[CONTRIBUTION FROM THE KEDZIE CHEMICAL LABORATORY, MICHIGAN STATE COLLEGE

THE SYNTHESIS OF CERTAIN 5-AMINOTETRAZOLE DERIVATIVES. IV. THE REARRANGEMENT OF CERTAIN MONOSUBSTITUTED 5-AMINOTETRAZOLE DERIVATIVES[1]

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Received March 6, 1953

In the course of work with the 5-monoalkylaminotetrazoles 5-methylaminotetrazole was observed to display a double melting point the higher of which corresponded almost exactly with that of 1-methyl-5-aminotetrazole (1). Before this observation could be examined further it was corroborated in a private communication from Dr. R. A. Henry who had characterized the high-melting form as 1-methyl-5-aminotetrazole. 5-Benzylaminotetrazole does not show a double melting point, probably due to the close proximity of its melting point to that of the isomeric 1-benzyl-5-aminotetrazole. However, when 5-benzylaminotetrazole was kept at the melting temperature for several minutes, complete rearrangement to 1-benzyl-5-aminotetrazole occurred. This observation explains the dependence of the melting point of 5-benzylaminotetrazole on the rate of heating. With very slow heating melting points as low as 181° have been observed, while on rapid heating the melting point may be as high as 193° without apparent decomposition [1].

Attention has been directed to the peculiar behavior of 1-phenyl-5-aminotetrazole and of 1-*p*-nitrophenyl-5-aminotetrazole on heating in capillary tubes (1). The former melted completely at about 160°, resolidified at about 165°, and melted again at 205–206°. No decomposition was apparent at the lower melting point. The nitrophenyl compound exhibited marked changes in appearance at about 170° and then melted with decomposition at 221–223°. This phenomenon was further investigated first with 1-phenyl-5-aminotetrazole. A small sample kept at 160–165° for a few minutes melted and resolidified at the bath temperature. The product had acquired an acidic character not present in the unheated material and was completely soluble in cold, dilute aqueous sodium hydroxide. After recrystallization the material melted at 205–206° without prior melting and resolidification. In a comparable manner a small sample of 1-*p*-nitrophenyl-5-aminotetrazole was heated at 170–175°. Although it did not melt and considerable charring was observed, an alkali-soluble product could be separated. After recrystallization it melted at 221–223° with decomposition without showing any changes prior to melting. Analysis showed that both thermal rearrangement products had the same composition as the original compounds. Subsequently it was found that the same change could be effected with less decomposition by boiling

[1] Based on a thesis submitted to the School of Graduate Studies at Michigan State College in 1952 by William L. Garbrecht in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

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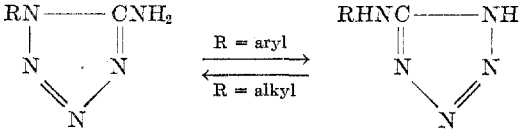
suspensions of either compound in xylene. The rearrangements were complete since no trace of alkali-insoluble material could be found in the products.[4]

A simple explanation of the changes is expressed by the rearrangement of the 1-aryl-5-aminotetrazoles (Ib) to 5-arylaminotetrazoles (IIb). When the substituent is an alkyl group, rearrangement takes place in the opposite direction, the 5-alkylaminotetrazole (IIa) going to a 1-alkyl-5-aminotetrazole (Ia).

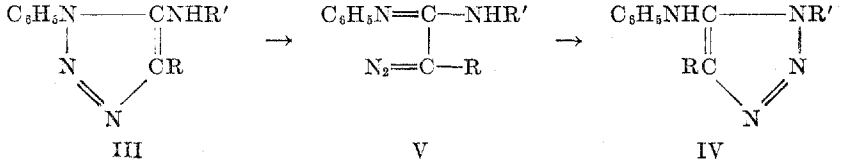


I, a, R = alkyl
b, R = aryl

II, a, R = alkyl
b, R = aryl

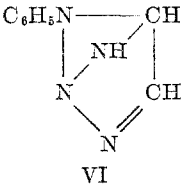
During the preparation of 1-phenyl-5-aminotetrazole from phenylthiourea Stollé observed the formation of a very small amount of material to which he assigned the structure of 5-phenylaminotetrazole (2). This product was described as an acidic compound melting at 206°, properties which were in agreement with those observed for the thermal rearrangement product of 1-phenyl-5-aminotetrazole.

Such rearrangements have been encountered in other heterocyclic systems containing the N—C—N arrangement where one of the nitrogens is an amino group. Dimroth (3) described the thermal rearrangement of a number of 1-phenyl-5-amino-, and 1-phenyl-5-methylamino-1,2,3-triazoles (III) to 5-phenylamino-, and 1-methyl-5-phenylamino-1,2,3-triazoles (IV), respectively. The suggestion that the rearrangement involved the intermediate formation of a substituted diazoacetamidine (V) was challenged by Dutt who suggested a nitrogen bridge structure (VI) for one of the products (4) or as an intermediate (5). Later Dimroth and Michaelis (6) presented further evidence in favor of the monocyclic structures for the two forms.



III V IV

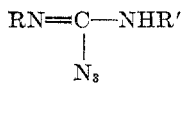
R = H, C_6H_5, $COOC_2H_5$; R' = H, CH_3



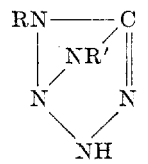
VI

[4] We have recently learned that Dr. R. A. Henry has studied this change in homogeneous media and found it to be an equilibrium process.

