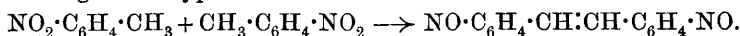


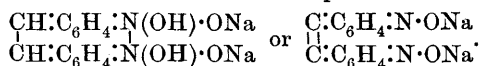
CCIV.—*The Colouring Matters of the Stilbene Group.*
Part IV. The Action of Caustic Alkalis on
para-Nitrotoluene and its Derivatives.

By ARTHUR GEORGE GREEN, ARTHUR HUGH DAVIES, and RONALD
 SMITH HORSFALL.

As the results of investigations conducted by Green in conjunction with former collaborators (*Ber.*, 1897, **30**, 3097; 1898, **31**, 1078; *Trans.*, 1904, **85**, 1424, 1432), the view was advanced that the deeply-coloured (red, violet, or blue), unstable intermediate products which mark the first stage of the action of caustic alkalis on *p*-nitrotoluene and its derivatives are to be regarded as nitrosostilbenes, formed according to the typical scheme:



This conclusion was arrived at from a study of the products of oxidation, the compounds themselves being too unstable to admit of isolation. The deep colour of the alkaline solutions of these compounds (when neutral they are pale yellow) was accounted for by assuming for the alkali salts a tautomeric quinonoid form, such as:



The reaction appears to be common to *p*-nitrotoluene and all its derivatives, but is greatly facilitated by the presence of electro-negative groups in the ortho-position with respect to the methyl group.* This is seen, for example, in the more ready condensation of *p*-nitrotoluenesulphonic acid compared with that of *p*-nitrotoluene itself. At the same time, it is noteworthy that in those cases in which the reaction is greatly accelerated by the presence of a strongly electronegative group, such as $\text{SO}_3 \cdot \text{C}_6\text{H}_5$, CN or NO_2 , the colour of the intermediate compound is blue instead of red.

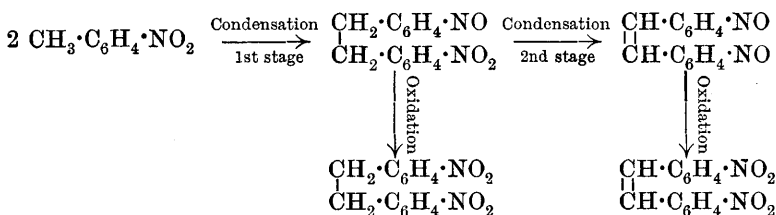
In order to investigate the effect of different ortho-substituents, and to obtain further light on the course of the reaction, we have examined the behaviour to caustic alkalis of *p*-nitrotoluene itself, and of its *o*-methyl-, *o*-methoxy-, *o*-cyano-, and *o*-carboxy-derivatives. As in the cases previously investigated, we have endeavoured to

* This fact was first recognised by Green and Stainton. The latter established a close parallelism between the influence of various ortho-substituents on the mobility of the hydrogen atoms of the methyl group when derivatives of *p*-nitrotoluene are submitted to the stilbene condensation, on the one hand, and to Sach's reaction (condensation with nitrosodimethylaniline), on the other.

characterise the intermediate compounds by oxidation to the stable nitro-compounds by means of air or hypochlorites.

In the cases examined by Green, Marsden, and Scholefield (the *o*-chloro-derivative and the *o*-phenylsulphonate), only stilbene compounds were obtained on oxidation, and no formation of a dinitrodibenzyl compound was observed, although Green and Wahl had previously obtained from *p*-nitrotoluenesulphonic acid both dinitrodibenzyl disulphonic acid and dinitrostilbenedisulphonic acid, according to the conditions under which the alkaline condensation was performed. We have now found that the ultimate product of oxidation largely depends on the reactivity of the particular derivative. Thus, whilst the *o*-cyano-derivative gave only the corresponding stilbene compound, we obtained from the methyl, methoxyl, and carboxyl derivatives the corresponding dibenzyl compounds; and from *p*-nitrotoluene itself, like its sulphonic acid, either dinitrodibenzyl or dinitrostilbene, according to the conditions employed. It is worthy of note that the derivatives which yield by preference dibenzyl compounds are those which react least easily and give red condensation products, whilst the derivatives which yield chiefly stilbene compounds are those which react most readily and form violet or blue condensation products.

