

LXXIII.—*Orientation Effects in the Diphenyl Series.*
Part VII. The Effect of Substituents in One Nucleus on the Ratio of Ortho:Para Nitration in the Other. The Nitration of 2- and 4-Nitro- and of 2:4- and 2:4'-Dinitro-diphenyl and of Diphenyl-4-carboxylic Acid.

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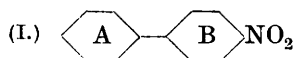
It was recently pointed out (Le Fèvre and Turner, J., 1928, 245) that the then-known facts, *viz.*, the semi-quantitative results of Bell and Kenyon (J., 1926, 2705), in connexion with the nitration of 2- and 4-nitrodiphenyl indicated that the two nuclei of diphenyl are independently conjugated. These two compounds have now been nitrated quantitatively. 4-Nitrodiphenyl is nitrated to the extent of 37% and 63% in the 2'- and the 4'-position respectively, and 2-nitrodiphenyl gives 39% of the 2'-nitro- and 61% of the 4'-nitro-compound. In neither case is 2:4-dinitrodiphenyl formed, nor, we think, would its formation be expected (compare, however, Bell and Kenyon, *loc. cit.*, for the converse opinion) in view of the known retarding influence of a nitro-group on further substitution

in the same nucleus. More important is the proof of the non-formation of detectable quantities of 3'-nitro-derivatives.

From the point of view of establishing the independence of the two nuclei, the nitration of 2 : 4-dinitrodiphenyl, hitherto unknown, is even more pertinent. This substance has been obtained by heating a mixture of iodobenzene and 1-chloro-2 : 4-dinitrobenzene with copper bronze (the first example, as far as we are aware, of the synthesis of an unsymmetrical diphenyl derivative by the Ullmann reaction), and has been found to be nitrated to the extent of 45% in position 2' and 55% in position 4', less than 1% of a third product being formed, a fact which clearly demonstrates the nuclear independence referred to above.

Since distortion of the diphenyl molecule such as leads to optical activity does not appear, so far as is known at present, until the 2 : 2' : 6 : 6'-positions are crowded, the 2'/4' ratio (corresponding to the *o/p* ratio in simple benzene substitution) for the nitration of 2-nitrodiphenyl should not be materially different from that of the 4-isomeride in so far as this ratio is determined by purely steric effects. This is in agreement with the results obtained.

The 2'/4' ratios for the nitration of 4-nitro-, 2-nitro-, and 2 : 4-dinitro-diphenyl are seen from the above figures to be in the proportion 59 : 64 : 82, and if it be assumed that the 2'/4' ratio is determined, as it is in the case of the monohalogenobenzenes, by the degree of electropositeness of the substituent (the *o/p* ratios for Cl, Br, and I in those compounds are as 43 : 61 : 70, corresponding to increasing positiveness of the halogen atom), then in 4-nitrodiphenyl (I) carbon atom 1 (in nucleus B) should be less positive than the corresponding atom in 2-nitrodiphenyl, this C₁ being in turn less positive than that in 2 : 4-dinitrodiphenyl. And this is the case, in effect if not in fact, owing to the polarising effect of the nitro-group or groups. It seems probable, therefore, that the properties of C₁, as affected by the substituents attached to the other carbon atoms of the B nucleus, determine the ratio of 2' to 4' nitration (*i.e.*, *o*- to *p*-nitration in nucleus A). It is possible that, if certain strongly polarising groups



could be introduced into B, C₁ would become so positive that some 3'-nitration would occur in A.

By nitrating 3-nitrodiphenyl, Blakey and Scarborough (J., 1927, 3000) obtained 11—12 g. of 3 : 4'- and 5—6 g. of 2 : 3'-dinitrodiphenyl out of a total possible 18 g. of dinitro-derivatives, and although these figures are only approximate, they are in accordance with the expectations of the above theory, which requires a 2'/4'

ratio even lower than that of 4-nitrodiphenyl, for C_1 in 3-nitrodiphenyl possesses a distinctly negative character.