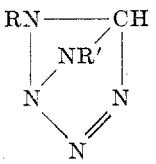
The rearrangement of the 5-aminotetrazoles could be explained on the basis of the intermediate formation of a substituted guanyl azide (VII); the direction of cyclization would be determined by the nature of the substituent groups.[5] However, a number of arylcyanamides are known to react with hydrazoic acid in homogeneous solution with the essentially exclusive formation of 1-aryl-5-aminotetrazoles [(7) and later section of this paper] presumably through the intermediate formation of a guanyl azide. Subsequently, when these 1-aryl-5-aminotetrazoles are heated to a higher temperature in the same solvent, they rearrange to the more stable 5-arylaminotetrazoles. It seems rather unlikely that the same intermediate should be involved in both processes. Should this be the case it is rather difficult to explain why any extensive formation of 1-aryl-5-aminotetrazoles occurs in the first place. Although cyclization of alkyl-substituted guanyl azides to 1-alkyl-5-aminotetrazoles can be explained easily on the basis of the inductive effect of the alkyl groups, no simple explanation is immediately apparent for the cyclization of the aryl-substituted guanyl azides in the same direction (7). The intermediate formation of a nitrogen bridge structure (VIIIa or b) during the rearrangement would avoid the postulation of the same intermediate for two apparently different reactions and appears attractive to us. The possibility must also be borne in mind that one of the isomeric forms might actually possess the bridge structure. The same type of intermediate would explain the rearrangement of the 5-alkylaminotetrazoles to 1-alkyl-5-aminotetrazoles. It is interesting to note that the nitrogens carrying the substituents in the bridge structure occupy equivalent positions. When R is aryl and R′ is hydrogen or alkyl, rupture of the bond from the aryl-substituted N to the adjacent N would cause formation of the 5-arylaminotetrazole. On the other hand rupture of the bond from the alkyl-substituted N to the bridgehead N would lead to the 5-alkylaminotetrazole structure. Both processes would require the shift of a hydrogen.



VII



VIIIa



VIIIb

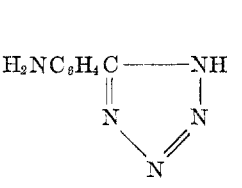
The explanations developed for the cyclization of substituted guanyl azides (7) may be applied here. The nature of R and R′ will determine the direction of ring opening. The bond from the bridgehead nitrogen to that nitrogen in the four-membered ring carrying the most negative substituent will be most easily ruptured. On this basis when R′ is hydrogen, if R is an aryl group formation of the 5-arylaminotetrazole will be favored, but if R is an alkyl group the 1-alkyl-5-aminotetrazole structure will be favored. If R and R′ are the same, the direction of ring opening is of no consequence. In general, the greater the difference in

[5] In a private communication Dr. R. A. Henry has suggested such a mechanism (See also Ref 21).

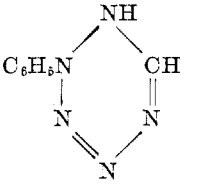
negativity between R and R′, the more completely should the rearrangement proceed in the favored direction.

It should be emphasized that structure VIII represents an asymmetric molecule when the substituents R and R′ are different. Should one of the isomeric forms possess such a structure, it should be resolvable into optically active forms provided that the lability of the bridged ring did not negate attempts at resolution.

Other structures can be written for the rearrangement products of the 1-aryl-5-aminotetrazoles. For example, a Fischer-Hepp type rearrangement could follow the formation of the 5-arylaminotetrazole. Such a change would lead to a structure in which the aryl group was attached directly at the 5 position of the tetrazole ring (IX) rather than through the amino-nitrogen. The absence of the N—C—N system should make such products less prone to rearrangement. This possibility is rather effectively ruled out by the absence in the rearrangement products of an amino group that can be diazotized and coupled. Qualitative tests with a variety of 1-aminophenyl- and 5-aminophenyl-tetrazoles demonstrated that such compounds can be diazotized and coupled easily. It should also be pointed out that 1-substituted 5-aminotetrazoles, excepting 5-aminotetrazole itself, form nitroso derivatives with nitrous acid but do not diazotize and couple (2, 8).



IX

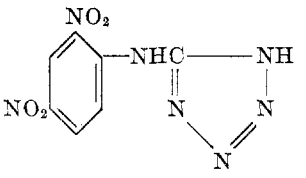


X

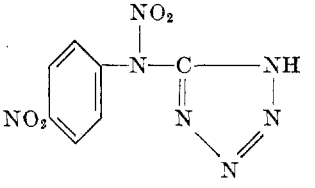
Rearrangement could also lead to a pentazine structure (X). This alternative is not very attractive. All attempts to prepare pentazine derivatives have led to 5-aminotetrazole structures (9). In this connection it may also be significant that many tetrazines are known to rearrange rather easily to 1,2,3-triazole or 1,2,4-triazole derivatives (10). Furthermore, interpretation of the ultraviolet absorption spectra of the arylaminotetrazoles can be made without resort to a pentazine structure.

