577. *The Reaction of Diazonium Salts with* β-2-*Thienylacrylic Acid.*

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Under Meerwein's conditions (Meerwein, Buchner, and van Emster, *J. pr. Chem.*, 1939, **152**, 237) β-2-thienylacrylic acid and *p*-nitrobenzenediazonium chloride give only a small amount of 5-*p*-nitrophenyl-2-4′-nitrostyrylthiophen, but with other diazo-compounds the 2-styrylthiophens are obtained; β-2-furylacrylic acid generally gives the diarylated compounds. The differing reactions of thiophen- and furan-acids are considered to favour the assumption of an ionic reaction mechanism.

FROM the reaction of diazonium salts with β-2-furylacrylic acid three classes of compounds were obtained, *viz.*, 5-aryl-2-styrylfurans, showing strong fluorescence in organic solvents, α-(5-aryl-2-furyl)acrylic acids, and 2-styrylfurans (Freund, *J.*, 1952, 3068), whereas the last were the only reaction products to be expected according to Meerwein, Buchner, and van Emster (*J. pr. Chem.*, 1939, **152**, 237). It appeared of interest to investigate whether double arylation, previously only encountered with quinones (G.P. 508,395; Kvalnes, *J. Amer. Chem. Soc.*, 1934, **56**, 2478), would take place with compounds similar to furylacrylic acid. β-2-Thienylacrylic acid underwent arylation under Meerwein's conditions (*loc. cit.*) with great ease, but with diazotised *p*-nitroaniline yielded only a small amount of 5-*p*-nitrophenyl-2-4′-nitrostyrylthiophen, which showed a green fluorescence in benzene similar to that of the corresponding furan compound. Such strong arylating agents as diazotised *p*-chloroaniline and *p*-aminobenzoic acid gave only 2-4′-chloro- and 2-4′-carboxy-styrylthiophen. It appears difficult to reconcile the different behaviour of β-2-furyl- and β-2-thienyl-acrylic acid with the claim that in the Meerwein reaction organic radicals are involved (Waters, *J.*, 1946, 411; " The Chemistry of Free Radicals," London, 1946; cf. Freund, *loc. cit.*). Polarisation of the double bonds seems to be the dominating factor as suggested by Meerwein *et al.* (*loc. cit.*).

EXPERIMENTAL

β-2-*Thienylacrylic Acid.*—Perkin condensation with thiophen-2-aldehyde according to Biedermann (*Ber.*, 1886, **19**, 1855) gave only a very poor yield of thienylacrylic acid. Doebner condensation (1 mol. of the aldehyde and 2 mols. of malonic acid in pyridine with a few drops of piperidine) gave the acid, m. p. 147—148°, in 70% yield (Cohn, *Z. physiol. Chem.*, 1893, **17**, 283; m. p. 144—145° : Nord, *J. Org. Chem.*, 1949, **14**, 409).

2-4′-*Carboxystyrylthiophen.*—A filtered diazonium solution, prepared from *p*-aminobenzoic acid (6·85 g.), sodium nitrite (3·7 g.) in water (40 c.c.), 25% hydrochloric acid (20 g.), and water (70 c.c.), was added to β-2-thienylacrylic acid dissolved in acetone (150 c.c.) in which crystalline sodium acetate (20 g.) was suspended. After the pH had adjusted itself to approx. 6, the mixture was warmed to 28—30° and a solution of copper chloride (1·5 g.) in water (10 c.c.) was added. Gas evolution was rapid at 30° and lasted for about 1 hr. After removal of the acetone a solid resin remained which was extracted with dilute aqueous ammonia. Approx. 4 g. of buff-coloured material remained. This dissolved in hot dilute alkali and crystallised from acetic acid from which the 2-4′-*carboxystyrylthiophen* separated in globuli, m. p. 251—254° (Found : C, 67·8; H, 4·5; S, 13·8. $C_{13}H_{10}O_2S$ requires C, 67·8; H, 4·4; S, 13·9%).

The ammoniacal solution was acidified and the precipitate boiled with water to remove unchanged β-2-thienylacrylic acid. Some brown material remained which after digestion with a small amount of cold alcohol was recrystallised from alcohol. The poorly developed brown crystals melted at 270—280°. This compound has not yet been closely investigated; it may be α-*p*-carboxyphenyl-β-2-thienylacrylic acid.

2-4′-*Chlorostyrylthiophen.*—A diazonium solution from *p*-chloroaniline (6·4 g.), sodium nitrite (3·65 g.), 25% hydrochloric acid (22 c.c.), and ice (10 g.) was filtered and added to a solution of β-2-thienylacrylic acid (7·7 g.) in acetone (150 c.c.) in which sodium acetate (20·22 g.) was suspended. The pH of the mixture was approx. 6. On addition of copper chloride (2 g.) in water (10 c.c.) gas evolution set in which lasted for about 40 min. After removal of the acetone the residue was extracted with dilute ammonia. Two recrystallisations of the residue (4 g.) from alcohol gave prisms of 2-4′-*chlorostyrylthiophen*, m. p. 137° (Found : C, 65·2, 65·1; H, 4·5, 4·3; Cl, 16·1; S, 14·5. $C_{12}H_9SCl$ requires C, 65·3; H, 4·1; Cl, 16·1; S, 14·5%). The ammoniacal solution on acidification gave only unchanged thienylacrylic acid.