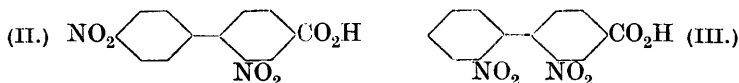
Bell, Kenyon, and Robinson (J., 1926, 1239) showed that diphenyl, when mononitrated by a mixture of nitric and acetic acids at 80—90°, gave 45—55% of 4-nitrodiphenyl. We have dinitrated diphenyl quantitatively, and find that 30% of the product is 4:4'-dinitrodiphenyl. Since this must have been derived from intermediately formed 4-nitrodiphenyl, which, as shown above, is nitrated to the extent of 63% in the 4'-position, it can be calculated that, of the original diphenyl, 47% must have been nitrated in position 4, and therefore 53% in position 2, a result not in disagreement with the observations of Bell, Kenyon, and Robinson.

4:4'-Dinitrodiphenyl is readily nitrated by hot fuming nitric acid, and the 2:4:4'-*trinitrodiphenyl* formed is nitrated in presence of mixed acids at 100° to give the known 2:4:2':4'-tetranitro-compound. 2:2'-Dinitrodiphenyl is similarly nitrated to give mainly 2:4:2'-*trinitrodiphenyl* (convertible in turn into the above tetranitro-compound), together with a small quantity of a second substance.

The mononitration of 2:4'-dinitrodiphenyl, which has been studied quantitatively, produces 47.5% of 2:4:2'- and 52.5% of 2:4:4'-*trinitrodiphenyl*, a result which appears to show the very small effects originating from mere steric influences.

When picryl chloride, iodobenzene, and copper bronze are heated together, the main product is 2:4:6-*trinitrodiphenyl*, the apparent non-formation of hexanitrodiphenyl being no doubt due to spatial effects.

We have also studied the nitration of diphenyl-4-carboxylic acid, in an attempt to prepare 4'-nitrodiphenyl-4-carboxylic acid, of which the mononitration (occurring, as it possibly would, in both rings) would have been of considerable interest as affording a method of comparing the retarding influence of the nitro- and the carboxyl group on further substitution. We have, however, been unable to obtain the mononitro-acid, although dinitration is readily accomplished, and has been studied quantitatively. Only two dinitro-acids are formed, and these are readily separated by fractional acidification of the alkaline solution of the mixture. One acid (m. p. 265°, corr.), constituting 49% of the total product, is clearly identical with that (m. p. 252°) described by Strasser and Schultz



(*Annalen*, 1881, **210**, 191), who obtained evidence that it was 2:4'-dinitrodiphenyl-4-carboxylic acid (II). That the conclusion

of these authors is correct has now been shown by decarboxylating the acid, whereby 2 : 4'-dinitrodiphenyl was isolated.

The second acid, forming 51% of the product, is 2 : 2'-*dinitrodiphenyl-4-carboxylic acid* (III), since decarboxylation affords 2 : 2'-dinitrodiphenyl. Strasser and Schultz suspected the presence of a second acid, but failed to isolate it.

Although the nitration of 4'-nitrodiphenyl-4-carboxylic acid could not be studied, the results obtained clearly show that the retarding influence of a nitro-group is far greater than that of a carboxyl group.

EXPERIMENTAL.

(All melting points given are corrected.)

Nitration of 4-Nitrodiphenyl.—4-Nitrodiphenyl (20 g.) was added to 285 c.c. of nitric acid (d 1.448), stirred, and kept at 40–50°. 4 : 4'-Dinitrodiphenyl gradually separated, and stirring was continued until the temperature of the suspension had fallen to 20°. The solid was then filtered off and washed with dilute nitric acid, 13.65 g. of 4 : 4'-dinitrodiphenyl, *m. p.* 239–243°, being obtained. The mother-liquor was precipitated with water, and yielded 10.75 g. of crude 2 : 4'-dinitrodiphenyl, so the total yield of dinitrodiphenyls was 99.5% of that theoretically possible. The amount of 4 : 4'-dinitrodiphenyl not separating under the above conditions was determined as follows: A "mother-liquor" having the same composition as that in the actual nitration was prepared by stirring a mixture of 71.5 c.c. of nitric acid (d 1.448), 0.5 c.c. of water, 2.7 g. of 2 : 4'-dinitrodiphenyl and 3.4 g. of 4 : 4'-dinitrodiphenyl, the temperature being allowed to fall slowly from 50° to 20°. The undissolved 4 : 4'-dinitrodiphenyl weighed 3.0 g. The corrected weight of 4 : 4'-isomeride is therefore $13.65 + 1.6 = 15.25$ g., whence the percentage in the total nitration product is 62.5.

