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# STUDIES ON SOME BENZOTRIAZOLE DERIVATIVES

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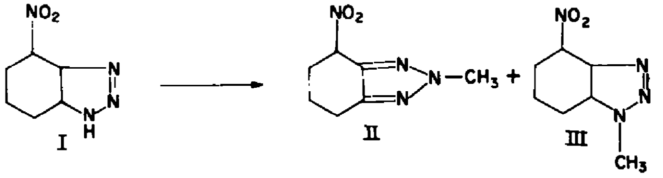
**Abstract**—Methylation of 4-nitrobenzotriazole (I) with dimethyl sulphate does not give as previously believed 1-methyl-4-nitrobenzotriazole but 2-methyl-4-nitrobenzotriazole (II) and 1-methyl-4-(7)-nitrobenzotriazole (III). 5-Nitrobenzotriazole (IV) yields on methylation, 2-methyl-5-nitrobenzotriazole (V) and 1-methyl-5-nitrobenzotriazole (VI). Nitration of 2-methylbenzotriazole furnishes a mixture of 2 products namely 2-methyl-5-nitrobenzotriazole and 2-methyl-4-nitrobenzotriazole.

Fries *et al.*[1] stated that the methylation of 4-nitrobenzotriazole (I) with dimethyl sulphate gave a 78% yield of a compound with a m.p. range (163–173°) which was identified as 1-methyl-4-nitrobenzotriazole. Fieser and Martin[2] repeated the same experiment and isolated a product which upon crystallization from dilute acetic acid showed a sharp m.p. 183°, and which was assigned the same structure. It has now been found, that methylation of I, using the experimental conditions outlined by the above authors, gives a mixture of 2 products, namely 2-methyl-4-nitrobenzotriazole (II), and 1-methyl-4-(7)-nitrobenzotriazole (III).


I
II
III

The structure of compound II was inferred from the fact that it is identical with a specimen of 2-methyl-4-nitrobenzotriazole prepared according to the method of Wiley and Hussung,[3] from 4-nitrobenzotriazole and diazomethane.

Furthermore, proof of the structure of III is based on the fact that it is identical with 1-methyl-4-(7)-nitrobenzotriazole prepared from 1-methyl-benzotriazole by nitration.[1]

Brady and Reynolds[4] studied the methylation of 5-nitrobenzotriazole (IV) and claimed to obtain a mixture of 1-methyl-5-nitrobenzotriazole (VI), and 1-methyl-6-nitrobenzotriazole respectively. It is now shown that the reaction of 5-nitrobenzotriazole and dimethyl sulphate gives a mixture of 2-methyl-5-nitrobenzotriazole (V), and 1-methyl-5-nitrobenzotriazole (VI).

The compound which was previously identified by Brady *et al.* as 1-methyl-6-nitrobenzotriazole has been proved to be 2-methyl-5-nitrobenzotriazole, since it is

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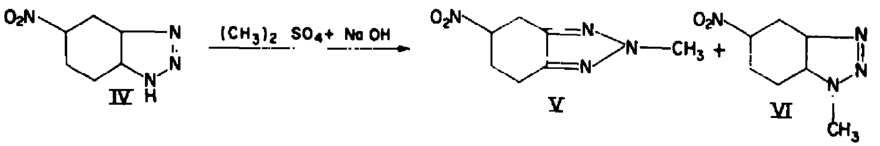
[1] K. Fries, H. Güterbock and H. Kuhn, *Liebigs Ann.* **511**, 213 (1934).

[2] L. F. Fieser and E. L. Martin, *J. Amer. Chem. Soc.* **57**, 1835 (1935).

[3] R. H. Wiley and K. H. Hussung, *J. Amer. Chem. Soc.* **79**, 4395 (1957).

[4] O. L. Brady and C. V. Reynolds, *J. Chem. Soc.* 2667 (1930).



identical with the product obtained from 2-methylbenzotriazole upon nitration as described below.

Recently, it was shown by Wiley and Hussung[3] that upon refluxing 2-methylbenzotriazole and dilute nitric acid for 60 hours, 2-methyl-5-nitrobenzotriazole (V; m.p. 150–152°) was obtained. On repeating this experiment it has now been found that this product is actually a mixture of 2 separable isomers, namely 2-methyl-5-nitrobenzotriazole (m.p. 187°) and 2-methyl-4-nitrobenzotriazole (m.p. 184°).

The same result was obtained when 2-methylbenzotriazole was nitrated at 0° using a mixture of nitric and sulphuric acids followed by heating at 100° for 45 minutes. The yields of the two nitro products are, however, higher when the latter method is used.

Proof of structure of V and/or II is based on the fact that they are identical with 2-methyl-5-nitrobenzotriazole and 2-methyl-4-nitrobenzotriazole respectively prepared as described above.

