

589. *A New Synthesis of Arsonic Acids. Part III.\* Coupling of Furan, Thiophen, and  $\beta$ -2-Thienylacrylic Acid with Arsanilic Acid.*

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Furan, thiophen, and  $\beta$ -2-thienylacrylic acid have been coupled with diazotised arsanilic acid. They yield (2?)-*p*-arsonophenyl-furan and -thiophen respectively and (2?)-4'-arsonostyrylthiophen.

THE arsonic acids described in preceding Parts were prepared by treating diazotised arsanilic acid (in one case 4-amino-2-nitrophenylarsonic acid) with  $\alpha\beta$ -unsaturated carbonyl compounds. The reaction has now been extended to the synthesis of arsonic acids of the furan and thiophen series.

Johnson (*J.*, 1946, 895) coupled diazotised *p*-chloroaniline with furan according to Meerwein's method (*J. pr. Chem.*, 1939, 152, 237), and obtained predominantly 2-*p*-chlorophenylfuran, with a small quantity of the 3-substituted furan. The reaction with *p*-arsanilic acid yielded only one compound which is probably 2-*p*-arsonophenylfuran. According to Gomberg and Bachmann (*J. Amer. Chem. Soc.*, 1924, 46, 2339), thiophen and diazotised aniline yield only the 2-phenylthiophen, m. p. 42—43°, previously synthesised from  $\beta$ -benzoylpropionic acid and phosphorus pentasulphide by Kues and Paal (*Ber.*, 1887, 20, 3141). On the other hand, Bamberger (*Ber.*, 1897, 30, 370) obtained a compound of

\* Part II, preceding paper.

m. p. 90—90.5° from nitrosoacetanilide and thiophen, and Möhlau and Berger (*Ber.*, 1893, 26, 1994) reported a melting point of 56—57° for their product from benzenediazonium chloride, thiophen, and aluminium chloride. However, the melting point of Möhlau and Berger's compound could be raised by recrystallisation (see Bamberger, *loc. cit.*, footnote 3). The compound is considered to be 3-phenylthiophen. It is thus uncertain whether our product is 2- or 3-*p*-arsonophenylthiophen, though the former structure is preferred.  $\beta$ -2-Thienylacrylic acid and diazotised arsanilic acid give 2-4'-arsonostyrylthiophen in good yield; it thus differs from  $\beta$ -2-furylacrylic acid, which gives  $\beta$ -(5-*p*-arsonophenyl-2-furyl)acrylic acid as sole isolable product although 2-*p*-arsonophenyl-5-*p*-arsonostyrylfuran is doubtless also formed.

## EXPERIMENTAL

M. p.s are uncorrected.

2-*p*-Arsonophenylfuran.—Arsanilic acid (10.85 g.) dissolved in aqueous sodium hydroxide (2.1 g. in *ca.* 100 c.c.) was mixed with aqueous sodium nitrite (3.65 g. in 10 c.c.) and treated with 25% hydrochloric acid (32 g.) in the usual way. The clear solution was added to furan (3.4 g.) in acetone (100 c.c.) containing crystalline sodium acetate (*ca.* 40 g.). Gas evolution set in immediately and cupric chloride (10 g.) in water (*ca.* 20 c.c.) was added slowly. After 1 hour gas evolution ceased. The buff-coloured precipitate formed was filtered off, washed with acetone, dried, and dissolved in 2*N*-sodium hydroxide. The mixture was filtered and acidified, (2?)-*p*-arsonophenylfuran being precipitated as a brown solid. This was digested with cold acetone which on evaporation left a crystalline mass. Recrystallisations from alcohol gave needles or yellowish globuli, m. p. >300° in small yield (Found: C, 44.9, 44.9; H, 3.6, 3.5; As, 28.2. C<sub>10</sub>H<sub>9</sub>O<sub>4</sub>As requires C, 44.8; H, 3.4; As, 28.0%).

(2?)-*o*-Arsonophenylthiophen.—Arsanilic acid (10.85 g.) was diazotised as above and added to thiophen (4.2 g.) in acetone (100 c.c.) containing crystalline sodium acetate (35—40 g.). Cupric chloride (10 g.) in water (20 c.c.) was added dropwise with stirring during 1 hour and the solution was warmed on the water-bath to 20—22°, whereupon gas evolution set in. The acid, worked up as described above, crystallised from alcohol or glacial acetic acid as yellowish globuli, m. p. >300° (yield, 20—25%) (Found: C, 42.1, 42.1; H, 3.3, 3.4; As, 26.6. C<sub>10</sub>H<sub>9</sub>O<sub>3</sub>SAs requires C, 42.3; H, 3.2; As, 26.4%).

$\beta$ -(5-*p*-Arsonophenyl-2-furyl)acrylic Acid.—Arsanilic acid (10.85 g.) was diazotised as above and added to a solution of furylacrylic acid (6.9 g.) in acetone (120 c.c.) in which crystalline sodium acetate (35—40 g.) was suspended. Gas evolution commenced immediately and became violent even without the addition of cupric chloride. The temperature which after the addition of the diazonium solution was approx. 8—10° rose to 24—25° and cooling was advisable. Addition of cupric chloride solution is advisable as the copper salt of the arsonic acid formed is easily separated. The solid was worked up as above. The dry arsonic acid was extracted with absolute alcohol which on evaporation deposited small not very well-developed crystals, m. p. >300° (Found: C, 46.1, 46.0; H, 3.4, 3.4; As, 22.3. C<sub>13</sub>H<sub>11</sub>AsO<sub>6</sub> requires C, 46.2; H, 3.3; As, 22.2%). The major part of the hydrochloric acid precipitate (insoluble in cold alcohol), probably the 2-*p*-arsonophenyl-5-4'-arsonostyrylfuran, could not be obtained free from nitrogen as it could not be recrystallised.

2-*p*-Arsonostyrylthiophen.—An attempt to prepare thienylacrylic acid from thiophen-2-aldehyde by a Perkin condensation according to Biedermann (*Ber.*, 1886, 19, 1855) gave a very poor yield, most of the aldehyde being resinified. A Doebner condensation with malonic acid (approx. 2 mols.) gave a 75—80% yield. After recrystallisation from water the  $\beta$ -2-thienylacrylic acid, m. p. 144—145° (Cohn, *Z. physiol. Chem.*, 1893, 17, 283, gives this m. p.).

Arsanilic acid (10.85 g.) was diazotised as above and added to a solution of  $\beta$ -2-thienylacrylic acid (7.7 g.) in acetone (125 c.c.) in which crystalline sodium acetate (*ca.* 40 g.) was suspended. After addition of a few drops of aqueous cupric chloride (10 g. in 20 c.c.), gas evolution set in and a buff-coloured precipitate began to form. At 20—22° gas evolution was considerable and lasted for approx. 1 hour during which all of the cupric chloride solution was added. After a few hours the precipitate was collected (from the solution 1.3 g. of unchanged thienylacrylic acid were recovered). The solid was dissolved in 2*N*-sodium hydroxide, which was filtered and acidified. The precipitated arsonic acid, a brown solid, was dried (yield, 8.8 g.) and twice recrystallised from acetic acid (orange-red solution), forming plates and prisms, m. p. >300° (yield, 30%) (Found: C, 46.3, 46.3; H, 3.8, 3.8; As, 22.1, 22.3; S, 10.1, 10.0. C<sub>12</sub>H<sub>11</sub>O<sub>3</sub>SAs requires C, 46.5; H, 3.6; As, 24.2; S, 10.3%).

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