LXXX.—*Unsymmetrically Substituted Dinitro- and Diamino-derivatives in the Stilbene and Tolane Series. Part I. The Elimination of Hydrogen Chloride from 3 : 4′-Dinitrostilbene Dichloride.*

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FLÜRSCHEIM was the first to point out the important principle that the alternate effects produced by substituents in aromatic nuclei can be rendered conspicuous by comparing the properties of isomeric *m*- and *p*-disubstituted derivatives. With groups in these two positions the possibility of ring closure is almost eliminated and anomalies caused by steric hindrance are largely curtailed, whilst the general polar effects are approximately equal. The present research was undertaken with the idea of testing the accuracy of certain apparently unequivocal forecasts derived by application of the alternate polarity rule to the diphenylethane series. The theory of non-polar alternating affinity, on the contrary, does not appear to afford any trustworthy *a priori* guidance in the types of reaction selected for investigation.

The dichlorides and dibromides of αβ-unsaturated acids, when deprived of one molecule of halogen hydride, invariably lose the β-halogen atom. It seemed desirable, therefore, to ascertain whether similarly unidirectional influences could be discovered in the dihalides of unsymmetrically substituted stilbene derivatives. The effect of two nitro-groups in the 3- and 4′-positions is cumulative and a strong difference in the reactivity of the two halogen atoms should accrue. The removal of one molecule of halogen hydride should therefore result in the preferential formation of one or other of the two possible monochlorostilbenes. Aa a matter of fact, *α-chloro-*4 : 3′-*dinitrostilbene* was the sole product of reaction, and this is in entire agreement with polarity principles.

3 : 4′-Dinitrostilbene had previously been prepared by Cullinane (J., 1923, **123**, 2060) by the condensation of *p*-nitrophenylacetic acid and *m*-nitrobenzaldehyde in presence of piperidine at 100° for 1 hour. Exact repetition of his method by the present authors resulted, however, in the isolation of a totally different product. Cullinane's supposed dinitrostilbene consisted of yellow needles, m. p. 155° (yield not stated), which gave green solutions in various organic solvents. The dinitrostilbene obtained by us, having been washed many times with boiling alcohol and recrystallised from glacial acetic acid, melted at 217°, and was sparingly soluble in most solvents, forming only pale yellow solutions.

From the alcoholic washings three other products were isolated in small quantity : *p*-nitrotoluene, formed by the partial decomposition of *p*-nitrophenylacetic acid by piperidine, and the *piperidine* salts of the two stereoisomeric forms of 3 : 4′-dinitro-α-phenylcinnamic acid, resulting from loss of water without carbon dioxide. Both of these acids were subsequently synthesised. They could be decarboxylated to give the same dinitrostilbene by heating with piperidine. Their properties will be described in a future paper.

Preliminary investigation showed that 3 : 4′-*dinitrostilbene dibromide* * on heating with pyridine lost both atoms of bromine ; the stilbene was therefore converted into a mixture of *dichlorides*, from each of which (although with much greater facility in the case of the low-melting β-variety), by prolonged heating with pyridine, one

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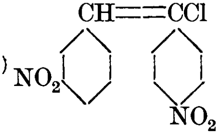
* A detailed description of this dibromide will be given in a subsequent paper.

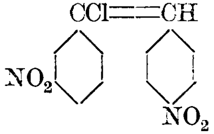
molecule of hydrogen chloride was eliminated, with the formation of only one monochlorodinitrostilbene, having one of the configurations I and II.

(I.)



α-Chloro-4 : 3′-dinitrostilbene.

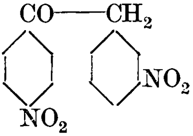
or



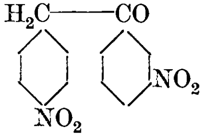
(II.)

α-Chloro-3 : 4′-dinitrostilbene.

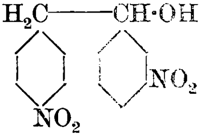
The chlorostilbene was eventually * decomposed by warm concentrated sulphuric acid, with the formation of a coloured intermediate compound (not isolated). This on decomposition with water passed through the transitory enol form to produce 4-*nitrophenyl* 3-*nitrobenzyl ketone* (III).



(III.)



(IV.)



(V.)

That this ketone had the structure shown was proved by oxidising the intermediate aldol, 3 : 4′-*dinitro*-αβ-*diphenylethyl alcohol*, isolated as a by-product from the stilbene condensation and therefore possessing the configuration (V), with chromic acid in acetic acid solution, when the isomeric 3-*nitrophenyl* 4-*nitrobenzyl ketone* (IV) was obtained.† Another proof of the constitution of (III), by its synthesis from 3 : 4′-dinitro-α-phenylcinnamamide, will be described shortly.

