LX.—*The Molecular Configurations of Polynuclear Aromatic Compounds. Part V. The Identity of the Nitration Products derived from 2 : 7- and 4 : 5-Dinitrophenanthraquinones.*

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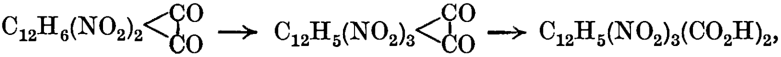
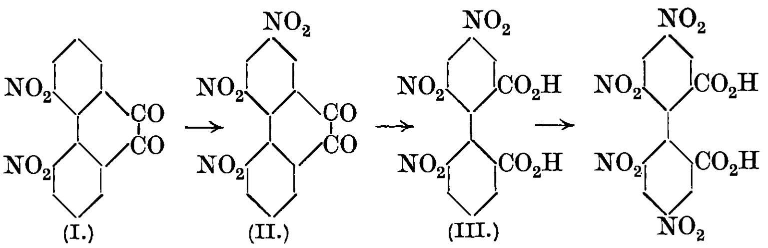
THE conversion of 2 : 7-dinitrophenanthraquinone successively into 2 : 4 : 7-trinitrophenanthraquinone and 4 : 6 : 4′-trinitrodiphenic acid,



$$C_{12}H_6(NO_2)_2<\begin{matrix}CO\\|\\CO\end{matrix} \longrightarrow C_{12}H_5(NO_2)_3<\begin{matrix}CO\\|\\CO\end{matrix} \longrightarrow C_{12}H_5(NO_2)_3(CO_2H)_2,$$

has been already described (Christie and Kenner, J., 1923, **123**, 779). At the same time, it was intimated that a similar set of reactions had been carried out in the case of the dinitro-quinone which is produced with the 2 : 7-isomeride by nitration of phenanthraquinone and which Schmidt and Kämpf (*Ber.*, 1903, **36**, 3745) concluded to be a 4 : 5-derivative (I). The new trinitroquinone was therefore thought to be a 2 : 4 : 5-derivative (II), and so different from the above-mentioned 2 : 4 : 7-isomeride, when it was oxidised to a diphenic acid (III) from which 4 : 6 : 4′ : 6′-tetranitrodiphenic acid was obtained by further nitration :



It was therefore remarkable that when the acid (III) was resolved into optically active forms by fractional crystallisation of the quinidine or, better, of the quinine salts, a very close correspondence was revealed between the physical constants of the various salts and of those derived from the 4 : 6 : 4′-trinitro-acid. This will be apparent from the following table :

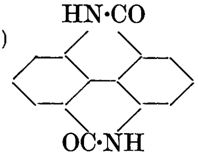
	4 : 6 : 4′-Acid.	New acid.
Melting point.	289—290°	291°
Quinine *d*-salt.	M. p. 222°; $[\alpha]_D$ −156·4°	M. p. 222°; $[\alpha]_D$ −156·1°
,, *l*-salt.	M. p. 175°; $[\alpha]_D$ − 69·1°	M. p. 176°; $[\alpha]_D$ − 77·5°
Quinidine *l*-salt.	M. p. 229°; $[\alpha]_D$ −191·1°	M. p. 228°; $[\alpha]_D$ −189·2°
,, *d*-salt.	M. p. 176°; $[\alpha]_D$ 85·5°	M. p. 178°; $[\alpha]_D$ 109·9°
Sodium salt, *d*-acid.	$[\alpha]_D$ −152·3°	$[\alpha]_D$ −151·1°

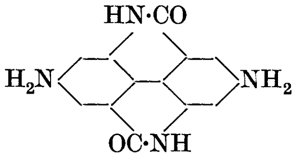
This agreement also extends to the original trinitro-quinones, each of which crystallises from benzene in yellow, hexagonal prisms, which melt at 209° and contain one molecular proportion of benzene of crystallisation.