In a second nitration, 10 g. of 4-nitrodiphenyl gave 4.98 g. of crude 2 : 4'-isomeride, and $7.02 + 0.69 = 7.71$ g. of 4 : 4'-compound, corresponding to 64% of 4 : 4'-nitration.

The crude 2 : 4'-compound was crystallised several times from alcohol. Although the amount of 4 : 4'-compound present was small, as the solubility control experiment showed, it was difficult to remove it, owing to the solubility of 4 : 4'-dinitrodiphenyl in concentrated alcoholic solutions of 2 : 4'-dinitrodiphenyl and its sparing solubility in dilute alcoholic solutions of its isomeride.

Dinitration of Diphenyl.—Diphenyl (20 g.) was added gradually to 440 c.c. of nitric acid (d 1.448), kept stirred and initially at 35°. The temperature rose to 50°, and was kept at that point by external cooling. After all the hydrocarbon had been added, the solution was stirred until it had cooled to 20°. 4 : 4'-Dinitrodiphenyl

crystallised out, and was filtered off; its weight, after correction for solubility in the mother-liquor (determined with the appropriate solution), was 9.43 g. Complete precipitation of the original mother-liquor gave 23.77 g. of solid. The total yield of isomeric dinitro-compounds was thus 97% of that theoretically possible. Since the 4 : 4'-dinitrodiphenyl (29.8% of total product) must have been formed from 4-nitrodiphenyl, which undergoes 63% of 4'-nitration, the original diphenyl must have undergone

$$\frac{9.43 \times 199 \times 154 \times 100}{244 \times 0.63 \times 20 \times 199} = 47\% \text{ of 4-nitration.}$$

In a second experiment, 9.83 g. of diphenyl gave a corrected weight of 4.61 g. of 4 : 4'-dinitrodiphenyl (total yield of dinitro-compounds, 15.53 g. = 98%). From this result, the original diphenyl must have undergone 47% of 4-nitration (4 : 4'-compound, 29.7% of total product).

Nitration of 4 : 4'-Dinitrodiphenyl.—The dinitro-compound was dissolved in 10 parts of nitric acid (*d* 1.5) and the solution was heated to boiling for a few minutes, cooled, and poured into water. The precipitated solid, when washed and dried, had m. p. 175—176°, and crystallised from glacial acetic acid or from nitric acid in pale yellow cubes, m. p. 176° (Found : N, 14.9. C₁₂H₇O₆N₃ requires N, 14.6%).

The 2 : 4 : 4'-trinitrodiphenyl so obtained was nitrated as follows : 1 G. was dissolved in 10 c.c. of concentrated sulphuric acid, 10 c.c. of nitric acid (*d* 1.5) were added, and the mixture was heated at 100° for an hour; the cooled solution was poured into water. The precipitated solid crystallised from glacial acetic acid in small needles, m. p. 165°, and was identical with 2 : 4 : 2' : 4'-tetranitrodiphenyl obtained by the Ullmann synthesis.

Preparation of 2-Nitrodiphenyl.—Diphenyl was nitrated by the method of Bell and Kenyon (J., 1926, 1239). The acetic acid mother-liquors, obtained after removal of solid 4-nitrodiphenyl, were poured into water. The oil was separated, washed with warm water, dried, and slowly distilled at 20 mm. through a short column. The fraction of b. p. 185—190° was almost pure 2-nitrodiphenyl. It was dissolved in methylated spirit so as to give a solution saturated at 20°. This was cooled to 0° and inoculated with 2-nitrodiphenyl. The material which crystallised was submitted to a similar process, whereupon pure 2-nitrodiphenyl was obtained, m. p. 37—38°.

Nitration of 2-Nitrodiphenyl.—(a) *Qualitative.* 2-Nitrodiphenyl (20 g.) was stirred with 270 c.c. of nitric acid (*d* 1.420) at 35°, and nitric acid (*d* 1.5) was added very slowly. The temperature rose slightly, and the 2-nitrodiphenyl first melted and then slowly

dissolved. After all had passed into solution, the liquid was stirred for a further $\frac{1}{4}$ hour, water added gradually until the temperature rose to 50° , and the liquid allowed to cool. 2:4'-Dinitrodiphenyl separated and, after being twice crystallised from alcohol, had m. p. $92.5-93.5^\circ$ (10 g.). The mother-liquor was completely precipitated with water, and the solid precipitate was crystallised repeatedly from benzene and then from alcohol, pure 2:2'-dinitrodiphenyl being obtained.

