Tetrahedron, 1967, Vol. 23, pp. 2863 to 2868. Pergamon Press Ltd. Printed in Northern Ireland

# STUDIES IN THE BENZOTRIAZOLE SERIES—III*

## CONDENSATION OF 2,4-DINITROCHLOROBENZENE WITH BENZOTRIAZOLE DERIVATIVES

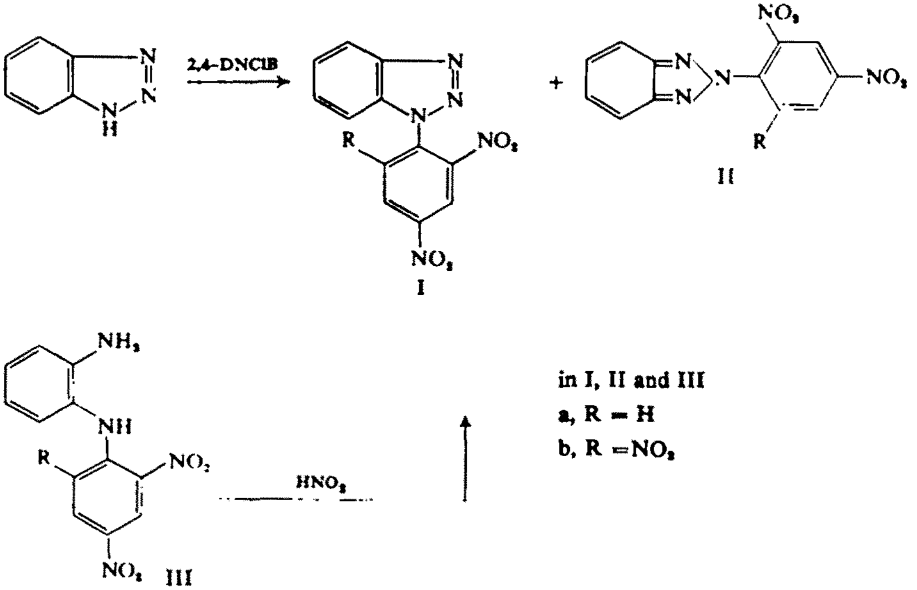
M. KAMEL, M. I. ALI and M. M. KAMEL
National Research Centre, Dokki, Cairo, U.A.R.

(*Received* 27 *September* 1966)

**Abstract**—Benzotriazole condenses with 2,4-dinitrochlorobenzene (and with picryl chloride) to give a mixture of 1-, and 2-(2,4-dinitrophenyl) benzotriazole (and 1-, and 2-picryl-benzotriazole). 5-Nitrobenzotriazole reacts with 2,4-dinitrochlorobenzene to afford a mixture of 1-(2,4-dinitrophenyl) 5- and 6-nitrobenzotriazole. Proof of the assigned structures is given. The compound reported to be 2-(2,4-dinitrophenyl) 5-nitrobenzotriazole is now shown to be 4,6-dinitro-2-(p-nitrophenyl) benzotriazole. 2-(2,4-Dinitrophenyl) 5-nitrobenzotriazole has been synthesized. 4- and 5-aminobenzotriazoles on reaction with 2,4-dinitrochlorobenzene give the corresponding 2,4-dinitroanilino derivatives.

FOLLOWING on the methylation and nitration of benzotriazole derivatives, we now report on the condensation of 2,4-dinitrochlorobenzene with benzotriazole and derivatives.

Benzimidazoles condense with 2,4-dinitrochlorobenzene to give the N-2,4-dinitrophenyl derivatives.[3] Compared with benzimidazoles, benzotriazoles devoid of substitution in the hetero-ring contain 3 nitrogen sites for the attack of the reagent. It is now found that condensation of benzotriazole with 2,4-dinitrochlorobenzene affords a mixture of 1- (Ia) and 2-(2,4-dinitrophenyl) benzotriazole (IIa) in the ratio of about 2·3:1.



I

II

III

in I, II and III
a, R = H
b, R = NO$_2$

---

* References 1 and 2 are to be considered as Parts I and II, respectively.

[1] M. Kamel, S. Sherif and M. M. Kamel, *Tetrahedron* **20**, 211 (1964).

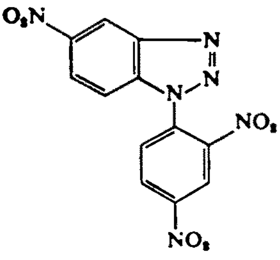
[2] M. Kamel, M. I. Ali and M. M. Kamel, *Tetrahedron* **22**, 3351 (1966).

