

CCLVI.—*The Existence of Quinonoid Salts of o-Nitroamines and their Conversion into Oxadiazole Oxides.*

By ARTHUR GEORGE GREEN and FREDERICK MAURICE ROWE.

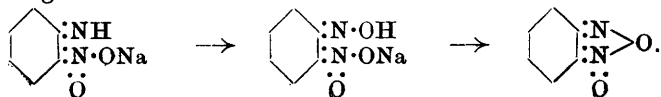
THE question of the existence of quinonoid forms of nitroamines has been the subject of frequent discussion and investigation. The proof afforded by Hantzsch of the existence of *aci*-salts of nitrophenols seems to render it not unlikely that in alkaline solution the nitroamines may also yield analogous *aci*-salts of the type

$C_6H_4 \begin{smallmatrix} \text{NH} \\ \text{NO} \cdot \text{OM} \end{smallmatrix}$. In the ortho-series this view receives some support from the fact that *o*-nitroaniline dissolves in alcoholic potassium hydroxide with a deep reddish-orange, and 2:4-dinitroaniline with a bluish-red, colour. Attempts to decide this question by physical methods (Baly, Steward, and Edwards, *Trans.*, 1906, **89**, 514; Baly, Tuck, and Marsden, *ibid.*, 1910, **97**, 580; Hantzsch, *Ber.*, 1910, **43**, 1669; Morgan and Clayton, *Trans.*, 1911, **99**, 1945; Morgan, Jobling, and Barnett, this vol., p. 1209) have not led to definite conclusions, and further evidence of a chemical nature is therefore desirable.

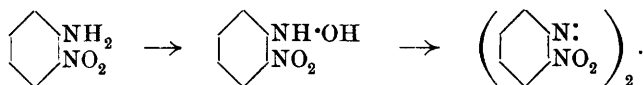
A recent observation made by Suida (*Chem. Zeit.*, 1912, **36**, 622) that the nitroanilines when dyed on wool cannot be diazotised by nitrous acid, would seem to indicate that the nitroamine is combined with the fibre in the form of a protein salt of a quinonoid nitronic acid, and the facts which follow also point unmistakably to the existence in the case of *o*-nitroaniline and other *o*-nitroamines of *aci*-quinonoid salts.

In the course of the previous investigation, in which it was observed that *o*-nitro-groups diminished the reactivity of basic nitrogen, we were led to examine the action of hypochlorites on *o*-nitroaniline. It was then found that when the oxidation was performed in warm aqueous solution with ordinary alkaline sodium hypochlorite almost the sole product was the so-called "dinitroso-benzene," and that the normal reaction only occurred when absolutely neutral conditions were maintained. The difference in the result is very striking when the oxidation is effected in both cases in cold methyl-alcoholic solution, using in one case completely neutral conditions, and in the other adding sufficient potassium hydroxide to render the solution a deep orange. In the first case only dinitroazobenzene is produced; in the second, "dinitroso-benzene" is obtained in theoretical yield, the orange colour disappearing as the reaction proceeds.

In view of the fact that "dinitrosobenzene" is undoubtedly a quinonoid compound (compare its conversion into *o*-benzoquinone-dioxime by reduction, and its analogy to the so-called "glyoxime peroxide," "benzildioxime peroxide," and "camphordioxime peroxide"), and considering the improbability of a migration of oxygen from a nitro-group to the adjacent nitrogen atom, we are led to the conclusion that the reaction in alkaline solution takes place according to the scheme:



This is supported by the fact that in neutral solution the oxidation takes an entirely different and more normal course:



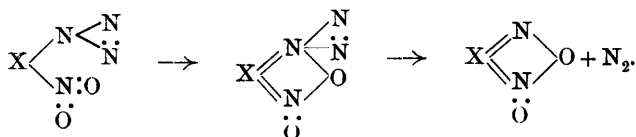
It follows, therefore, with great probability that in an alkaline solution the *aci*-salt of the quinonoid nitronic acid is present, whilst in neutral solution *o*-nitroaniline exists mainly in the benzenoid form.