(b) *Quantitative.* 2-Nitrodiphenyl (4 g.) was nitrated under the foregoing conditions. After the addition of water, resulting in a rise of temperature to 50° , the whole was poured into excess of cold water and left over-night. The solid deposit was filtered off, well washed with boiling water, partly dried, powdered, and then dried in a vacuum over calcium chloride. In this way, 4.79 g. (yield, 97.7%) and 4.83 g. (yield, 98.5%) of mixed dinitrodiphenyls were obtained in two different experiments. Both specimens had f. p. 68.3° . The f. p.'s of a number of mixtures of 2:2'- and 2:4'-dinitrodiphenyl were then accurately determined :

2:4'-Com- pound, %	0.0	21.5	47.5	59.9	60.8	69.6	78.2	88.7	100.0
F. p.	123.6°	109.2°	85.6°	70.4°	69.1°	74.2°	79.2°	85.4°	91.3°

The f. p. of the nitration product is thus 0.5° lower than the eutectic point (39% of 2:2'-compound). Addition of 0.6218 g. of 2:4'-compound to 1.3643 g. of nitration product gave a mixture of f. p. 75.6° , corresponding with 28.2% of 2:2'-dinitrodiphenyl, or with 27.4% of that compound if it be assumed that the nitration product has the same composition as the eutectic. It follows from this that 2-nitrodiphenyl undergoes about 61% of 4'-nitration, and therefore about 39% of 2'-nitration, the amount of nitration in any other sense being of the order of 1%.

Preparation of 2:4-Dinitrodiphenyl.—A mixture (equimolecular) of 21 g. of iodobenzene and 20 g. of 1-chloro-2:4-dinitrobenzene was heated in a wide-mouthed conical flask in a metal-bath, initially at 210° . Copper bronze (40 g.) was added gradually, the mixture being well stirred with a thermometer. The temperature of the mixture rose slowly to 225° , and reaction proceeded rapidly. After all the copper had been added, heating was continued (230°) for 10 minutes. The cooled product was extracted with hot benzene, and the extract distilled in steam. No diphenyl was detected. The non-volatile oil was crystallised from 200 c.c. of hot methylated spirit. 2:4-Dinitrodiphenyl was then obtained (3–5 g.) in golden-yellow plates, m. p. 110° (Found: N, 11.6. $C_{12}H_8O_4N_2$ requires N, 11.5%). A further quantity remained in the mother-liquors.

Nitration of 2:4-Dinitrodiphenyl.—2:4-Dinitrodiphenyl (2 g.)

was dissolved in 50 c.c. of nitric acid (*d* 1.5). The solution was heated at 100° for a minute, cooled, and poured into water. The precipitated solid was filtered off, washed with warm water, and dried in a vacuum over calcium chloride. In this way, 2.35 g. (yield, 99%) of mixed trinitro-derivatives were obtained, f. p. 139.5°. The f. p.'s of a number of mixtures of 2 : 4 : 4'- and 2 : 4 : 2'-trinitrodiphenyl (see below) were then determined :

2 : 4 : 4'-Com- pound, %	0.0	50.6	53.9	55.6	65.1	80.7	90.1	100.0
F. p.	150.5°	134.6°	138.0°	140.8°	148.7°	162.4°	169.2°	175.5°

A mixture of 1.0028 g. of nitration product with 0.9614 g. of pure 2 : 4 : 4'-trinitrodiphenyl had f. p. 159°, corresponding to 23.5% of 2 : 4 : 2'-trinitrodiphenyl. The calculated percentage of 2 : 4 : 2'-derivative in this new mixture is 23.0%, the absence of any third substance being assumed. It follows that the nitration product contained 55% of 2 : 4 : 4'- and 45% of 2 : 4 : 2'-trinitrodiphenyl.

