CCCLXXI.—*Derivatives of Stilbene.*

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THIELE and ESCALES (*Ber.*, 1901, **34**, 2842) have shown that 2 : 4-dinitrostilbene is reduced to 2-nitro-4-aminostilbene by ammonium sulphide in boiling alcoholic solution and to the isomeric nitroamine by stannous chloride. This suggested that the very readily accessible condensation products of aromatic aldehydes and 2 : 4-dinitrotoluene might be transformed into phenanthrene derivatives by following one of two routes, but unfortunately neither of these has proved to be practicable. All attempts to obtain a phenanthrene derivative from 4-nitro-2-aminostilbene and from 4-nitro-2-amino-3′ : 4′-methylenedioxystilbene,

$$NO_2\cdot C_6H_3(NH_2)\cdot CH{:}CH\cdot C_6H_3{:}O_2CH_2$$

(Gulland, Robinson, and Stafford, J., 1925, **127**, 1502), by treatment of the diazo-derivatives with copper powder were fruitless. In order to test the less direct process, in a case which was considered to be a favourable one, 2-*nitro*-4-*amino*-3′ : 4′-*dimethoxystilbene*,

$$NO_2\cdot C_6H_3(NH_2)\cdot CH{:}CH\cdot C_6H_3(OMe)_2 \quad (I),$$

was converted into 4-*chloro*-2-*nitro*-3′ : 4′-*dimethoxystilbene*,

$$NO_2\cdot C_6H_3Cl\cdot CH{:}CH\cdot C_6H_3(OMe)_2 \quad (II),$$

and then into 4-*chloro*-2-*amino*-3′ : 4′-*dimethoxystilbene*,

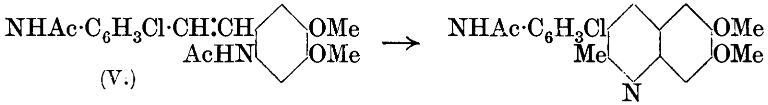
$$NH_2\cdot C_6H_3Cl\cdot CH{:}CH\cdot C_6H_3(OMe)_2 \quad (III).$$

When an aqueous or alcoholic suspension of the corresponding diazonium sulphate was treated with copper powder, the only isolable product was an amorphous nitrogenous compound.

The chloronitrodimethoxystilbene (II) is readily nitrated, yielding, doubtless, 4-*chloro*-2 : 6′-*dinitro*-3′ : 4′-*dimethoxystilbene*,

$$NO_2{\cdot}C_6H_3Cl{\cdot}CH{:}CH{\cdot}C_6H_2(OMe)_2{\cdot}NO_2 \quad (IV),$$

and after reduction and acetylation this affords 4-*chloro*-2 : 6′-*diacetylamino*-3′ : 4′-*dimethoxystilbene* (V). Gulland, Robinson, and Stafford (*loc. cit.*) mention the possibility that *oo*′-diacylaminostilbenes might be dehydrated (losing $2H_2O$) with formation of 2 : 6-naphthyridines, but the substance (V) loses only $1H_2O$ when it is heated with phosphoryl chloride.



(V.)

Only one of the possible directions of condensation is represented in the above scheme.

EXPERIMENTAL.

2-*Nitro*-4-*amino*-3′ : 4′-*dimethoxystilbene* (I).—Hydrogen sulphide was passed for 3 hours through a gently refluxing mixture of 2 : 4-dinitro-3′ : 4′-dimethoxystilbene (20 g.; Gulland, Robinson, and Stafford, *loc. cit.*), alcohol (250 c.c.), and aqueous ammonia (40 c.c.; *d* 0·880). After cooling, the bright red, crystalline solid was collected and heated for 2 hours with an excess of carbon disulphide, in which it was very sparingly soluble. The residual amine (78% yield) crystallised from *iso*butyl alcohol in bright red prisms, m. p. 186—187° (Found: C, 63·7; H, 5·5. $C_{16}H_{16}O_4N_2$ requires C, 64·0; H, 5·4%). 2-Nitro-4-amino-3′ : 4′-dimethoxystilbene is readily soluble in acetone, ethyl acetate, or chloroform, moderately readily soluble in alcohol or acetic acid, and very sparingly soluble in carbon tetrachloride or carbon disulphide. The solutions in the last two cases exhibited a weak green fluorescence. The *hydrochloride*, prepared by the action of alcoholic hydrogen chloride, formed long, golden needles melting at 223° with previous darkening at 200° (Found: Cl, 10·5. $C_{16}H_{16}O_4N_2$,HCl requires Cl, 10·5%). The *acetyl* derivative crystallised from dilute acetic acid in pale orange parallelipipeds, m. p. 183—184° (Found: C, 62·9; H, 5·3. $C_{18}H_{18}O_5N_2$ requires C, 63·2; H, 5·3%). Oxidation of this acetyl derivative with potassium permanganate in the presence of magnesium sulphate yielded a mixture of veratric and 2-nitro-4-acetylaminobenzoic acids. The latter acid melted at 219°, alone or mixed with an authentic specimen. This proves that it is the *p*-nitro-group in the original stilbene which is reduced by ammonium sulphide.