[3] A. M. Simonov and N. D. Vitkevich, *Zh. Obsch. Kim.* **29**, 2404 (1959) English translation, p. 2369.

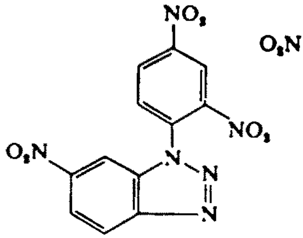
Compound I is identical with the product obtained by the action of nitrous acid on 2-amino-2′,4′-dinitrodiphenylamine (IIIa)[4] thus leaving the other product with structure II.

Similarly, benzotriazole and picryl chloride give rise to a 3:1 mixture of 1- (Ib) and 2-picrylbenzotriazole (IIb). An authentic sample of Ib was prepared by the action of nitrous acid on 2-amino-2′,4′,6′-trinitrodiphenylamine (IIIb).

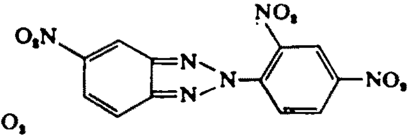
The reaction of 5-nitrobenzotriazole with 2,4-dinitrochlorobenzene can, theoretically, afford one or more of the 3 products IV, V and VI. It is now found that this reaction leads to the formation of a mixture of two products only, a major product m.p. 222°, and a minor product, m.p. 185°. That the 2,4-dinitrophenyl group became attached to the nitrogen atom in position 1 in these two compounds is evident from: (a) their preparation from the appropriate starting materials which leaves no doubt as to the 1- position of the 2,4-dinitrophenyl group. (b) they are different from 2-(2,4-dinitrophenyl) 5-nitrobenzotriazole (see below). Thus each of the two products may be represented by either formulae IV or V.



IV



V



VI

A compound which is believed to have structure V was prepared as follows: 4-Nitro-*o*-phenylenediamine was heated with 2,4-dinitrochlorobenzene to give a product (VII) which was cyclized by the action of nitrous acid to give V m.p. 222° and identical with the major product described above. In favour of the assigned structure VII, is the formation of 2-amino-5-nitroacetanilide (VII with acetyl group in place of the 2,4-dinitro phenyl group) from the reaction between 4-nitro-*o*-phenylenediamine and acetic anhydride.[5,6]

The minor product has the 2,4-dinitrophenyl group in the 1-position, i.e., it is 1-(2,4-dinitrophenyl) 5-nitrobenzotriazole (IV), since an identical compound has been obtained by the nitration of 1-(2,4-dinitrophenyl) benzotriazole. The introduction of a nitro group in position 5 appears to be contradictory to the general rules of orientation in the benzotriazole series, where a nitro group invariably enters the 4-position.[7]

A compound having the structure 2-(2,4-dinitrophenyl) 5-nitrobenzotriazole, has been reported by the nitration of 5-nitro-2-phenylbenzotriazole.[8]

---

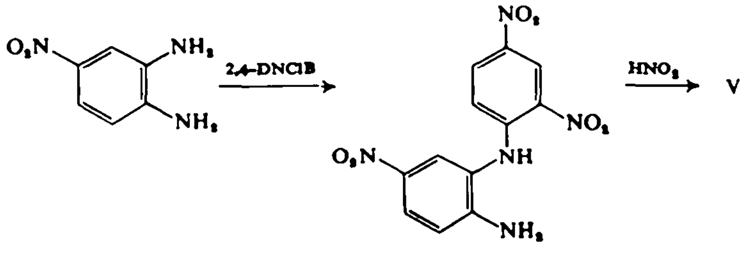
[4] W. Borsche and D. Rantscheff, *Liebigs Ann.* **379**, 152 (1911); p. 169.

[5] M. A. Philips, *J. Chem. Soc.* 1409 (1930).

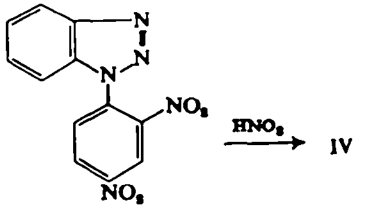
[6] cf. also the formation of 2,3-diamino-5-nitroacetanilide on acetylation of 3,4,5-triaminonitrobenzene (R. Nietzki and H. Hagenbath, *Ber. Dtsch. Chem. Ges.* **30**, 539 (1897).