Nitration of 2 : 2'-Dinitrodiphenyl.—The dinitro-compound (6 g., m. p. 124°) was added gradually to 60 c.c. of nitric acid (*d* 1.5), which was kept at 75–80°; water was then slowly added, the temperature being kept below 80°, until crystallisation began, whereupon the whole was allowed to cool. The solid was filtered off, washed with water, and twice crystallised from glacial acetic acid, 5.4 g. of pure 2 : 4 : 2'-trinitrodiphenyl being obtained as pale yellow rectangular prisms, m. p. 150–151° (Found: N, 14.8. $C_{12}H_7O_6N_3$ requires N, 14.6%).

The nitration mother-liquor, when treated with excess of water, gave 1 g. of a mixture of trinitro-compounds, and the acetic acid mother-liquor yielded 0.5 g. of gummy material. The results show that 2 : 2'-dinitrodiphenyl is nitrated to the extent of 80–85% in position 4.

Nitration of 2 : 4 : 2'-Trinitrodiphenyl.—The foregoing compound (1 g.) was heated with 10 c.c. of concentrated sulphuric acid and 10 c.c. of nitric acid (*d* 1.5) at 100° for 1 hour, the solution cooled, and poured into water. The precipitated solid, after being twice crystallised from glacial acetic acid, melted at 165°, and was identical with a specimen of 2 : 4 : 2' : 4'-tetranitrodiphenyl prepared by the Ullmann process from 1-chloro-2 : 4-dinitrobenzene.

Nitration of 2 : 4'-Dinitrodiphenyl.—A solution of 5 g. of the dinitro-compound (m. p. 93.5°) in 30 c.c. of nitric acid (*d* 1.5) was heated at 100° for one minute and poured into water; the precipitated solid was carefully washed and dried, and then had f. p. 136.9°. The addition of a weighed quantity of pure 2 : 4 : 4'-trinitrodiphenyl raised the f. p. by the amount corresponding to the absence of a third substance. Hence, from the data given above,

2 : 4'-dinitrodiphenyl undergoes 52.5% of 4-nitration and 47.5% of 2'-nitration.

2 : 4 : 6-*Trinitrodiphenyl*.—A mixture of 30 g. of picryl chloride and 30 g. of iodobenzene was heated in a bath at 195—200°. The mixture was stirred with a thermometer, and 25 g. of copper bronze were gradually added, the temperature not being allowed to rise above 205°. The cooled mixture was extracted with hot alcohol. The crystalline solid separating on cooling was recrystallised from light petroleum (b. p. 80—100°; Soxhlet extractor) and then from alcohol. 2 : 4 : 6-*Trinitrodiphenyl* forms pale yellowish needles, m. p. 130° (Found: N, 15.2. $C_{12}H_7O_6N_3$ requires N, 14.6%). No hexanitrodiphenyl was detected.

Preparation of Diphenyl-4-carboxylic Acid.—(a) *From 4-aminodiphenyl*. This compound gives very poor yields of 4-cyanodiphenyl by the diazo-method (compare Kaiser, *Annalen*, 1890, 257, 95; Ferriss and Turner, J., 1920, 117, 1140).

(b) *From 4-acetyldiphenyl*. This compound was prepared by a modification of the method given previously (Ferriss and Turner, *loc. cit.*): To a mixture of 125 g. of diphenyl, 40 g. of acetyl chloride, and 500 c.c. of carbon disulphide, 90 g. of well-powdered aluminium chloride were slowly added (10 mins.; efficient cooling). The whole was heated on the water-bath for 2 hours and then cooled and decomposed with water. Carbon disulphide and excess of diphenyl were removed in a current of steam, and the residual oil was distilled in superheated steam from a flask kept in a bath at 200°. The crude 4-acetyldiphenyl so obtained was suitable for the next preparation; after crystallisation from alcohol it had m. p. 120.5° (60—70 g.). It was oxidised by one of the following methods.

Hypochlorite oxidation. A mixture of 5 g. of acetyldiphenyl with 150 c.c. of water was boiled and 30 c.c. of commercial sodium hypochlorite solution were added gradually. Boiling was continued until chloroform was no longer evolved, the hot liquid was then filtered and acidified, and the precipitated solid crystallised twice from alcohol to remove terephthalic acid; 2 g. of diphenyl-4-carboxylic acid were thus obtained.