It is interesting that the behaviour of 2-methylbenzotriazole upon nitration is different from that of the 1-methyl-derivative which is known to give 1-methyl-4-(7)-nitrobenzotriazole[1] only. The analogy between the benzotriazole derivatives and naphthalene upon nitration seems to be confined to benzotriazole itself or its 1-methyl derivatives.

The UV spectra of benzotriazole and its derivatives has been extensively studied by several investigators,[3,5,6] who found that the UV absorption spectra of benzotriazole and its 1-alkyl derivatives are nearly identical and are quite different from 2-alkyl benzotriazoles. Wiley and Hussung[3] stated that the presence of a nitro group obscures the usual absorption differences between the 1-, and 2-methyl derivatives. In confirmation it is now shown that, 1-methyl-4-(7)-nitro-, 2-methyl-4-nitro-, and 2-methyl-5-nitro-benzotriazoles do not show the characteristic differences between the 1-, and 2-alkyl derivatives, as can be seen from the data in Table 1.

TABLE 1

| Compound | Max | | Min | | m.p. °C |
|---|---|---|---|---|---|
| | $\lambda$ | log $\varepsilon$ | $\lambda$ | log $\varepsilon$ | |
| 2-Methyl-4-nitrobenzotriazole | 308 | 3·98 | 255 | 3·33 | 184 |
| 2-Methyl-5-nitrobenzotriazole | 248 | 4·30 | 210 | 3·83 | 187 |
| | 289 | 4·04 | 257 | 3·76 | |
| 1-Methyl-4-(7)-nitrobenzotriazole | 215 | 3·88 | 256 | 3·30 | 203 |
| | 304 | 3·98 | | | |
| 2-Methyl-4-aminobenzotriazole | 225 | 4·45 | 255 | 3·08 | 48 |
| | 280 | 3·35 | 290 | 3·26 | |
| | 325 | 4·45 | | | |

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[5] K. V. Auwers, *Ber. Dtsch. Chem. Ges.* **71B**, 604 (1938).

[6] D. Dal Monte, A. Mangini, and R. Passerini, *Bull. Sci. facolta chim. ind. Bologna* **12**, 168–9 (1954); *Chem. Abstr.* **49**, 10739ᶠ (1955).

In view of the fact that the compound previously identified by Fries *et al.*[1] as 1-methyl-4-nitrobenzotriazole has now been proved to be a mixture of two products, the UV data recorded in the literature for this compound cannot be considered valid. On the other hand, the UV data previously determined by Passerini *et al.*[6] and its correctness confirmed by us now for 1-methyl-6-nitrobenzotriazole, must be considered as representing 2-methyl-5-nitrobenzotriazole.

## EXPERIMENTAL

### *Methylation of 4-nitrobenzotriazole*

*2-methyl-4-nitrobenzotriazole* (II) *and 1-methyl-4-(7)-nitrobenzotriazole* (III). A solution of 4-nitrobenzotriazole (10 g) in 2 N NaOH (126 ml) was treated with dimethyl sulphate (20 g). The mixture was shaken for 30 min, and then, left to cool at room temp. The pale yellow product (A) was filtered off (9 g) and crystallized from ethyl alcohol. It showed no sharp m.p. (range between 163–173°) indicating that it was a mixture. The separation of the components of this mixture was carried out as follows:

9 gm of the above mixture were stirred with cold methyl alcohol (150 ml) for 30 min and the insoluble fraction (B) filtered off. Repeated fractional crystallization of (B) from chloroform (4 times) yielded a product m.p. 184° which was identified as II by m.p. and mixed m.p. (Found: C, 47·02; H, 3·47; N, 32·05. Calc. for $C_7H_6O_2N_4$: C, 47·23; H, 3·40; 31·48%).

The combined methyl alcohol and chloroform mother liquors were distilled off, whereby, a residue (C) was obtained. After several crystallizations from chloroform, a further crop of II was obtained (total yield of II 4 g 36·2%).

On concentration of the chloroform mother liquors, another compound was obtained, it was crystallized several times from ethyl alcohol m.p. 203° (yield 2·3 gm. 20·89%) and identified as III (m.p. and mixed m.p.).

### *Methylation of 5-nitrobenzotriazole*

*1-methyl-5-nitrobenzotriazole* (VI) *and 2-methyl-5-nitrobenzotriazole* (V). When 5-nitrobenzotriazole (2 g) was dissolved in 2 N NaOH aq. (25 ml) and then methylated with dimethyl sulphate (4 ml) an almost theoretical yield of a solid was obtained which on fractional crystallization from benzene and ethyl alcohol alternatively gave 2-methyl-5-nitrobenzotriazole as pale yellow needles m.p. 187° in 22% yield. (Found: C, 47·05; H, 3·53; N, 31·80. $C_7H_6O_2N_4$ requires: C, 47·23; H, 3·40; N, 31·48%).

