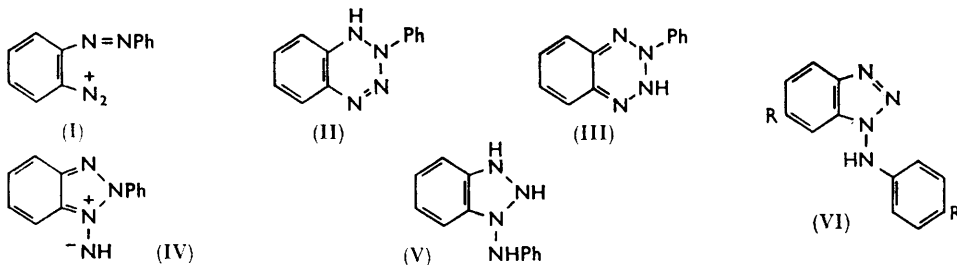


843. N-Oxides and Related Compounds. Part XXV.¹ The So-called "Dihydrobenzo-1,2,3,4-tetrazines."

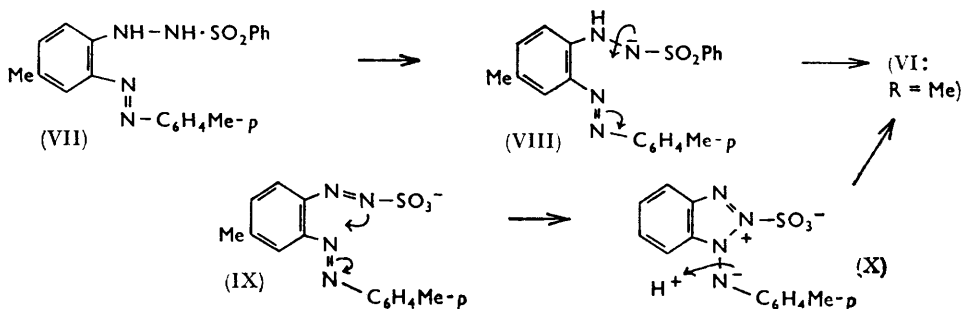
By H. BAUER and A. R. KATRITZKY.

The compounds referred to in the title are shown to be 1-aminobenzotriazole derivatives.

ZINCKE and LAWSON^{2,3} reduced diazotised *o*-aminoazo-compounds of type (I) and obtained dihydro-products which are stable to concentrated acid, alkali, hydrogen iodide, and stannous chloride-hydrochloric acid. The products have been assigned a dihydrotetrazine (III),² benzotriazole (IV),⁴ and (for a related naphtho-derivative) a dihydrobenzotriazole



structure (V);⁵ in recent compilations, dihydrotetrazine formulations have been favoured: *e.g.*, (III)⁶ or (II).⁷ In view of our work on *o*-bisazo-compounds,¹ it appeared probable that all previously suggested structures were incorrect and that these compounds were 1-aminobenzotriazoles (cf. VI): we have now proved this for a typical compound (VI; R = Me).



We obtained 7-methyl-1-*p*-toluidinobenzotriazole (VI; R = Me) by (a) reduction of 4-methyl-2-*p*-tolylazobenzenediazonium chloride,¹ (b) heating the hydrazine derivative (VII) with alkali in ethylene glycol, and (c) by spontaneous conversion of the diazosulphonate (IX).⁸ We suggest the mechanisms (VII) → VIII → VI; R = Me ← X ← IX for reactions (b) and (c). Reaction (a) probably involves an intermediate ArN=NSnCl₃ which reacts analogously to compound (IX).

¹ Part XXIV, Bauer, Bedford, and Katritzky, *J.*, 1964, 751.

² Zincke and Lawson, *Ber.*, 1886, **19**, 1452.

³ Zincke and Lawson, *Ber.*, 1887, **20**, 2896.

⁴ Bamberger and Hübner, *Ber.*, 1903, **36**, 3822.

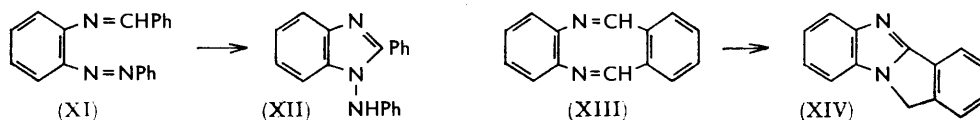
⁵ Hodgson and Forster, *J.*, 1942, 435.

⁶ Hoggarth in Rodd, "Chemistry of Carbon Compounds," IVc, Elsevier, London, 1960, p. 1577.

⁷ Wystrach in "The 1,2,3- and 1,2,4-Triazines, Tetrazines, and Pentazines," by Erickson, Wiley, and Wystrach, Interscience, 1956, p. 166.

⁸ Potassium *p*-(phenylazo)benzenediazosulphonate is stable for months.

