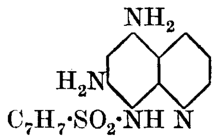
305. *Quinoline Compounds containing Arsenic. Part V. Synthesis of 7 : 8-Triazolquinoline-5-arsonic Acid.*

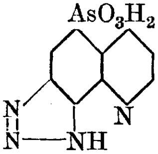
By R. H. SLATER.

SINCE it was not possible to obtain 8-bromo- or 8-chloro-7-nitroquinoline-5-arsonic acid by nitration of the corresponding 8-halogenoquinoline-5-arsonic acids (this vol., p. 2104), attempts were made to prepare them in another way. 5 : 7-Dinitro-8-amino-quinoline (Kaufmann and Zeller, *Ber.*, 1917, **50**, 1627) could not be diazotised, and 8-chloro-5 : 7-dinitroquinoline was obtained by Dikshoorn's method (*Rec. trav. chim.*, 1929, **48**, 556) in very small yield, so these two compounds were useless for the object in view.

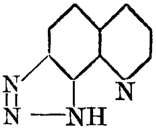
Reduction of 5 : 7-dinitro-8-*p*-toluenesulphonamidoquinoline with ammonium sulphide gave, not the expected 7-nitro-5-amino-compound, but 5 : 7-*diamino*-8-p-*toluenesulphonamidoquinoline* (I) in practically quantitative yield. This diamine, after bis-diazotisation, reacted with sodium arsenite solution to give 7 : 8-*triazolquinoline*-5-*arsonic acid* (II) and 7 : 8-*triazolquinoline* (III). The absence of a group in the 5-position in (III) is presumably due to reduction of the 5-diazonium group by arsenious acid.



(I.)



(II.)



(III.)

The facile removal of the *p*-toluenesulphonyl group by the action of nitrous acid is remarkable, for ring-closure can take place without the elimination of this group. Morgan and Godden (J., 1910, **97**, 1717) observed that, when the analogous 1 : 3-diamino-4-benzenesulphonamidonaphthalene was diazotised in presence of alcohol, the benzenesulphonyltriazole compound produced was contaminated with the deacylated triazole.

EXPERIMENTAL.

5 : 7-*Diamino*-8-p-*toluenesulphonamidoquinoline* (I).—A cold solution of 5 : 7-dinitro-8-*p*-toluenesulphonamidoquinoline (10 g.) (Kaufmann and Zeller, *loc. cit.*) in EtOH (150 c.c.) and NH_3 aq. (30 c.c.; *d* 0·880) was treated with H_2S for 1 hr., boiled for a few mins., cooled, and again treated with H_2S for 1 hr. The yellow *base* pptd. by H_2O (2 l.) was dissolved in boiling 5% HCl aq., repptd. by Na_2CO_3 aq. (yield, 8 g.), and crystallised from EtOH; sheaves of long, flat, light brown needles, m. p. 207—208° (decomp.) (Found :

C, 58·3; H, 5·0; N, 16·7; S, 9·6. $C_{16}H_{16}O_2N_4S$ requires C, 58·5; H, 4·9; N, 17·1; S, 9·8%), moderately easily sol. in $CHCl_3$, sparingly in C_6H_6, and almost insol. in light petroleum. The base is readily sol. in dil. NaOH aq., slightly in NH_3 aq., but almost insol. in Na_2CO_3 aq. It readily forms orange-red solutions in AcOH, HCl aq., HNO_3, and H_2SO_4. The diazo-solution gives a crimson azo-dye with alkaline β-naphthol.

7 : 8-*Triazolquinoline*-5-*arsonic Acid* (II) *and* 7 : 8-*Triazolquinoline* (III).—5 : 7-Diamino-8-*p*-toluenesulphonamidoquinoline (4·1 g.), suspended in HCl aq. (30 c.c., *d* 1·12; 12 c.c. H_2O), was bis-diazotised (2 g. $NaNO_2$ in 5 c.c. H_2O) at 0—5°; a marked odour of *p*-toluenesulphonyl chloride was perceptible. The diazo-solution was after 1 hr. poured into a solution of sodium arsenite (10·5 g. in 25 c.c. H_2O and 2·5 c.c. sat. $CuSO_4$ aq.). After 5 hrs., the mixture was heated until evolution of N ceased, then made slightly alkaline with NaOH aq., boiled for a few mins., and filtered. The dark brown residue was extracted thrice with 5% NaOH aq., and the reaction of the combined filtrates adjusted with HCl aq. to p_H 3—4; the arsonic acid thereby pptd. was collected, dissolved in Na_2CO_3 aq., and repptd. by HCl aq. at p_H 3—4; pale yellow, microscopic needles (1·3 g.), unmolten at 310° (Found: C, 37·1; H, 2·7; N, 19·3. $C_9H_7O_3N_4As$ requires C, 36·7; H, 2·4; N, 19·1%).*

7 : 8-*Triazolquinoline*-5-*arsonic acid* is insol. in H_2O and the usual organic solvents, but readily sol. in dil. NaOH aq. and NH_3 aq. and in moderately conc. HCl aq., H_2SO_4, and HNO_3. The Na salt is not pptd. by conc. NaOH aq. The following salts are precipitable from the NH_4 salt aq.: white Ca, buff Ag, white Pb, green Cu, white Hg (on boiling); all are gelatinous and insol. in hot H_2O.

When the acid mother-liquor from which the above arsonic acid had been originally pptd. was neutralised with NaOH aq., a white gelatinous compound (0·6 g.) separated. It crystallised from hot H_2O in stellate clusters of slender needles, m. p. 256—257°, of 7 : 8-*triazolquinoline* (Found: C, 63·5; H, 3·4; N, 32·7. $C_9H_6N_4$ requires C, 63·5; H, 3·6; N, 32·9%), readily sol. in AcOH, slightly in EtOH and $CHCl_3$, but almost insol. in C_6H_6 and light petroleum. This compound dissolves in boiling dil. Na_2CO_3 aq. and NaOH aq. to about the same extent as it does in hot H_2O; these solutions deposit needles on cooling. The base is sol. in HCl aq., H_2SO_4, and HNO_3. A dil. AcOH solution gives with *N*/1000-I a deep reddish-brown coloration which disappears on warming: the other two compounds described do not give a coloration.

The author thanks the Court of the Grocers' Company, London, for a scholarship.

ROYAL COLLEGE OF PHYSICIANS' LABORATORY,
EDINBURGH.

[*Received, May 3rd*, 1932.]

---

* Owing to the great stability of this arsonic acid, it was not possible to estimate As in the usual way.