The structure of 1-*p*-nitrophenyl-5-aminotetrazole was supported by its formation both from *p*-nitrophenylcyanamide and by nitration of 1-phenyl-5-aminotetrazole (7). It was thought that the relationship between the rearrangement products of 1-*p*-nitrophenyl- and 1-phenyl-5-aminotetrazole might be established in a similar manner. Unfortunately, nitration of 5-phenylaminotetrazole with mixed acid at 0° resulted in a dinitro derivative. Although the distribution of the nitro groups in this product has not been determined, several possible structures must be considered. Both nitro groups may have become attached to the benzene ring, presumably in the *ortho* and *para* positions (XI), or one of the nitro groups may be attached to the amino group (XII). A choice

between these structures cannot be made at this time. The mildness of the conditions under which nitration was accomplished would point to the nitrophenylnitraminotetrazole structure. It has been shown that both 5-aminotetrazole (11) and 5-methylaminotetrazole (12) can be converted into nitramino derivatives under very mild conditions. However, these nitramino derivatives are fairly strong acids, at least ten times as strong as the dinitro 5-phenylaminotetrazole. The rather strongly acidic character of the dinitro compound could be explained on the basis of either structure.



XI

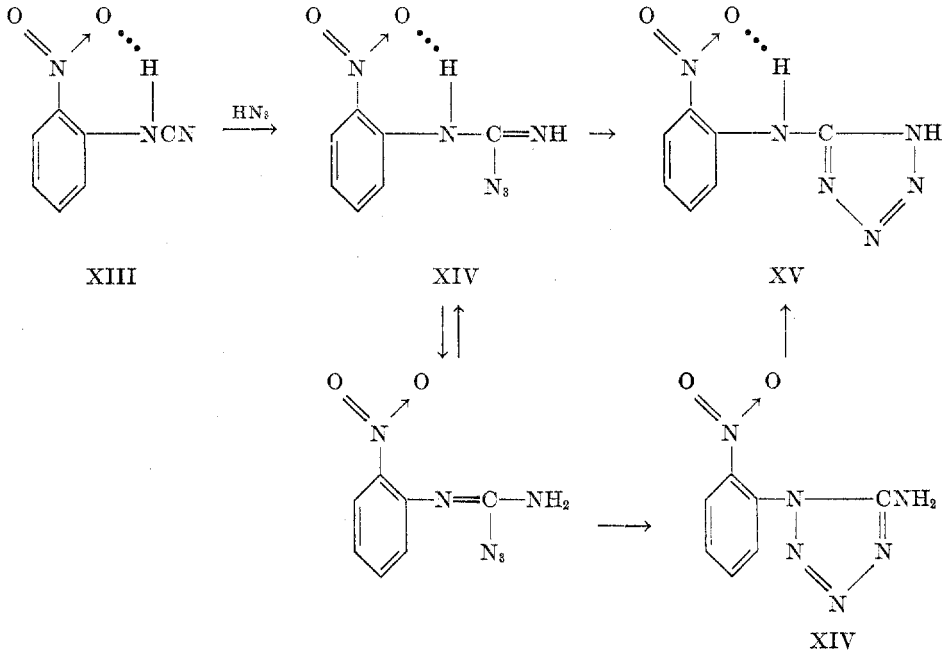


XII

Before the nitration product of 5-phenylaminotetrazole had been identified as a dinitro compound, the synthesis of the isomeric *meta*- and *ortho*-nitrophenyl derivatives was undertaken. *m*-Nitrophenylcyanamide on treatment with hydrazoic acid gave only a neutral product to which the structure of 1-*m*-nitrophenyl-5-aminotetrazole was assigned on the basis of elementary analysis and its chemical properties. On heating in a capillary tube this compound showed the same type of behavior noted for the *para* isomer. On boiling a suspension of the *meta* compound in xylene a change in physical appearance was apparent. After this treatment the compound was soluble in dilute aqueous sodium hydroxide and no longer showed the typical changes observed before rearrangement on heating in a capillary tube. These observations support the belief that rearrangement to 5-*m*-nitrophenylaminotetrazole had taken place. Potentiometric titration and ultraviolet absorption spectrum also support this conclusion.

The same sequence of reactions was undertaken with *o*-nitrophenylcyanamide. In this instance the course of the reaction with hydrazoic acid could be influenced not only by the electrical nature of the substituent but also by intramolecular hydrogen bonding involving the nitro group and the amino hydrogen of the cyanamide (XIII). It was conceivable that hydrogen bonding could prevent the tautomeric shift of the hydrogen in the *o*-nitrophenylguanyl azide (XIV) and cause the direct formation of 5-*o*-nitrophenylaminotetrazole (XV) upon cyclization. The steric effect of the *o*-nitro group could also influence cyclization in the same direction. In an initial experiment with *o*-nitrophenylcyanamide and hydrazoic acid the product was an alkali-insoluble material, possibly 1-*o*-nitrophenyl-5-aminotetrazole (XVI). The crude product showed the double melting point characteristic of 1-aryl-5-aminotetrazoles. After recrystallization from xylene the product was soluble in aqueous alkali, showed only a single melting point, and appeared to be 5-*o*-nitrophenylaminotetrazole. Attempts to duplicate the preparation of an alkali-insoluble product were not successful. At lower temperatures, 50 and 60°, no reaction took place; *o*-nitrophenylcyanamide was

recovered. At 70° *o*-nitrophenylcyanamide reacted slowly with hydrazoic acid to form only 5-*o*-nitrophenylaminotetrazole. At 80° the reaction was quite rapid and formation of 5-*o*-nitrophenylaminotetrazole was complete in two hours. Potentiometric titration, ultraviolet absorption spectrum, and the behavior of the product on heating were all in conformity with the structure assigned. Although, with one exception, the product formed by the interaction of *o*-nitrophenylcyanamide and hydrazoic acid has always been 5-*o*-nitrophenylaminotetrazole, it is impossible to exclude 1-*o*-nitrophenyl-5-aminotetrazole as an intermediate in the sequence.