The results point to the conclusion that the alkaline condensation occurs in two stages, which may be more or less concurrent according to the degree of reactivity of the substance. The product of the first stage gives rise on oxidation to a dinitrodibenzyl, that of the second stage to a dinitrostilbene. This is shown by the following scheme:



When oxidation accompanies condensation, as in the experiments described, it would only depend on the speed with which stage one passes into stage two whether the first or the second condensation product was that chiefly attacked by the oxygen. Substituents which increase the reactivity of the substance would therefore favour the formation of stilbene compounds. That this is in fact the case will be shown later.

Relative Influence of Various ortho-Substituents on the Reactivity of the Methyl Group in para-Nitrotoluene Derivatives.

We have endeavoured to obtain an approximate measure of the relative influence exerted by different ortho-substituting groups on the reactivity of the *p*-nitrotoluene complex by observing the relative temperatures at which the colour formation commences under constant conditions of alkalinity and molecular concentration. The experiments were performed as follows: 0.1 gram of *p*-nitrotoluene or the corresponding molecular quantity of one of its derivatives was dissolved in 1 c.c. of pyridine and 5 c.c. of pure methyl alcohol. The solution was contained in a test-tube which could be warmed or cooled as required. Five c.c. of a saturated solution of potassium hydroxide in methyl alcohol (33 per cent. KOH) were added, the mixture was kept well stirred with a thermometer, and the minimum temperature was noted at which colour formation set in. The following results were obtained:

Substance.	Ortho-substituent.	Coloration produced.	Minimum temperature of reaction.
<i>p</i> -Nitrotoluene	H	Crimson	78°
<i>p</i> -Nitro- <i>o</i> -xylene	CH ₃	„	79° to 80°
<i>p</i> -Nitro- <i>o</i> -tolylmethyl ether ...	O·CH ₃	„	75° to 77°
<i>p</i> -Nitro- <i>o</i> -toluidine	NH ₂	„	81°
<i>p</i> -Nitro- <i>o</i> -toluic acid	CO ₂ H	„	78° to 79°
<i>o</i> -Chloro- <i>p</i> -nitrotoluene	Cl	Violet	23° to 24°
Phenyl <i>p</i> -nitrotoluene- <i>o</i> -sulphonate	SO ₃ ·C ₆ H ₅	Blue	about -20°
<i>p</i> -Nitro- <i>o</i> -cyanotoluene	CN	„	„ -20°
2:4-Dinitrotoluene	NO ₂	„	below -20°

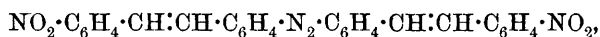
The reaction temperatures have, of course, only a relative significance, as they vary greatly with the concentration of alkali employed.

The comparison shows that, whilst the methyl, methoxyl, amino-, and carboxy-groups have but little influence on the reactivity of the compound, the more strongly electronegative groups, sulphophenyl, cyano- and nitro-, exert a powerful effect, that of the nitro-group being greatest. This result is very analogous to the effect on the lability of the chlorine atom in chlorobenzene derivatives exerted by electronegative groups, such as the nitro- and sulphonic acid groups, when occupying an ortho-position.

Action of Caustic Alkalis and Air Oxidation on para-Nitrotoluene.

