

to 50° without illumination, no ethylene dichloride was formed and free chlorine was still observed.

For the purpose of collecting a glpc sample a different reactor was used. Into 75 ft of Saran tubing (0.375-in. i.d.) was introduced at 2 mm pressure the 2:1 ethylene-isoprene mixture, and chlorine at the ratio of 5 mol % of the isoprene. The gas flow was 3×10^{-4} mol/min. The product was condensed with liquid nitrogen, and no chlorine was visible. Ethylene dichloride is resolvable from 2-chloromethylbutadiene, although it appears close to it, and none was observed. The actual conversions were 1,2-hydrochloride, 1.4%; 1-chloro-*cis*-2-methylbutadiene, 0.3%; 1-chloro-*trans*-2-methylbutadiene, 0.4%; 2-chloromethylbuta-

diene, 0.8%; 1,2-dichloride, 0.5%; *cis*-1,4-dichloride, 0.09%; *trans*-1,4-dichloride, 0.9%.

Registry No.—Isoprene, 78-79-5.

Acknowledgment.—We acknowledge with appreciation the assistance of C. Bredeweg, The Dow Chemical Co., and of Professor Lewis Hatch who sent us the M.S. thesis of J. L. A. Rodrigues, University of Texas (1965), on the vapor phase reaction between chlorine and dienes.

Thermal Decomposition of *o*-Azidoazobenzenes. I. *o,o'*-Diazidoazobenzene¹

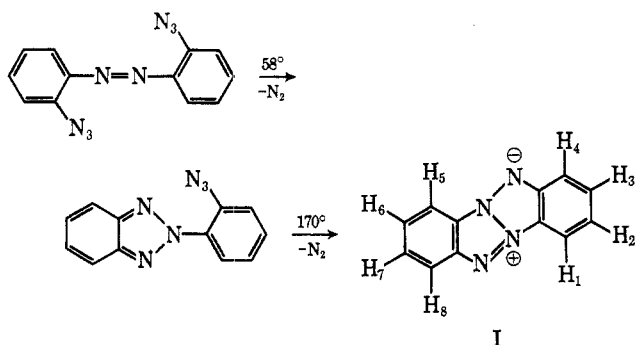
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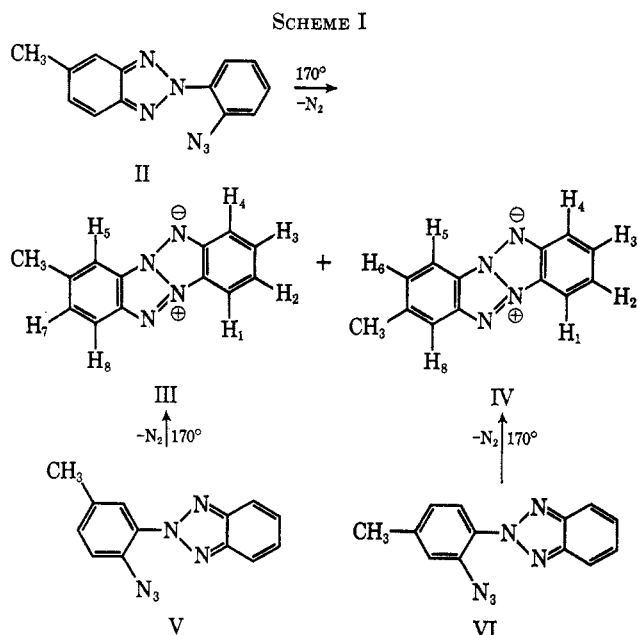
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Thermal decomposition of 2-(2-azidophenyl)-5-methylbenzotriazole has been found to give a mixture of 2-methyl- and 3-methyl-5,6H-dibenzo[*b,f*]-1,3a,4,6a-tetraazopentalenes. Each of these products was prepared separately by decomposition of 2-(2-azido-5-methylphenyl)benzotriazole and 2-(2-azido-4-methylphenyl)benzotriazole, respectively. The results of an nmr study on the parent 5,6H-dibenzo[*b,f*]-1,3a,4,6a-tetraazopentalene as well as the 2-methyl and 3-methyl derivatives is presented. The chemical shifts were found to be constant with electron distribution calculations of Chia and Simmons^{5d} and with the observations of Carboni, *et al.*,^{5d} on orientation effects in electrophilic substitution reactions.