XIII XIV XV XIV

Potentiometric titrations were done on all the acidic rearrangement products. The apparent dissociation constants are given in Table I. A typical titration curve is shown in Figure 1. The acids in order of decreasing strength are dinitro 5-phenylamino-, 5-*o*-nitrophenylamino-, 5-*p*-nitrophenylamino-, 5-*m*-nitrophenylamino-, and 5-phenylamino-tetrazole.

The ultraviolet absorption spectra, Figures 2–6, support the formulation of the acidic rearrangement products as 5-arylaminotetrazoles. It has been shown that tetrazole, 5-aminotetrazole, and 5-dimethylaminotetrazole are transparent throughout the range 230–450 mμ (13). The introduction of a phenyl group at the 5-position causes the appearance of a maximum in the range 232–240 mμ (14), although a phenyl group in the 1-position as in 1-phenyl-5-methyl- or 1-phenyl-5-amino-tetrazole is without effect. On the other hand nitration of the 1-phenyl group causes the appearance of a maximum at 250 mμ for the *meta* compound and 265 for 1-*p*-nitrophenyl-5-aminotetrazole. When the phenyl group is sepa-

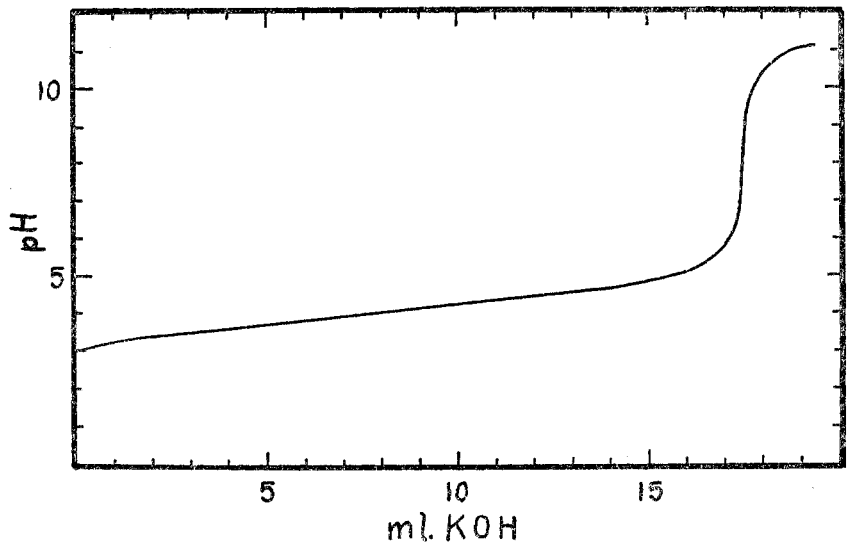


FIG. 1. POTENTIOMETRIC TITRATION OF 0.3773 g. OF 5-*o*-NITROPHENYLAMINOTETRAZOLE in 200 ml. of 50% (by volume) methanol with 0.1043 *N* potassium hydroxide.

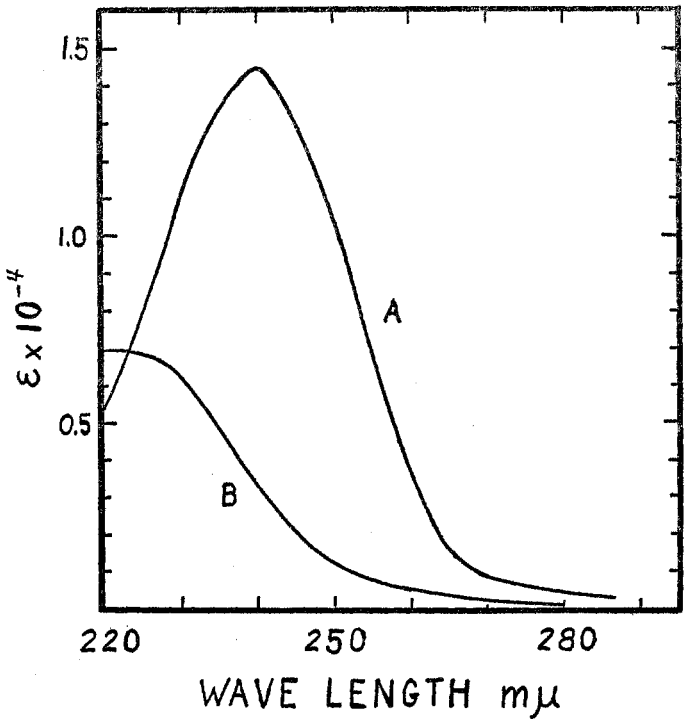


FIG. 2. ULTRAVIOLET ABSORPTION CURVES: A, 5-phenyltetrazole (0.017 g. per l.): B, 1-phenyl-5-methyltetrazole (0.020 g. per l.), both in 95% ethanol.

tated from the tetrazole by an amino group in the 5-position, only a small shift in the maximum to 250 mμ is noted. However, the further introduction of nitro groups into 5-phenylaminotetrazole causes the appearance of a second maximum

