The other tetrazoles all gave black tars on pyrolysis, from which identifiable samples of arimidazoles could not be obtained. However, 1-phenyl-5-*p*-nitrophenyltetrazole did yield a trace of solid of indefinite m.p. above 230°, but the amount was too small for further purification. The tar from 1-(3-quinolyl)-5-phenyltetrazole yielded a small amount of a mixture of basic solids, which was chromatographed on an alumina column with chloroform-alcohol mixture as eluent. A trace of an unidentified white solid was thus obtained, m.p. 288–290°.

Anal. Found: C, 67.24, 69.91; H, 5.61, 5.90; N, 17.35, 17.41.

Pyrolysis products of 1-phenyl-5-(p-chlorophenyl)tetrazole and 1-phenyl-5-p-tolyltetrazole. In additional experiments, the nature of all the pyrolysis products was examined, without special reference to yield. A 3.5-g. sample of 1-phenyl-5-*p*-chlorophenyltetrazole was heated for 5 hr. at 230–235° and worked up as previously described. The cooled dioxane–hydrochloric acid solution deposited 0.1 g. of solid, m.p. 305° dec., undepressed by mixture with an authentic sample of *p,p'*-dichlorocarbanilide (reported m.p. 305–306° dec.[11]). The filtrate was evaporated and the residue recrystallized from ethanol, giving a further quantity (0.35 g.), m.p. 300–301° dec. The filtrate was acidified with a little hydrochloric acid and enough water was added to cause crystallization. The precipitate (1.15 g.) melted at 235° after gradual shrinkage, and showed no melting point depression when mixed with authentic *p*-chlorocarbanilide.[12] The filtrate deposited more solid on standing; this proved to be 2-(*p*-chlorophenyl)benzimidazole, wt. 0.15 g., m.p. 305°. The filtrate from this substance gave only small amounts of impure material on further treatment.

In an analogous manner, 2.0 g. of 1-phenyl-5-*p*-tolyltetrazole yielded 0.2 g. of carbo-*p*-toluidide, m.p. 260–261°, 0.2 g. of 2-*p*-tolylbenzimidazole, and 0.65 g. of mixed ureas, from which repeated recrystallization from ethanol produced a pure sample of *p*-methylcarbanilide, m.p. 212°.

Catalyzed pyrolysis of 1,5-diphenyltetrazole. Samples of approximately equal volume each of 1,5-diphenyltetrazole and the potential catalytic agent were carefully mixed, and the behavior of the mixtures was observed while they were heated in melting point capillaries. Ground soft glass, alumina, silver powder, iron powder, and manganese powder did not alter the decomposition temperature (*ca.* 240°) significantly. Copper powder lowered the decomposition temperature to 175–180°. A 2.0-g. sample of 1,5-diphenyltetrazole was then mixed with 1.0 g. of copper powder and and heated at 190–200° for 2.25 hr. We could extract no 2-phenylbenzimidazole from the resulting black mass by the usual means, however, and the experiment was therefore abandoned.

ANN ARBOR, MICH.

(11) C. Manuelli and E. Ricca-Rossellini, *Gazz. chim. ital.*, **29II**, 124 (1899).

(12) H. Goldschmidt and B. Bardach, *Ber.*, **25**, 1364 (1892).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, MICHIGAN STATE UNIVERSITY]

Acetylation of Aryl Aminotetrazoles

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Acetylation of both 1-aryl-5-aminotetrazoles and 5-arylaminotetrazoles with boiling acetic anhydride leads to 1-aryl-5-acetamidotetrazoles. Acetylation of 5-arylaminotetrazoles in the cold with acetic anhydride in the presence of aqueous alkalies leads to 1-acetyl-5-arylaminotetrazoles that rearrange on heating to the 1-aryl-5-acetamidotetrazoles. Prolonged treatment of either 1-*p*-nitrophenyl-5-aminotetrazole, its acetyl derivative or 5-*p*-nitrophenylaminotetrazole with boiling acetic anhydride causes loss of nitrogen and rearrangement to 2-methyl-5-*p*-nitrophenylamino-1,3,4-oxadiazole. The latter was identified by degradation and by independent synthesis.