The identity of our product with the "dinitrosobenzene" obtained by Noelting and Kohn (*Chem. Zeit.*, 1894, **18**, 1905) and by Zincke and Schwarz (*Annalen*, 1899, **307**, 28) by decomposition of *o*-nitrodiazobenzeneimide, was established by its conversion into the corresponding dioxime and furazan. Other *o*-nitroamines when submitted to oxidation with hypochlorites in alkaline solution behave similarly, and the reaction affords a ready method of preparing compounds of this type; thus, from *m*-nitro-*p*-toluidine we have prepared the "dinitrosotoluene" obtained by Zincke and Schwarz from *m*-nitro-*p*-diazotolueneimide.

When, however, 2:4-dinitroaniline dissolved in methyl alcohol was submitted to similar treatment, there was obtained in place of the expected "*p*-nitrodinitrosobenzene" of Zincke and Schwarz a compound melting at 80°, which on investigation proved to be a chloromethoxy-derivative, $\text{C}_6\text{H}_2\text{Cl}(\text{OMe})\text{N}_2\text{O}_2$. The oxidation, therefore, is accompanied in this case by a very remarkable replacement of the *p*-nitro-group by a methoxy-group followed by the introduction of a chlorine atom. The substitution of ethyl alcohol for methyl gave rise to the corresponding chloroethoxy-derivative, $\text{C}_6\text{H}_2\text{Cl}(\text{OEt})\text{N}_2\text{O}_2$, but we failed to find conditions under which the nitro-group could be preserved intact.

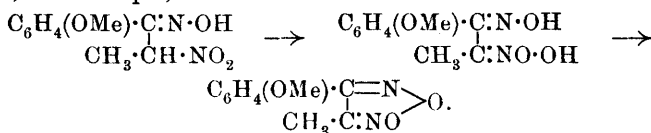
The constitution of these compounds as benzisooxadiazole (furazan) oxides, $\text{X} \llcorner \text{N} \text{N} \text{O} \text{O}$, which is indicated by the new method

of formation, also agrees well with their production from nitrodiazoidimides, and does not necessitate a transference of an oxygen atom:



The furazan oxide constitution stands, moreover, in better accord with the properties of this class of compounds (for example, their

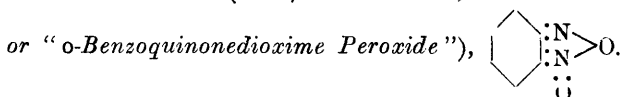
stability to acids and resistance to reduction and oxidation) than the dioxime peroxide formula, $X \begin{smallmatrix} \text{N} \cdot \text{O} \\ \diagup \quad \diagdown \\ \text{N} \cdot \text{O} \end{smallmatrix}$, advocated by Forster and Fierz (Trans., 1907, **91**, 1943). It may be noted also that in the fatty series, Wieland and Angeli (*Annalen*, 1903, **329**, 239) have described for the similarly constituted "glyoxime peroxides" a method of formation somewhat analogous to the above, which consists in treating the nitroketoximes with alkalis. Anetholenitroxime, for example, reacts thus:



Wieland and Semper (*Annalen*, 1908, **358**, 36) accordingly attribute to these aliphatic "glyoxime peroxides" a furazan oxide constitution similar to that which is here proposed for their aromatic analogues.

EXPERIMENTAL.

Benzisooxadiazole Oxide (*Benzfurazan Oxide*, "Dinitrosobenzene,"



Ten grams of *o*-nitroaniline were dissolved in 150 c.c. of saturated alcoholic potassium hydroxide. A solution of sodium hypochlorite was then added in the cold with constant shaking until the crimson colour had entirely disappeared. The mixture was poured into an open dish and left to crystallise, when the product (9.5 grams) separated out in a nearly pure state. When crystallised from water or alcohol it forms white needles melting at 72°, as stated by Zincke and Schwarz. It is volatile with steam, and has a peculiar, pungent odour.