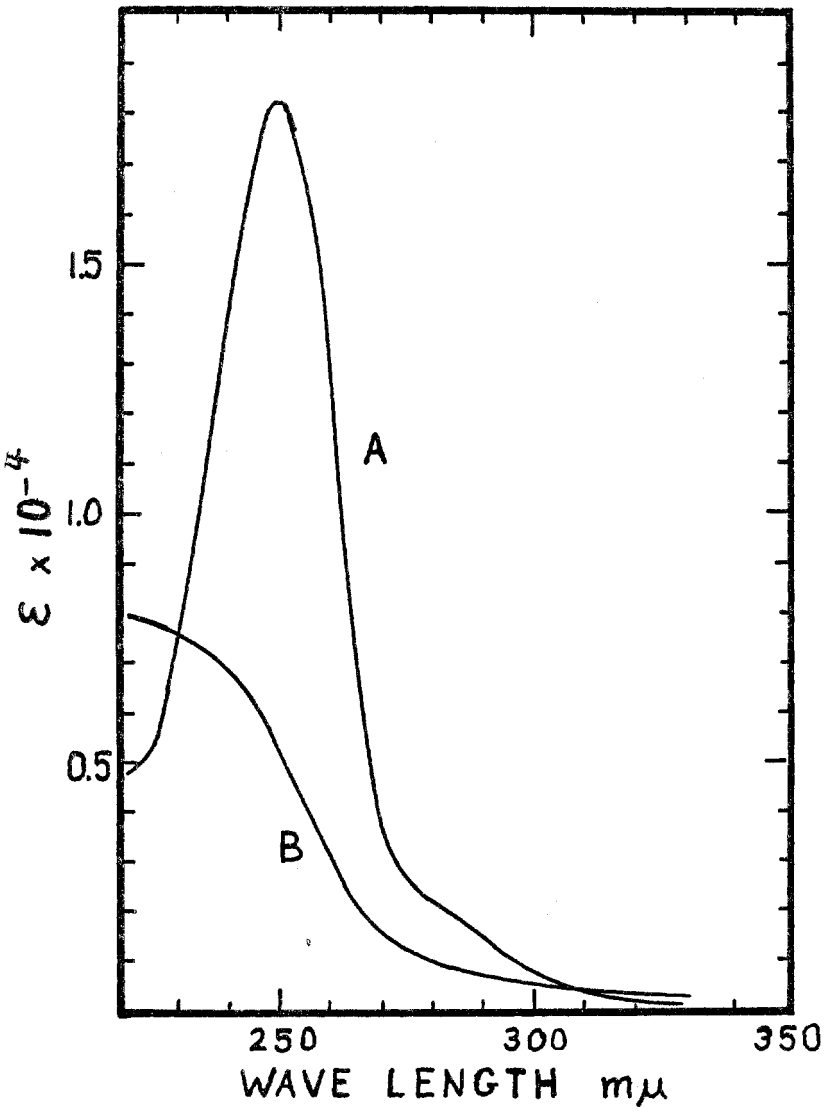


FIG. 3. ULTRAVIOLET ABSORPTION CURVES: A, 5-phenylaminotetrazole (0.011 g. per l.); B, 1-phenyl-5-aminotetrazole (0.010 g. per l.), both in 95% ethanol.

o-Nitrophenylaminotetrazole shows maxima at 243 and 415 mμ, while the *m*-nitro analog shows maxima at 253 and 360 mμ and the *p*-nitro derivative at 230 and 370 mμ. There is a rough correspondence of this second maximum with

the peaks shown by the nitroanilines at 400 mμ for the *ortho*, and 375 for both *m*- and *p*-nitroaniline (15). The similarity of the ultraviolet absorption of the nitroanilines and the 5-nitrophenylaminotetrazoles makes it rather unlikely that

