Anal. Calcd for $C_{13}H_{10}N_6$: C, 62.40; H, 4.00; N, 33.60. Found: C, 62.17; H, 3.95; N, 33.43.

2-(2-Azido-4-methylphenyl)benzotriazole.—In 30 ml of water was slurred 1.03 g (0.046 mol) of finely powdered 2-(2-amino-4-methylphenyl)benzotriazole and 10 ml of concentrated hydrochloric acid was added all at once. The slurry was cooled 0° by the addition of ice and then diazotized by the dropwise addition of 0.37 g of sodium nitrite. After stirring for 1 hr, all of the hydrochloride salt had dissolved. The solution was filtered to remove trace impurities. To the cold solution was added 0.30 g of sodium azide in a minimim of water. After 30 min, the precipitated solid was filtered and washed with water: yield 1.02 g (89%); mp 88°.

Anal. Calcd for $C_{13}H_{10}N_6$: C, 62.40; H,4.00; N, 33.60. Found: C, 62.28; H, 4.02; N, 33.52.

2-(2-Azido-5-methylphenyl)benzotriazole.—In 25 ml of water was placed 2.9 g (0.013 mol) of finely powdered 2-(2-amino-5-methylphenyl)benzotriazole. To this slurry was added all at once 10 ml of concentrated hydrochloric acid. Ice was added to cool the mixture to 0° and it was then diazotized by dropwise addition of 1.0 g of sodium nitrite in 10 ml of water. After 40 min, the hydrochloride salt had all dissolved. The solution was filtered and to the filtrate was added 1.0 g of sodium azide in water. After 30 min, the solid azide was filtered and washed with water: yield 2.85 g (88%); mp 90°. Recrystallization from petroleum ether (bp 60–90°) gave an analytical sample, mp 91°.

Anal. Calcd for $C_{13}H_{10}N_6$: C, 62.40; H, 4.00; N, 33.60. Found: C, 62.56; H, 4.11; N, 33.79.

2-Methyl-5,6H-dibenzo[*b,f*]-1,3a,4,6a-tetraazapentalene (III).—2-(Azido-5-methylphenyl)benzotriazole (2.85 g, 0.0114 mol) was dissolved in 8 ml of decalin and the solution was refluxed for 80 min. At the end of this time it was cooled in ice. The solid which separated was filtered and washed with petroleum ether: yield 1.83 g (72%): mp 185–188°. Recrystallization from ethanol gave an analytical sample, mp 194°.

Anal. Calcd for $C_{13}H_{10}N_4$: C, 70.27; H, 4.50; N, 25.23. Found: C, 70.42; H, 4.60; N, 24.90.

3-Methyl-5,6H-dibenzo[*b,f*]-1,3a,4,6a-tetraazapentalene (IV).—2-(2-Azido-4-methylphenyl)benzotriazole (0.91 g 0.00364 mol) was placed in 10 ml of decalin and the solution was heated to 165–175° for 15 min, followed by 15 min of refluxing at 195°. On cooling, needles separated, which were filtered and washed with petroleum ether: yield 0.68 g (94%) of IV; mp 198°. Recrystallization from methanol and acetone gave an analytical sample.

Anal. Calcd for $C_{13}H_{10}N_4$: C, 70.27; H, 4.50; N, 25.23. Found: C, 70.48; H, 4.56; N, 24.89.

Thermal Decomposition of 2-(2-Azidophenyl)-5-methylbenzotriazole.—In 50 ml of decalin was placed 4.74 g (0.0189 mol) of the azide and the solution was heated to 165–175° for 40 min. After standing overnight at room temperature, the mixture of III and IV was filtered and washed with petroleum ether: yield 3.36 g (80%); mp 184–185°. Recrystallization did not raise the melting point. Attempts to separate the mixture by chromatography on alumina were unsuccessful.

Anal. Calcd for $C_{13}H_{10}N_4$: C, 70.27; H, 4.50; N, 25.23. Found: C, 70.22; H, 4.64; N, 25.19.

