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ELECTROCHEMICAL PREPARATION OF 4,5,9,10-TETRAAZAPYRENE AND ITS N-OXIDES

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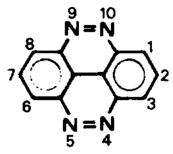
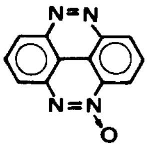
4,5,9,10-tetraazapyrene and its derivatives have been the subject of only a few studies[1-4]. Tetraazapyrene itself[1,3] and its 2,7-dimethyl derivative[4] have been obtained only recently in poor yields (15-20 %) by catalytic hydrogenation of the corresponding 2,2',6,6'-tétranitrobiphenyl. Attempts to reduce tetranitrobiphenyl using twelve other reducing agents have failed[5,6]. 2,7-Dicarbomethoxytetraazapyrene was prepared by oxidation of the corresponding tetraaminobiphenyl[4] (yield 18 %). Until now, only dioxides of tetraazapyrene have been reported. Holt and Oakland have prepared what they claimed to be the di 4,9(10?)-N-oxide in low yield by catalytic hydrogenation of tetranitrobiphenyl[3]. Castle *et alii* have similarly prepared what they consider to be 2,7-disubstituted N-oxides[4] (yield 20 to 50 %). N-oxides have also been obtained by oxidation of tetraazapyrenes[3,4] and of 1,10-diaminobenzocinnoline[2].





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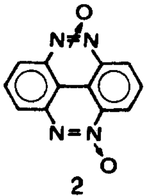

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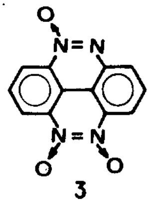

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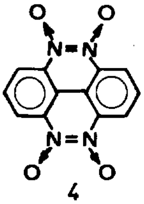

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We have prepared tetraazapyrene N-oxides in excellent yields by electrochemical reduction of 2,2',6,6'-tetranitrobiphenyl on a Hg electrode (- 1 V versus S.C.E, water-ethanol 1:1, pH 6.8) followed by *in situ* oxidation, either by air, or electrochemically (+ 0,15 V), of the 2,2',6,6'-tetrahydroxylamine obtained. The yields are given in table I. The products were separated by column chromatography (alumina, ligroin-methylene chloride 3:2) and identified by mass spectrometry and polarography. A study of the results obtained by these methods also shows conclusively that the dioxide is either tetraazapyrene 4,9 or tetraazapyrene 4,10-dioxide, or a mixture of the two isomers, and excludes the presence of tetrazapyrene 4,5-dioxide.

Table I

Preparation of 4,5,9,10-tetraazapyrene N-oxides

	têtra-azapyrene	monoxide **1**	dioxide **2**	trioxide **3**	tetroxyde **4**	total yield
air oxidation of the hydroxylamine	(3)	7.5	75	7.5		93
electrochemical oxidation of the hydroxylamine		11	48	32	1	92
catalytic reduction of tetranitrobiphenyl		3.7	10.5	3.3		17.5

The electrochemical reduction of the crude mixture of the N-oxides gives either (water-DMF 1:1 ; pH 6.8 ; - 0.90 V) tetraazapyrene in 72 % yield (based on tetranitrobiphenyl), or (water-acetone 3:2 ; pH 6.1 ; - 0.45 V) the monoxide in 65 % yield (based on tetranitrobiphenyl).

We repeated the catalytic hydrogenation of tetranitrobiphenyl under the conditions given by Holt and Oakland. A mixture of mono, di and trioxide is obtained ; the mono and the trioxide are formed in equivalent amounts (table I), which accounts for the fact that the results of the analysis found by Holt and Oakland agree with the percentages calculated for the dioxide. Under these conditions, the possibility that the N-oxides prepared by Castle *et alii* are also a mixture cannot be excluded.

The oxidation of tetraazapyrene by 30 % H_2O_2 in acetic acid yields a mixture of the monoxide and of the dioxide in a 3:2 ratio.

The excellent yields obtained show the advantages of the electrochemical method, which is moreover the only method for preparing the tetroxide.

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