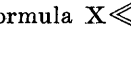
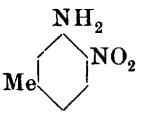
XCII.—*The Constitution of Oxadiazole Oxides (Furazan Oxides or Dioxime Peroxides).*

By Arthur George Green and Frederick Maurice Rowe.

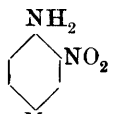
In a former communication (T., 1912, **101**, 2452) we have published a new method of formation of compounds belonging to the class described originally by Noelting and Kohn and by Zincke and Schwarz as "ortho-dinitroso-derivatives," but regarded later by Forster and Fierz (T., 1907, **91**, 1942) as *o*-quinonedioxime peroxides. This reaction consists in the oxidation of *o*-nitroamines with sodium hypochlorite in an alkaline solution. In view of the improbability of a transference of an oxygen atom from the nitro- to the amino-nitrogen, the new method of formation appeared to indicate for these compounds an unsymmetrical structure represented by the formula  , in place of the dioxime-peroxide constitution,  , advocated by Forster and Fierz. On the other hand, these authors have stated that one and the same "β-naphthaquinonedioxime peroxide" melting at 127° (identical with Koreff and Ilinki's "1 : 2-dinitrosonaphthalene" formed by oxidation of β-naphthaquinonedioxime) is obtained on heating either 2-nitro-1-naphthylazoimide or 1-nitro-2-naphthylazoimide, $NO_2 \cdot C_{10}H_6 \cdot N_3$, thus indicating a symmetrical structure for the product.

In order to obtain further evidence on the point in question, we have submitted to the sodium hypochlorite oxidation the pair of nitrotoluidines:



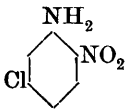
M. p. 109°.

and



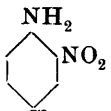
M. p. 114°.

and the pair of chloronitroanilines:



M. p. 125°.

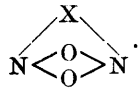
and



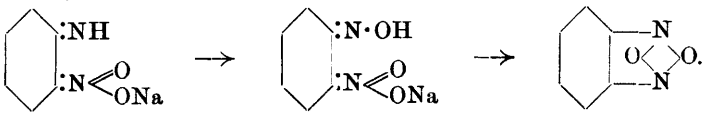
M. p. 116°.

with the object of ascertaining whether isomeric or identical furazan oxides result.

In each case the same oxidation product was obtained from both isomerides, thus confirming Forster and Fierz's observations in the naphthalene series. Symmetrical structure for the furazan oxides is thus definitely established, but in view of the objections already stated to the glyoxime-peroxide formula it appears more probable that the compounds in question have the constitution



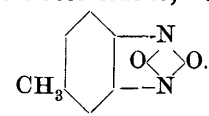
This formula would represent their formation from the nitro-amines without requiring the transference of an oxygen atom from the nitro-group, and it also stands in better accord with their chemical properties. The reaction may be regarded as taking place through the intermediate formation of quinonoid compounds, according to the scheme:



Experimental.

5-*Methylbenz*isooxadiazole Oxide.

(*Tolufurazan Oxide, Tolufuroxan, "Dinitrosotoluene," or "o-Toluquinonedioxime Peroxide"*),



The preparation of this compound from *m*-nitro-*o*-toluidine (m. p. 114°) by oxidation with sodium hypochlorite has already been described in our former paper (*loc. cit.*).

In order to subject *p*-nitro-*m*-toluidine to the same treatment, this base was prepared according to Städel and Kolb's method (*Annalen*, 1898, **259**, 208). Pure *m*-cresol was nitrated in glacial acetic acid solution below 0°, and the portion of the product volatile with steam, nitro-*m*-cresol (m. p. 56°), was converted into the potassium salt and then through the silver salt into the ethyl ether. The nitro-*m*-tolyl ethyl ether obtained melted at 50—51°. To convert this into the nitrotoluidine it was dissolved in a little alcohol and heated with aqueous ammonia in a sealed tube for twelve hours at 200° (heating with aqueous ammonia at 140—150° as prescribed by Städel and Kolb gave only a small yield). When crystallised

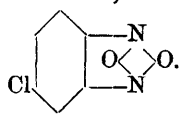
from dilute alcohol the *p*-nitro-*m*-toluidine formed yellow plates melting at 109°.

The oxidation with sodium hypochlorite was effected in alkaline alcoholic solution in a similar manner to that employed for the isomeric base. The product formed white needles melting at 97° (Found, N = 18·69), which proved to be completely identical with that from *m*-nitro-*p*-toluidine (Found, N = 18·81. Calc., N = 18·66 per cent.). It had the same crystalline form, and melted at exactly the same temperature. Mixtures of the two products also had the same melting point.