The compound can also be conveniently prepared by adding a solution of sodium hypochlorite to a hot aqueous solution of *o*-nitroaniline, rendered alkaline with sodium hydroxide, until the solution is nearly colourless. On cooling, the product crystallises in small, yellowish-white needles. (Found, N = 20.69. Calc., N = 20.58 per cent.)

o-Benzoquinonedioxime, $\text{C}_6\text{H}_4 \begin{smallmatrix} \text{N} \cdot \text{OH} \\ \diagup \quad \diagdown \\ \text{N} \cdot \text{OH} \end{smallmatrix}$, was prepared by reducing the product of the previous reaction by means of alkaline hydroxylamine in the manner described by Zincke and Schwarz (*loc. cit.*). It crystallises from hot water or dilute alcohol in small, brownish-

yellow needles, which melt and evolve gas at 145° (Zincke and Schwarz give 142°). It gives deep red solutions with alkalis, and dissolves with the same red colour in concentrated acids. It is interesting to note that the compound is a mordant dyestuff giving brown lakes with the oxides of chromium and copper, and a black lake with oxide of iron.

Benzisooxadiazole (benzfurazan), $C_6H_4 \begin{smallmatrix} \text{N} \\ \text{N} \end{smallmatrix} \text{O}$, was obtained by dissolving the dioxime in sodium hydroxide, and distilling it in a current of steam. The product, when recrystallised from alcohol, forms long, white needles, melting at 55° (as given by Zincke and Schwarz), readily soluble in most solvents, and very volatile.

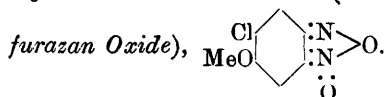
5-Methylbenzisooxadiazole Oxide (*Tolufurazan Oxide*, "*Dinitroso-toluene*," or "*o-Toluquinonedioxime Peroxide*"), $CH_3 \begin{smallmatrix} \text{N} \\ \text{N} \end{smallmatrix} \text{O}$.

Ten grams of *m*-nitro-*p*-toluidine were dissolved in 200 c.c. of alcoholic potassium hydroxide, and a solution of sodium hypochlorite was added in the cold with constant shaking until the deep red colour had disappeared. The product separated as a pale yellow precipitate, which after crystallisation from dilute alcohol or hot water forms readily soluble, white needles, melting at 97° (Zincke and Schwarz give $96-97^{\circ}$).

3:4-Toluquinonedioxime, $CH_3 \begin{smallmatrix} \text{N} \cdot \text{OH} \\ \text{N} \cdot \text{OH} \end{smallmatrix}$, was obtained by reduction of the preceding compound with alkaline hydroxylamine. It forms small, yellow needles, melting and decomposing at 128° (Zincke and Schwarz give $127-128^{\circ}$). It forms deep red solutions with alkalis or strong acids, and possesses mordant-dyeing properties similar to its lower homologue. (Found, $N=18.55$. Calc., $N=18.43$ per cent.)

5-Methylbenzisooxadiazole (*Tolufurazan*), $CH_3 \begin{smallmatrix} \text{N} \\ \text{N} \end{smallmatrix} \text{O}$, was obtained from the preceding substance by distillation of its sodium hydroxide solution in a current of steam. It separates from dilute alcohol in long, white needles, melting at 37° (as given by Zincke and Schwarz), which are readily soluble in solvents and very volatile. (Found, $N=20.91$. Calc., $N=20.89$ per cent.)

6-Chloro-5-methoxybenzisooxadiazole Oxide (Chloromethoxybenz-



Ten grams of 2:4-dinitroaniline were dissolved in 350 c.c. of methyl alcohol, and 75 c.c. of a concentrated methyl-alcoholic solution of potassium hydroxide were added. To the deep crimson solution warmed to 50° there was added, with constant shaking, sodium hypochlorite solution (containing 5 per cent. of active chlorine) until decolorisation occurred, and the colour was not restored by adding more alcoholic potassium hydroxide. The crystals which separated after some time were recrystallised from alcohol. The compound forms long, pale yellow needles, which melt at 80.5°. It is readily soluble in alcohol, acetic acid, or benzene, and insoluble in water.

Analysis demonstrated that the product is not the expected nitrobenzfurazan oxide, but that the oxidation is accompanied by a displacement of the second nitro-group by methoxyl and the introduction of a chlorine atom:

0.0859 gave 10.3 c.c. N₂ at 19° and 761 mm. N=14.14.