By acting on *p*-nitrotoluene with alcoholic sodium hydroxide, O. Fischer and Hepp (*Ber.*, 1893, **26**, 2231) obtained small quantities of dinitrodibenzyl and dinitrostilbene. The main product of the

reaction was, however, a sparingly soluble, orange-yellow substance, which the above authors term "dinitrosostilbene," but which is probably the dinitroazodistilbene,



formed by further condensation of the true dinitrosostilbene which is first produced. In order to prevent the formation of this condensation product, it is necessary to proceed in such a manner that the intermediate nitroso-compounds are oxidised as soon as they are formed. If, for instance, powdered *p*-nitrotoluene is covered with 33 per cent. alcoholic potash and slightly warmed, the formation of the red nitroso-compound commences at once. The conditions preclude the employment of hypochlorites, but the oxidation of the intermediate compound is readily effected by means of air. To obtain good results and prevent contamination of the product with coloured compounds it is only necessary to take care that the oxidation keeps pace with the colour formation, since the nitroso-compound, if not at once oxidised, quickly undergoes further condensation. Five grams of *p*-nitrotoluene were placed in a wide-necked, conical flask together with 100 c.c. of cold 33 per cent. methyl-alcoholic potash. The red coloration which forms immediately disappears again on vigorous shaking, giving place to a pale yellow, granular precipitate. The operation was continued in the cold with constant shaking until the colour formation only took place slowly and the mixture had become a pale yellow, crystalline magma. This was then filtered by the aid of the pump, the precipitate washed with hot water and hot alcohol, and dried. The product recrystallised from benzene, formed pale yellow needles melting at 180—182°. It was evidently the known 4 : 4'-dinitrodibenzyl, $\text{NO}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{NO}_2$:

Found, N = 10.56, 10.52.

$\text{C}_{14}\text{H}_{12}\text{O}_4\text{N}_2$ requires N = 10.29 per cent.

Under the conditions employed above (reaction in the cold), dinitrodibenzyl appears to be almost the sole product. If, however, the temperature of the mixture is slowly raised and the operation continued for a longer period, until finally the colour formation has practically ceased, the product is of a deeper yellow than before and then consists chiefly of a compound which, after alternate crystallisation from nitrobenzene and from glacial acetic acid, was obtained in bright yellow leaflets or flat needles, melting at 292—294°. It proved to be 4 : 4'-dinitrostilbene, $\text{NO}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{CH} : \text{CH} \cdot \text{C}_6\text{H}_4 \cdot \text{NO}_2$, and probably represents this substance in a somewhat purer state than previously obtained. Fischer and Hepp assign to dinitrostilbene the melting point 272°, whilst Walden and Kernbaum (*Ber.*, 1890, 23, 1958) give 280—285° as the melting point of their higher melting

isomeride. We have obtained no evidence of the formation by our reaction of a second isomeride. Analysis gave the following results:

Found, C = 61.95; H = 3.57; N = 10.65, 10.55.

$C_{14}H_{10}O_4N_2$ requires C = 62.2; H = 3.7; N = 10.37 per cent.

The yield of the crude product is nearly theoretical.

In order to distinguish with certainty between stilbene and dibenzyl derivatives in the above and other cases described in this paper, we have made use of the following test, which depends on the more ready oxidation of the ethylene group. A small quantity of the substance is dissolved in a little pyridine, and to the cold solution is added two or three drops of an acetone solution of calcium permanganate. With stilbene compounds, the solution is at once decolorised, whilst with dibenzyl compounds the pink colour persists for several minutes even if gently warmed.

Action of Caustic Alkalis and Air on p-Nitro-o-xylene.

The operation was carried out in the cold in the same manner as described above. In this case, also, the crude yield was almost theoretical. The product, after recrystallisation from glacial acetic acid, formed lemon-yellow needles, melting at 222—224°. It is not oxidised by permanganate under the conditions described above, and is without doubt 4:4'-dinitro-2:2'-dimethyldibenzyl (4:4'-dinitro-s-di-o-tolyethane), $NO_2 \cdot C_6H_3Me \cdot CH_2 \cdot CH_2 \cdot C_6H_3Me \cdot NO_2$.