After it had been shown that 5-alkylaminotetrazoles undergo rearrangement on heating to form 1-alkyl-5-aminotetrazoles[2,3] and on acetylation to give 1-alkyl-5-acetamidotetrazoles,[4] it became of interest to investigate the behavior of arylaminotetrazoles under similar conditions. The formation of 1-phenyl-5-acetamidotetrazole on acetylation of 1-phenyl-5-aminotetrazole had been observed.[5] Since many 1-aryl-5-aminotetrazoles can be converted easily into 5-arylaminotetrazoles on heating near their melting points or even in refluxing xylene,[2,3] it was of particular interest to determine whether this rearrangement could be reversed by acetylation.

For reference 1-phenyl-5-acetamidotetrazole (Ia) was prepared from 1-phenyl-5-aminotetrazole (IIa) in boiling acetic anhydride. The same product (Ia) was obtained from 5-phenylaminotetrazole (IIIa) in boiling acetic anhydride. Hydrolysis of Ia with concentrated hydrochloric acid regenerated IIa. As already noted by von Braun and Keller[5] the acetyl derivative (Ia) is acidic and dissolves easily in aqueous alkalies or alkali carbonates. It is precipitated unchanged from these solutions on acidification. It resists hydrolysis in boiling, dilute, aqueous alkalies.

When IIIa was acetylated in cold, aqueous, alkaline solution by treatment with acetic anhydride, a different acetyl derivative (IVa) was obtained. IVa is not readily soluble in aqueous alkalies or alkali carbonates. Although IVa can be dissolved in aqueous potassium carbonate on pro-

(1) Present address: Abbott Laboratories, North Chicago, Ill.

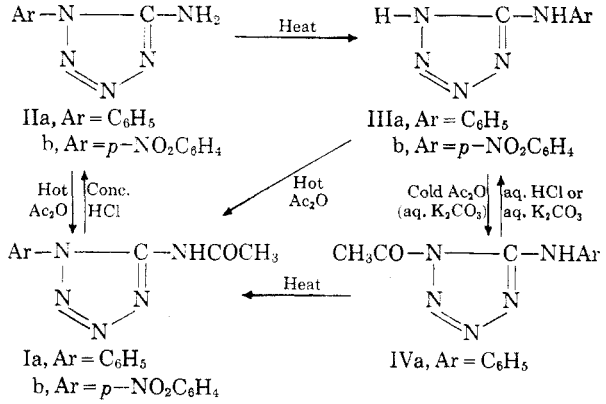
(2) W. G. Finnegan, R. A. Henry, and E. Lieber, *J. Org. Chem.*, **18**, 779 (1953).

(3) W. L. Garbrecht and R. M. Herbst, *J. Org. Chem.*, **18**, 1269 (1953).

(4) R. M. Herbst and W. L. Garbrecht, *J. Org. Chem.*, **18**, 1283 (1953).

(5) J. von Braun and W. Keller, *Ber.*, **65**, 1677 (1932).

longed shaking (several hours) at room temperature, the process is accompanied by hydrolysis; only IIIa precipitates on acidification of the solution. Similarly hydrolysis of IVa with concentrated hydrochloric acid regenerates IIIa. Although IVa has about the same melting point as Ia and mixture melting points are not depressed significantly, slight changes in the appearance of the solid (IVa) suggest rearrangement to Ia while heating in a capillary. When a solution of IVa in warm xylene is heated to boiling, complete conversion to Ia takes place rapidly. The latter precipitates from the boiling solution. The product so obtained is identical in all respects with the material obtained by acetylation of IIa or IIIa with hot acetic anhydride.



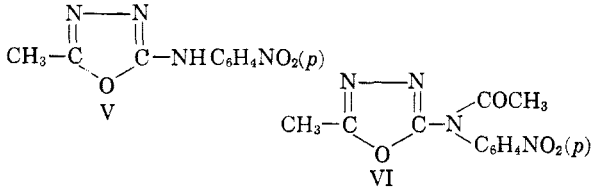
It is suggested that IVa is 1-acetyl-5-phenylaminotetrazole. The thermal rearrangement to Ia in boiling xylene is most easily accounted for on this basis either by way of an intermediate guanyl azide[2] or a bicyclic complex.[3] The possibility of the 2-acetyl-5-phenylaminotetrazole structure cannot be excluded although this would require rearrangement to the 1-acetyl derivative or dissociation in the process of going to Ia.