Registry No.—I, 7120-73-2; II, 16710-40-0; III, 16710-41-1; IV, 16710-42-2; 2-(2-nitrophenyl)-5-methylbenzotriazole, 16710-43-3; 2-(2-nitro-5-methylphenyl)benzotriazole, 16710-44-4; 2-(2-nitro-4-methylphenyl)benzotriazole, 16710-45-4; 2-(2-amino-4-methylphenyl)benzotriazole, 16710-46-6; 2-(2-amino-5-methylphenyl)benzotriazole, 16710-47-7; 2-(2-aminophenyl)-5-methylbenzotriazole, 16710-48-8; *o,o'*-diazidoazobenzene, 3364-08-7; V, 16710-49-9; VI, 16710-50-2.

Notes

Thermal Decomposition of *o*-Azidoazobenzenes. II. Synthesis of 2-Substituted Benzotriazoles[1]

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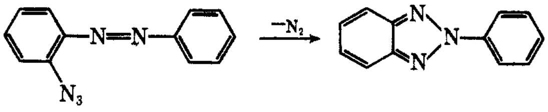
The fact that thermal decomposition of *o*-azidoazobenzenes results in cyclization to give 2-benzotriazoles was reported by Zincke and coworkers[2] many years ago. Since this early work, the reaction has escaped attention until more recent times when Carboni and coworkers[3] reported a number of examples. The lack of study of the reaction has undoubtedly been due in part to the difficulty in synthesizing *o*-aminoazobenzenes, from which the *o*-azidoazobenzenes could be prepared.



The report of the synthesis of *o*-azidoaniline,[4] however, has provided the needed starting material for two routes to *o*-azidoazobenzenes. The first of these involves the condensation of *o*-azidoaniline with arylnitroso compounds, examples of which are reported in paper I.[5] The second involves the diazotization of *o*-azidoaniline, followed by coupling of the diazonium salt with various phenols and amines. It is this latter method that is described in this paper.

o-Azidoaniline was found to diazotize smoothly at 0° using sodium nitrite in dilute hydrochloric acid. The cold diazonium salt solution was quite stable. No explosions were encountered. When the diazonium salt solution was added to cold basic solutions of phenol, *p*-cresol, and 2-naphthol, coupling occurred to give the

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(1) Presented at 149th National Meeting of the American Chemical Society, Detroit, Mich., April 1965.

(2) (a) T. Zincke and J. Jaenke, *Ber.*, **21**, 540 (1888); (b) T. Zincke and A. T. Lawson, *ibid.*, **20**, 1176 (1887).

(3) (a) R. A. Carboni and J. E. Castle, *J. Amer. Chem. Soc.*, **84**, 2453 (1962); (b) R. A. Carboni, U. S. Patent 2,904,544 (Sept 1959); (c) R. A. Carboni, U. S. Patent Reissue 25,238 (Sept 1962); (d) R. A. Carboni, J. E. Castle, and H. E. Simmons, *J. Amer. Chem. Soc.*, **89**, 2618 (1967); (e) R. A. Carboni, J. C. Kauer, W. R. Hatchard, and R. J. Harder, *ibid.*, 2626 (1967); (f) J. C. Kauer and R. A. Carboni, *ibid.*, 2633 (1967).

(4) (a) P. A. S. Smith, J. H. Hall, and R. O. Kan, *ibid.*, **84**, 485 (1962); (b) L. Krbechek and H. Takimoto, *J. Org. Chem.*, **29**, 3630 (1964).

(5) J. H. Hall, J. G. Stephanie, and D. K. Nordstrom, *ibid.*, **33**, 2951 (1968).