[7] K. Fries, *Liebigs Ann.* **454**, 121 (1927); K. Fries, H. Guterbock and H. Kuhn, *Ibid.* **511**, 213 (1934).

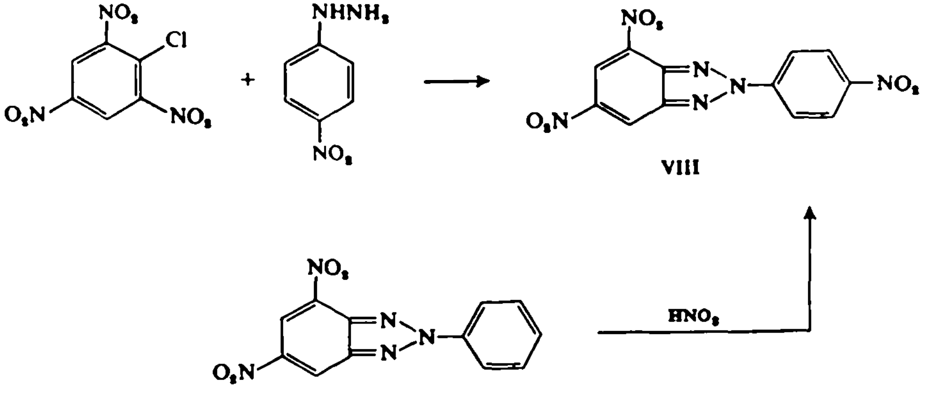
[8] C. Willgerodt and B. Hermann, *J. Prakt. Chem.* **40**, 252 (1889); *Ibid.* **42**, 126 (1890); C. Willgerodt, *Ibid.* **55**, 390 (1897).



VII



On repeating this work a compound of m.p. 232°, which was found to be identical with the trinitrobenzotriazole derivative prepared by the condensation of *p*-nitrophenylhydrazine and picryl chloride was obtained. This shows that Willgerodt's compound is actually, 4,6-dinitro-2-(*p*-nitrophenyl) benzotriazole (VIII). Compound VIII has also been obtained by the nitration of 4,6-dinitro-2-phenylbenzotriazole.

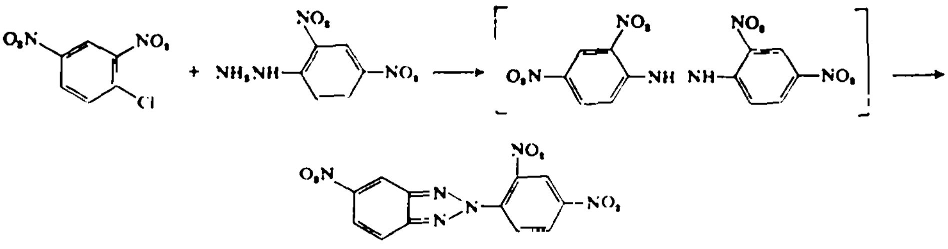


VIII

In an attempt to prepare an authentic sample of 2-(2,4-dinitrophenyl) 5-nitrobenzotriazole (IX) we investigated the condensation of 2,4-dinitrophenylhydrazine with 2,4-dinitrochlorobenzene. Green and Rowe[9] reported that condensation of these two compounds under a wide variety of conditions did not lead to the formation of any tetranitrohydrazobenzene. However, we found that when these two components were refluxed in ethanol or 2-propanol, in presence of sodium carbonate, a substance, m.p. 170°, which analysed correctly for $C_{12}H_6N_8O_6$, could be separated. This substance, more likely, will have the structure 2-(2,4-dinitrophenyl) 5-nitrobenzotriazole (IX).

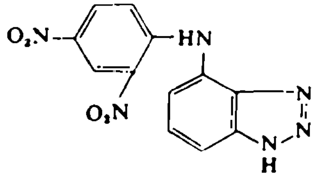
---

[9] A. G. Green and F. M. Rowe, *J. Chem. Soc.* **101**, **2443** (1912).

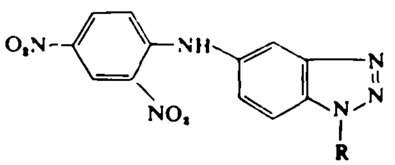


IX

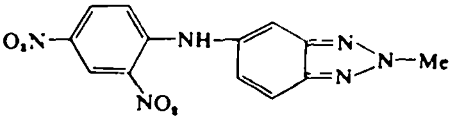
When aminobenzotriazoles were reacted with 2,4-dinitrochlorobenzene the 2,4-dinitrophenyl group became attached to the amino group, being the more basic centre. Thus, when 4- and 5-aminobenzotriazoles were condensed with 2,4-dinitrochlorobenzene, the respective 2,4-dinitroanilinobenzotriazoles (X and XIa) were obtained. These products when treated with nitrous acid followed by $\beta$-naphthol did not produce azo compounds, thus showing that the amino group has been attacked.