The thermal decomposition of *o,o'*-diazidoazobenzene has been shown to proceed by stepwise loss of nitrogen to give 5,6H-dibenzo[*b,f*]-1,3a,4,6a-tetraazopentalene (I).^{2,3} A preliminary report of an X-ray study of I described it as having two different N-N bond distances and as probably being planar.⁴ In recent work, chemical evidence for structure I was presented and alternate methods of synthesis were described.⁵



In a further investigation of this interesting aromatic system, we prepared 2-(2-azidophenyl)-5-methylbenzotriazole (II) and studied the decomposition in decalin at 170° (Scheme I). A yellow solid was obtained, mp 184–185°. Because of the sharpness of the melting



point, this solid was initially felt to be a single compound. However, in order to be certain, the two possible products, III and IV, were independently synthesized. Compound III was prepared by thermal decomposition of 2-(2-azido-5-methylphenyl)benzotriazole (V) and compound IV was prepared by thermal decomposition of 2-(2-azido-4-methylphenyl)benzotriazole (VI). The syntheses of V and VI were accomplished by condensation of 2-azidoaniline with the corresponding nitroso compound in acetic acid to give the substituted nitroso-2-azido-2'-nitroazobenzene. The azo compound was not isolated but was decomposed during the work-up of the reaction mixture to give the substituted 2-(2-nitrophenyl)benzotriazole. The nitro group was reduced with iron and acetic acid to the amine. Diazotization of the amine followed by treatment of the diazonium salt solution with sodium azide gave the sub-

(1) (a) Acknowledgment is made to the donors to the Petroleum Research Fund, administered by the American Chemical Society, for partial support of this research. (b) This work was taken in part from the M.A. Thesis of John G. Stephanie.

(2) (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).

(3) Other names that have been used include 5,11-dehydrobenzotriazole-[2,1-*a*]benzotriazole, dibenzo[*c,g*]-1,2,5,6-tetraazocine, 5H,11H-benzotriazol[2,1-*a*]benzotriazol-6-ium salt, and dibenzo[2,3;4,5]-1,3a,4,6a-tetraazopentalene.

(4) M. E. Burke, R. A. Sparks, and K. N. Trueblood, *Acta Cryst.*, **16**, A64 (1963).

(5) (a) R. A. Carboni, J. C. Kauer, J. E. Castle, and H. E. Simmons, *J. Amer. Chem. Soc.*, **89**, 2618 (1967); (b) R. A. Carboni, J. C. Kauer, W. R. Hatchard, and R. J. Harder, *ibid.*, 2626 (1967); (c) J. C. Kauer and R. A. Carboni, *ibid.*, 2633 (1967); (d) Y. T. Chia and H. E. Simmons, *ibid.*, 2638 (1967); R. J. Harder, R. A. Carboni, and J. E. Castle, *ibid.*, 2643 (1967).

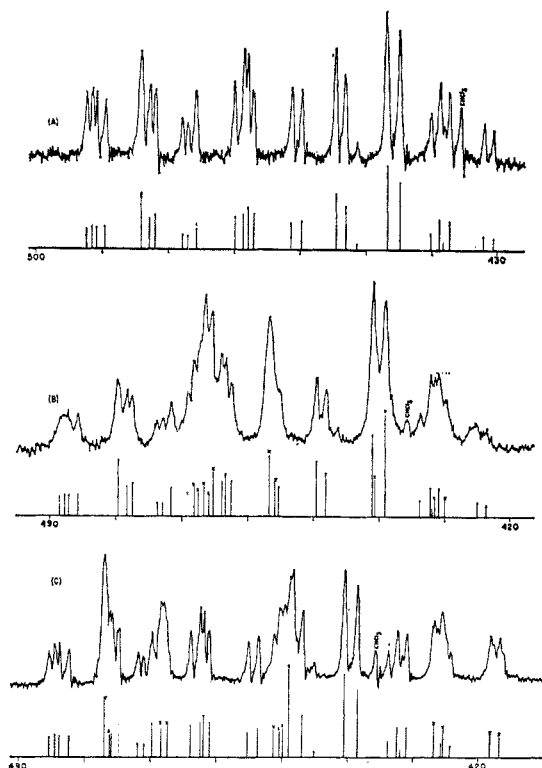
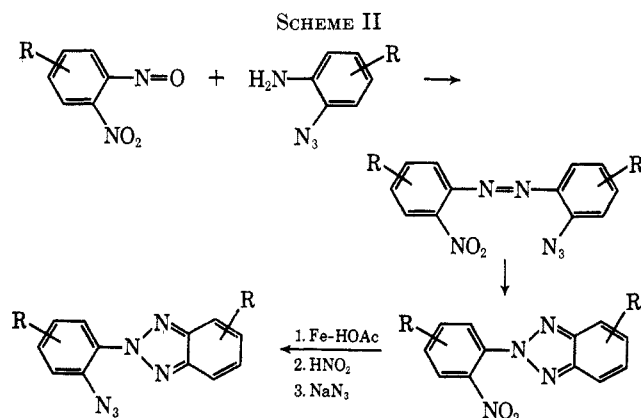