TABLE I

PHYSICAL PROPERTIES AND ANALYTICAL DATA

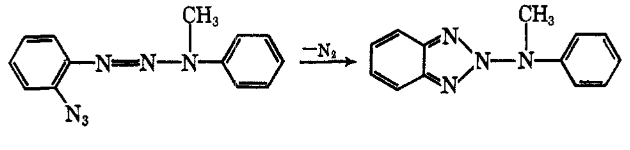
Compound[a]	Yield, %	Mp, °C	Crystallization solvent	Formula	Calcd, % C	Calcd, % H	Calcd, % N	Found, % C	Found, % H	Found, % N
			Azides							
4-(2-Azidophenylazo)phenol	18	53–61 dec	*b*							
2-(2-Azidophenylazo)-4-methylphenol	78	73–76 dec	EtOH–H_2O	$C_{13}H_{11}N_5O$	61.6	4.37		67.6[c]	4.92[c]	
1-(2-Azidophenylazo)-2-naphthol		*d*	C_6H_6	$C_{16}H_{11}N_5O$	66.42	3.84		65.82	3.75	
N-Methyl-N-(2-azidophenylazo)aniline	90	64–66 dec	Petroleum ether	$C_{13}H_{12}N_6$	61.89	4.79		62.05	4.85	
4-(2-Azidophenylazo)-N,N-dimethylaniline	86	102 dec[e]	MeOH	$C_{14}H_{14}N_6$	63.14	5.30		63.38	5.20	
2-Azidodiazoaminobenzene		81–86	EtOH							
2,2′-Diazidodiazoaminobenzene	81	123	EtOH	$C_{12}H_9N_9$	51.61	3.25	45.14	51.37	3.25	45.39
			Benzotriazoles							
2-(2-Hydroxy-5-methylphenyl)-	99	131.5–133[f,g]	EtOH	$C_{13}H_{11}N_3O$	69.32	4.93		69.82	5.02	
2-(4-Hydroxyphenyl)-		220.5–221.5[h]								
2-(4-Dimethylaminophenyl)-	100	185.5–186.0	EtOH	$C_{14}H_{14}N_4$	70.56	5.92	23.64	70.95	6.04	23.15
2-(N-Methylanilino)-	63	99–101	EtOH	$C_{13}H_{12}N_4$	69.62	5.39		69.65	5.29	
2-(2-Hydroxy-1-naphthyl)-	45	144	EtOH–H_2O	$C_{16}H_{11}N_3O$	73.55	4.24		73.43	4.40	
2-(4-Hydroxy-1-naphthyl)-	20	202–203	EtOH–H_2O	$C_{16}H_{11}N_3O$	73.55	4.24		73.46	4.30	

[a] Registry no. are given in descending order: 16675-37-9, 16675-38-0, 16675-39-1, 16675-40-4, 16675-41-5, 16675-42-6, 16703-92-7, 2440-22-4, 3682-83-5, 16675-45-9, 16675-46-0, 16675-47-1, 16675-48-2. [b] Purified by dissolving in base and treating with charcoal. Acidification, followed by crystallization from aqueous ethanol, gave the product as needles. The C, H, and N analyses indicated that the compound had decomposed by the time it was analyzed. [c] The compound decomposed before it could be analyzed. Calculated C/H ratio, 1.41. Found, 1.38. This ratio should not change since the decomposition involves loss of only nitrogen. [d] Decolorizes without melting to give the benzotriazole. [e] Rapid heating. The crystals were square hollow needles. [f] This compound exists in two crystal forms. When crystallized from hot ethanol, rhombohedrons are obtained, mp 131.5–133°. When crystallized from ethanol at room temperature, needles are obtained which melt at 100°. The melt then solidifies and remelts at 131.5–133°. [g] No melting point depression with a sample prepared by electrolytic reduction of 2-(2-nitrophenylazo)-4-methylphenol; an adoption of a method reported by H. Itomi [*Mem. Coll. Sci. Kyoto, Ser. A,* *12,* 343 (1929)] for 2-(4-hydroxyphenyl)benzotriazole. [h] No melting point depression of a sample prepared by electrolytic reduction of 4-(2-nitrophenylazo)phenol (see footnote *g*).

expected *o*-azidoazo compounds. In the case of 1-naphthol it was not found possible to purify the *o*-azidoazo compound. Attempts at purification gave the cyclized product, 2-(4-hydroxy-1-naphthyl)benzotriazole. Coupling of the diazonium salt with aniline, *o*-azidoaniline, and N-methylaniline in sodium acetate–acetic acid buffer likewise proceeded normally giving the corresponding *o*-azidodiazoamino compound. Coupling with N,N-dimethylaniline in sodium acetate–acetic acid buffer gave the brilliant red *o*-azido-*p′* dimethylaminoazobenzene. The yields are given in Table I.