In spite, therefore, of the apparently conclusive nature of the evidence in favour of the constitutional formulæ assigned to these various compounds, the possibility suggested itself that the two series might in reality be identical. This was confirmed when it was found that the melting point of the two acids was not depressed by mixing them, and that the same applied to the *quinoxaline* derivative, m. p. 307°, prepared by condensing each of the trinitro-quinones with *o*-phenylenediamine. It followed either that the orientation of the two dinitro-quinones, from which the same trinitro-quinone had been obtained, was in some respect faulty or that, in the course of nitration of these dinitro-compounds, migration of a nitro-group had occurred in one case. Whichever of these be correct, it seemed advisable if possible to determine the orientation of the trinitro-compound by an independent method.

It had previously been shown (Kenner and Stubbings, J., 1921, **119**, 593) that γ-6 : 6′-dinitrodiphenic acid was converted by reduction into a phenanthridone derivative (IV), and it was now found that 4 : 6 : 4′ : 6′-tetranitrodiphenic acid is similarly convertible into the corresponding diamino-compound (V), of which both neutral and basic sulphates were isolated.

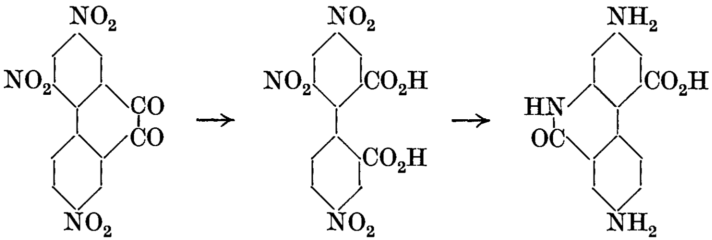
(IV.)





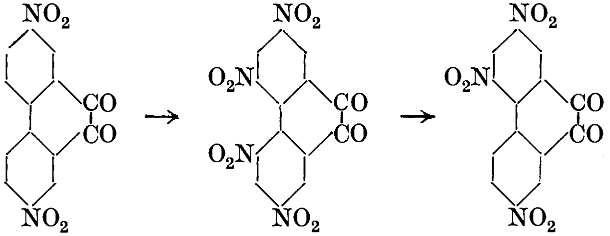
(V.)

The trinitrodiphenic acid, however, under similar conditions yielded an amino-acid soluble both in alkali and in excess of mineral acid. Clearly this result indicates that the trinitro-acid is a 4 : 6 : 4′-derivative, derived from a 2 : 4 : 7-trinitrophenanthraquinone :



It has been pointed out (J., 1923, **123**, 780) that a 2 : 4 : 5 : 7-tetranitrophenanthraquinone could not be obtained from the trinitro-compound under very vigorous conditions of nitration. Hence it was just conceivable that the production of the same trinitro-compound from the two dinitrophenanthraquinones was due to the formation of the tetranitro-derivative in the first place, followed by elimination of a nitro-group under the conditions of experiment :

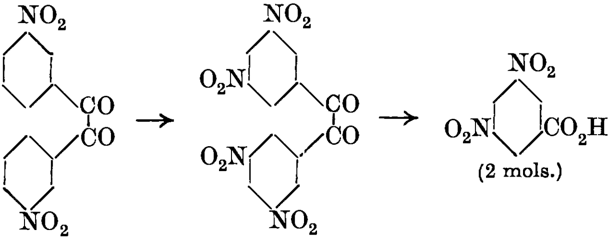
(I.) and



Although this would be a novel reaction, and is not observed in the case of the compound 4 : 6 : 4′ : 6′-tetranitrodiphenic acid, it was deemed advisable to examine the behaviour of the closely related compound, 3 : 3′-dinitrobenzil (VI), on nitration. No difficulty was experienced in converting this into the corresponding

3 : 5 : 3′ : 5′-*tetranitrobenzil*, the constitution of which was proved by its oxidation to 3 : 5-dinitrobenzoic acid :

(VI.)



EXPERIMENTAL.

