CLIX.—*Unsymmetrically Substituted Dinitro- and Diamino-derivatives in the Stilbene and Tolane Series. Part II. The Mode of Addition of Water to* 3 : 4′-*Dinitro- and Diamino-tolanes.*

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IN a former communication (this vol., p. 577) it was shown that two nitro-groups unsymmetrically situated in the two benzene nuclei of stilbene exert a definite influence on the reactivity of chlorine atoms attached to the carbon atoms in the side chain. The experiments now described indicate that similar influences are discernible in the unsymmetrically substituted dinitro- and diamino-tolanes, as exemplified by the mode of addition of the elements of water to the triple bond. Polarity considerations again appear to furnish a guide in determining the seat of reactivity.

3 : 4′-*Dinitrotolane* (I) was obtained from the dichloride or dibromide of 3 : 4′-dinitrostilbene, or from α-chloro-4 : 3′-dinitrostilbene, by the action of alcoholic potassium hydroxide. In the preparation from the dibromide, although traces of the stilbene were undoubtedly produced by loss of bromine (compare Pfeiffer and Kramer, *Ber.*, 1913, **46**, 3655), no difficulty was experienced in obtaining the pure tolane.

3 : 4′-Dinitrotolane assumed the elements of water only with great reluctance.* With the nitro-groups in these positions it was to be expected from the alternating polarity rule that harmonious combination of directing influences would exist, tending to make such a configuration exceedingly reactive and prone to attack at

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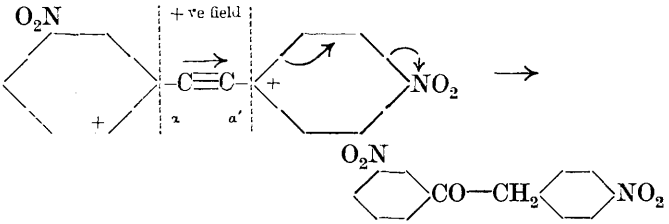
* All the ortho-substituted nitrotolanes prepared by Reinhardt (*Ber.*, 1913, **46**, 3598), by Pfeiffer and Kramer (*ibid.*, 1913, **46**, 3655), and by Pfeiffer (*Annalen*, 1916, **411**, 72) take up the elements of water with remarkable ease. It is significant, however, that neither Reinhardt nor Pfeiffer mentions the addition of water to 4 : 4′-dinitrotolane.

the carbon atoms in the side chain. But no such enhanced reactivity was manifested and the yield of 3-nitrophenyl 4-nitrobenzyl ketone (II) was small. Robinson, Allan, Oxford, and Smith (this vol., p. 401) recognise the existence of two quite distinct effects when a nitro-group is attached to the benzene ring : the one arising from the conjugation of the nitroxyl with the nucleus and resulting in positive charges on the ortho- and para-carbon atoms and the other a general electrical effect over the nucleus and the side chain. Applying these conceptions to 3 : 4′-dinitrotolane, one deduces respectively that a smaller density of electrons exists in the region of the two carbon atoms marked + than in the region of their immediate neighbours, and that the acetylenic carbon atoms $\alpha\alpha'$ are under the influence of a strong positive field, which inhibits reactivity towards positive ions at both centres. Since, however, the positive charge in the *p*-nitrophenyl group is nearer the acetylenic bond than is that in the *m*-nitrophenyl group, the electrons of the acetylenic bond will be displaced in the direction of the arrow, that is, from $\alpha \longrightarrow \alpha'$.[*] Addition of water, therefore, though difficult, takes place as follows :

(I.)



(II.)

It is also possible that the *p*-nitrophenylacetylene group is a conjugated system, but the existence of such conjugation could only be disclosed by experiments with anionoid reagents.

An attempt to investigate the influence of the amino-groups on the elimination of hydrogen chloride from 3 : 4′-diaminostilbene dichloride was unsuccessful, owing to the impossibility of retaining the chlorine atoms in the molecule during the reduction; 3 : 4′-*diaminostilbene* was the sole product.[†]

3 : 4′-*Diaminotolane*, like the nitrotolane, was very reluctant to assume the elements of water; this inertness is at first sight the more surprising in view of the peculiar ease with which 4 : 4′-diaminotolane passes into the deoxybenzoin, warm dilute hydrochloric acid

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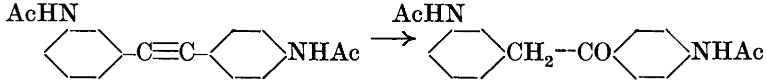
[*] Similar cases have been considered by Lucas and his colleagues (*J. Amer. Chem. Soc.*, 1924, **46**, 2475; 1925, **47**, 1459, 1462).