In order to determine whether the electrical character of the aromatic substituent would influence the rearrangement, both 1-*p*-nitrophenyl-5-aminotetrazole (IIb) and 5-*p*-nitrophenylaminotetrazole (IIIb) were acetylated in boiling acetic anhydride. In both instances 1-*p*-nitrophenyl-5-acetamidotetrazole (Ib) was formed rapidly. Identity of the products was established by elemental analysis, melting point behavior, and hydrolysis to IIb.

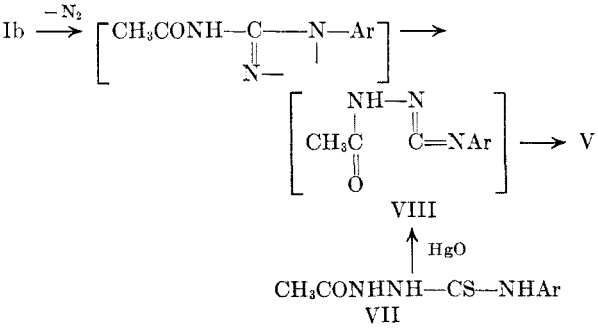
It should be emphasized that these rearrangements of arylaminotetrazoles make possible a complete cycle. Thermal rearrangement of II leads to III. Acetylation of III or thermal rearrangement of IV followed by hydrolysis leads back to II. This cycle was not realized with the alkylaminotetrazoles where the direction of rearrangement either thermally or on acetylation was the same.

During the acetylation of both IIb and IIIb the yield of acetyl derivative began to decrease when the heating period with acetic anhydride was extended beyond 0.5 hour. A second product of molecular formula $C_9H_8N_4O_3$ (V) began to appear as the heating period was extended and eventually became the only product excepting a small amount of a third product, $C_{11}H_{10}N_4O_4$ (VI). Inspection of the molecular formulas indicated that V might be formed from Ib by loss of a molecule of nitrogen. The behavior of Ib on heating, when it melted with gas evolution, resolidified, and remelted at approximately the melting point of V, was in accord with such a relationship. Prolonged heating of Ib with acetic anhydride caused almost complete conversion to V along with a small amount of VI. The molecular formulas indicated that VI might be the acetyl derivative of V, a relationship that was established by experiment. Hydrolysis of both V and VI with concentrated hydrochloric acid gave *p*-nitroaniline and hydrazine dihydrochloride. This accounted for all the nitrogen. By assuming that the methyl group was still present in V and VI all the hydrogen could be accounted for. A heterocyclic system containing two adjacent nitrogens, two carbons and an oxygen, with a methyl and a *p*-nitrophenylamino group as substituents, as in 2 - methyl - 5 - *p* - nitrophenylamino - 1,3,4 - oxadiazole, would satisfy the molecular formula and the observed behavior of V. In this case VI could be 2-methyl-5-*p*-nitrophenylacetamido-1,3,4-oxadiazole.

It should be pointed out that Ia did not undergo a similar decomposition. Even after heating with boiling acetic anhydride for five days, only Ia could be recovered.



The formation of the 1,3,4-oxadizaole from Ib requires the elimination of two nitrogen atoms from the tetrazole ring and the shift of an acetamido group from carbon to nitrogen. Stollé,[6] who had observed the formation of 2-acetamido-5-methyl-1,3,4-oxadiazole from 5-acetamidotetrazole on pro-



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

longed heating with acetic anhydride, has suggested a mechanism involving such a shift. A similar rearrangement involving an *N*-acetamidocarbodiimide (VIII) could apply in the present case.

Recently Huisgen *et al.*,[7] described the formation of 2,5-disubstituted 1,3,4-oxadiazoles upon acylation of 5-alkyl- and 5-aryltetrazoles in pyridine solution. The reaction is said to occur rapidly under mild conditions and in almost quantitative yields. An initial attack by the acylating agent at the 2-position is postulated followed by elimination of the 3 and 4 ring nitrogens and recyclization without rearrangement to form the oxadiazole. The formation of V from either Ib, IIb, or IIIb in the present case requires elimination of the 2 and 3 ring nitrogens followed by rearrangement and cyclization as already outlined. It is quite possible that the reaction described by Huisgen *et al.*, follows the same course, *i.e.*, acylation at the 1-position, elimination of the 2 and 3 ring nitrogens, rearrangement, and recyclization. Since the same products would result from either reaction course, the latter cannot be excluded categorically. Acylation of 5-substituted tetrazoles in the 1-position has been observed in this work and in earlier studies.[4]