The *o*-azidoazo compounds differed considerably in stability. The *o*-azidoazophenols and naphthols were found to undergo slow decomposition even at room temperature. In each case, by the time elemental analyses were obtained, appreciable loss of nitrogen had occurred. In contrast, *o*-azido-*p′*-dimethylaminoazobenzene, N-methyl-N-(*o*-azidophenylazo)aniline, and *o,o′*-diazidodiazoaminobenzene were all quite stable at room temperature. *o*-Azidodiazoaminobenzene, although formed readily and moderately stable, was never obtained in pure form. Numerous attempts at recrystallization failed to remove an impurity in the compound.

Thermal decomposition of 2-azido-4′-hydroxy-, 2-azido-4′-dimethylamino-, and 2-azido-2′-hydroxy-5′-methylazobenzenes in refluxing dioxane gave the corresponding 2-substituted benzotriazoles in high yields (Table I). A considerably lower yield was obtained in the decomposition of 1-(2-azidophenylazo)-2-hydroxynaphthalene. *o*-Azidodiazoaminobenzene decomposed in refluxing dioxane to an intractable tar. N-methyl-N-(*o*-azidophenylazo)aniline was found to be much more stable and had to be refluxed in a higher boiling solvent, xylene, before decomposition was complete. The benzotriazole was obtained in 63% yield. Suspecting that the failure of *o*-azidodiazoaminobenzene to cyclize to the benzotriazole might be due to the fact that the proton was on the nitrogen next to the azido group, *o,o*-diazidodiazoaminobenzene was also synthesized and decomposed. However only a polymer was obtained. Apparently the diazoamino linkage is less stable than the azido group.



Experimental Section

All of the melting points were determined on a Kofler hot stage. The elemental analyses were performed by Weiler and Strauss Microanalytical Laboratory, Oxford, England. The physical properties and analytical data are given in Table I. The following procedure is typical of that used for coupling of *o*-azidobenzenediazonium chloride with phenol, *p*-cresol, and 2-naphthol.

4-(2-Azidophenylazo)phenol.—In 3 ml of concentrated hydrochloric acid and 30 ml of water was dissolved 1.34 g (0.01 mol) of *o*-azidoaniline.[4] The solution was cooled to 0° and diazotized by the dropwise addition of 0.71 g of sodium nitrite in 10 ml of water. After standing 15 min, the solution was filtered into a stirred solution of 0.94 g (0.01 mol) of phenol in 100 ml of water containing 1.20 g (0.03 mol) of sodium hydroxide. A bright red precipitate formed immediately. After standing 1 hr, the solution was acidified and the yellow solid filtered and washed with water. The crude material was dissolved in 150 ml of ethanol and filtered to remove 0.33 g of an insoluble solid (not investigated). Dilution of the filtrate with water gave 1.90 g (81%) of 4-(2-azidophenylazo)phenol. The compound melted with decomposition at 53–61°. Attempts to recrystallize the solid resulted in decomposition. It was purified by dissolving it in sodium hydroxide, treating with charcoal, and filtering. Acidification of the filtrate gave the solid back. It was then dissolved in a minimum amount of aqueous ethanol and cooled in ice to give needles.

The coupling of *o*-azidobenzenediazonium chloride with aniline, N-methylaniline, and N,N-dimethylaniline was accomplished by means of the following general procedure.

N-Methyl-N-(*o*-azidophenylazo)aniline.—*o*-Azidoaniline (1.34 g, 0.01 mol) was dissolved in 30 ml of water containing 3 ml of concentrated hydrochloric acid. The solution was cooled to 0° and diazotized with 0.71 g of sodium nitrite. The diazonium salt solution was filtered into an ice-cold solution of N-methylaniline (1.07 g, 0.01 mol) in 50 ml of water containing 3 ml of concentrated hydrochloric acid. Sodium acetate (5 g) was added to the solution. After 1 hr stirring, the precipitated solid was filtered and washed with water: yield 2.26 g (90%); mp 55–60°. Recrystallization from petroleum ether (bp 30–60°) gave sulfur-colored granuals, mp 64–66° with partial decomposition.