0.2326 „ 0.1646 AgCl. Cl=17.51.

0.3062 „ 0.3523 AgI. OMe=15.18.

C₇H₅O₃N₂Cl requires N=13.96; Cl=17.70; OMe=15.46 per cent.

On complete reduction with zinc dust and alcoholic hydrochloric acid the product gave a base, the acetyl compound of which melted at 203°. This base was characterised as an ortho-diamine by its yielding an azimino-compound (m. p. 227°) and its condensation to a yellow glyoxaline with phenanthraquinone.

Chloromethoxy-*o*-benzoquinonedioxime,

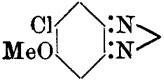
was obtained by reduction of an alcoholic solution of the preceding compound with alkaline hydroxylamine. The substance crystallises from dilute alcohol in small, brownish-yellow prisms, which melt at 152°. It is readily soluble in alcohol or acetic acid, but less so in water or benzene. In alkali hydroxides, carbonates, or acetates it dissolves with a deep red colour, and also gives similar-coloured solutions with strong acids. It has mordant dyeing properties:

0.0886 gave 10.6 c.c. N₂ at 18° and 757 mm. N=14.09.

0.2062 „ 0.1467 AgCl. Cl=17.60.

C₇H₇O₃N₂Cl requires N=13.82; Cl=17.53 per cent.

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6 - Chloro - 5 - methoxybenzisoaxadiazole (Chloromethoxybenz-furazan), , was prepared from the dioxime by sub-

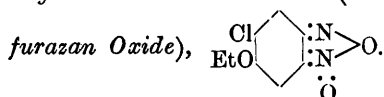
jecting its alkali hydroxide solution to steam distillation. The oil which passed over crystallised on cooling, and was collected and recrystallised from alcohol. It forms slender, white needles, which melt at 76°, and are readily soluble in the usual solvents. It is volatile with steam :

0.0964 gave 12.5 c.c. N₂ at 18° and 757 mm. N=15.30.

0.2192 „ 0.1694 AgCl. Cl=19.13.

C₇H₅O₂N₂Cl requires N=15.18; Cl=19.24 per cent.

6-Chloro-5-ethoxybenzisoaxadiazole oxide (Chloroethoxybenz-

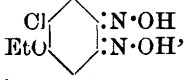


Ten grams of 2:4-dinitroaniline are dissolved in 600 c.c. of absolute ethyl alcohol at 50°, and mixed with 80 c.c. of concentrated alcoholic potassium hydroxide. The deep crimson-coloured mixture is then treated with sodium hypochlorite solution in the same way as for the methoxy-compound. The product which separates out on allowing the mixture to remain overnight is collected and crystallised from ethyl alcohol. It forms yellow, prismatic crystals, melting at 55°, which are readily soluble in alcohol, acetic acid, or benzene, but insoluble in water :

0.1610 gave 0.1068 AgCl. Cl=16.42.

0.3176 „ 0.3433 AgI. OEt=20.69.

C₈H₇O₃N₂Cl requires Cl=16.55; OEt=20.97 per cent.

Chloroethoxy-o-benzoquinonedioxime, , was ob-

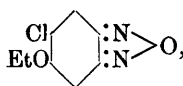
tained by reduction of an alcoholic solution of the preceding compound with alkaline hydroxylamine. The substance crystallises from dilute alcohol in small, yellow needles, melting at 136°. It is readily soluble in alcohol or acetic acid, but less so in benzene or water.

Its properties are closely similar to those of the methoxy-compound :

0.2273 gave 0.1496 AgCl. Cl=16.29.

C₈H₉O₃N₂Cl requires Cl=16.40 per cent.

6-Chloro - 5 - ethoxybenzisoaxadiazole (chloroethoxybenz-furazan),


 was prepared from the dioxime in the usual manner. It forms small, pale yellow prisms, melting at 48°, which are readily soluble in solvents and volatile with steam:

0.1694 gave 0.1213 AgCl. Cl=17.71.

C₈H₇O₂N₂Cl requires Cl=17.88 per cent

The investigation is being continued.

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