Each of these ketones (III and IV) was converted into the corresponding monochlorodinitrostilbene by treatment with phosphorus pentachloride, and although these two products melted at approximately the same temperature, a mixed melting point determination showed a depression of 20°, and further, each chlorodinitrostilbene, on treatment with sulphuric acid as before, was reconverted into the corresponding ketone.

Without doubt the monochlorodinitrostilbene formed by loss of the elements of hydrogen chloride from 3 : 4′-dinitrostilbene dichloride is I and not II.

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* Prolonged boiling with silver acetate in acetic acid, with potassium acetate, or with formic acid was ineffectual. An attempt to prepare the ozonide met with no greater success.

† Finzi had shown (*Monatsh.*, 1905, **26**, 1128) that oxidation of a substituted deoxybenzoin to the benzil cannot be carried out with chromic acid in acetic acid.

EXPERIMENTAL.

3 : 4′-*Dinitrostilbene*.—A mixture of *p*-nitrophenylacetic acid (76 g.) and *m*-nitrobenzaldehyde (63·5 g.) was heated with piperidine (13 g.) at 110° for 1 hour (carbon dioxide and water were expelled; the liquid then set to a semi-solid mass); thereafter the temperature was raised to 150° * during 2 hours. The product was boiled with alcohol (200 c.c.) until the solid cake had disintegrated, and the dinitrostilbene was then filtered off, pulverised, and repeatedly washed with boiling alcohol (about 300 c.c.) until it was bright yellow. It crystallised from acetic acid, nitrobenzene or pyridine in yellow needles, m. p. 217° (Found: C, 62·35; H, 3·75. $C_{14}H_{10}O_4N_2$ requires C, 62·2; H, 3·7%). It is slightly soluble in hot benzene, acetone, ethyl acetate, or chloroform, but very sparingly soluble in boiling alcohol. The yield was 30%. On standing, the mother-liquor and washings deposited a dark brown, viscous oil which could not be purified; treatment of this with cold strong sulphuric acid increased the total yield of dinitrostilbene to 55%.

3 : 4′-*Dinitro-αβ-diphenylethyl Alcohol* (V).—After removal of this oil, addition of water precipitated a light yellow solid which, after crystallisation from acetic acid and then from alcohol, melted at 147—148° (Found: C, 58·1; H, 4·3. $C_{14}H_{12}O_5N_2$ requires C, 58·3; H, 4·2%). This substance is soluble in alcohol, acetic acid, ethyl acetate, or acetone, and sparingly soluble in ether or benzene. Heating with piperidine or treatment with cold strong sulphuric acid produces the dinitrostilbene. Slow evaporation of the solution after removal of the aldol compound caused the separation of a little *p*-nitrotoluene, and on long standing the residual liquors deposited thin leaflets which crystallised from alcohol in straw-coloured needles, m. p. 168—169° (Found: C, 59·7; H, 5·2. $C_{20}H_{21}O_6N_3$ requires C, 60·15; H, 5·3%). This compound is therefore the *piperidine* salt of one of the two stereoisomeric 3:4′-dinitro-α-phenylcinnamic acids, m. p. 221°.† If the temperature of condensation is allowed to rise to 160° after 1 hour, the yield of dinitrostilbene is even less than usual, much more *p*-nitrotoluene being formed. After removal of the normal reaction products (no pure aldol can be isolated) a crop of crystals separates, which after crystallisation from alcohol consists of bright yellow needles, m. p. 204—205° (decomp.) (Found: C, 59·85; H, 5·5. $C_{20}H_{21}O_6N_3$ requires C, 60·15; H, 5·3%). This is the *piperidine* salt of the other stereoisomeric substituted cinnamic acid, m. p. 205·5°.†

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* Above this temperature much decomposition takes place.

† The free acids were obtained by treatment of the piperidine salts with warm sodium carbonate solution, and subsequent acidification; the melting points were not depressed by admixture with authentic samples.

α- *and* β-*Forms of* 3 : 4′-*Dinitrostilbene Dichloride.*—Finely divided 3 : 4′-dinitrostilbene (20 g.) was suspended in chloroform (750 c.c.),* and dry chlorine passed in during 4 hours. After standing for 4 days, the excess of chlorine was removed from the filtered solution by shaking carefully with dilute sodium bisulphite, and then with sodium hydroxide. After having been washed and dried, the chloroform solution was evaporated to a small bulk until deposition of the dichloride commenced (concentration beyond this stage tends to blacken the product). When cold, the white crystals were filtered off, washed with a little chloroform, and dried (15 g.; 60% yield). They consisted of a mixture of the α- and β-forms, and melted at 188—196°. By two crystallisations from acetic acid the pure α-form could be obtained in thin plates, m. p. 207° (Found: Cl, 20·9. $C_{14}H_{10}O_4N_2Cl_2$ requires Cl, 20·8%). The more soluble β-form, m. p. 132—138°, was never obtained quite pure (Found: Cl, 21·1%). Both forms are appreciably soluble in alcohol.