o,o′-Diazidodiazoaminobenzene.—o-Azidoaniline (1.34 g, 0.01 mol) was dissolved in 30 ml of water and 3 ml of concentrated hydrochloric acid. The solution was half-diazotized by the addition of 0.35 g (0.05 mol) of sodium nitrite at 0°. A solution of 5 g of sodium acetate in 50 ml of water was added all at once. The solution was kept cold by the addition of ice. After stirring for 40 min, the solution was allowed to stand overnight at room temperature. The precipitate was filtered and washed with water. Recrystallization from absolute ethanol (charcoal) gave 1.13 g (81%), mp 123°. Thermal decomposition of this solid in refluxing dioxane gave only polymeric products.

The following procedure is typical of that used for the decomposition of the o-azidoazobenzenes. Procedure A was used to prepare 2-(2-hydroxy-5-methylphenyl)-, 2-(4-hydroxyphenyl)-, 2-(4-dimethylaminophenyl)-, and 2-(2-hydroxy-1-naphthyl)-benzotriazoles.

2-(2-Hydroxy-5-methylphenyl)benzotriazole. A.—In 5 ml of dioxane was placed 0.05 g (0.002 mol) of 2-(o-azidophenylazo)-4-methylphenol and the solution was heated. Evolution of nitrogen was noticeable at 65°. After refluxing for a few minutes, the colorless solution was cooled and poured into 50 ml of water, and the precipitated solid was filtered: yield 0.44 g (99%); mp 130–132°. This compound exists in two crystalline forms. When it crystallizes from hot 95% ethanol, rhombohedrons are obtained which melt at 131.5–133°. When crystallization from 95% ethanol occurs at room temperature, long needles are formed which melt at *ca.* 100° when heated rapidly. The melt then solidifies and remelts at 131.5–133°.

B.—2-(2-Nitrophenylazo)-4-methylphenol (0.05 g, 0.019 mol) was dissolved in 80 ml of water containing 1.6 g of sodium hydroxide. The solution was electrolyzed for 1.5 hr using a copper cathode and carbon anode.[6] The current through the cell varied from 2 to 0.5 A. The temperature during the electrolysis rose to 65°. At the end of this time, the solution was treated with charcoal and filtered, and the filtrate was acidified. The small amount of solid which precipitated was filtered and recrystallized from ethanol, yield 0.04 g (9%). This product had the same melting point characteristics and the same ir spectrum as the compound prepared by thermal decomposition of 2-(2-azidophenylazo)-4-methylphenol.

2-(N-Methylanilino)benzotriazole.—N-Methyl-N-(o-azidophenylazoaniline (0.05 g, 0.002 mol) was decomposed by refluxing it in *m*-xylene (5 ml) for 1 hr. The xylene was distilled off on the steam bath under vacuum. The residual oil solidified on cooling. Recrystallization of the solid from 95% ethanol gave 0.28 g (63%) of the benzotriazole, mp 99–101°.

2-(4-Hydroxy-1-naphthyl)benzotriazole.—o-Azidoaniline (2.69 g, 0.02 mol) was dissolved in 60 ml of water containing 6 ml of concentrated hydrochloric acid, cooled to 0°, and diazotized with 1.44 g of sodium nitrite. This solution was added with stirring to a cold solution of 2.88 g (0.02 mol) of 1-naphthol in 100 ml of water containing 2.40 g of sodium hydroxide. The resulting dark red precipitate (3.7 g) was filtered and washed thoroughly with water. This solid was stirred with 52 ml of 3 *N* sodium hydroxide for 1 hr. The dark red base-insoluble solid (A) was then filtered, washed with water, and air dried. The sodium hydroxide solution was treated with charcoal and then filtered. Acidification of the solution with hydrochloric acid gave 1.16 g (20%) of a flesh-colored precipitate (B).

Several recrystallizations of B from aqueous alcohol gave an analytical sample, mp 202–203°. The infrared spectrum of this material showed the azide group to be absent, indicating that the decomposition to the benzotriazole had already occurred. The analysis was correct for 2-(4-hydroxy-1-naphthyl)benzotriazole.