4-*Chloro*-2-*nitro*-3′ : 4′-*dimethoxystilbene* (II).—A hot solution of 2-nitro-4-amino-3′ : 4′-dimethoxystilbene (20 g.) in glacial acetic acid (225 c.c.) was poured into a cold solution of cupric sulphate (40 g.) in hydrochloric acid (1000 c.c. of 15%), and the mixture cooled to 0°. Sodium nitrite (24 g.) in water (100 c.c.) was gradually added with stirring. The chocolate-coloured mixture was then poured slowly into an almost boiling solution of cuprous chloride (prepared from cupric sulphate, 45 g., sodium chloride, 22 g., water, 110 c.c., concentrated hydrochloric acid, 300 c.c., and an excess of copper) and vigorously shaken. Copper bronze (20 g.) was then introduced, and next day the solid was collected, washed, and thoroughly dried. After extraction with light petroleum (b. p. 60—80°), a product separating in orange, leaf-like crystals, m. p. 124—125°, was obtained (yield 22—24%) (Found : C, 60·1; H, 4·6. $C_{16}H_{14}O_4NCl$ requires C, 60·1; H, 4·4%). 4-Chloro-2-nitro-3′ : 4′-dimethoxystilbene is readily soluble in most organic solvents, and dissolves in sulphuric acid to a dull green solution.

4-*Chloro*-2-*amino*-3′ : 4′-*dimethoxystilbene* (III).—A solution of 4-chloro-2-nitro-3′ : 4′-dimethoxystilbene (5 g.) in glacial acetic acid (70 c.c.) was treated alternately with small quantities of hydrochloric acid (30 c.c. in all) and zinc dust (10 g.). The amine, which was precipitated on the addition of excess of dilute aqueous ammonia, crystallised from alcohol in very pale brown prisms, m. p. 147—148° [Found : C, 66·0; H, 5·6; MeO, 21·35. $C_{14}H_{10}NCl(OMe)_2$ requires C, 66·3; H, 5·5; MeO, 21·4%]. The pale brown solution of the amine in ether, benzene, or ethyl acetate exhibits an intense violet fluorescence; a solution in acetone fluoresces with a slightly more bluish tinge. The *hydrochloride* and *sulphate* are stable in the presence of the corresponding acid, but are hydrolysed by water. The *acetyl* derivative crystallised from alcohol in white needles, m. p. 180° [Found : MeO, 18·6. $C_{16}H_{12}ONCl(OMe)_2$ requires MeO, 18·7%]. A trace of the acetyl compound dissolved with a very pale brown colour in concentrated sulphuric acid. Addition of a crystal of potassium nitrate produced a purple coloration, which quickly changed to yellowish-brown.

4-*Chloro*-2 : 6′-*dinitro*-3′ : 4′-*dimethoxystilbene* (IV).—4-Chloro-2-nitro-3′ : 4′-dimethoxystilbene (3 g.) was triturated with glacial acetic acid (6 c.c.), and nitric acid (5 c.c.; *d* 1·42) gradually added. The yellow solid obtained on the addition of water crystallised from glacial acetic acid in yellow needles, m. p. 175° (Found : C, 52·5; H, 3·8. $C_{16}H_{13}O_6N_2Cl$ requires C, 52·7; H, 3·6%). This dinitro-derivative is readily soluble in chloroform, benzene, ethyl acetate, or acetone, and moderately readily soluble in alcohol.

4-*Chloro*-2 : 6′-*diacetylamino*-3′ : 4′-*dimethoxystilbene* (V).—Zinc dust (12 g.) and hydrochloric acid (30 c.c. in all) were added alternately to a solution of 4-chloro-2 : 6′-dinitro-3′ : 4′-dimethoxystilbene (3 g.) in glacial acetic acid (60 c.c.). After filtration, an excess of aqueous ammonia was added, and the crude diamine (which dissolved readily in ether, forming a brown solution with an intense sky-blue fluorescence) was acetylated by acetic anhydride (10 c.c.) in the cold. The product (yield, 60%) crystallised from glacial acetic acid in pale yellow rods, m. p. 275° (decomp.) (Found : C, 61·4; H, 5·4. $C_{20}H_{21}O_4N_2Cl$ requires C, 61·8; 5·4%). This diacetyl compound is soluble in alcohol or acetone, and very sparingly soluble in most other solvents. A minute amount of the substance dissolved in concentrated sulphuric acid to a pale pink solution, which was momentarily decolorised and then became yellow on the addition of a crystal of potassium nitrate.

Action of phosphoryl chloride on 4-*chloro*-2 : 6′-*diacetylamino*-3′ : 4′-*dimethoxystilbene*. The deep blood-red solution obtained by heating the diacetylamino-compound (2 g.) with phosphoryl chloride (10 c.c.) on the steam-bath for 4 hours was poured slowly into cold caustic soda (250 c.c. of 12%). The pale brown precipitate was triturated with carbon disulphide, and the residue was extracted with chloroform. On the addition of twice the volume of light petroleum (b. p. 60—80°), a deep brown material was precipitated, and the filtrate, after the addition of a little more light petroleum, deposited a pale brown solid melting at about 230° (decomp.) after darkening at 160° (Found : C, 64·4; H, 5·3; N, 7·9. $C_{20}H_{19}O_3N_2Cl$ requires C, 64·8; H, 5·1; N, 7·55%). The substance, which could not be crystallised, contained no diazotisable amino-group, but after it had been heated for a short time with hydrochloric acid, diazotisation, followed by coupling with β-naphthol in alkaline solution, gave a red azo-compound.

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