X



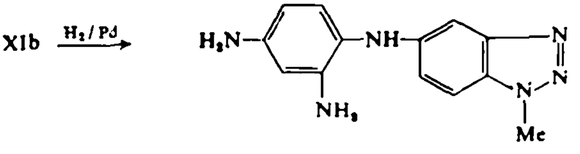
XIa, R = H
b; R = Me



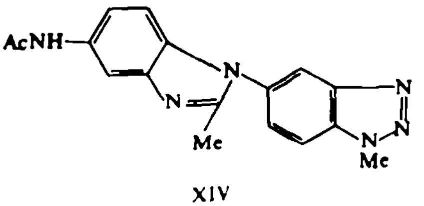
XII

Similarly, 5-amino-1-, and -2-methylbenzotriazole reacted with 2,4-dinitrochlorobenzene to give XIb and XII, respectively.

5-(2,4-Dinitroanilino) 1-methylbenzotriazole (XIb) was catalytically reduced to the corresponding amino derivative XIII, which was not isolated, but was heated with acetic anhydride in presence of hydrochloric acid to give 5-(5-acetylamino-2-methylbenzimidazol-1-yl) 1-methylbenzotriazole (XIV). The latter compound was hydrolysed to the free amino compound XIV (with H instead of Ac).



XIII



XIV

## EXPERIMENTAL

*UV spectra.* A Carl Zeiss (JENA) Universal-Spectrophotometer model VSUI was used. A hydrogen lamp being employed as light source. Spectra were taken in a soln of 95% EtOH. Readings were taken 5 $m\mu$ apart. The wave lengths were measured to 1 $m\mu$ in the important regions of the spectra.

*Condensation of benzotriazole with* 2,4-*dinitrochlorobenzene*

1- (Ia), *and* 2-(2,4-*dinitrophenyl*) *benzotriazole* (IIa). Benzotriazole (11·9 g; 1 mole), 20·2 g (1 mole) 2,4-dinitrochlorobenzene and 8·2 g (1 mole) of anhyd AcONa were refluxed in 400 ml EtOH for 6 hr and cooled. The ppt was filtered off and triturated with water giving 12 g of a mixture having m.p. 150–160°. It was crystallized twice from AcOH to give 7 g of Ia (yellow crystals), m.p. 186°, not depressed on admixture with an authentic sample.[4] (Found: C, 50·60; H, 2·29; N, 24·21. $C_{12}H_7N_5O_4$ requires: C, 50·54; H, 2·47; N, 24·57%.)

The filtrates from the above two crystallizations were concentrated and the product crystallized several times from AcOH to give ca. 3 g of 2-(2,4-dinitrophenyl) benzotriazole as pale yellow crystals, m.p. 165°. (Found: C, 50·36; H, 2·60; N, 24·40. $C_{12}H_7N_5O_4$ requires: C, 50·54; H, 2·47; N, 24·57%.)

*Condensation of benzotriazole with picryl chloride*

Benzotriazole (3 g), picryl chloride (5·5 g) and anhyd AcONa (1·6 g) were refluxed in 200 ml of EtOH for 8 hr and cooled. The ppt, was filtered off (filtrate A) and washed with water. It was then crystallized twice from EtOH to give Ib (3 g) as yellow crystals, m.p. 212°, not depressed when mixed with an authentic sample. (Found: C, 43·51; H, 2·06; N, 25·15. $C_{12}H_6N_6O_6$ requires: C, 43·65; H, 1·83; N, 25·46%.)

The filtrate A was concentrated to a small volume and the product, collected, washed with water, and dried. It was then crystallized from benzene to give IIb as yellow crystals, m.p. 168°; yield 1 g. (Found: C, 43·89; H, 2·04%.)

2-Amino-2′,4′,6′-trinitrodiphenylamine (1 g, prepared from *o*-phenylenediamine and picryl chloride[10]) was dissolved in 15 ml cold conc. $H_2SO_4$ diluted with 40 ml water. The soln was filtered and the filtrate cooled to 0–5°. Then 0·3 g $NaNO_2$ was gradually added with stirring. The product (Ib) was crystallized from EtOH, m.p. 212°.