[†] Replacement of the chlorine atoms by hydrogen does not occur, since 3 : 4′-*diaminodibenzyl* (prepared for purposes of comparison) coincided with none of the products obtained during the whole investigation.

effecting its quantitative conversion (Reinhardt, *Ber.*, 1913, **46**, 3598). Under no conditions * did sulphuric acid bring about the corresponding reaction in the case of 3 : 4′-diaminotolane; during one reduction experiment only, in which zinc and hydrochloric acid were employed, was a small amount of 4-*aminophenyl* 3-*aminobenzyl ketone* produced. From the *diacetyl* derivative of the aminotolane (III), however, the action of concentrated sulphuric acid resulted in the formation of the *diacetyl* derivative of this ketone (IV) in good yield, its constitution being inferred from its non-identity with 3-*acetylaminophenyl* 4-*acetylaminobenzyl ketone*, prepared from the corresponding nitrophenyl nitrobenzyl ketone (this vol., p. 579).



(III.) (IV.)

The conception of combined general and alternating polar effects again proves valuable here. Electronic repulsion from the two acetylamino-groups, resulting from their conjugation with the respective benzene nuclei, produces a strongly negative field in the region of the acetylenic carbon atoms, which are consequently in a highly reactive state. Addition of water thus takes place with great ease.

The mechanism of reaction of the free aminotolane, on the other hand, is obscured by salt formation, but to account for the great difference in reactivity between 4 : 4′- and 4 : 3′-diaminotolane it is only necessary to suppose that the former exists in hydrochloric acid as its mono-acid salt, and the latter as its di-acid salt. In fact, the author ventures to suggest that the diquaternary ammonium base derived from 4 : 4′-diaminotolane would assume the elements of water with great difficulty.

EXPERIMENTAL.

3 : 4′-*Dinitrostilbene Dibromide*.—Finely-divided 3 : 4′-dinitrostilbene (21·6 g.) (this vol., p. 580) was suspended in chloroform (1 litre), bromine (12 c.c.) added, and the whole kept during 2—4 days. The stilbene gradually dissolved and later the dibromide partly crystallised. The solvent and excess of bromine were then distilled off, and the solid residue † was recrystallised from boiling glacial acetic acid (about 925 c.c.). The yield was 90%. As with the dichloride, two forms could be obtained by fractional crystallisation. The pure α-form is sparingly soluble in acetic acid,

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* The concentration and temperature were varied over a wide range.

† This, unlike the dichloride (this vol., p. 581), did not char during removal of the last few c.c. of solvent.

crystallising in almost white, thick prisms, m. p. 234° (Found: Br, 36·9. $C_{14}H_{10}O_4N_2Br_2$ requires Br, 37·2%). Its production seems to be favoured by longer exposure of the chloroform solution to daylight. The pure β-form is more soluble in acetic acid or chloroform, crystallising from the former solvent in pale brown, minute plates, m. p. 214° (Found: Br, 36·95%). Both forms are sparingly soluble in most organic solvents; they separate from boiling nitrobenzene in small prisms. Even the β-form, which in substances of this type usually reacts differently from the α- form (compare Pfeiffer, *Ber.*, 1912, **45**, 1810), on being heated with pyridine at 90° for 2 hours loses both bromine atoms, reverting to the stilbene.*

3 : 4′-*Dinitrotolane* (I).—The mixture of dibromides (22·8 g.) was suspended in boiling alcohol (220 c.c.), and a solution of potassium hydroxide (6·6 g.) in water (15 c.c.) added. After being boiled under reflux for 1 hour, the mixture was allowed to cool to 50° and the brown solid filtered off. After being well washed with cold alcohol and then with water, the product was crystallised twice from glacial acetic acid, and then from a large volume of alcohol to free it from traces of stilbene (see p. 1232). The pure tolane melted at 173—174°; the yield was 70% (Found: C, 62·3; H, 3·2. $C_{14}H_8O_4N_2$ requires C, 62·7; H, 3·0%). It is easily soluble in hot benzene, nitrobenzene, acetone, or ethyl acetate, less readily in acetic acid or chloroform, somewhat sparingly soluble in ethyl alcohol, and very sparingly soluble in carbon tetrachloride, carbon disulphide, ether, or light petroleum. It produces a deep red solution in strong sulphuric acid.†

Addition of water. The nitrotolane (1 g.), obtained in a fine state of division by pouring an alcoholic solution into water, was dissolved in cold concentrated sulphuric acid. After being maintained at 15° for 30 minutes,‡ the solution was slowly poured on to ice, and the slightly resinous deposit filtered off and dissolved in acetone. Slow evaporation of the solvent left behind dark glistening plates, which after three crystallisations from alcohol (charcoal) melted at 101°, alone or mixed with an authentic specimen of 3-nitrophenyl 4-nitrobenzyl ketone (this vol., p. 582). Although the yield was only fair, no other product was isolated.