Stollé[8] described the preparation of 2,5-dimethyl-1,3,4-oxadiazole from diacetylhydrazine and acetic anhydride on heating. Attempts to adapt this procedure by heating either 4-*p*-nitrophenylsemicarbazide or 1-acetyl-4-*p*-nitrophenylsemicarbazide with acetic anhydride were unsuccessful. The procedure of Hoggarth[9] involving thermal decomposition of *S*-methyl-1-acylthiosemicarbazides was applied to *S* - methyl - 1-acetyl - 4 - phenylthiosemicarbazide. In one instance a small amount of 2-methyl-5-phenylamino-1,3,4-oxadiazole was isolated but the principal product was usually a sulfur containing, alkali in soluble material, probably 3-methylmercapto-4-phenyl-5-methyl-1,2,4-triazole. An attempt to adapt the procedure of Stollé and Fehrenbach[10] which involves treatment of 1-acylthiosemicarbazides with lead oxide was likewise unsuccessful. When 1-acetyl-4-phenylthiosemicarbazide (VII, Ar = C_6H_5) was warmed with lead oxide in 95% ethanol, very little lead sulfide formed. From the reaction mixture a small quantity of an alkali soluble, sulfur containing product was isolated. The product, which is isomeric with 2-methyl-5-phenylamino-1,3,4-thiadiazole[11] and melts about 20° higher, may be the previously undescribed 3-mercapto-4-phenyl-5-methyl-1,2,4-triazole. Modification of Stollé and Fehrenbach's procedure by using mercuric oxide as a more active desulfurizing agent and boiling toluene to attain a higher reaction temperature gave reproducible, good yields of 2-methyl-5-phenylamino-1,3,4-oxadiazole from VII (Ar = C_6H_5). The reaction probably involves formation of a substituted carbodiimide (VIII, Ar = C_6H_5) as intermediate.

Nitration of 2-methyl-5-phenylamino-1,3,4-oxadiazole with cold mixed acid gave a mixture of V and 2-methyl-5-(2′,4′-dinitrophenylamino)-1,3,4-oxadiazole. The latter was separated by virtue of its greater solubility in cold chloroform. Its structure was established by elemental analysis and hydrolysis with concentrated hydrochloric acid to 2,4-dinitroaniline and hydrazine dihydrochloride.

EXPERIMENTAL[12]

1-Phenyl-5-aminotetrazole (IIa) was prepared from phenylthiourea by the procedure of Finnegan *et al.*,[2] without isolation of intermediates in 70% over-all yield. A procedure adapted from Herbst and Froberger[13] involving interaction of aniline successively with cyanogen bromide and hydrazoic acid[14] in aqueous ethanol gave 55–60% over-all yields.

1-p-Nitrophenyl-5-aminotetrazole (IIb) was prepared by nitration of IIa.[15]

5-Phenylaminotetrazole (IIIa) and *5-p-nitrophenylaminotetrazole* (IIIb) were made by rearrangement of IIa and IIb in boiling xylene.[3]

1-Phenyl-5-acetamidotetrazole (Ia). *A.* A solution of 5 g. of IIa in 50 ml. of acetic anhydride was boiled under reflux for 8 hr. (small amounts of IIa could usually be recovered with shorter heating periods). After dilution with 50 ml. of 95% ethanol the solution was evaporated to dryness on a steam bath. The product crystallized from 50% isopropyl alcohol as fine, colorless needles, yield 5.8 g. (91%), m.p. 214° with decomposition. (Von Braun and Keller[5] report m.p. 211°). The product is readily soluble in cold, aqueous alkalies and precipitates unchanged on acidification.

Anal. Calcd. for $C_9H_9N_5O$: C, 53.2; H, 4.5; N, 34.5. Found: C, 53.2; H, 4.7; N, 34.8.

A solution of 4 g. of IIa in 30 ml. of acetic anhydride was boiled under reflux for 120 hr. Ia was isolated in almost quantitative yield from the reaction mixture.

B. A solution of 1 g. of IIIa in 10 ml. of acetic anhydride was boiled under reflux for 2.5 hr. The product, Ia, was isolated as in the foregoing example. It was completely soluble in cold, dilute potassium hydroxide, precipitated on acidification, and crystallized from 99% isopropyl alcohol as fine, colorless needles, yield 0.6 g., m.p. and mixture m.p. 213° with decomposition.