*Condensation of* 5-*nitrobenzotriazole with* 2,4-*dinitrochlorobenzene*

5-Nitrobenzotriazole (3·3 g), 2,4-dinitrochlorobenzene (4 g) and anhyd AcONa (1·3 g) were refluxed in 150 ml EtOH for 8 hr and cooled. The solid was collected and washed with water to give 4 g which was crystallized twice from AcOH to give 2·8 g of V, m.p. 222°, identical with V prepared below. (Found: C, 43·79; H, 1·80; N, 25·14. $C_{12}H_6N_6O_6$ requires: C, 43·65; H, 1·83; N, 25·46%.) UV spectrum $\lambda_{max}$ 235 and 270 (log $\epsilon$, 4·01 and 3·81).

The mother liquors from the above crystallizations were evaporated and the residue crystallized several times from AcOH to yield 0·2 g of IV as pale yellow prisms, m.p. 185° identical with IV prepared below. (Found: C, 43·59; H, 2·12. $C_{12}H_6N_6O_6$ requires: C, 43·65; H, 1·83%.) UV spectrum: $\lambda_{max}$ 237 and 279 (log $\epsilon$, 4·36 and 4·13), $\lambda_{min}$ 260 (log $\epsilon$, 4·1).

2-*Amino*-2′,4′,5-*trinitrodiphenylamine* (VII). 4-Nitro-*o*-phenylenediamine (1·5 g) and 2,4-dinitrochlorobenzene (2 g) were melted together and heated at 160° for 3 hr. The product was washed with EtOH and crystallized from ethylene glycol as orange brown crystals, m.p. 244° (yield, 1·5 g). (Found: C, 45·30; H, 3·01; N, 22·0. $C_{12}H_9N_5O_6$ requires: C, 45·14; H, 2·84; N, 21·95%.)

*Action of nitrous acid on* VII. The preceding compound (1 g) was dissolved in 20 ml conc $H_2SO_4$ diluted with 10 ml water, cooled, stirred, and slowly treated with 7 ml 10% $NaNO_2$aq. After complete addition, the reaction mixture was stirred for 1 hr, and the product (0·5 g) washed with water, and crystallized from AcOH, m.p. 222°, not depressed when mixed with V prepared above. (Found: C, 43·87; H, 2·00; N, 25·18%.)

*Nitration of* 1-(2,4-*dinitrophenyl*) *benzotriazole* (Ia). Compound Ia (2 g) were dissolved in 10 ml conc $H_2SO_4$ cooled to 0–5°, 1·5 ml conc $HNO_3$ were gradually added. The temp was raised to 60° for ½ hr, then the reaction mixture was poured into cold water and the product (IV) crystallized from AcOH, m.p. 185° (not depressed on admixture with IV obtained above. (Found: C, 43·30; H, 2·1; N, 25·20%.)

---

[10] H. Leemann and E. Grandmougin, *Ber. Dtsch. Chem. Ges.* **41**, 1306 (1908).

4,6-*Dinitro-2-(p-nitrophenyl) benzotriazole* (VIII)

(a) 5-Nitro-2-phenylbenzotriazole was prepared and nitrated,[8] to give VIII, crystallized from AcOH, m.p. 232° (Lit.[8] gives 238°).

(b) *p*-Nitrophenylhydrazine (1·7 g), picryl chloride (2·5 g) and $Na_2CO_3$ (0·53 g) in 100 ml EtOH were refluxed for 6 hr. The soln was then concentrated and the product, dissolved in ethanolic NaOH, filtered, and the filtrate acidified with dil AcOH. The product (1 g) was crystallized from AcOH (charcoal) to give VIII as yellow crystals, m.p. 232°, not depressed when mixed with the product obtained in (a). (Found: C, 43·43; H, 2·06; N, 25·24. $C_{12}H_6N_6O_6$ requires: C, 43·65; H, 1·83; N, 25·47%.)

(c) *From 4,6-dinitro-2-phenylbenzotriazole.* Phenylhydrazine (2·1 g) and picryl chloride (5 g) were dissolved in ca. 100 ml EtOH and 1 g KOH in little water was added with shaking and the reaction left overnight. The ppt was washed with water and crystallized from AcOH to give 4,6-dinitro-2-phenylbenzotriazole, m.p. 230° (Lit.,[8] m.p. 220°). (Found: C, 50·72, H, 2·33. $C_{12}H_7N_5O_4$ requires: C, 50·54; H, 2·47%.) 4,6-Dinitro-2-phenylbenzotriazole (1 g) was heated with a mixture of 10 ml conc $H_2SO_4$ and 14 ml fuming $HNO_3$ (*d*, 1·52) on the water bath for 1 hr. The reaction mixture was poured on ice and the product was crystallized from AcOH to give VIII, m.p. 232°, not depressed when mixed with the preceding compounds. (Found: C, 43·51; H, 1·73%.)