The structure (VI; R = Me) was proved by its conversion into a monoacetyl derivative which showed no N-H stretching band in the infrared spectrum and which yielded aceto-*p*-toluidide on hydrogenation. The ultraviolet spectra (in methanol) of compound (I;



R = Me) (λ_{max} 231, 265, inflexion at 275 $m\mu$; $\log \epsilon$ 4.12, 3.90, 3.87) and of the acetyl derivative (λ_{max} 260, inflexion at 290 $m\mu$; $\log \epsilon$ 3.92, 3.52) are typical for benzotriazoles.⁹

The ring-closure reactions discussed in this Paper are similar to many others involving benzenes with two *ortho*-substituents containing double bonds, e.g., (XI) \longrightarrow (XII)¹⁰ and (XIII) \longrightarrow (XIV).¹¹

EXPERIMENTAL

5,4'-Dimethyl-2-(*p*-phenylsulphonylhydrazino)azobenzene (VII).—5-Methyl-2-*p*-tolylbenzotriazole 1-phenylsulphonimide¹ (2 g.) in ethanol (10 c.c.) was treated with yellow ammonium sulphide solution (10 c.c.). After 2 hr. at room temperature, the crystalline *hydrazine derivative* was collected; it separated from ethanol in red needles (1.3 g., 65%), m. p. 133.5—134° (Found: C, 63.1; H, 5.8; N, 14.3' C₂₀H₂₀N₄O₂S requires C, 63.2; H, 5.3; N, 14.7%).

7-Methyl-1-*p*-toluidinobenzotriazole (VI; R = Me).—(a) Sodium nitrite (2 g.) in water (4 c.c.) was added at 5° to 2-amino-5,4'-dimethylazobenzene (5 g.) in ethanol (20 c.c.) and 12*N*-hydrochloric acid (10 c.c.). The diazonium solution was added dropwise to stannous chloride dihydrate (10 g.) in ethanol (10 c.c.), water (10 c.c.), and 2*N*-hydrochloric acid (15 c.c.), and the whole heated 1 hr. at 100°. The precipitate of triazole (4.7 g., 89%) was collected and washed with dilute hydrochloric acid. It separated from aqueous ethanol as needles, m. p. 167—168° (lit.,² 168°).

(b) The hydrazine derivative (VII) (0.16 g.) and potassium hydroxide (0.2 g.) were heated in ethylene glycol (1.5 c.c.) until the initial red suspension had become successively violet and colourless (ca. 5 min.). After cooling, acidification with 2*N*-hydrochloric acid, and brief heating at 100°, the triazole separated. It was recrystallised from aqueous ethanol (0.087 g., 87%) and had m. p. and mixed m. p. 167—168°.

(c) Potassium 4-methyl-2-*p*-tolylazobenzenediazosulphonate (IX) (cf. ref. 12) was left in air for 10 days: the orange colour faded to brown. The product was extracted with methanol (charcoal) and water added to yield needles of the triazole.

1-(*N*-Acetyl-*p*-tolylamino)-7-methylbenzotriazole.—The 1-*p*-toluidino-derivative (VI; R = Me) (4 g.) was refluxed with acetyl chloride (20 c.c.) for 2 hr., and the whole evaporated at 100°/20 mm. Aqueous methanol was added to the residue to yield the *N*-acetyl derivative (3.5 g., 75%) which formed needles, m. p. 152° (lit.,² 132—134°) from ethanol (Found: C, 68.8; H, 5.4; N, 20.1. C₁₆H₁₄N₄O requires C, 68.6; H, 5.7; N, 20.0%).

The acetyl compound (1 g.) in ethanol (70 c.c.) was shaken over Raney nickel under hydrogen at 20° and normal pressure. After the slow adsorption had apparently ceased, ethanol (60 c.c.) was removed by distillation. Unchanged starting material (0.6 g.) then crystallised. Evaporation and crystallisation of the residue from water gave plates of aceto-*p*-toluidide, m. p. 147—148°, in almost quantitative conversions. Infrared and ultraviolet spectra and mixed m. p. proved the identity of the compound.

This work was carried out during the tenure (by H. B.) of a NATO post-doctoral Fellowship.

UNIVERSITY CHEMICAL LABORATORY, CAMBRIDGE.

[Present addresses: MAX PLANCK INSTITUTE, HEIDELBERG (H. B.)
and UNIVERSITY OF EAST ANGLIA, NORWICH (A. R. K.).]

[Received, January 29th, 1964.]

⁹ Fagel and Ewing, *J. Amer. Chem. Soc.*, 1951, **73**, 4360.

¹⁰ Fischer, *J. prakt. Chem.*, 1922, **104**, 102; 1924, **107**, 16.

¹¹ Thiele and Falk, *Annalen*, 1906, **347**, 112.

¹² Tröger and Puttkammer, *Ber.*, 1907, **40**, 206.