Summary

The work described in this paper has resulted in adding two new mixed aquo-ammonocarbonic acids, namely, unsymmetrical dicarbethoxy-guanidine and carbethoxy-cyanoguanidine, to the list of those already known. The manner in which one compound of this type may be synthesized from another by partial solvolysis has been illustrated by several typical reactions.

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THE STRUCTURE OF FURAZAN OXIDES

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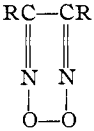
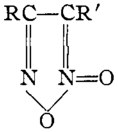
The structure of furazan oxides, other than fused aromatic derivatives, has never been conclusively proved. At various times four structures have been proposed. The first, an internal peroxide (I), does not correctly represent the properties of these substances. This was first pointed out by Wieland and Semper[1] who favored either Formula II or III. Structure II, however, was first suggested by Werner.[2] These two formulas were based largely on the reactions by which furazan oxides were formed. A few years later Green and Rowe,[3] as well as Forster and Fierz,[4] showed that the aromatic fused ring oxides have a symmetrical structure (IV). They suggested further, on the basis of this work, that all furazan ozides have a similar structure (V). Angeli[5] and later Bigiavi,[6] studying the behavior of furazan oxides with the Grignard reagent, also favored Structure V.


I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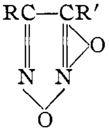
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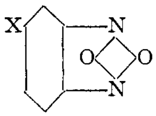
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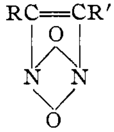
V

Wieland, in defense of his contention that these substances have an unsymmetrical structure, next offered evidence of two isomeric monophenyl furazan oxides[7] (VIa and VIb). This evidence has been largely vitiated by the work of Ponzio,[8] who showed that probably the two sub-

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[1] Wieland and Semper, *Ann.*, **358**, 36 (1908).

[2] Werner, "Lehrbuch der Stereochemie," Gustav Fischer, Jena, **1904**, p. 260.

[3] Green and Rowe, *J. Chem. Soc.*, **103**, 897 (1913).

[4] Forster and Fierz, *ibid.*, **103**, 1918 (1913).

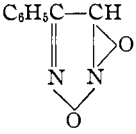
[5] Angeli, *Gazz. chim. ital.*, **46**, 300 (1916); *Atti. accad. Lincei*, [V] **25** (2), 7 (1916).

[6] Bigiavi, *Gazz. chim. ital.*, [2] **51**, 324 (1921).

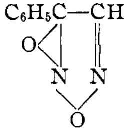
[7] Wieland, *Ann.*, **424**, 107 (1921).

[8] Ponzio, *Gazz. chim. ital.*, [1] **53**, 379 (1923).

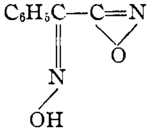
stances are identical, but of different degrees of purity; and further that the substance is likely the oxime of benzoyl nitrile oxide (VII). All of these inconclusive and contradictory results are of little value for structural considerations.



VIa



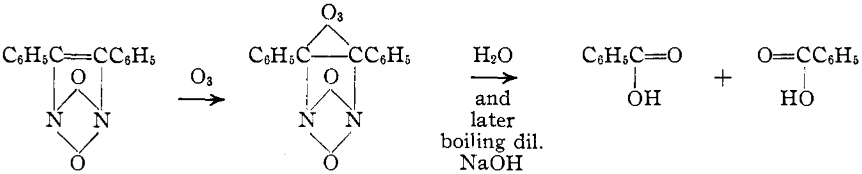
VIb



VII

Furazan oxides are easily prepared by oxidizing 1,2-dioximes, but no cases have been reported in which two furazan oxides have resulted from the oxidation of isomeric dioximes. This may be due to the fact that the maximum number[9] of isomeric dioximes of a dissimilarly substituted α-diketone have not been oxidized.[10] The only case reported in the literature in which four dioximes of an unsymmetrical α-diketone have been isolated is that of Forster's dioximes of camphor quinone.[10e] Forster, however, oxidized only two of the four isomers. The two remaining have now been oxidized in this Laboratory. The only oxidation product isolated was identical in all characteristics with the oxide obtained by Forster. This is negative evidence in favor of Formula V and in itself must be considered as inconclusive.

Structure V differs from II and III in the position of the double bonds. Formula V has an ethylenic linkage and should, therefore, react with ozone. Structures II and III, on the other hand, should not react.[11] Diphenyl furazan oxide reacted with ozone in the manner to be expected on the basis of Formula V. The chief decomposition product of the ozonides was benzoic acid, clearly showing the presence of an ethylenic linkage between the carbon atoms of the furazan oxide ring. The process of ozonization can be indicated as follows.



Since an ethylenic linkage must occur in the furazan oxide nucleus, Formula V seems the most probable structure for these substances.

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[9] On the basis of the Hantzsch-Werner theory.

[10] Five cases have been reported in the literature in which two out of four isomeric dioximes have been oxidized. (a) Angeli, *Gazz. chim. ital.*, [2] **22,** 445 (1892). (b) Boeris, *ibid.*, [2] **23,** 165 (1893). (c) Malagnini, *ibid.*, [2] **24,** 1 (1894). (d) Avogadro, *ibid.*, **54,** 545 (1924). (e) Forster, *J. Chem. Soc.*, **83,** 525 (1903).

[11] Meisenheimer found that the ethylenic linkage in triphenylisoxazole was attacked by ozone, while the imino linkage was not.

Experimental Part

The Oxidation of γ- and δ-Camphor-quinone Dioximes was carried out in a manner very similar to that described by Forster.[10e] The products melted at 144–145°, which is the melting point of the oxide obtained from the α and β isomers. Mixed melting points of any pairs of the preparations were identical. The specific rotation of the substances in absolute alcohol was not quite that given by Forster, but the rotation of each of the products was the same within the experimental error. These values are given in Table I.

TABLE I

SPECIFIC ROTATIONS OF OXIDES FROM ISOMERIC DIOXIMES

Solvent, absolute alcohol; length of tube, 20 cm.; zero reading 2.89°.

Oxide from	Wt. of oxide, g.	Number of readings	Average of readings	Difference	$[\alpha]^{28}_{D}$
β-Dioxime	0.5042	12	3.77°	0.88°	21.84°
γ-Dioxime	.5449	6	3.84°	.95°	21.88°
δ-Dioxime	.5262	6	3.80°	.91°	21.66°

The Ozonization of Diphenyl Furazan Oxide.—One g. of diphenyl furazan oxide was dissolved in 30 cc. of pure, dry carbon tetrachloride and a current of oxygen containing about 3% of ozone was passed through for seven hours. In about five hours the solution became yellow and when the ozonization was stopped a small amount of yellow solid had separated. The ozonides were decomposed with water and the carbon tetrachloride solution extracted with dil. sodium hydroxide solution. This removed 0.31 g. of benzoic acid. The carbon tetrachloride was evaporated and the residue boiled for an hour with dil. sodium hydroxide solution, whereby the yield of benzoic acid was increased to 0.75 g. Continued boiling with alkali increased the amount of benzoic acid slightly and, since a few tests were made with the residue before boiling with sodium hydroxide, it is probable that the yield of benzoic acid could be increased somewhat. The water solutions gave brown ring tests with ferrous sulfate and sulfuric acid.

Summary

1. The four dioximes of camphor quinone yield but one oxidation product, indicating a symmetrical structure for furazan oxides.

2. The symmetrical structure was proved by ozonizing diphenyl furazan oxide.

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