Compound A was very insoluble in all solvents and could not be purified. When 0.11 g of A was refluxed several hours in dioxane, the dark red color was discharged. Cooling of the dioxane solution gave 0.008 g of colorless needles, mp 289–299°. The analysis of the compound is consistant with an empirical formula of $C_{22}H_{14}N_6O$. This product is base insoluble, does not give an acetyl derivative with acetyl chloride, and does not show an OH absorption in its infrared spectrum.

Anal. Calcd for $C_{22}H_{14}N_6O$: C, 69.83; H, 3.73; N, 22.21. Found: C, 69.81; H, 3.94; N, 21.98.

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[6] See Table I, footnote *g*.

Nuclear Magnetic Resonance Studies of Triazoles. I. Tautomerism of 1,2,4-Triazole[1a]

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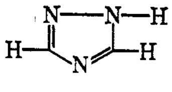
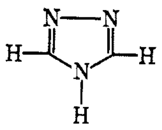
If tautomerism involving only N–H hydrogen is considered, all triazoles, tetrazoles, and unsymmetrically substituted imidazoles and pyrazoles can exist in at least two tautomeric forms similar in form to 1 and 2.



1



2

Under appropriate conditions proton magnetic resonance has been shown to provide valuable information as to the nature of tautomerism in heterocycles.[2] Previous publications concerning the nmr spectrum of 1,2,4-triazole have either not treated the problem of tautomerism[3] or worked in solvents contaminated with water.[4]

Experimental Section

Proton magnetic resonance data was taken with a Varian A-60 spectrometer equipped with a Varian Model V-6057 variable temperature accessory. Temperature given was accurate to ±2°. Each spectrum was taken a minimum of five times with the indicated chemical shift determined by weighted average. Concentrations given as percentages are weight per unit weight and are accurate to 0.0001 g. Concentrations given in terms of moles are accurate to ±0.01 *M*. Each sample contained tetramethylsilane (TMS) as an internal reference.

The solvents used were spectroscopy grade hexadeuteriodimethyl sulfoxide (DMSO-d_6) and reagent grade hexamethylphosphoramide (HMPT). The DMSO-d_6 was dried by distillation at reduced pressure from sodium sulfate and kept in an anhydrous nitrogen atmosphere. The HMPT was purified by distillation at reduced pressure and stored in an anhydrous nitrogen atmosphere. The nmr tubes used were filled in an anhydrous nitrogen atmosphere and stored with pressure caps in a calcium chloride desiccator. No changes in the spectra due to water were observed over an interval of 6 months.

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[1] (a) This work was supported by Research Grant No. CY3908, from the National Institutes of Health and a North Texas State University Faculty Grant. (b) Address inquiries to this author at Texas Instruments Incorporated, Richardson, Tex.

[2] (a) S. Gronowitz and R. A. Hoffman, *Ark. Kemi*, **16**, 459 (1960); (b) D. O'Brien and J. Gates, Jr., *J. Org. Chem.*, **31**, 1538 (1966); (c) J. Pople, W. Schneider, and H. Bernstein, "High-Resolution Nuclear Magnetic Resonance," McGraw-Hill Book Co., Inc., New York, N. Y., 1959, p 223; (d) D. W. Moore and A. G. Whittaker, *J. Amer. Chem. Soc.*, **82**, 5007 (1960); (e) C. L. Habraken and J. A. Moore, *J. Org. Chem.*, **30**, 1892 (1965); (f) L. Tensmeyer and C. Ainsworth, *ibid.*, **31**, 1878 (1966).

[3] (a) R. Child, *J. Heterocycl. Chem.*, **2**, 98 (1965); (b) M. Hauser and O. Logush, *J. Org. Chem.*, **29**, 972 (1964); (c) G. B. Barlin and T. J. Battersham, *J. Chem. Soc., Sect. B*, 516 (1967); (d) K. T. Potts and R. M. Huseby, *J. Org. Chem.*, **31**, 3538 (1966); (e) H. Zimmermann, *Z. Electrochem.*, **66**, 440 (1961).

[4] W. Frieberg and C. F. Kroger, *Tetrahedron Lett.*, 2109 (1967).