2 : 4 : 7-*Trinitrophenanthraquinone from* 4 : 5-*Dinitrophenanthraquinone.*—When the procedure described in the case of 2 : 7-dinitrophenanthraquinone (Christie and Kenner, *loc. cit.*, p. 783) was applied to the 4 : 5-isomeride, the trinitro-derivative was obtained, after crystallisation from benzene, in stout, yellow prisms, m. p. 209° (Found : loss of weight at 120°, 18·6. $C_{14}H_5O_8N_3,C_6H_6$ requires loss, 18·5%. Found for material previously heated at 120°. N, 12·3. $C_{14}H_5O_8N_3$ requires N, 12·25%). Solutions of the quinone (0·75 g.) and *o*-phenylenediamine (0·38 g.) in glacial acetic acid reacted at once when mixed. The precipitated *quinoxaline* derivative separated from benzene in clusters of colourless needles, m. p. 307° (Found : N, 16·75. $C_{20}H_9O_6N_5$ requires N, 16·9%). An identical product was obtained from the quinone derived from 2 : 7-dinitrophenanthraquinone.

4 : 6 : 4′-*Trinitrodiphenic Acid from* 4 : 5-*Dinitrophenanthraquinone.*—The acid prepared from the above trinitroquinone by the usual process of oxidation with potassium dichromate and sulphuric acid was obtained first as an oil and then as a solid, m. p. 292° [Found : equiv., 188·3. $C_{12}H_5O_6N_3(CO_2H)_2$ requires equiv., 188·5]. Solutions of the acid (4·6 g.) in alcohol (100 c.c.) and of quinine hydrate (9·2 g.) in alcohol (70 c.c.) were mixed and boiled; a salt (5·8 g.) separated on cooling. On evaporating the alcoholic liquor, an oil remained from which a second salt (5·8 g.) was obtained by treatment with dry ether.

Quinine d-4 : 6 : 4′-*trinitrodiphenate*, the less soluble of the two salts so obtained, forms colourless, octahedral prisms, m. p. 222·5° (decomp.) and free from alcohol. For a 1·25% solution in 10*N*-acetic acid, $[\alpha]_D^{19^\circ} = -156{\cdot}1^\circ$ (Found : N, 9·6. $C_{54}H_{55}O_{14}N_7$ requires N, 9·6%).

Quinine l-4 : 6 : 4′-*trinitrodiphenate* melts at 176° (decomp.) after repeated purification by solution in alcohol and precipitation by ether. For a 0·5% solution in chloroform, $[\alpha]_D^{19°}$ = − 77·5° (Found : N, 9·7. $C_{54}H_{55}O_{14}N_7$ requires N, 9·6%).

Quinidine salts, m. p. 228° and 178°, agreeing in crystalline form with those previously described (Christie and Kenner, *loc. cit.*) were also obtained. For 0·7% solutions in chloroform, the respective observed values for $[\alpha]_D$ were − 189·2° and + 109·9°. The poor agreement between the latter value and that previously recorded is to be attributed partly to a clerical error, which led to the value 56·04° being quoted in place of the correct value of 85·55°, and partly to the lower melting point of the salt employed on the previous occasion.

d-4 : 6 : 4′-Trinitrodiphenic acid, prepared from the quinine salt in the manner described in the earlier papers, was an oil which very slowly solidified to colourless prisms, m. p. 281—282° (decomp.). For a 3·11% solution in ether, $[\alpha]_D$ = + 23·47°, and on conversion into a 1·48% solution of the sodium salt, $[\alpha]_D$ = − 149·0°. For a 0·84% solution of sodium salt prepared without investigating the rotatory power of the acid, $[\alpha]_D$ = − 151·1°. For a 1·36% solution of the sodium salt from the quinidine salt, m. p. 178°, $[\alpha]_D$ = − 146·1°, and the acid melted at 281—282° (decomp.).

l-4 : 6 : 4′-Trinitrodiphenic acid, from the quinine salt, melted and decomposed at 280—282°, and showed $[\alpha]_D$ = − 15·14° for a 2·80% solution in ether. For a 1·05% solution of the sodium salt subsequently prepared, $[\alpha]_D$ = + 136·6°. The changes in sign of rotatory power thus observed in passing from the acid to the sodium salt show that the prefixes *d*- and *l*- as used in the previous paper require to be interchanged.