2-4′-*Nitrostyrylthiophen.*—*p*-Nitroaniline (13·8 g.) was diazotised and the filtered solution added to one of β-2-thienylacrylic acid (15·4 g.) in acetone (200 c.c.) in which sodium acetate (*ca.* 45 g.) was suspended. Gas evolution set in immediately and became violent on the addition of a solution of copper chloride (5 g.) in water (10 c.c.); it was over in a few minutes. The mass of crystals was filtered off (filtrate *A*), washed with dilute aqueous ammonia and cold ethanol, and dried in a desiccator (yield, 7 g.). This was boiled with alcohol (400 c.c.) in which 1·5 g. (substance *B*) remained undissolved. The alcoholic solution, on cooling, yielded yellowish crystals (6·9 g.), m. p. 168—169°. These were passed in benzene through alumina and once more recrystallised, yielding 2-4′-*nitrostyrylthiophen*, needles, m. p. 174° (Found : C, 61·8, 61·9; H, 4·0, 4·0; N, 6·0, 5·8; S, 13·6. $C_{12}H_9O_2NS$ requires C, 62·3; H, 3·9; N, 6·1; S, 13·9%).

5-p-*Nitrophenyl*-2-4′-*nitrostyrylthiophen.*—Substance *B* was twice recrystallised from glacial acetic acid and then melted (const.) at 220—222°. It was passed in benzene through alumina where a dark brown impurity was removed. The substance crystallised in short scarlet prisms from the concentrated benzene solution; from glacial acetic acid, 5-p-*nitrophenyl*-2-4′-*nitrostyrylthiophen* crystallised in red needles or prisms, m. p. 232°, and showed in benzene a strong yellow-green fluorescence (Found : C, 62·2; H, 3·8; N, 8·6; S, 9·3. $C_{18}H_{12}O_4N_2S$ requires C, 61·3; H, 3·4; N, 8·0; S, 9·1%).

Filtrate *A* was subjected to steam-distillation which removed the acetone and some *p*-chloronitrobenzene. The dark residue (*C*) was digested with dilute aqueous ammonia, and the solution filtered. On acidification a solid was precipitated which was repeatedly extracted with boiling water to free it from unchanged thienylacrylic acid, and then dried on a porous plate. After recrystallisations from alcohol and acetic acid, olive needles, m. p. 235—238°, were obtained. The *p*-nitrophenyl group may have entered position 5 of the thiophen nucleus or the α-position of the side chain. The latter constitution is tentatively suggested, namely, α-p-*nitrophenyl*-β-2-*thienylacrylic acid* (Found : C, 56·4, 56·3; H, 3·5, 3·5; N, 5·2, 5·0; S, 11·5, 11·6. $C_{13}H_9O_4NS$ requires C, 56·7; H, 3·3; N, 5·1; S, 11·6%).

The residue *C* (after the ammoniacal extraction; approx. 7·2 g.) was dried and twice recrystallised from ethanol and acetic acid, and 1·5 g. of still impure 2-*p*-nitrostyrylthiophen were obtained.

2-4′-*Aminostyrylthiophen.*—2-4′-Nitrostyrylthiophen (m. p. 168—169°; 4·4 g.) was gradually introduced into a solution of anhydrous stannous chloride in glacial acetic acid (55 c.c.) (240 g. of $SnCl_2$ in 500 c.c. of acid), saturated with dry hydrochloric acid, and stirred for 3 hr. at 35°, left overnight, and then filtered. The precipitate was washed with a little acetic acid and decomposed with 25% aqueous sodium hydroxide (130 c.c.) under external and internal cooling with ice. The solid material was filtered off, washed until neutral with water, dried in a desiccator, and extracted with benzene. The solution was passed through alumina. Solid (1·55 g.) was obtained which melted constantly at 128—129° after two recrystallisations from ethanol. 2-4′-*Aminostyrylthiophen* forms slightly yellow prisms (Found: C, 71·7, 71·6; H, 5·6. 5·5; N, 7·2, 7·1; S, 15·9, 15·7. $C_{12}H_{11}NS$ requires C, 71·8; H, 5·5; N, 7·0; S, 15·9%). In hot dilute hydrochloric acid it gave the grey hydrochloride.

When boiled with a small amount of acetic anhydride in acetic acid, it gave the acetyl derivative as greenish-yellow needles, m. p. 222°.

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