α-*Chloro*-4 : 3′-*dinitrostilbene* (I).—Preliminary investigation having shown that the α- modification of the dichloride is much more stable to pyridine than the β-, the crude mixture of dichlorides (75 g.) was heated (water-bath) with pyridine (160 g.) for 90 hours. On cooling, bright yellow, glistening needles of the monochlorodinitrostilbene crystallised out, which after recrystallisation from acetic acid melted at 161° (Found: C, 54·9; H, 3·1; Cl, 11·5. $C_{14}H_9O_4N_2Cl$ requires C, 55·2; H, 2·95; Cl, 11·6%). Precipitation of the mother-liquors with alcohol resulted in a further small quantity (total yield = 77%). No other product was isolated.† This compound crystallises well from pyridine, acetic or formic acid, benzene, chloroform, or acetone. It is but sparingly soluble in alcohol, ether, or carbon tetrachloride.

4-*Nitrophenyl* 3-*Nitrobenzyl Ketone* (III).—Finely powdered α-chloro-4 : 3′-dinitrostilbene (I) (5 g.) was gently warmed with strong sulphuric acid (20 c.c.) during 1 hour (above 60°, charring takes place). When the evolution of hydrogen chloride had ceased, the deep red solution was cooled and poured on to ice. The almost white precipitate was crystallised from alcohol, and then from acetic acid; clusters of white needles, m. p. 134°, were thus obtained

* A smaller quantity of solvent is inadvisable, owing to the slow speed of absorption of chlorine by the stilbene.

† The liquors were concentrated almost to dryness on the water-bath and warmed with strong sulphuric acid. After the vigorous evolution of hydrogen chloride (chiefly from the pyridine hydrochloride) had ceased, the product was poured into water, and the lutarious deposit crystallised from alcohol (charcoal). It melted at 129° and did not depress the melting point of III. It had therefore been formed from the same chlorodinitrostilbene.

(Found : C, 58·5; H, 3·6. $C_{14}H_{10}O_5N_2$ requires C, 58·7; H, 3·5%). This ketone is easily soluble in all the usual solvents except ether, light petroleum, or carbon tetrachloride. It gives a *semicarbazone* which crystallises from alcohol in pale yellow needles, m. p. 219°. Treatment of the ketone at its melting point with phosphorus pentachloride reconverted it into the monochlorodinitrostilbene.

3-*Nitrophenyl* 4-*Nitrobenzyl Ketone* (IV).—A solution of the aldol compound (V) (4·5 g.) in hot glacial acetic acid (45 c.c.) was cooled to 50° without allowing deposition of solid, treated with a 10% solution of chromic acid [prepared from crystalline sodium dichromate (7·5 g.), sulphuric acid (10 g.), and water (35 g.)] during 1 hour, and then, while still warm, with water (10 c.c.). The ketone which separated crystallised from 95% alcohol in pearly plates (yield 75%), m. p. 102° (Found : C, 58·65; H, 3·45. $C_{14}H_{10}O_5N_2$ requires C, 58·7; H, 3·5%). The solubilities of this ketone approximate very closely to those of the isomeric ketone (III), m. p. 134°. It gives a *semicarbazone* which crystallises from alcohol in bright yellow rhombs, m. p. 230°.

α-*Chloro*-3 : 4′-*Dinitrostilbene* (II).—Treatment of the ketone (IV) at its melting point (brine-bath) with phosphorus pentachloride furnished the corresponding monochlorodinitrostilbene in fair yield; on crystallisation from acetic acid, it formed small clumps of light brown needles, m. p. 162° (Found : C, 55·0; H, 3·0; Cl, 11·8. $C_{14}H_9O_4N_2Cl$ requires C, 55·2; H, 2·95; Cl, 11·6%). A mixture of the two isomeric monochlorostilbenes melted at 142—145°. The solubilities of this isomeride (m. p. 162°) are almost identical with those of the other (m. p. 161°). The degrees of stability, too, are comparable, since prolonged boiling with formic acid or with silver acetate in acetic acid does not remove the chlorine atom. Pyridine is also without action. Concentrated sulphuric acid at 60° converts it into the ketone (IV) from which it was derived, but so far as could be ascertained there was no difference in the rate of decomposition of the two monochlorodinitrostilbenes.

Action of Concentrated Sulphuric Acid.—The dinitrostilbene furnishes a bright red solution, from which the unchanged product is recovered on dilution with water : both monochlorodinitrostilbenes (I and II) give deep red solutions on warming and evolve hydrogen chloride vigorously; they char considerably at 80° : the dinitrostilbene dichloride yields a faintly pink solution, with very slight evolution of gas; it chars somewhat at about 80° : the dinitrostilbene dibromide gives a pink colour and evolves hydrogen bromide at 70—80°; there is no sign of charring, and the product after dilution with water and crystallisation from alcohol still contains bromine.

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