Hydrolysis of 1-phenyl-5-acetamidotetrazole. A. A solution of 0.5 g. of Ia in 10 ml. of concentrated hydrochloric acid was evaporated to dryness on the steam bath. Recrystallization of the residue from 50% isopropyl alcohol gave 0.4 g. of IIa, m.p. 159.5–160.5° followed by resolidification and remelting at 202–203°.[15]

B. A solution of 0.5 g. of Ia in 10 ml. of 5% aqueous potassium hydroxide was boiled under reflux for 2 hr. Only faint turbidity developed on cooling the solution. Acidification of the clear filtrate with hydrochloric acid precipitated

(7) R. Huisgen, J. Sauer, and H. J. Sturm, *Angew. Chem.*, **70**, 272 (1958).

(8) R. Stollé, *Ber.*, **32**, 797 (1899).

(9) E. Hoggarth, *J. Chem. Soc.*, 1918 (1949).

(10) R. Stollé and K. Fehrenbach, *J. prakt. Chem.*, **122**, 289 (1929).

(11) G. Pulvermacher, *Ber.*, **27**, 613 (1894).

(12) Analyses were done by Micro-Tech Laboratories, Skokie, Ill. Melting points were taken in open capillaries and are not corrected.

(13) R. M. Herbst and C. F. Froberger, *J. Org. Chem.*, **22**, 1050 (1957).

(14) Reactions with cyanogen bromide or hydrazoic acid must be done in a well ventilated hood. Contact or inhalation of the highly toxic vapors should be avoided.

(15) W. L. Garbrecht and R. M. Herbst, *J. Org. Chem.*, **18**, 1014 (1953).

Ia quantitatively, m.p. and mixture m.p. 214° with decomposition after crystallization from 99% isopropyl alcohol.

Acetyl-5-phenylaminotetrazole (IVa). A solution of 3.2 g. (0.02 mole) of IIIa in 35 ml. of water containing 8.3 g. (0.06 mole) of anhydrous potassium carbonate was chilled in an ice bath. Acetic anhydride (6.1 ml., 90%, 0.06 mole) was added dropwise during 10 min. with continuous manual agitation and cooling. A drop of caprylic alcohol helped control foaming near the end of the reaction. The product, which started to precipitate almost immediately upon addition of acetic anhydride, was filtered off, washed with ice cold 10% potassium hydroxide and then water; crude yield 3.9 g., air dried. Recrystallization was effected by dissolving the crude product in cold benzene (125 ml.) and diluting the clear solution with 250 ml. of petroleum ether. The acetyl derivative separated as small, rod-like prisms, yield 3.1 g., m.p. 209° with decomposition on slow heating, 213° after softening at 210° on rapid heating. Mixture m.p. with Ia is only slightly depressed.

Anal. Calcd. for $C_9H_9N_5O$: C, 53.2; H, 4.5; N, 34.5. Found: C, 55.3; H, 4.6; N, 34.6.

The product is moderately soluble in cold acetone, ethyl acetate, ethylene chloride, and benzene, insoluble in petroleum ether, water, cold aqueous potassium carbonate, or potassium hydroxide. It dissolves in the latter two solvents slowly on prolonged (several hours) agitation at room temperature.

Hydrolysis of acetyl-5-phenylaminotetrazole. A. IVa, 0.5 g., dissolved completely in 5 ml. of cold concentrated hydrochloric acid. After evaporation to dryness on a steam bath the residue of 5-phenylaminotetrazole (IIIa) was recrystallized from 50% isopropyl alcohol, yield 0.4 g., m.p. and mixture m.p. 202.5–203° with decomposition.

B. IVa, 0.5 g., was suspended in 25 ml. of cold 4% potassium carbonate solution. On standing at room temperature for 1.5 hr. with frequent shaking the acetyl derivative dissolved completely. On acidification 5-phenylaminotetrazole (IIIa) precipitated and was recrystallized from 75% isopropyl alcohol, yield 0.3 g., m.p. and mixture m.p. 202.5–203° with decomposition.

Rearrangement of IVa in boiling xylene. IVa, 0.5 g., was suspended in 10 ml. of cold xylene. The slightly turbid solution, formed on warming gently and quickly, was filtered rapidly. The clear filtrate was heated to boiling and maintained at this temperature for about a minute while a voluminous, finely crystallized product separated. The mixture was cooled, dilute with petroleum ether, and filtered. The product crystallized from 99% isopropyl alcohol as a cottony mass of needles typical of Ia, yield 0.35 g., m.p. and mixture m.p. 214° with decomposition.