On concentration of the ethyl alcohol and benzene mother liquors another product m.p. 163° was obtained which was identified as 1-methyl-5-nitrobenzotriazole by m.p. and mixed m.p. (13·6% yield).

*Nitration of 2-methylbenzotriazole:* (*2-methyl-4-nitrobenzotriazole* (II) *and 2-methyl-5-nitrobenzotriazole* (V); *Method* A. To a solution of 2-methylbenzotriazole (13·3 g) in conc $H_2SO_4$ (40 ml) at 0°, conc $HNO_3$ (7 ml) was added gradually taking care that the temp did not exceed 5°. After these additions, the mixture was left at room temp for some time, and then heated for 45 min at 100° (steam bath). After cooling, the mixture was poured into ice water, whereby, a pale yellow precipitate (11 g) was obtained. This was filtered off and crystallized from ethyl alcohol, m.p. 145–155° indicating a mixture. The separation of the components of this mixture was carried out as follows:

Repeated fractional crystallizations (8 times) of the above mixture from ethyl alcohol and benzene alternately yielded a product m.p. 184° and which was identified as II (m.p. and mixed m.p.).

The combined ethyl alcohol and benzene mother liquors were distilled off, whereby, a solid (D) was obtained. After several crystallizations from ethyl alcohol and benzene respectively, a further crop of II was obtained (total yield 7 g; 39·30%).

On concentration of the ethyl alcohol and benzene mother liquors another product m.p. 150–152° was obtained. It was crystallized from pet ether (80–100°) and finally from ethyl alcohol to give a product m.p. 187° which was identified as V by m.p. and mixed m.p. (yield 3·5 g 18·6%).

*Method* B. A solution of 2-methylbenzotriazole (4 g) in dil $HNO_3$ aq. (20 ml conc $HNO_3$, $d = 1{\cdot}4$, 40 ml $H_2O$) was heated for 60 hr under reflux. The solution was cooled, and the pale yellow crystalline product filtered off. On repeated recrystallization from pet ether (70–80°) and then from ethyl alcohol, 2-methyl-5-nitrobenzotriazole (V) was obtained (1 g; 20%) as colourless crystals m.p. 187°. (Found: N, 31·50. $C_7H_6O_2N_4$ requires N, 31·48%.)

The above acid filtrate was neutralized ($NaHCO_3$ aq.) and then extracted several times with chloroform. On distillation, a pale yellow product was obtained. Repeated fractional crystallization from ethyl alcohol and light petroleum (70–80°) alternately gave another compound m.p. 184° (0·7 g; 12% yield) which was identified as II (m.p. and mixed m.p. with an authentic sample of II prepared as described above).

*2-Methyl-4-aminobenzotriazole.* 2-Methyl-4-aminobenzotriazole was prepared from 2-methyl-4-nitrobenzotriazole (10 g) in ethyl alcohol (1500 ml), by reduction with hydrogen using 10% Pd-C catalyst[7] (1 g). It was crystallized from ether and pet ether (40-60°) m.p. 48° (yield 6 g; 75%). (Found: C, 56·58; H, 5·52; N, 37·73. $C_7H_8N_4$ requires: C, 56·75; H, 5·40; N, 37·83%).

2-Methyl-4-aminobenzotriazole was soluble in hot water, methyl alcohol, ethyl alcohol and chloroform.

*4-Acetylamino-2-methylbenzotriazole.* Calculated amounts of 2-methyl-4-amino-benzotriazole, acetic acid, and acetic anhydride, were heated for 1 hr. The mixture was then poured into cold water and neutralized ($Na_2CO_3$ aq.). The acetyl derivative was extracted with ether and the residue crystallized from pet ether (40–60°) and benzene (95–5%) as white needles m.p. 130°. (Found: C, 56·62; H, 5·50; N, 29·87. $C_9H_{10}ON_4$ requires: C, 56·84; H, 5·28; N, 29·47%).

4-Acetylamino-2-methylbenzotriazole was soluble in ether, chloroform, ethyl alcohol and benzene.

*2-Methyl-5-aminobenzotriazole.* From 2-methyl-5-nitrobenzotriazole (5 g), ethyl alcohol (700 ml), and Pd-C catalyst (0·5 g). It was crystallized from benzene–pet ether m.p. 101°. (Found: N, 37·90. $C_7H_8N_4$ requires: N, 37·83%).

*UV absorption measurements.* A CARL ZEISS (JENA) Universal–Spectrophotometer model VSUI was used. A hydrogen lamp being employed as light source. Spectra were taken in a solution of 95% ethyl alcohol. Readings were taken 5 mμ apart. The wavelengths were measured to 1 mμ in the important regions of the spectra.

[7] R. Morzingo, *Organic Syntheses* **26**, 77 (1948).