Figure 1.—Nmr spectra of A, 5,6H-dibenzo[*b,f*]-1,3a,4,6a-tetraazopentalene (I); B, the 2-methyl derivative (III); and C, the 3-methyl derivative (IV). The bands in the calculated spectra B and C that are marked with X are the bands of the methyl-substituted ring.

stituted 2-(2-azidophenyl)benzotriazole. The synthesis of II was accomplished by a similar method in which 2-nitronitrosobenzene was condensed with 2-azido-4-methylaniline. This method seems to be a general method for the production of the heterocyclic ring system I. The general procedure is outlined in Scheme II.



Thermal decomposition of V gave a yellow solid, mp 194°. Decomposition of VI gave a yellow solid, mp 198°. The infrared spectra of these two compounds were almost identical. However, a mixture melting point gave a depression. Also, the nmr spectra of each of these compounds was found to be different as shown in Figure 1. Furthermore, the nmr spectrum of the material obtained by decomposition of II contained all of the peaks present in the spectra of III and IV. Thus, decomposition of IV does give a mixture of isomeric products. Careful analysis of the nmr spectrum in-

dicates that the ratio of IV/III produced by decomposition of II is 1.9. The preference for cyclization to the position *para* to the methyl group to give IV is consistent with the known electrophilic character of the intermediate produced in azide decompositions.

The nmr spectrum of I would be expected to be an ABCD-type spectrum. In order to verify that the observed pattern was an ABCD type, a detailed study of the nmr spectrum of I, III, and IV was undertaken. One of the first observations on these spectra was the unusual width of the absorption band. In each case, these bands were spread out over a range of about 70 cps. In general, such broad bands are normally observed in *ortho* substituted benzenes when the groups attached are greatly different in electronic character; that is, one is electron donating and the other is electron withdrawing. Often such spectra are first order. The 60-Mc nmr spectrum of I has 26 observable peaks compared to the expected 32 for first-order behavior, indicating that the spectrum is not first order. However, examination of this spectrum (Figure 1) reveals that it has considerable symmetry. The right half of the spectrum has a center of symmetry and also the left half has a center symmetry. Careful analysis of this spectrum shows that it is almost first order. The nmr spectra of I, III, and IV (Figure 1) were compared. All of the peaks found in the spectrum of I were also found in the spectra of III and IV. In fact it was found possible to subtract the spectrum of I from the spectra of III and IV and obtain the ABC spectra of the methyl substituted rings of III and IV. Examination of the ABC systems allowed assignment of the peaks to particular protons in III and IV and also in the parent compound I. Estimation of the chemical shifts and approximate coupling constants were made for each of these compounds. This information was fed into an IBM 7040 computer. Using the LAOCN-3 program,⁶ the theoretical spectra, the accurate chemical shifts, and accurate coupling constants were calculated. This information is tabulated in Table I. The H₁ and H₄ of I, *ortho* to the nitrogens, are located further downfield than H₂ and H₃. However, H₄ is further upfield than H₁, a reflection of its location *ortho* to the nitrogen carrying the formal negative charge. Similarly, the H₂ proton is located further upfield than the H₃ proton due to its location *para* to the negative charge. Examination of the chemical shifts of the methyl-substituted derivatives, III and IV, reveal a similar situation, *i.e.*, the protons located *ortho* and *para* to the nitrogen with the formal negative charge are further upfield than the protons located *ortho* and *para* to the nitrogen with the formal positive charge. These results are in excellent agreement with the shifts expected based on the electron distribution calculations of Chia and Simmons.^{5d} Also, it is in agreement with the observed orientation effects in electrophilic substitution reactions.^{5b}

The upfield shift of the protons *ortho* and *para* to one nitrogen and the downfield shift of the protons *ortho* and *para* to the second nitrogen accounts for the unusually broad nmr spectra of I and its derivatives and provides further evidence that the mesionic structure I as proposed by Carboni and Castle² is correct. The fact that the nmr spectrum of I can be completely accounted for

(6) A. A. Bothner-By and S. Castellano, "LAOCN-3," Mellon Institute, Pittsburgh, Pa.