The entire product was dissolved in 5 ml. of cold concentrated hydrochloric acid and evaporated to dryness on a steam bath. The residue of 1-phenyl-5-aminotetrazole (IIa) crystallized from 50% isopropyl alcohol as needles, yield 0.3 g., m.p. and mixture m.p. 159° followed by resolidification and remelting at 203° with decomposition.

1-p-Nitrophenyl-5-acetamidotetrazole (Ib). *A.* Acetic anhydride (20 ml.) containing 2 g. of IIb was boiled under reflux for 0.5 hr. The hot solution was diluted with 10 ml. of isopropyl alcohol and 5 ml. of water and evaporated to dryness on a steam bath. The residue crystallized from 99% isopropyl alcohol as pale, yellow needles, yield 1.7 g. (74%), m.p. 191° with gas evolution followed by resolidification and remelting at 224–225°. The product is not soluble in dilute aqueous alkalies.

Anal. Calcd. for $C_9H_8N_6O_3$: C, 43.6; H, 3.3; N, 33.9. Found: C, 43.5; H, 3.3; N, 34.1.

In a similar experiment the reflux time was extended to 1 hr. Only 44% of Ib, m.p. 190° with gas evolution, resolidification and remelting at 223–224° was obtained. When the reflux period was extended to 3 hr. only a small amount of Ib separated from the isopropyl alcohol solution of the crude product. Evaporation of the filtrate left a yellow solid that dissolved in aqueous alkali with an intense red color. Recrystallization of the residue from a small volume of 99% isopropyl alcohol gave V as a yellow powder, m.p. 233–234°.

B. A solution of 1.5 g. of IIIb in 20 ml. of acetic anhydride was boiled under reflux for 45 min. The reaction mixture was diluted with 20 ml. of isopropyl alcohol and evaporated to dryness on a steam bath. The residue crystallized from 99% isopropyl alcohol as pale, yellow needles, yield 0.9 g., m.p. 189° with gas evolution, resolidification and remelting at 221°. Mixture m.p. with the material from IIb was not depressed.

Hydrolysis of 1-p-nitrophenyl-5-acetamidotetrazole. One gram of Ib was dissolved in 40 ml. of 20% hydrochloric acid. The solution was evaporated to dryness on a steam bath. The residue was dissolved in hot water, the solution made just acid to Congo red with hydrochloric acid and chilled. The solid that separated was recrystallized from 50% isopropyl alcohol, m.p. and mixture m.p. with IIb 175° followed by resolidification and remelting at 221°.[15]

2-Methyl-5-p-nitrophenylamino-1,3,4-oxadiazole (V). *A.* A solution of 20 g. of IIb in 200 ml. of acetic anhydride was boiled under reflux for 12 hr. About 125 ml. of acetic anhydride was removed by distillation and the residual solution was diluted with 50 ml. of isopropyl alcohol and evaporated almost to dryness on a steam bath. Crystallization of the crude product from 99% isopropyl alcohol gave a solid that appeared to be a mixture of two crystal types one of which could be extracted with cold chloroform. The chloroform insoluble material crystallized from 99% isopropyl alcohol as yellow needles, m.p. 232–233°. The product dissolves in dilute aqueous alkalies with an intense red color.

Anal. Calcd. for $C_9H_8N_4O_3$: C, 49.1; H, 3.7; N, 25.5. Found: C, 49.4; H, 3.9; N, 25.3.

The chloroform extracts were evaporated to dryness. The residue crystallized from 99% isopropyl alcohol as transparent, pale, yellow prisms, m.p. 158°. Elemental analysis suggested that this material might be 2-methyl-5-*p*-nitrophenylacetamido-1,3,4-oxadiazole (VI) the acetyl derivative of V.

Anal. Calcd. for $C_{11}H_{10}N_4O_4$: C, 50.4; H, 3.8; N, 21.4. Found: C, 50.5; H, 4.0; N, 22.0.