Permanganate oxidation. To a vigorously stirred, boiling suspension of 50 g. of finely powdered acetyldiphenyl in 1 l. of water were added 120 g. of potassium permanganate in six portions at $\frac{3}{4}$ -hour intervals. The mixture was finally boiled for a further hour, filtered whilst hot, and then decolorised with sulphur dioxide. On addition of hydrochloric acid, crude diphenylcarboxylic acid was precipitated. After removal of terephthalic acid by two crystallisations from alcohol, 40 g. of acid, m. p. 228°, were obtained. If all

the permanganate is added at the beginning, more terephthalic acid is produced.

Experiments on the Nitration of Diphenyl-4-carboxylic Acid.—

(a) *In concentrated sulphuric acid.* Nitration with mixed acids is impossible, owing to the readiness with which the carboxylic acid undergoes sulphonation. The ready sulphonation of diphenyl compounds has been noted frequently in this series of investigations, but has not been reported previously.

(b) *In glacial acetic acid.* Trial experiments showed that nitration did not occur, or was incomplete, unless about 4 mols. of nitric acid were present. Mononitration could not be effected. For dinitration, the most satisfactory conditions were as follows: 2 G. of diphenylcarboxylic acid were dissolved in 15 c.c. of boiling glacial acetic acid, and 1.4 c.c. (4 mols.) of nitric acid (d 1.5) were added. After the mixture had been kept at the b. p. for a short time, dinitration was complete, the product having m. p. 180—245°.

(c) *In nitric acid.* Diphenylcarboxylic acid does not dissolve in nitric acid of d 1.4, but dissolves in the acid of d 1.5 at 0°, to give the result recorded by Strasser and Schultz (*loc. cit.*). Their dinitro-acid was isolated with m. p. 254° (265° corr.). The very sparingly soluble compound described by them is apparently a polynitro-compound.

Diphenylcarboxylic acid dissolved slowly in well-stirred nitric acid (d 1.5) at -15° to give only dinitro-acids. The solution was poured into water, and the precipitated solid collected, washed, and dried (Found: N, 9.9. $C_{13}H_8O_6N_2$ requires N, 9.7%).

Quantitative Dinitration of Diphenyl-4-carboxylic Acid.—The acid (16.24 g.) was added to 610 c.c. of well-stirred nitric acid (d 1.5) kept at -15° , stirring being maintained until a clear solution was obtained. This was poured on ice, and the solid obtained was filtered off, washed, and dried in a vacuum over calcium chloride (20.2 g.). The mother-liquor was almost neutralised with sodium carbonate. The gum which separated became crystalline when the whole was heated at 100°. The solid, after being collected and purified as before (3.34 g.), had m. p. 194—195°. The total yield (23.54 g.) is almost theoretical.

The fraction weighing 20.2 g. was suspended in 400 c.c. of hot water, and just sufficient sodium carbonate added to give a clear solution, which was diluted to 4 l. and stirred vigorously. Hydrochloric acid (about 0.75*N*) was added drop by drop, and from time to time precipitates were filtered off. In this way, a sharp separation into two main fractions was effected: (1) m. p. 240—254°, 11.60 g., crystallising from alcohol-acetic acid in small colourless needles, m. p. 265° (corr.); (2) m. p. 191—197°, 8.55 g. The above substance

of m. p. 194—195° was the same, so that the total yield of (2) was 11.89 g., whence the percentages of (1) and (2) are respectively 49 and 51.

The constitutions of the two acids were determined by decarboxylation. After several methods had been tried, the following proved successful: 1.5 G. of acid (1) were well ground with 2 g. of sodium hydrogen carbonate and 3.5 g. of copper bronze, and the mixture was slowly heated in a bath. At 305°, the metallic appearance of the copper suddenly vanished, and the mixture became pasty. It was cooled, and extracted twice with boiling benzene. Four similar experiments were carried out, and the combined extracts were evaporated. The oily residue became crystalline on cooling. After being crystallised first from light petroleum (b. p. 80—100°) and then from alcohol, it (0.4 g.) had m. p. 92.5—93.5°, unaffected by admixture of pure 2:4'-dinitrodiphenyl. Acid (1) is therefore 2:4'-dinitrodiphenyl-4-carboxylic acid.

Acid (2), similarly treated, gave a crude product melting at 110—118°. After successive crystallisation from light petroleum (b. p. 80—100°) and alcohol, it melted at 124°, either alone or when mixed with pure 2:2'-dinitrodiphenyl. Acid (2) is therefore 2:2'-dinitrodiphenyl-4-carboxylic acid.

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