The substance is somewhat sparingly soluble in most solvents. It gave the following results on analysis:

Found, C = 64.14; H = 5.55; N = 9.58, 9.54.

$C_{16}H_{16}O_4N_2$ requires C = 64.0; H = 5.33; N = 9.33 per cent.

Under the conditions of the experiment, the corresponding stilbene derivative was not obtained.*

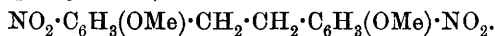
Action of Caustic Alkalis and Air on p-Nitro-o-tolyl Methyl Ether.

The p-nitro-o-tolyl methyl ether employed was obtained by methylation of nitro-o-cresol prepared by decomposition of the diazo-compound of p-nitro-o-toluidine and purification in the manner described by Witt, Noelting, and Grandmougin (*Ber.*, 1890, 23, 3636). After recrystallisation from alcohol, the ether melted at about 72°.

The condensation and oxidation were effected in the same manner as before. The yield of the crude product, insoluble in alcohol, was nearly theoretical, namely, 4.9 grams from 5 grams of tolyl ether taken. The substance was crystallised two or three times from ethyl

* The dinitrodimethylstilbene and dinitrodimethoxystilbene have been since obtained and are at present undergoing investigation. A. G. G.

acetate, and then formed lemon-yellow leaflets melting at 178—180°. It proved to be 4 : 4'-*dinitro-2 : 2'-dimethoxydibenzyl* (4 : 4'-*dinitro-2 : 2'-dimethoxy-s-diphenylethane*),



Analysis gave the following results :

Found, C = 58.43 ; H = 4.80 ; N = 8.72.

$\text{C}_{16}\text{H}_{16}\text{O}_6\text{N}_2$ requires C = 57.83 ; H = 4.81 ; N = 8.43 per cent.

A methoxyl determination by Zeisel's method gave :

Found, CH_3 = 8.78.

$\text{C}_{16}\text{H}_{16}\text{O}_6\text{N}_2$ requires CH_3 = 9.03 per cent.

The substance is not oxidised by permanganate under the conditions prescribed above.

Under the conditions employed, there was no formation of the corresponding stilbene derivative.*

Action of Caustic Alkalis and Hypochlorites on p-Nitro-o-toluic Acid.

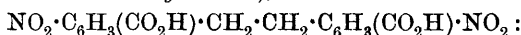
The *p*-nitro-*o*-toluic acid employed was obtained by saponification of the nitrile (see later) by boiling it for two or three hours with sulphuric acid diluted with half its volume of water. After recrystallisation from dilute alcohol, it formed long, colourless needles which melted at about 178°. When heated with aqueous sodium hydroxide, it gives a deep violet-red coloration, which is converted into a yellow stilbene dyestuff on longer heating. This colouring matter dyes unmordanted cotton direct in bright yellow shades, and is similar to Direct Yellow. The behaviour of the carboxylic acid is therefore quite analogous to that of the corresponding sulphonic acid.

In order to oxidise the violet-red intermediate compound, we have proceeded in a similar manner to that employed for the sulphonic acid by Green and Wahl. Five grams of *p*-nitrotoluic acid were dissolved in 12 c.c. of water by means of 1.4 grams of sodium carbonate. To the hot solution were added 35 c.c. of sodium hypochlorite solution (7.4 per cent. active chlorine), followed immediately by 50 c.c. of sodium hydroxide (33 per cent. NaOH). The mixture was then rapidly heated to the boiling point, when the reaction sets in vigorously and the liquid boils spontaneously for about half a minute. Directly the reaction slackens and the mixture becomes pasty, but before any coloration appears, and whilst there is still a small excess of hypochlorite left (that is, in about one minute from the commencement of the reaction), the whole contents of the flask must be poured quickly into an excess of dilute hydrochloric acid (100 c.c. of concentrated hydrochloric acid and 300 c.c. of water) contained in a large beaker. The operation is somewhat difficult to carry out, as, if the