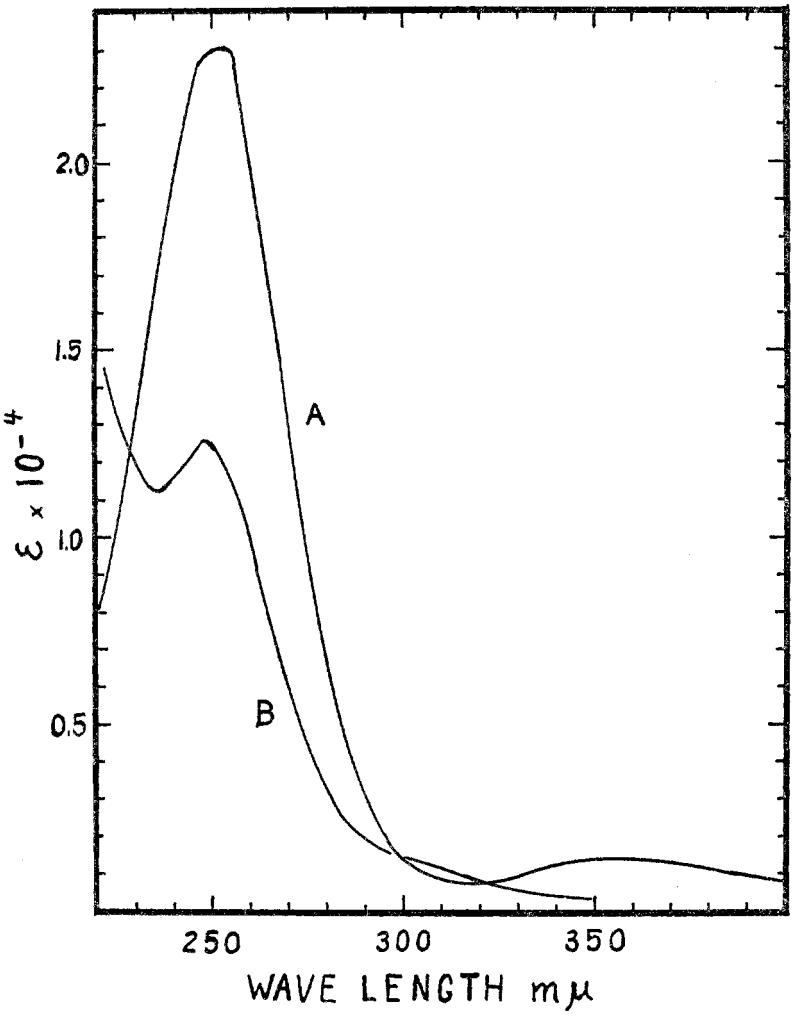


FIG. 4. ULTRAVIOLET ABSORPTION CURVES: A, 5-*m*-nitrophenylaminotetrazole (0.016 g. per l.): B, 1-*m*-nitrophenyl-5-aminotetrazole (0.019 g. per l.), both in 95% ethanol.

they could possess the pentazine structure (X) or other structures which do not retain the aniline configuration.

In the case of dinitro 5-phenylaminotetrazole, the first peak is shifted toward the red which suggests that the nitro groups are not both on the phenyl ring. Comparison of the 5-mononitrophenylaminotetrazoles with 5-phenylaminotetrazole indicates that nitration of the benzene ring causes a shift toward the

shorter wave lengths. However, the minimum and second maximum exhibited by the dinitro compound suggest that the nitroaniline structure is still intact.

EXPERIMENTAL[6, 7]

THERMAL REARRANGEMENT OF ALKYL AND ARYL 5-AMINOTETRAZOLES

5-Benzylaminotetrazole. 5-Benzylaminotetrazole (1) (1 g.) was heated in an oil-bath at 180–185° for five minutes. After cooling, the product was extracted with a few ml. of 0.1 *N* aqueous potassium hydroxide. The alkali-insoluble residue was then recrystallized from

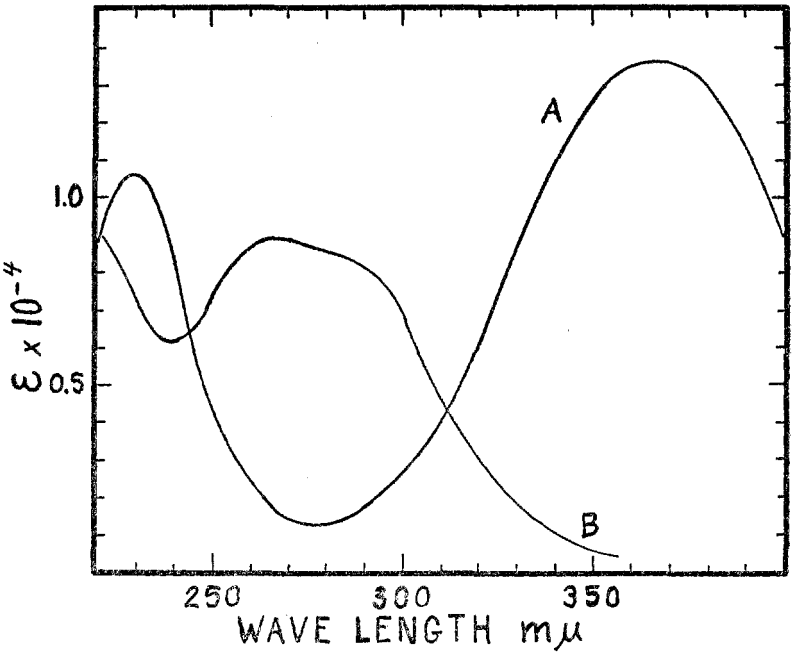


FIG. 5. ULTRAVIOLET ABSORPTION CURVES: A, 5-*p*-nitrophenylaminotetrazole (0.014 g. per l.); B, 1-*p*-nitrophenyl-5-aminotetrazole (0.020 g. per l.), both in 95% ethanol.

the minimum amount of 50% aqueous ethanol, yield 0.7 g. of fine, colorless needles, m.p. 190.5–191.5°. The product was identical with 1-benzyl-5-aminotetrazole (7). No organic product could be separated from the alkaline extract on neutralization.

1-Phenyl-5-aminotetrazole. 1-Phenyl-5-aminotetrazole (2 g.) (7) was suspended in 20 ml. of xylene and heated under reflux for one hour. After chilling, the solid was collected, dissolved in dilute aqueous potassium hydroxide, and filtered. The alkaline solution was almost colorless. Neutralization precipitated 5-phenylaminotetrazole as a colorless solid which crystallized from ethanol as needles, yield 1.8 g., m.p. 205–206°.

Anal. Calc'd for $C_7H_7N_5$: C, 52.2; H, 4.4; N, 43.5.

Found: C, 51.9, 52.2; H, 4.6, 4.4; N, 43.7, 43.5.

The presence of a primary amine function on the phenyl group of the rearrangement product was rendered unlikely by the following experiment. In identical qualitative tests the rearrangement product, 1-*p*-aminophenyl-5-methyltetrazole (16), 1-*p*-aminophenyl-5-amino-

[6] All melting points were taken in open capillaries; temperatures are corrected.

[7] Micro-analyses were done by the Micro-Tech Laboratories, Skokie, Illinois.

