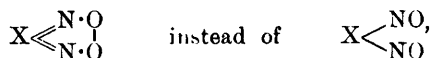


CCVI.—*Constitution of Furoxans (Dioxime "Peroxides").*

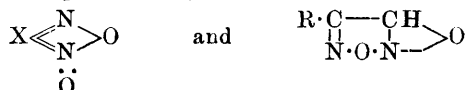
By MARTIN ONSLOW FORSTER and MATTHEW FELIX BARKER.

IN a communication dealing with the nature of the compounds which arise by heating the *o*-nitrotriazio-derivatives of benzene and naphthalene (Forster and Fierz, T., 1907, **91**, 1942), it was suggested that the numerous aromatic substances previously regarded as dinitroso-compounds should be classified as dioxime peroxides:



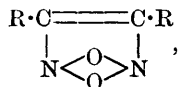
and this proposal remained unchallenged until Green and Rowe (T., 1912, **101**, 2452) claimed for these materials the constitution of furoxans (oxides of furazan), similar in constitution to the aliphatic derivatives described by Wieland and Semper (*Annalen*, 1907, **358**, 36).

During the discussion which followed their paper, however, it was pointed out by one of us that the particular oxide of furazan adopted by Green and Rowe, like the one previously advocated by Wieland and Semper, namely:



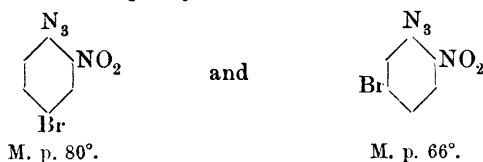
respectively, conflicts with the observation of Forster and Fierz (*loc. cit.*) that when 1-nitro-2-naphthylazoimide and 2-nitro-1-naphthylazoimide are heated, elimination of nitrogen leads to the same dioxime "peroxide" in each case, an origin which points unmistakably to a symmetrical constitution for the furazan oxide.

A reasonable objection to this argument, however, follows from the fact that the transference of oxygen from one atom of nitrogen to the other, demanded in the case of the nitronaphthylazoimides if the formula of Green and Rowe is correct, might be due to the steric effect of the second benzene ring, and we have therefore made experiments to ascertain whether the change in question is independent of the naphthalene nucleus. We find that it is, and are therefore led to the conclusion that these furazan oxides are symmetrical in structure. As stated in a preliminary communication (P., 1913, **29**, 152), we believe the formula:

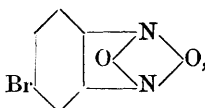


to be the most satisfactory representation of these compounds, a conviction in which we are now supported by Green and Rowe (this vol., p. 897), whose preliminary announcement appeared simultaneously with our own.

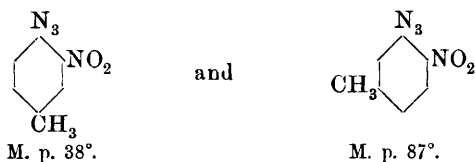
The authors mentioned base their conclusion on the course followed by the oxidation of *o*-nitroamines with alkaline sodium hypochlorite. They produced the same toluhafuran oxide alike from *p*-nitro-*m*-toluidine and *m*-nitro-*p*-toluidine, whilst from *m*-chloro- and *p*-chloro-*o*-nitroanilines the same chlorobenzfuran oxide was obtained. Our inquiry depends on the decomposition of *o*-nitroazoimides. Having first repeated the earlier experiments with 1-nitro-2-naphthylazoimide and 2-nitro-1-naphthylazoimide, assuring ourselves that the same naphthafuran oxide arises from both, two bromonitrophenylazoimides:



were prepared, and found to yield the same bromobenzfuran oxide,



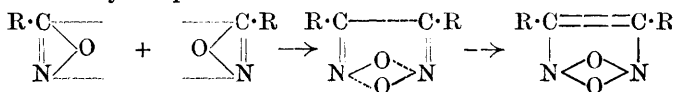
when heated. Furthermore, from the isomeric nitrotriazotoluenes,



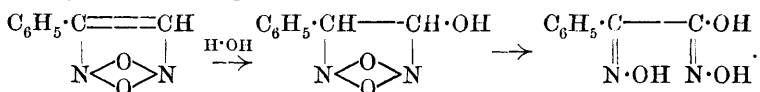
the toluhafuran oxide prepared by Green and Rowe from the nitro-toluidines has been obtained, and it seems to us that all these experiments taken together place the symmetrical structure of the aromatic furazan oxides on a firm basis.