B. A solution of 3 g. of Ib in 20 ml. of acetic anhydride was boiled under reflux for 4.5 hr. After dilution with 10 ml. of glacial acetic acid and 5 ml. of water the solution was evaporated to dryness on a steam bath. The residue was allowed to stand under saturated potassium bicarbonate solution for 36 hr. The insoluble material was washed several times with dilute hydrochloric acid and water and crystallized from 50% isopropyl alcohol, pale, yellow needles, m.p. and mixture m.p. with V 230–231°.

Hydrolysis of 2-methyl-5-p-nitrophenylamino-1,3,4-oxadiazole. A solution of 1 g. of V in 20 ml. of concentrated hydrochloric acid was boiled under reflux for 2 hr. The solid that crystallized on cooling was separated by filtration and appeared to be hydrazine dihydrochloride, m.p. 192–194°. It gave a positive test for chloride ion with silver nitrate and when shaken with an ethanolic solution of benzaldehyde, a yellow precipitate of benzalazine formed, m.p. and mixture m.p. 90–91°. The aqueous filtrate from the hydrazine dihydrochloride was evaporated to dryness on a steam bath. The residue crystallized from water as yellow needles identical with *p*-nitroaniline, m.p. and mixture m.p. 146°.

Hydrolysis of 2-methyl-5-p-nitrophenylacetamido-1,3,4-oxadiazole. VI was hydrolyzed with concentrated hydrochloric acid as described for V in the foregoing example. Hydrazine dihydrochloride and *p*-nitroaniline were isolated from the hydrolyzate and identified as just described.

Synthesis of 2-methyl-5-p-nitrophenylamino-1,3,4-oxadiazole (V). *A.* Attempts to adapt the procedure of Stollé[8] followed two courses. Equimolar amounts of *p*-nitrophenyl isocyanate and monoacethydrazide were melted together. The mixture resolidified almost immediately to form a product, m.p. 300–301°, which was refluxed with acetic anhydride for 16 hr. Evaporation of the acetic anhydride left a

solid, m.p. 209–210° after recrystallization from 99% isopropyl alcohol.

The same product was obtained when 2 g. of 4-*p*-nitrophenylsemicarbazide was boiled under reflux with 50 ml. of acetic anhydride for 20 hr. Since the material was not identical with either V or VI, it was not further characterized.

B. Following the technique described by Hoggarth[9] 10 g. of 1-acetyl-4-phenylthiosemicarbazide[16] was dissolved in 50 ml. of *N* sodium hydroxide. A solution of 7.6 g. of methyl iodide in 10 ml. of 99% isopropyl alcohol was added and the mixture shaken thoroughly for 5 min. The precipitate of *S*-methyl derivative was filtered off and air dried, yield 4.2 g. (39%), m.p. 121–124°. The crude *S*-methyl derivative (3 g.) was dissolved in 60 ml. of 99% isopropyl alcohol and boiled under reflux for 20 hr. Evaporation of the solvent gave a small amount of 2-methyl-5-phenylamino-1,3,4-oxadiazole, m.p. 174–175°, dense, pyramidal prisms, after several crystallizations from isopropyl alcohol.

Anal. Calcd. for $C_9H_9N_3O$: C, 61.7; H, 5.2; N, 24.0. Found: C, 61.6; H, 5.2; N, 23.9.

The major product of the thermal decomposition was always a sulfur containing material that was soluble in dilute acids but insoluble in bases. The material crystallized from isopropyl alcohol as transparent prisms, m.p. 119–120°. Elemental analysis indicated that the product might be 3-methylmercapto-4-phenyl-5-methyl-1,2,4-triazole.

Anal. Calcd. for $C_{10}H_{11}N_3S$: C, 58.5; H, 5.4; N, 20.5; S, 15.6. Found: C, 58.3; H, 5.7; N, 20.7; S, 15.3.

C. In an attempt to adapt the procedure of Stollé and Fehrenbach[10] 3.3 g. of 1-acetyl-4-phenylthiosemicarbazide was heated with stirring for 26 hr. with 3.5 g. of lead oxide suspended in 150 ml. of 95% ethanol. The lead oxide failed to darken beyond a faint gray. From the hot ethanolic filtrate 2 g. of a sulfur containing product was isolated, m.p. 217–218° after several crystallizations from 95% ethanol. Elemental analysis and the solubility of the compound in dilute aqueous alkalies suggested that the compound might be 3-mercapto-4-phenyl-5-methyl-1,2,4-triazole. The isomeric 2-methyl-5-phenylamino-1,3,4-thiadiazole structure has already been assigned to a compound, m.p. 193–194°.[11]