On reduction with alkaline hydroxylamine the tolufurazan oxide from *p*-nitro-*m*-toluidine gave 3 : 4-toluquinonedioxime (m. p. 128°: Found, N = 18·55. Calc., N = 18·43 per cent.) From this the methylbenz*iso*oxadiazole (tolufurazan) melting at 37° was obtained by distilling the alkaline solution in a current of steam (Found, N = 20·91. Calc., N = 20·89 per cent.). Both compounds were completely identical with those obtained previously from *m*-nitro-*p*-toluidine.

*Chlorobenz*isoo*xadiazole oxide.*

(*Chlorobenzfurazan Oxide, Chlorobenzfuroxan*),



(1) *Preparation from* m-*Chloro-o-nitroaniline.*—This base was obtained by Beilstein and Kurbatov's method (*Annalen*, 1876, **182**, 102) by nitration of *m*-chloroacetanilide, saponification of the product and separation from the chloro-*p*-nitroaniline by distillation in a current of steam. When crystallised from benzene it was obtained in golden crystals melting at 125°. The oxidation with sodium hypochlorite was effected in alkaline alcoholic solution in the usual way. The product, which separates on keeping, was crystallised from alcohol, and found to melt at 48°:

0·1809 gave 25·8 c.c. N_2 at 17° and 747 mm. N = 16·63.

0·1392 „ 0·1167 AgCl. Cl = 20·74.

$C_6H_3O_2N_2Cl$ requires N = 16·43; Cl = 20·83 per cent.

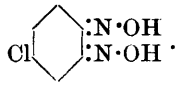
(2) *Preparation from* p-*Chloro-o-nitroaniline.*—This base was obtained in theoretical yield by heating 2 : 5-dichloronitrobenzene (m. p. 55°), dissolved in sufficient alcohol, with aqueous ammonia under pressure at 190° for eight hours. The product melted at 116·5°. The oxidation with alkaline sodium hypochlorite can be conducted in alcoholic or in aqueous solution. In the latter case the base is dissolved in hot water, rendered alkaline with sodium

hydroxide, and sodium hypochlorite added until the deep orange-red colour disappears. The product which separates on cooling is crystallised from alcohol:

0·1053 gave 14·3 c.c. N_2 at 14° and 758 mm. N = 16·46.
0·1697 „ 0·1418 AgCl. Cl = 20·66.

$C_6H_3O_2N_2Cl$ requires N = 16·43; Cl = 20·83 per cent.

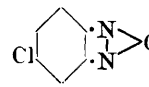
The products are completely identical in properties. They crystallise from alcohol in large, pale yellow, readily soluble crystals, melting at 48°. A mixture of the two compounds also melted at the same temperature.

Chloro-o-benzoquinonedioxime,  .

This compound was obtained by reduction of the chlorofurazan oxide prepared from either *m*- or *p*-chloro-*o*-nitroaniline. The reduction was effected in alcoholic solution with alkaline hydroxylamine. The product was a brown, crystalline powder, melting at 128°, having the general properties of *o*-dioximes:

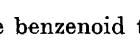
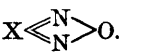
0·0758 * gave 10·7 c.c. N_2 at 17° and 746 mm. N = 16·44.
0·0926 † „ 12·7 c.c. N_2 „ 14° „ 758 mm. N = 16·40.
0·1018 * „ 0·0845 AgCl. Cl = 20·54.
0·1426 † „ 0·1184 AgCl. Cl = 20·54.

$C_6H_5O_2N_2Cl$ requires N = 16·24; Cl = 20·58 per cent.

*Chlorobenz*isoo*xadiazole* (*Chlorobenzfurazan*),  , was prepared by subjecting to steam distillation an alkaline solution of chlorobenzoquinonedioxime (from *p*-chloro-*o*-nitroaniline). The product forms long, white, silky needles, which melt at 44°. It is readily volatile with steam:

0·0743 gave 11·35 c.c. N_2 at 15° and 758 mm. N = 18·20.
0·1202 „ 0·1108 AgCl. Cl = 22·97.

$C_6H_3ON_2Cl$ requires N = 18·12; Cl = 22·98 per cent.

This and other compounds of the same class are probably more correctly represented by formulæ of the benzenoid type,  , than by those of the quinonoid type,  . The absence of colour, and resistance to reduction and oxidation stand in better accord with the former than with the latter view of their structure.

* From *m*-chloro-*o*-nitroaniline. † From *p*-chloro-*o*-nitroaniline.

Whilst the dioximes are readily converted into the furazan oxides by oxidation in alkaline solution with sodium hypochlorite, the furazans remain unchanged under this treatment. The latter are also strongly basic compounds, forming readily soluble hydrochlorides.

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