of products with the major component comprising approximately 95% of the mixture. A mixed melting point with the acetylated mixture obtained with Tetracene showed no depression.

(c) **3-Methyl-5-amino-1,2,4-triazole.**—The acetylation of 3-methyl-5-amino-1,2,4-triazole<sup>22</sup> was carried out in the manner described by Birkoff.<sup>35</sup> This procedure yielded a white solid, m.p. 203–206° (lit.<sup>36</sup> 204–206°).

**Reduction of IX.**—To a solution of 5.4 g. of IX (0.23 mole) in 400 cc. of liquid ammonia was added an excess of freshly cut sodium (5.4 g., 0.23 mole). The reaction mixture was exposed to air and the ammonia allowed to evaporate overnight, during which time the excess sodium appeared to be destroyed. The yellow residue was taken up in water and the mixture adjusted to a pH of 1 with 6 *N* nitric acid.

(35) L. Birkoff, *Ber.*, **76B**, 769 (1943).

(36) The original investigation described this material as a pure compound. However, microscopic studies in the present study indicated the same mixture as that obtained with both Tetracene and aminoguanidinium nitrate.

The cloudy mixture was filtered and the filtrate evaporated to dryness on a steam-bath in a stream of air. The brown residue was then dried in a vacuum desiccator and the dry solid refluxed with acetone in a Soxhlet extractor. Evaporation of the acetone extract left an oily residue which crystallized as a tan solid on cooling. Recrystallization from water gave 0.5 g. of 5-aminotetrazole, m.p. 204–206° dec. (lit.<sup>32</sup> 203° dec.).

**1-Guanyl-4-(5'-tetrazolyl)-tetrazene Nitrate (XV).**—The diazotization of 5-aminotetrazole (2.06 g., 0.02 mole) was carried out in the same manner as that already described in connection with the preparation of IX. The diazonium salt solution was then partially neutralized<sup>37</sup> with a solution of 1.64 g. of sodium acetate (0.02 mole) in 10 cc. of water. The cold clear solution was next added dropwise with stirring to a solution of 2.74 g. of aminoguanidinium nitrate (0.02 mole) in 25 cc. of water. The gelatinous solid, which appeared almost immediately, was collected, washed with cold water and dried overnight, wt. 3.7 g. (80% yield), m.p. 90–93° dec. The crude solid was dissolved in 30 cc. of cold, concentrated nitric acid and the clear solution poured into 450 cc. of water. The reprecipitated solid was collected, washed with water, ethanol and finally ether, wt. 2.6 g., m.p. 93–94° dec.<sup>38</sup> The analytical sample was dried *in vacuo* at the temperature of refluxing acetone.

*Anal.* Calcd. for  $\text{C}_2\text{H}_7\text{N}_{11}\text{O}_3$ : C, 10.30; H, 3.03; N, 66.09. Found: C, 10.61; H, 3.21; N, 65.71.

**Acid Degradation of XV.** (a) **5-Aminotetrazole Nitrate (XIV).**—A suspension of 9.73 g. of XV (0.04 mole) in a mixture of 30 cc. of concentrated hydrochloric acid and 470 cc. of water was refluxed for 15 minutes. The clear solution was evaporated just to the inception of crystallization and the mixture allowed to cool to room temperature. The product was collected and dried, wt. 2.84 g. (46% yield), m.p. 162–178° dec.

*Anal.* Calcd. for  $\text{CH}_4\text{N}_5\text{O}_3$ : C, 8.19; H, 2.72; N, 56.75. Found: C, 8.16; H, 2.73; N, 57.37.

The infrared spectrum of this product was identical with that of 5-aminotetrazole nitrate; principal maxima in each case occurring at 1715, 1490, 1390 and 1030  $\text{cm}^{-1}$ .

(b) **Guanyl Azide Hydrochloride.**—The filtrate from "a" was evaporated to near dryness and the mixture allowed to solidify. The solid was collected, washed with a little acetone and dried *in vacuo*, wt. 2.2 g. (44% yield), m.p. 117–140° dec. A single recrystallization from ethanol afforded a white crystalline solid, m.p. 126–146° dec.

*Anal.* Calcd. for  $\text{CH}_4\text{N}_5\text{Cl}$ : C, 9.92; H, 3.31; N, 57.85. Found: C, 10.10; H, 3.22; N, 57.80.

The infrared spectrum of this product proved to be essentially superimposable with that of guanyl azide hydrochloride with principal maxima occurring at 2175, 1660 and 1470  $\text{cm}^{-1}$ .

**Alkaline Degradation of XV.**—To a solution of 500 cc. of 0.2 *N* barium hydroxide was added 4.0 g. of XV (0.017 mole) and the mixture refluxed for two hours. The hot solution was then adjusted to a pH of 2 (Hydrion paper) with 1 *N* sulfuric acid and the barium sulfate removed by filtration. The filtrate was concentrated to a volume of approximately 30 cc. and resulting solid collected and dried, wt. 1.31 g. (74%), m.p. 188–200 dec. Recrystallization from water gave 1.0 g. of white crystalline solid, m.p. 197–200° dec., alone or with a genuine sample of 5-aminotetrazole hydrate.

**Decomposition of XV in  $\text{H}_2\text{O}$ .**—A finely divided suspension of 2.0 g. of XV (0.009 mole) in 100 cc. of water was stirred for 30 minutes and then allowed to stand overnight (12 hours) at room temperature. The clear solution was evaporated to dryness on a steam-bath in a stream of air and the solid residue crystallized from water to give 0.4 g. (45% yield) of 5-aminotetrazole hydrate, m.p. 203–204° dec. (lit.<sup>39</sup> 203° dec.).

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(37) The elimination of this step was subsequently found to diminish the yield (73%) of XV only slightly.

(38) It was noted the resolidified melt, which is presumably a mixture of acid degradation products, exhibits a much broader melting point, 110–135° dec.

(39) J. Thiele, *Ann.*, **270**, 54 (18922).