D. A mixture of 15 g. of 1-acetyl-4-phenylthiosemicarbazide and 15.5 g. of yellow mercuric oxide suspended in 800 ml. of toluene was boiled under reflux with stirring for 20 min. The mercuric oxide darkened rapidly and became black a few minutes after the toluene started to boil. The hot suspension was filtered rapidly. The colorless needles that separated from the filtrate on cooling were recrystallized from 99% isopropyl alcohol, yield 8 g. (64%), m.p. 175°, dense, pyramidal prisms. Mixture m.p. with 2-methyl-5-phenylamino-1,3,4-oxadiazole (see *B* above) not depressed.

Finely powdered 2-methyl-5-phenylamino-1,3,4-oxadiazole (16.8 g.) was added in small portions with stirring to an ice cold mixture of 25 ml. each of concentrated sulfuric and nitric acids. Stirring and cooling were continued until the solid dissolved completely. The nitration mixture was poured onto 400 g. of ice. The yellow, flocculent precipitate was filtered off, washed with water and dried at room temperature under reduced pressure. The crude product (21 g.) was extracted with several portions of cold chloroform. The insoluble portion was recrystallized several times from absolute methanol, pale, yellow needles, m.p. 232–233°. The mixture m.p. with V was not depressed.

The chloroform extracts were evaporated to dryness. The yellow residue was separated manually from a trace of orange material on the sides of the flask and recrystallized several times from absolute methanol, m.p. 218–219°. The product proved to be 2-methyl-5-(2′,4′-dinitrophenylamino)-1,3,4-oxadiazole.

Anal. Calcd. for $C_9H_7N_5O_5$: C, 40.8; H, 2.7; N, 26.4. Found: C, 40.7; H, 2.7; N, 26.9.

On hydrolysis of a small amount of the dinitro compound with boiling hydrochloric acid, 2,4-dinitroaniline, m.p. and mixture m.p. 178–180°, separated from the aqueous hydrolyzate. On standing the filtrate deposited crystals of hydrazine dihydrochloride, m.p. 195–200° with gas evolution; benzalazine, m.p. and mixture m.p. 92–93° was formed with benzaldehyde in alcoholic solution.

The 2-methyl-5-*p*-nitrophenylamino-1,3,4-oxadiazole (1.5 g.) synthesized above was acetylated by boiling for 8.5 hr. with 30 ml. of acetic anhydride. After dilution with isopropyl alcohol the reaction mixture was evaporated to dryness on a steam bath. The residue was extracted with chloroform. The chloroform soluble acetyl derivative was recrystallized several times from absolute methanol, m.p. and mixture m.p. with VI 157–159°.

Anal. Calcd. for $C_{11}H_{10}N_4O_4$: C, 50.4; H, 3.8; N, 21.4. Found: C, 50.2; H, 3.9; N, 21.6.

EAST LANSING, MICH.

(16) P. K. Bose, *J. Indian Chem. Soc.*, **2**, 102 (1925).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, DE PAUL UNIVERSITY]

Relative Acidities of 5-(Substituted Phenyl)amino-4-phenyl-1,2,3-triazoles

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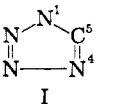
The relative acidities of 5-(substituted phenyl)amino-4-phenyl-1,2,3-triazoles have been studied by ultraviolet absorption spectrophotometry and electrometric titrations in dimethylformamide. The results are in agreement with the electronic mechanism proposed earlier, for the equilibria in the substituted amino tetrazoles and triazoles.

There is considerable evidence that the tetrazole ring, I, is electronegative and about as strongly so as an acetyl group.[1] Considering the electronegativities of carbon and nitrogen, one would expect the 1,2,3-triazole ring, II, to be less electronegative than in the tetrazole ring. One principal difference



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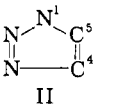

II

between structures I and II is that the latter is able to have different substituents in the 4-position. In this communication a further study of the electrical effects of these two ring systems is reported, involving an investigation of the acidities of 5-(substi-

(1) R. A. Henry, W. G. Finnegan, and E. Lieber, *J. Am. Chem. Soc.*, **77**, 2264 (1955); C. N. R. Rao, *J. Sci. Ind. Research (India)*, **17B**, 89 (1958).