Whether this conclusion is applicable also to the aliphatic compounds of Wieland and Semper cannot be stated so definitely, but there is much in favour of extending it to these derivatives; for instance, the statement that the most general and most important source of the dioxime "peroxides" is the polymerisation of the nitrile oxides (*Annalen*, 1907, **358**, 37) involves, on the basis of the formula put forward by those authors, behaviour different on the part of one molecule from that of another, which appears

improbable, whereas according to our formula the polymerisation would be very simple:

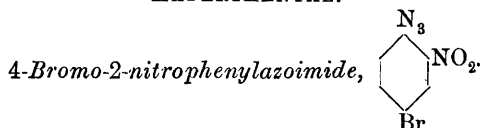


Furthermore, decomposition of diphenylglyoxime "peroxide" into phenylcarbimide (2 mols.) is more in accordance with a symmetrical structure, whilst the action of alkali on phenylfuroxan, leading to oximinobenzoylformhydroxamic acid (*loc. cit.*, p. 59), would be represented as follows:



Green and Rowe found that with hydroxylamine the furazan oxides may be reduced to the dioximes, a change which takes place also when reduction is effected with zinc dust and a limited amount of acetic acid (Forster, T., 1903, **83**, 525). We have studied the behaviour of these compounds towards hydrazine hydrate, which leads in some cases to the furazan, in others to the diamine.

EXPERIMENTAL.



4-Bromo-2-nitroaniline (6.5 grams) suspended in a mixture of glacial acetic acid (40 c.c.) and sulphuric acid (20 c.c.) was treated with ice and solid sodium nitrite until a clear solution was formed. Excess of nitrite having been destroyed with carbamide, aqueous sodium azide (4 grams) was added, when the substituted azoimide was precipitated in very pale yellow crystals. After recrystallisation from cold acetone diluted with water, followed by precipitation from cold benzene with petroleum, a felted mass of almost colourless needles was formed, melting at 80°:

0.1972 gave 38.3 c.c. N₂ at 13.5° and 766 mm. N = 23.2.

C₆H₃O₂N₄Br requires N = 23.1 per cent.

The substance is freely soluble in cold benzene or acetone, less readily in methyl or ethyl alcohol, and very sparingly soluble in petroleum.

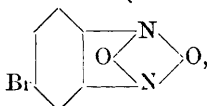
Decomposition by Heat.—In quantities of 2 decigrams, 4-bromo-2-nitrophenylazoimide was heated at 80–90°, the temperature being raised very gradually to 110° as the liberation of nitrogen

slackered. On extracting with warm petroleum (b. p. 60—80°), only a very slight tarry residue was left, the solvent depositing opaque masses of pale yellow, lustrous prisms, melting at 69°:

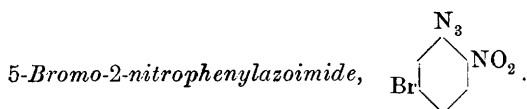
0.2004 gave 21.4 c.c. N_2 at 15° and 775 mm. $N=12.9$.

$C_6H_3O_2N_2Br$ requires $N=13.0$ per cent.

4-Bromobenzisooxadiaxole oxide (4-bromobenzfurazan oxide),



is freely soluble in cold organic media excepting petroleum.



The base required for making this material was prepared by heating 2:4-dibromo-1-nitrobenzene with alcoholic ammonia during two days at 150°, unchanged dibromonitrobenzene being removed by extracting the product several times with warm petroleum, in which 3-bromo-6-nitroaniline is only sparingly soluble. Conversion into the substituted phenylazoimide was effected by the process used in the case of the isomeride, the pale yellow oil precipitated from the diazonium solution by sodium azide solidifying almost immediately. The substance melts at 66°:

0.2000 gave 39.5 c.c. N_2 at 15° and 751 mm. $N=22.9$.