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* Unlike the dibromide of the parent substance (Limpricht. *Annalen*, 1868, **145**, 338), 3 : 4′-dinitrostilbene dibromide does not yield the corresponding benzil when heated with water under pressure, even at 215° for 60 hours.

† Compare the bluish-violet colour given under similar conditions by 2 : 4-dinitrotolane (Pfeiffer, *loc. cit.*).

‡ Any other conditions, such as alteration of temperature, use of solvents, change in concentration or duration, resulted in a charred product or recovery of the unchanged nitrotolane.

3 : 4′-*Diaminostilbene*.—A solution of the dinitrostilbene (2 g.) in boiling acetic acid (15 c.c.) was cooled to 70° and zinc dust (10 g.) and hydrochloric acid (40 c.c.) were gradually added with stirring; the reaction was complete in ¾ hour. The boiling solution was filtered, and, on cooling, the *hydrochloride* separated in yellow, pearly plates or needles.* The free amine after recrystallisation from alcohol formed small, yellow plates or needles, m. p. 156° (Found: C, 80·0; H, 6·9. $C_{14}H_{14}N_2$ requires C, 80·0; H, 6·7%). It is very soluble in ethyl acetate or acetone, less readily in alcohol, ether or benzene, and sparingly soluble in chloroform, carbon tetrachloride, carbon disulphide or light petroleum. The *diacetyl* derivative crystallises from methyl alcohol in clumps of needles, m. p. 226—227° (Found: C, 73·3; H, 6·3. $C_{18}H_{18}O_2N_2$ requires C, 73·5; H, 6·1%). This derivative is very soluble in ethyl acetate, soluble in acetone or alcohol, and sparingly soluble in benzene or chloroform. It gives no colour with cold concentrated sulphuric acid.

3 : 4′-*Diaminodibenzyl*.—The diaminostilbene (1·2 g.) was reduced with sodium (2 g.) in boiling ethyl alcohol (30 c.c.), the reaction being complete in ½ hour. When cold, the opaque solution was acidified with dilute hydrochloric acid and a small amount of tar removed by extraction with ether. The free base crystallised from the warm solution on addition of dilute sodium hydroxide (weight of crude product = 0·95 g.), and when recrystallised from aqueous alcohol formed small, white plates, m. p. 73—75°. It is easily soluble in acetone, alcohol, ether or benzene; the *hydrochloride* is readily soluble in water, from which it crystallises in needles. The *diacetyl* derivative crystallises from aqueous alcohol in small clusters of thick needles, m. p. 177° (Found: C, 72·7; H, 6·9. $C_{18}H_{20}O_2N_2$ requires C, 73·0; H, 6·8%). It is readily soluble in alcohol, acetone, or ethyl acetate, moderately easily soluble in hot chloroform, and almost insoluble in benzene. It gives no colour with cold sulphuric acid.

Reduction of 3 : 4′-*Dinitrostilbene Dichloride*.—3 : 4′-Diaminostilbene was also obtained, though with difficulty, from 3 : 4′-dinitrostilbene dichloride by reduction in alcoholic solution with zinc and hydrochloric acid at 15°.† The reduction was incomplete, and the light brown *substance* which remained after filtration of the normal reaction product, when crystallised from alcohol melted

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* It is essential to isolate this amine as its hydrochloride, otherwise the melting point varies over a range of 50°.

† No reduction took place with iron powder and calcium chloride, whilst stannous chloride and acetic acid yielded a mixture of products exceedingly difficult to purify.

at 202—205° (Found: C, 65·2; H, 3·0%). It contained chlorine, but gave an immediate intense purple colour with cold concentrated sulphuric acid, and was therefore not the unchanged dichloride (see this vol., p. 582). On the other hand, it could not be diazotised. Its constitution was not further investigated.

Reduction of α-Chloro-4 : 3′-dinitrostilbene.—Facile reduction occurred when crystalline stannous chloride (25 g.) in 80% acetic acid (25 c.c.) was added to the chlorostilbene (5 g.) dissolved in boiling glacial acetic acid (50 c.c.). The solution was almost neutralised with sodium hydroxide,* and the tin precipitated by hydrogen sulphide. The filtrate was boiled and neutralised, and the free ketonic base recrystallised several times from alcohol (charcoal); after purification, it formed rosettes of almost colourless needles, m. p. 153°, which were not identical with 3 : 4′-diaminostilbene, m. p. 156°, obtained from the dichloride (see above), since an intimate mixture melted about 15° below this temperature.

A better yield of the diacetyl derivative of this base was obtained by shaking the crude reduction liquor, while still warm, with acetic anhydride in presence of sodium acetate. After standing over-night, the solution was poured into water and the suspended solid extracted with methyl ethyl ketone. The ketone layer, which separated after the addition of a large quantity of calcium chloride, was dried over potassium carbonate, the solvent removed, and the diacetyl compound recrystallised three times from methyl alcohol with the addition of ether; it then melted at 204°. (The properties of these two compounds are described below.)