Quinine salts prepared from the acid derived from 2 : 7-dinitrophenanthraquinone melted at 222° and 175°, respectively, and exhibited specific rotatory powers of − 156·4° (1·28% solution in 10*N*-acetic acid) and − 69·11° (0·63% solution in chloroform).

Reduction of 4 : 6 : 4′ : 6′-*Tetranitrodiphenic Acid.*—When a solution of stannous chloride (33 g.) in hydrochloric acid (30 c.c.) was slowly added to a solution of the acid (3 g.) in glacial acetic acid (30 c.c.) and hydrochloric acid (24 c.c.), heat was evolved, a red colour was produced which slowly disappeared, and a precipitate formed. This was collected after the mixture had been boiled for an hour, and after being washed with hydrochloric acid it was dissolved in concentrated sulphuric acid. By cautious dilution with water, yellow plates were obtained which turned green when exposed to the air and light, and left no residue on ignition. They blackened, but did not melt, when heated to 300° (Found : N, 15·2. $C_{14}H_{10}O_2N_4,H_2SO_4$ requires N, 15·4%). The aqueous extract obtained by warming the material with sodium carbonate solution was shown in the usual manner to contain sulphate ions.

When a solution of the material in sulphuric acid was added to sodium acetate solution, a green precipitate was obtained which still contained sulphur after being thoroughly washed and was apparently a basic sulphate (Found : N, 17·7. $C_{14}H_{10}O_2N_4,\frac{1}{2}H_2SO_4$ requires N, 17·8%).

Reduction of 4 : 6 : 4′-*Trinitrodiphenic Acid.*—The result of applying the procedure described above to 4 : 6 : 4′-trinitrodiphenic acid was less satisfactory than that of heating a suspension of the finely ground acid in hydrochloric acid at 100° with an amount of tin about 50% in excess of that theoretically necessary for complete reduction. By collecting the almost colourless solid portion of the product, washing it with hydrochloric acid, and cautious precipitation with water of its solution in sulphuric acid, a yellow material was obtained which turned green on exposure to air and exhibited the properties of an amino-acid [Found : N, 11·3; equiv., 120·6. $C_{13}H_{10}ON_3(CO_2H),H_2SO_4$ requires N, 11·45%; equiv., 122·3].

3 : 5 : 3′ : 5′-*Tetranitrobenzil.*—Dinitrobenzil (30 g.) reacted vigorously with nitric acid (150 g.; *d* 1·5) and sulphuric acid (180 g.) when heated at 100° for 10 minutes, so that it was necessary to cool the liquid. Finally, the mixture was heated for 20 hours at 100° and then poured on to ice. The solid product consisted of 3 : 5-dinitrobenzoic acid (m. p. 205°, equiv. 213·1) and a neutral substance insoluble in cold sodium carbonate solution. By crystallisation from benzene, yellow needles of a tetranitrobenzil, m. p. 168°, were obtained (Found : N, 14·35. $C_{14}H_6O_{10}N_4$ requires N, 14·35%). Its orientation was demonstrated by adding excess of hydrogen peroxide to a solution of the compound in dilute aqueous sodium hydroxide. Heat was evolved and after about ½ hour the dark coloration first produced had given place to a pale yellow. An excellent yield of 3 : 5-dinitrobenzoic acid was obtained on acidification. Tetranitrobenzil was, however, unchanged by prolonged heating with the above nitration mixture, so that it was not an intermediate product in the formation of dinitrobenzoic acid from dinitrobenzil.

The *quinoxaline* derivative of tetranitrobenzil, prepared in the usual manner by condensation in glacial acetic acid solution, formed colourless needles, m. p. 274° (Found : N, 18·4. $C_{20}H_{10}O_8N_6$ requires N, 18·2%).

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