TABLE I
 COUPLING CONSTANTS AND 60-Mc CHEMICAL SHIFTS

Chemical shifts	Compound		
	I	III	IV
H ₁	486.7	482.7	479.7
H ₂	440.0	433.8	433.7
H ₃	453.1	448.2	447.0
H ₄	471.5	467.0	465.5
H ₅	486.7	467.9	471.9
H ₆	440.0		422.1
H ₇	453.1	436.2	
H ₈	471.5	460.1	450.1
CH ₃		150	149
Coupling constants			
J _{1,2}	8.47	9.17	8.56
J _{1,3}	1.05	1.06	1.16
J _{1,4}	0.79	0.75	0.87
J _{2,3}	7.00	7.59	7.05
J _{2,4}	0.93	0.70	0.79
J _{3,4}	8.73	9.30	8.82
J _{5,6}	8.47		8.72
J _{5,7}	1.05	1.52	
J _{5,8}	0.79	0.87	0.89
J _{6,7}	7.00		
J _{6,8}	0.93		1.40
J _{7,8}	8.73	9.21	

by treatment as an ABCD system indicates that both of the benzenoid rings are identical. The fact that the aromatic rings are benzenoid is indicated by the coupling constants in Table I. All of the values are normal for benzene derivatives. Finally, on examination of the data in Table I, it can be seen that the introduction of a methyl group in one of the rings affects the chemical shifts of protons in the other ring. For example, in compound IV, the presence of the methyl group on one ring has shifted the H₁₋₄ protons upfield by 6-7 cps. The fact that the electronic effect of the methyl group is felt over such large distances is consistent with the aromatic character of I.^{5d}

Experimental Section

All of the microanalyses were performed by Alfred Bernhardt Microanalytical Laboratories, Mulheim, West Germany. All melting points were taken on a calibrated Kofler hot bench. The nmr spectra were run on a Varian A56/60 spectrometer. The theoretical spectra, coupling constants, and chemical shifts were calculated using the LAOCN-3 program on a 7040 IBM computer.

2-(2-Nitrophenyl)-5-methylbenzotriazole.—Finely powdered *o*-nitrosobenzene (8.8 g, 0.058 mol) was placed in 250 ml of glacial acetic acid. To this stirred slurry was added 8.6 g (0.058 mol) of 2-azido-4-methylaniline in 50 ml of acetic acid. After stirring for 4 days at room temperature, the mixture was poured into water and the product was extracted with ether. The ether was washed with dilute acid, sodium carbonate solution, and water. Evaporation of the ether gave a red semisolid. Recrystallization from boiling ethanol completed the cyclization of the intermediate 2-azido-4-methyl-2'-nitrobenzene and gave 11.9 g (81%) of the benzotriazole, mp 85-87°. Further recrystallizations from ethanol raised the melting point to 91.5-92°.

Anal. Calcd for C₁₃H₁₀N₄O₂: C, 61.42; H, 3.94; N, 22.05. Found: C, 61.32; H, 4.07; N, 22.25.

2-(2-Nitro-5-methylphenyl)benzotriazole.—In 250 ml of hot glacial acetic acid was dissolved 4.14 g (0.025 mol) of 2-nitro-5-methylnitrosobenzene. The solution was cooled rapidly in ice with shaking to crystallize the nitroso compound in finely divided form. The mixture was warmed up to room temperature and 3.41 g (0.025 mol) of *o*-azidoaniline was added. After stirring for 3 hr, the solution was poured into 1 l. of water and the

product was extracted into ether. The ether was washed with sodium hydroxide solution to remove the remaining acetic acid. Evaporation of the ether under an air stream gave a gummy red solid. The 2-nitro-5-methyl-2'-azidoazobenzene obtained could not be purified due to its low decomposition temperature. The crude product was dissolved in 100 ml of dioxane and the solution was refluxed until the nitrogen evolution had ceased. The dioxane was evaporated. The residue was dissolved in a minimum of benzene and the solution placed on a 1.5 × 25 cm alumina column. Elution of the column with benzene (45 ml) gave the product in the first band, yield 3.50 g. After two recrystallizations from carbon tetrachloride, an analytical sample, mp 100-102°, was obtained.

Anal. Calcd for C₁₃H₁₀N₄O₂: C, 61.41; H, 3.96; N, 22.03. Found: C, 61.23; H, 4.37; N, 22.17.