3 : *4′-Diaminotolane.*—The nitrotolane (3 g.) was boiled with alcohol (25 c.c.), and the suspension quickly cooled to 10°. Zinc dust (5 g.) was added, and then, very slowly, hydrochloric acid (17 c.c.) † during 1 hour, the temperature being maintained at 10—15°. The solution of the hydrochloride was filtered from much (2 g.) unreduced nitrotolane and the precipitated amine was extracted with ether and recrystallised from aqueous alcohol, when it formed light brown needles, m. p. 124—125° (Found: C, 80·6; H, 6·1. $C_{14}H_{12}N_2$ requires C, 80·8; H, 5·8%). It dissolves easily in alcohol, ether, ethyl acetate or acetone, rather less readily in hot benzene or chloroform, and is sparingly soluble in carbon disulphide or light petroleum. It is not converted into the deoxybenzoin by boiling with hydrochloric acid. Its *diacetyl* derivative crystallises from methyl alcohol in thick needles, m. p. 226° (Found: C, 73·8;

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* The free amine appears to be somewhat unstable to hydrogen sulphide in presence of alkali; possibly a sulphur atom is incorporated in the molecule (compare Jones and Robinson, J., 1917, **111**, 911).

† Zinc and acetic acid give coloured by-products.

H, 5·55. $C_{18}H_{16}O_2N_2$ requires C, 74·0; H, 5·5%). This diacetyl derivative, unlike those of diaminostilbene (m. p. 226—227°) and diaminodibenzyl (m. p. 177°), gives an immediate red colour with cold concentrated sulphuric acid.

4-*Acetylaminophenyl* 3-*Acetylaminobenzyl Ketone* (IV).—Pure 3 : 4′-diacetyldiaminotolane (III) (0·3 g.) was dissolved in cold concentrated sulphuric acid (3·0 c.c.), and the temperature maintained at 15° for ½ hour. No hydrolysis took place under these conditions. The deep red solution was then poured on to ice, and the mauve-coloured solid at once filtered off. It slowly changed to a grey non-crystalline mass, which by purification from alcohol was transformed into almost white needles, m. p. 204° (Found : C, 69·3; H, 6·1. $C_{18}H_{18}O_3N_2$ requires C, 69·7; H, 5·8%). The yield was good, and no other product was detected. This diacetyl compound was identical with that obtained from the reduction of α-chloro-4 : 3′-dinitrostilbene (see above). It is soluble in alcohol, dilute acetic acid, or ethyl acetate, but sparingly soluble in ether. It no longer gives a red colour with cold concentrated sulphuric acid.

4-*Aminophenyl* 3-*Aminobenzyl Ketone.*—During the course of one experiment on the reduction of 3 : 4′-dinitrotolane with zinc and hydrochloric acid at 70—80°, after separation of the hydrochloride of the normal reduction product, precipitation of the mother-liquors with alkali yielded a brown solid which, after being twice crystallised from aqueous alcohol, melted at 156°. Its melting point was depressed 20° by admixture of an authentic specimen of 3 : 4′-diaminostilbene (m. p. 156°),* but not at all by addition of the amine (m. p. 153°) formed on reduction of α-chloro-4 : 3′-dinitrostilbene; its diacetyl derivative, m. p. 204°, was identical with that obtained by the action of sulphuric acid on 3 : 4′-diacetyldiaminotolane. Without doubt it was a deoxybenzoin produced by addition of water to the triple bond of the tolane, probably under the influence of the metal, since boiling hydrochloric acid alone effected no change (Found : C, 74·0; H, 6·4. $C_{14}H_{14}ON_2$ requires C, 74·3; H, 6·2%). This amine is soluble in all the usual organic solvents, and crystallises in clusters of slightly brown, flat needles from alcohol.

3-*Acetylaminophenyl* 4-*acetylaminobenzyl ketone* was obtained when the corresponding dinitro-ketone (1·3 g.) was reduced at 10° with zinc and hydrochloric acid, as in previous experiments. The crude amine isolated from the hydrochloride was at once acetylated, and the product recrystallised from alcohol, when it melted at 184—186° (Found : C, 69·35; H, 6·0. $C_{18}H_{18}O_3N_2$ requires C, 69·7; H, 5·8%). The solubilities of this diacetyl derivative were similar to those of

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* Which even under these conditions, therefore, is not produced (compare Reinhardt, *loc. cit.*).

the isomeric ketone, m. p. 204°, but a mixture of the two melted at 170—179°. This dissimilarity definitely establishes the constitution of 4-acetylaminophenyl 3-acetylaminobenzyl ketone, and consequently the mode of addition of water to 3 : 4′-diaminotolane and to its diacetyl derivative.

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