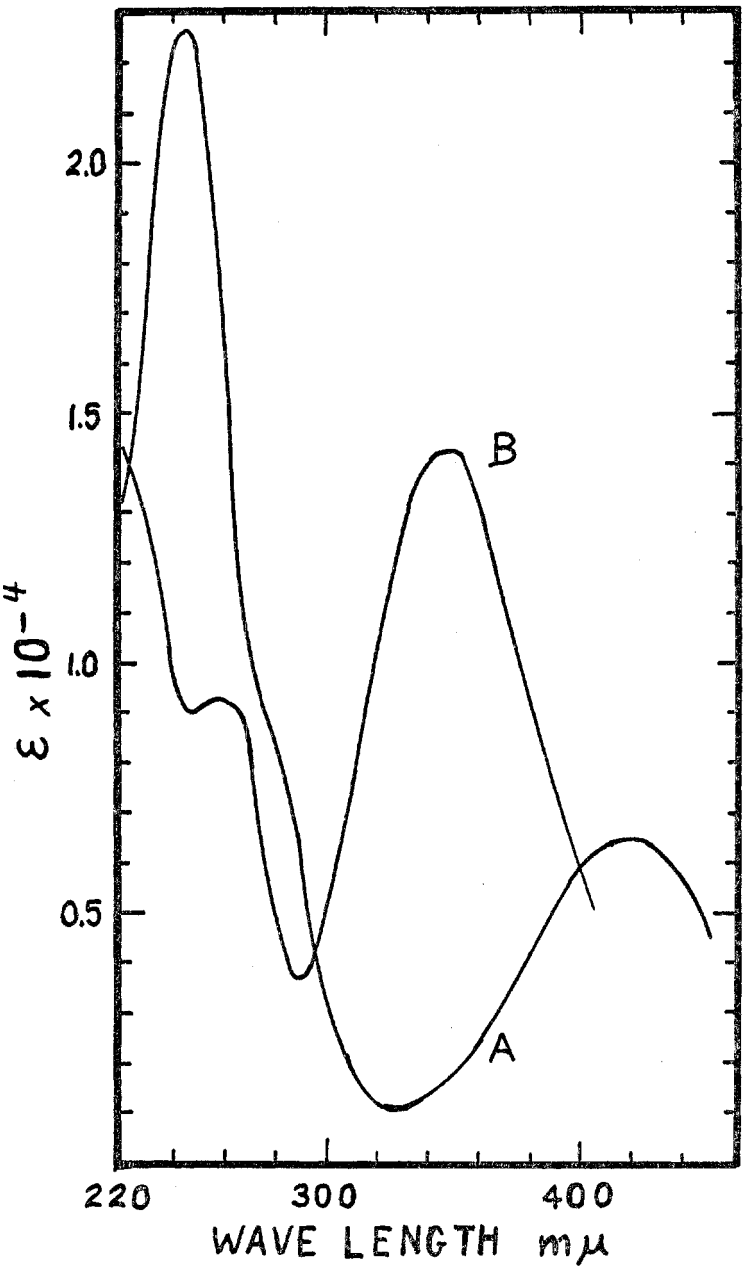


FIG. 6. ULTRAVIOLET ABSORPTION CURVES: A, 5-*o*-nitrophenylaminotetrazole (0.006 g. per l.); B, dinitro 5-phenylaminotetrazole (0.021 g. per l.), both in 95% ethanol.

tetrazole (7), and 1-methyl-5-*p*-aminophenyltetrazole (17) were treated with nitrous acid and then with an alkaline solution of β-naphthol. All gave typical red coupling products except the rearrangement product. It should be noted that the primary amine function of

the 1-substituted 5-aminotetrazoles is not diazotized on treatment with nitrous acid rather a nitroso derivative which does not couple is formed (2, 8).

1-p-Nitrophenyl-5-aminotetrazole (2 g.), obtained by interaction of hydrazoic acid and *p*-nitrophenylcyanamide (7), was suspended in 20 ml. of xylene and heated under reflux for two hours. After chilling, the yellow solid was collected and dried. Two recrystallizations of the 5-*p*-nitrophenylaminotetrazole from acetonitrile gave pale yellow needles, m.p. 221–223° with decomposition, yield 1.9 g. This material was readily soluble in dilute aqueous potassium hydroxide giving a deep red solution and was insoluble in dilute aqueous hydrochloric acid.

Anal. Calc'd for $C_7H_6N_6O_2$: C, 40.8; H, 2.9; N, 40.8.
Found: C, 40.2, 40.2; H, 3.3, 3.3; N, 40.9, 41.0.

The product obtained by nitration of 1-phenyl-5-aminotetrazole (7) behaved in exactly the same manner when heated in boiling xylene. The rearranged material dissolved in aqueous alkali to give a deep red solution. It crystallized from acetonitrile as pale yellow needles, m.p. 221–223° with decomposition.

Anal. Calc'd for $C_7H_6N_6O_2$: C, 40.8; H, 2.9; N, 40.8.
Found: C, 40.6, 40.8; H, 3.0, 3.0; N, 41.1, 41.0.

Reaction of hydrazoic acid with m-nitrophenylcyanamide. A solution of 6 g. of *m*-nitrophenylcyanamide (18) in 100 ml. of xylene containing 0.37 mole of hydrazoic acid and 50 ml. of absolute ethanol was heated under reflux for 14 hours. After distilling off most of the alcohol, cooling caused 1-*m*-nitrophenyl-5-aminotetrazole to separate as fine, tan needles, crude yield 6.3 g. Crystallization from acetonitrile gave fine, yellow needles, m.p. 226.5–228° with decomposition after shrinking at about 170°. The product was soluble in warm, dilute hydrochloric acid from which it separated on cooling, and was insoluble in dilute aqueous potassium hydroxide.