2-(2-Nitro-4-methylphenyl)benzotriazole.—In a mixture of 80 ml of methylene chloride and 10 ml of glacial acetic acid was placed 1.66 g (0.01 mol) of 4-nitroso-3-nitrotoluene and 1.34 g (0.01 mol) of 2-azidoaniline. The mixture was stirred at room temperature for 4 days. It was then extracted with sodium carbonate solution to remove the acetic acid. The methylene chloride was evaporated and the residue dissolved in a minimum of benzene. Chromatography on a 2 × 25 cm alumina column (Fisher A-540) gave 2.44 g of crude product in the first 180 ml of benzene eluent. Recrystallization from ethanol gave 1.87 g (74%) of pure material, mp 94°. The infrared spectrum of this compound indicated by the absence of an azido peak that cyclization of the intermediate 2-nitro-4-methyl-2'-azidoazobenzene had occurred.

2-(2-Amino-4-methylphenyl)benzotriazole.—In 45 ml of acetone was dissolved 1.68 g (0.00661 mol) of the nitro compound. To this refluxing solution was added 5 ml of glacial acetic acid and 5 ml of water. Over a period of 30 min, 5 g of powdered iron was added in small portions. After stirring vigorously for 3 hr, the solution was cooled and filtered to remove the insoluble salts. The acetone filtrate was washed with concentrated sodium carbonate solution to remove any remaining acetic acid. Dilution of the acetone with water gave 1.14 g (77%) of the amine, mp 105°.

Anal. Calcd for C₁₃H₁₂N₄: C, 69.54; H, 5.36; N, 25.00. Found: C, 69.44; H, 5.40; N, 24.90.

2-(2-Amino-5-methylphenyl)benzotriazole.—The corresponding nitro compound (3.50 g, 0.0138 mol) was dissolved in a mixture of 100 ml of acetone, 12 ml of water, and 12 ml of glacial acetic acid. To this stirred refluxing solution was added 7 g of powdered iron in small portions over a period of 30 min. Refluxing and stirring was continued for 20 hr. The solution was then cooled and filtered to remove the iron salts. The filtrate was washed with a concentrated sodium carbonate solution to remove acetic acid. The acetone layer was concentrated until a precipitate started to form. It was then poured into 450 ml of water. The solid was filtered, washed with water, and dried: yield 2.9 g (93%); mp 133-134°.

Anal. Calcd for C₁₃H₁₂N₄: C, 69.54; H, 5.36; N, 25.00. Found: C, 69.63; H, 5.63; N, 24.54.

2-(2-Aminophenyl)-5-methylbenzotriazole.—To 100 ml of acetone was added 0.50 g (1.97 mmol) of 2-(2-nitrophenyl)-5-methylbenzotriazole. To the solution was added 10 ml of glacial acetic acid, 10 ml of water, and 0.67 g (12 mmol) of powdered iron. The mixture was refluxed and stirred for 12 hr. It was then cooled and filtered to remove the iron salts. The filtrate was shaken with a nearly saturated solution of sodium carbonate to remove the acetic acid. Separation of the acetone layer followed by its dilution with 400 ml of water gave 0.29 g (66%) of the amine. Recrystallization from ethanol gave an analytical sample which melted 78-79° if the melting point was taken in the usual manner. However, if the melting point was taken rapidly, the solid melted at 68-70°. The compound appears to exist in two different crystal structures.

Anal. Calcd for C₁₃H₁₂N₄: C, 69.64; H, 5.36; N, 25.00. Found: C, 69.60; H, 5.35; N, 24.90.

2-(2-Azidophenyl)-5-methylbenzotriazole.—In 10 ml of 6 *N* hydrochloric acid was dissolved 0.28 g (1.25 mmol) of 2-(2-aminophenyl)-5-methylbenzotriazole. The solution was cooled to 0° and diazotized by the addition of 0.10 g (1.45 mmol) of sodium nitrite in water. After 15 min, 0.18 g (2.5 mmol) of sodium azide in water was added. After standing 3 hr, the solid was filtered and washed thoroughly with water, yield 0.26 g (84%). Recrystallization from ethanol gave colorless needles, mp 83.7-84°.

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 slurried 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 minimum 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 Benzotriazoles¹

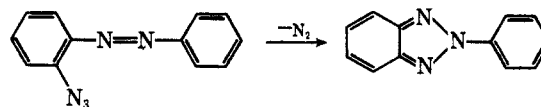
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The fact that thermal decomposition of *o*-azidoazobenzenes results in cyclization to give 2-benzotriazoles was reported by Zincke and coworkers² many years ago. Since this early work, the reaction has escaped attention until more recent times when Carboni and coworkers³ 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 aryl-nitroso 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.

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