* *Ibid.*

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reaction is allowed to proceed a few seconds too long until the hypochlorite is exhausted, colour formation sets in, and the product cannot be subsequently purified. When the operation is correctly conducted, the product is obtained as a pale yellow precipitate, sparingly soluble in water or alcohol. It was purified by several extractions with boiling dilute alcohol (30 per cent.), dried, and recrystallised from cresol. The product separated in colourless plates, which melted with decomposition at 299—300°. Its analysis and properties indicate that it is 4 : 4'-dinitrodibenzyl-2 : 2'-dicarboxylic acid (4 : 4'-dinitro-s-diphenylethane-2 : 2'-dicarboxylic acid),



Found, C = 53·4, 52·9, 53·5 ; H = 3·51, 3·28, 3·38 ; N = 8·07, 7·83.

$\text{C}_{16}\text{H}_{12}\text{O}_8\text{N}_2$ requires C = 53·33 ; H = 3·33 ; N = 7·77 per cent.

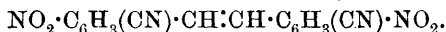
It is not oxidised by permanganate in cold pyridine solution or in cold dilute aqueous solution.

We have not yet obtained the corresponding stilbene derivative in a pure state, although in several of our experiments, in which rather different conditions from the above were employed, a product was obtained which gave the reactions of a stilbene compound. The melting point of this substance was about 270°. It is reduced to a crimson-red compound on adding phenylhydrazine or dextrose to the aqueous solution rendered alkaline with sodium hydroxide.

Action of Caustic Alkalis and Air on p-Nitro-o-cyanotoluene.

The nitrile was prepared from *p*-nitro-*o*-toluidine by Sandmeyer's reaction, and purified by recrystallisation from alcohol. It formed pale yellow needles which melted at 103°. On adding alcoholic potash or strong aqueous potassium or sodium hydroxides to a cold alcoholic solution of the nitrile, excluding air by a current of hydrogen, a brilliant deep blue coloration is produced. This coloration after some minutes slowly changes to violet, and, if air is admitted, it quickly becomes brown, and a dark tarry precipitate is deposited. The blue compound therefore, like other members of its class, is extremely unstable. Since its isolation was impossible, it was at once submitted to oxidation. Both air and sodium hypochlorite were employed as oxidising agents, the product in each case being the same. The hypochlorite, however, gave the best results. Ten grams of the nitrile were dissolved in 30 c.c. of warm pyridine and mixed with 300 c.c. of alcohol. To the cold solution were added 160 c.c. of sodium hypochlorite (4·75 per cent. active chlorine), followed immediately by 60 c.c. of strong aqueous sodium hydroxide. The mixture became warm, and a precipitate separated. This was immediately collected by the aid of the pump, and washed with

boiling alcohol. The crude product was a pale yellow, granular precipitate, which melted above 200°. For purification, it was recrystallised several times from nitrobenzene and glacial acetic acid. It proved to be 4:4'-dinitro-2:2'-dicyanostilbene,



The compound is sparingly soluble in nitrobenzene, chloroform, or glacial acetic acid, moderately so in pyridine, and almost insoluble in alcohol. It crystallises from glacial acetic acid in small, indistinct, yellow crystals, which melt with decomposition at about 258°. Analysis gave the following results:

Found, C = 60.9, 60.0, 60.2; H = 2.75, 2.5, 2.39; N = 17.50, 17.87.

$\text{C}_{16}\text{H}_8\text{O}_4\text{N}_4$ requires C = 59.9; H = 2.52; N = 17.54 per cent.

The substance at once decolorises permanganate in a cold pyridine solution. On reduction in cold alcoholic solution by addition of sodium hydroxide and a drop of phenylhydrazine, it is reconverted into the deep blue nitrosostilbene from which it is derived.

We have not been able to isolate a second isomeride. Attempts to convert the nitrile into the carboxylic acid were also unsuccessful, owing to the occurrence of by-reactions on heating with mineral acids.

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