$C_6H_3O_2N_4Br$ requires $N=23.1$ per cent.

5-Bromo-2-nitrophenylazoimide is freely soluble in cold benzene, acetone, or ethyl acetate, and dissolves readily in warm petroleum (60—80°), separating in pale yellow, transparent plates or rectangular prisms.

Decomposition by Heat.—Proceeding as before, the substituted phenylazoimide was transformed into 4-bromobenzisooxadiaxole oxide melting at 69°, not depressed by admixture with the product of heating 4-bromo-2-nitrophenylazoimide.



Diazotised nitrotoluidine ($CH_3:NO_2:NH_2=1:3:4$) was treated in the manner described above, when the azoimide separated as an oil, which rapidly solidified; after recrystallisation from acetone

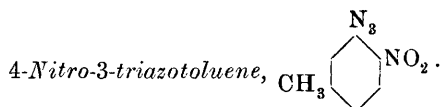
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and finally from alcohol, diluted in each case with water, it separated in long, pale yellow needles, melting at 38°:

0.1307 gave 36.0 c.c. N₂ at 24° and 764 mm. N=31.5.

C₇H₆O₂N₄ requires N=31.5 per cent.

Decomposition by Heat.—When heated carefully the azoimide began to effervesce at 70—75°, and decomposition became complete after raising the temperature to 110°; recrystallisation from hot petroleum (80—100°) gave a specimen of tolufurazan oxide melting at 96° (Green and Rowe give 97°).



The substituted azoimide was derived from diazotised nitrotoluidine (CH₃:NO₂:NH₂=1:4:3) in the usual manner, and after recrystallisation from cold acetone diluted with water separated in pale yellow needles melting at 87°:

0.1202 gave 33.9 c.c. N₂ at 26° and 763 mm. N=31.5.

C₇H₆O₂N₄ requires N=31.5 per cent.

Decomposition by Heat.—A somewhat higher temperature was required to complete this change; gas was liberated most freely at 90—100°, and 110—120° was finally attained. Some tar remained after extracting with hot petroleum (80—100°), which deposited the tolufurazan oxide melting at 96°, identical with the product from 3-nitro-4-triazotoluene.

Behaviour of the Furazan Oxides towards Hydrazine Hydrate.

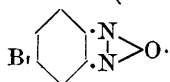
Benzfurazan oxide, prepared by heating *o*-nitrophenylazoimide, was treated in alcoholic solution with considerable excess of hydrazine hydrate, when the liquid became dark red; effervescence began, and became vigorous on gentle warming. After five to six hours on the water-bath the liquid remained clear on dilution, and was then evaporated to dryness; on extracting the residue with hot petroleum (60—80°) the latter deposited *o*-phenylenediamine in lustrous, rectangular plates melting at 103°. Similarly, tolufurazan oxide (m. p. 96°) gave tolylenediamine (CH₃:NH₂:NH₂=1:3:4) melting at 89°, and *p*-benzoquinonedioxime "peroxide" gave *p*-phenylenediamine melting at 141°.

In the case of naphthafurazan oxide, however, arising alike from 2-nitro-1-naphthylazoimide and 1-nitro-2-naphthylazoimide, 1:2-naphthylenediamine was not produced, the product consisting of naphthafurazan (m. p. 79°), the anhydride of naphthaquinone-

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dioxime (Found, $N=16.5$; $C_{10}H_6ON_2$ requires $N=16.5$ per cent.). This compound has a marked odour of bitter almonds, a property which has hitherto escaped notice.

4-Bromobenzisooxadiazole (4-Bromobenzfurazan),



On adding hydrazine hydrate (5 c.c.) to a solution of bromobenzfurazan oxide (2 grams) in alcohol (40 c.c.) a deep red colour was developed, and gas was liberated; after being gently warmed during three to four hours, water precipitated long, yellow needles, melting at 75° after recrystallisation:

0.1473 gave 17.5 c.c. N_2 at 15° and 773 mm. $N=14.2$.

$C_6H_3ON_2Br$ requires $N=14.1$ per cent.

The substance has a distinct odour of menthol; it is freely soluble in most organic media, and does not reduce ammoniacal silver oxide.

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