Anal. Calc'd for $C_7H_6N_6O_2$: C, 40.8; H, 2.9; N, 40.8.
Found: C, 40.7, 40.9; H, 2.9, 3.1; N, 40.8, 40.9.

Thermal rearrangement of 1-m-nitrophenyl-5-aminotetrazole. A suspension of 2 g. of 1-*m*-nitrophenyl-5-aminotetrazole in xylene was boiled under reflux for two hours. After cooling, the yellow solid was collected, dissolved in dilute aqueous potassium hydroxide and filtered. Neutralization precipitated 5-*m*-nitrophenylaminotetrazole as a pale yellow solid that crystallized from 95% ethanol as fine, pale yellow needles, m.p. 226° with decomposition. The product was readily soluble in dilute aqueous potassium hydroxide with a yellow color and was insoluble in dilute aqueous hydrochloric acid. Yield, 1.9 g.

Anal. Calc'd for $C_7H_6N_6O_2$: C, 40.8; H, 2.9; N, 40.8.
Found: C, 41.1, 41.2; H, 3.2, 3.2; N, 41.1, 41.1.

Reaction of hydrazoic acid with o-nitrophenylcyanamide. A solution of 3.9 g. of *o*-nitrophenylcyanamide[8] in 50 ml. of xylene containing 0.18 mole of hydrazoic acid and 50 ml. of absolute ethanol was heated under reflux for two hours. The temperature of the boiling reaction mixture was 78°. After distillation of most of the alcohol, the product separated as yellow needles on chilling. The crude product, yield 3.1 g., was completely soluble in dilute aqueous potassium hydroxide with a deep red color. Neutralization of the clear solution precipitated a yellow solid which crystallized from acetonitrile as very fine, bright yellow needles, m.p. 211° with decomposition. The acidic character of the product indicated that it was 5-*o*-nitrophenylaminotetrazole.

Anal. Calc'd for $C_7H_6N_6O_2$: C, 40.8; H, 2.9; N, 40.8.
Found: C, 41.0, 40.9; H, 3.1, 3.1; N, 41.0, 40.9.

When the reaction was repeated at 50° and 60°, the starting material was recovered unchanged; at 70° only the acidic product was isolated along with some unchanged starting material.

In a single experiment in which *o*-nitrophenylcyanamide was boiled under reflux in a

[8] *o*-Nitrophenylcyanamide was prepared essentially as described by Pierron (18). Better results were obtained when the reaction time was reduced from one hour to 30–40 minutes.

xylene solution of hydrazoic acid for about two hours (temperature of the boiling reaction mixture was not determined), the crude product that separated on cooling was insoluble in dilute aqueous alkali. On heating in a capillary tube the crude product melted at 151–153°, resolidified and then melted again at 201°. This material was not characterized more completely because on recrystallization from xylene it was converted into the alkali-soluble product described above. All attempts to repeat this experiment were unsuccessful; in each instance only the alkali-soluble material could be isolated as already described.

Potentiometric titrations. The acidic rearrangement products were titrated potentiometrically to determine their equivalent weights and apparent acidic dissociation constants. Weighed samples of the compounds sufficient to make approximately 0.01 *molar* solutions in 200 ml. of 50% (by volume) methanol were titrated with 0.1043 *N* potassium hydroxide solution. The *p*H was determined after each addition of alkali with a Beckman *pH* Meter, Model G. From these data the region of half neutralization was plotted on a large scale, the *p*H at half neutralization was determined from the plot, and the apparent acidic dissociation constant was calculated. Equivalent weights were also calculated from the titration data. The results are summarized in Table I and a typical titration curve is shown in Figure 1.

TABLE I

APPARENT ACIDIC DISSOCIATION CONSTANTS AND EQUIVALENT WEIGHTS OF SOME 5-ARYLAMINOTETRAZOLES IN 50% (BY VOLUME) AQUEOUS METHANOL

5-SUBSTITUTED TETRAZOLE	APPARENT pK_a	APPARENT $K_a \times 10^6$	EQUIVALENT WT.	
			Calc'd	Found
Phenylamino	5.49	3.2	161	161
p-Nitrophenylamino	4.34	46	206	209
m-Nitrophenylamino	4.85	14	206	208
o-Nitrophenylamino	4.08	83	206	207
Dinitro 5-phenylamino	3.38	420	251	254

Ultraviolet absorption measurements. The ultraviolet absorption spectra were determined with a Beckman quartz spectrophotometer, Model DU, using 10-mm. quartz cells and 95% ethanol as solvent. In addition to the aryl-5-aminotetrazole derivatives spectra of 5-phenyltetrazole (19) and 1-phenyl-5-methyltetrazole (20) were determined for comparison. The results are shown graphically in Figures 2–6.

SUMMARY

The rearrangement of a number of monosubstituted 5-aminotetrazoles has been described. At their melting points 5-alkylaminotetrazoles rearrange to the corresponding 1-alkyl-5-aminotetrazoles. However, in boiling xylene 1-aryl-5-aminotetrazoles rearrange to the corresponding 5-arylaminotetrazoles. This constitutes a convenient method for the synthesis of the otherwise difficultly available 5-arylaminotetrazoles. Possible mechanisms for the rearrangement are discussed. Apparent acidic dissociation constants in 50% methanol have been determined for the 5-arylaminotetrazoles. Ultraviolet absorption spectra for the 1-aryl-5-aminotetrazoles and the related 5-arylaminotetrazoles have been described and a correlation of their structures with the ultraviolet absorption spectra has been discussed.

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