5-*Nitro-2-(2,4-dinitrophenyl (benzotriazole* (IX). 2,4-Dinitrophenylhydrazine (2 g), 2,4-dinitrochlorobenzene (2 g) and $Na_2CO_3$ (0·53 g) were refluxed in ca. 200 ml EtOH (or 2-propanol) for 6 hr. The soln was then concentrated and the ppt (IX) filtered off and crystallized from EtOH as yellowish crystals, m.p. 170°; yield 0·5 g. (Found: C, 43·93; H, 2·01; N, 24·98. $C_{12}H_6N_6O_6$ requires: C, 43·65; H, 1·83; N, 25·46%.)

*Condensation of aminobenzotriazoles with 2,4-dinitrochlorobenzene*

The aminobenzotriazole (0·01 mole), 2,4-dinitrochlorobenzene (2·02 g) and anhyd AcONa (0·83 g) were refluxed in 50–100 ml EtOH for 3–4 hr then cooled, and the ppt filtered off, washed with water, and crystallized.

4-(2,4-*Dinitroanilino) benzotriazole* (X), was obtained in 66% yield and crystallized from benzene–pet ether (b.p. 70–80°) as orange brown crystals, m.p. 205°. (Found: C, 48·21; H, 2·65; N, 27·75. $C_{12}H_8N_6O_4$ requires: C, 48·00; H, 2·69; N, 28·00%.)

5-(2,4-*Dinitroanilino) benzotriazole* (XIa) was obtained in 76% yield and crystallized from EtOH as orange crystals, m.p. 248° (Lit.,[11] 248–249°). (Found: C, 47·83; H, 2·72; N, 28·35. $C_{12}H_8N_6O_4$ requires: C, 48·00; H, 2·69; N, 28·00%.)

5-(2,4-*Dinitroanilino) 1-methylbenzotriazole* (XIb) was obtained in 87% yield and crystallized from AcOH as yellow crystals, m.p. 253°. (Found: C, 50·07; H, 3·33; N, 26·70. $C_{13}H_{10}N_6O_4$ requires: C, 49·68; H, 3·21; N, 26·74%.)

5-(2,4-*Dinitroanilino) 2-methylbenzotriazole* (XII) was obtained in 83% yield and was crystallized from chf as orange crystals, m.p. 227°. (Found: C, 49·51; H, 3·09; N, 26·45. $C_{13}H_{10}N_6O_4$ requires: C, 49·68; H, 3·21; N, 26·74%.)

5-(5-*Acetylamino-2-methylbenzimidazol-1-yl) 1-methylbenzotriazole* (XIV). Compound XIb (10 g) was dissolved in 200 ml glacial AcOH and was catalytically reduced using 3 g of 5% Pd–C.[12] When the reduction was complete, the soln was filtered and the filtrate was concentrated under vacuum to a small volume; then 20 ml $Ac_2O$ and a few drops of HCl were added and the whole was refluxed for 3 hr. The reaction mixture was poured into ice-water and neutralized with $NH_4OH$. The ppt was filtered off and crystallized from EtOH to give XIV, m.p. 302°, yield 6·5 g . (Found: C, 63·45; H, 5·02; N, 25·86. $C_{17}H_{16}N_6O$ requires: C, 63·74; H, 5·04; N, 26·23%.)

5-(5-*Amino-2-methylbenzimidazol-1-yl) 1-methylbenzotriazole.* The preceding acetyl deriv (3 g) was refluxed with 10 ml 40% $H_2SO_4$ for 2 hr. The reaction mixture was cooled and neutralized with $NH_4OH$. The ppt formed was dried and crystallized from benzene, m.p. 230°; (Found: C, 64·92; H, 4·29; N, 29·95. $C_{15}H_{14}N_6$ requires: C, 64·73; H, 5·07; N, 30·20%.)

---

[11] Agfa, Ger. 121,156; Frdl. 6, 707 (1900–2).

[12] R. Mozingo, *Org. Synth.* **26**, 77 (1948).