THE REACTION OF FURAZANO[3,4-*b*]QUINOXALINE 1-OXIDE WITH CYCLOPENTADIENE: TRAPPING OF THE 2,3-DINITROSOQUINOXALINE INTERMEDIATE

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Abstract- *The trapping of the 2,3-dinitrosoquinoxaline by reaction of furazano[3,4-b]quinoxaline 1-oxide with cyclopentadiene is reported.*

The existence of *cis*-dinitrosoalkenes or 1,2-dinitrosoarenes as intermediates in the interconversion of the two isomeric forms of furazan *N*-oxides and their fused derivatives[1] was a reasonable hypothesis before 1,2-dinitrosobenzene was isolated and characterised[2] in Argon matrices at 12-14 K. However, these dinitroso intermediates have not been trapped by butadienes in attempted hetero-Diels-Alder reactions of nitro-substituted benzofurazan *N*-oxides[3] despite the strong dienophilic reactivity of the nitroso group,[4] the products obtained being cycloadducts to the partially localized double bonds of the benzene ring.

In case of furazano[3,4-*b*]quinoxaline 1-oxide (**1**),[5] the strong electron withdrawing ability of the quinoxaline group increases the dienophilic character of the nitroso groups in the 2,3-dinitrosoquinoxaline intermediate (**2**). Furthermore, the less localized carbon-carbon double bonds in **1**, compared to those of benzofurazan *N*-oxides, overcome the problem of a possible addition of the diene to these double bonds.

When an excess of freshly distilled cyclopentadiene was added to an ice-cold solution of

1 in dry methylene dichloride, a reaction occurred rapidly and the red colored solution changed immediately to dark yellow-orange. Careful chromatographic separation of the mixture on silica gel using ethyl acetate as the eluant yielded two main fractions.

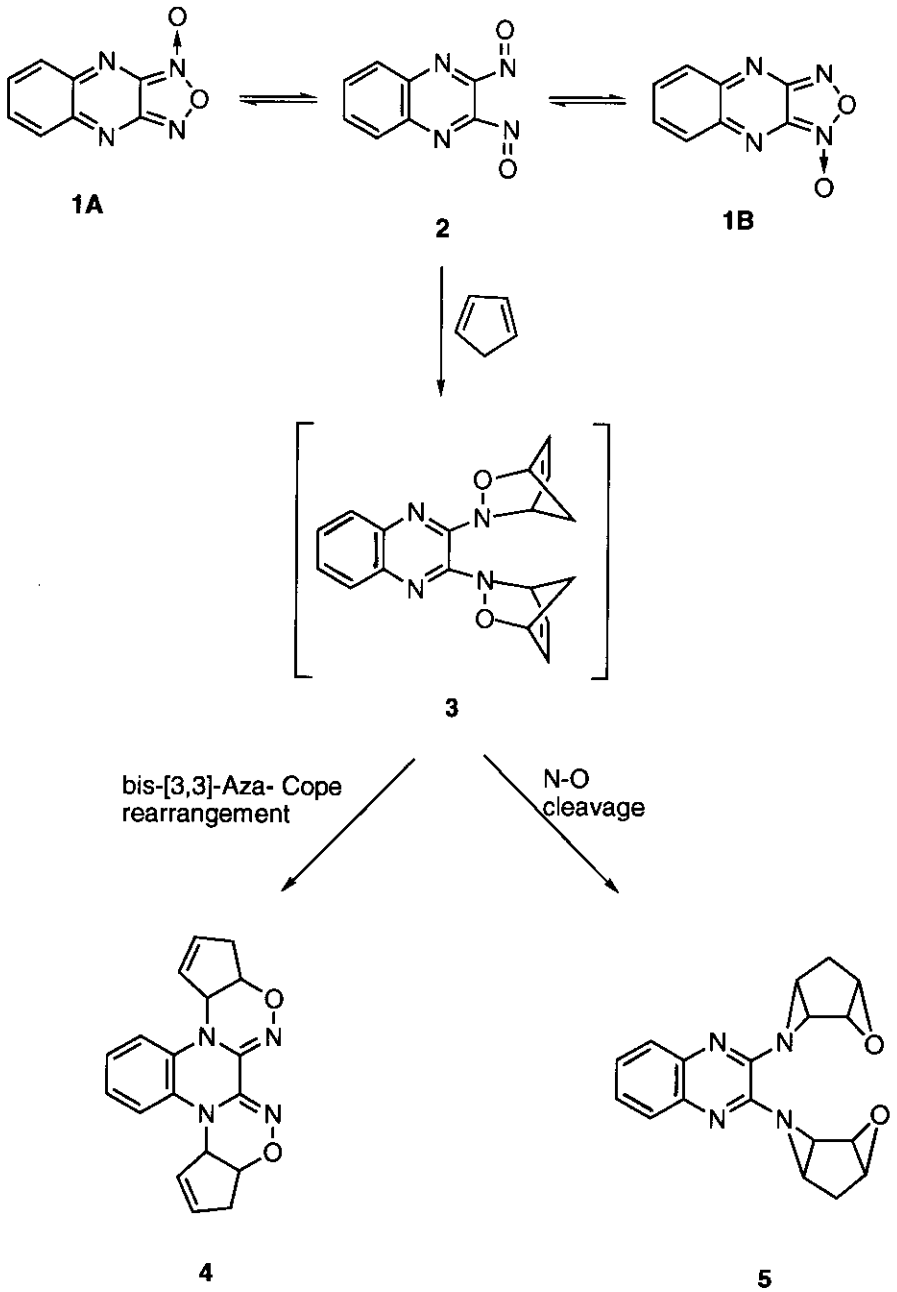
The first product, with R_f 0.55 (in ethyl acetate) and mp 88-90 °C, isolated in 10% yield, was an adduct of cyclopentadiene to furazano[3,4-*b*]quinoxaline 1-oxide (1) in ratio 2:1, as shown by its mass spectrum and the exact molecular weight measurement, whereas both ^{1}H- and ^{13}C-nmr spectra, recorded in the Table, are consistent with the structure (4). The aromatic proton and carbon chemical shifts are reminiscent of an *o*-phenylenediamine structure, namely, the pyrazine ring has been changed to a 1,4-dihydropyrazine derivative. The olefinic, CH_2, -CHO- and -CHN- groups of the cyclopentene rings give characteristic signals[6] in both the ^{1}H- and ^{13}C-nmr spectra and reveal that they can not belong to bicyclic oxazine systems as in 3. In the ^{1}H-nmr spectra of simple bicyclic oxazines analogous to 3 in the literature,[7,8] the CH_2 signal appeared at *ca.* δ 2.0, the -CHO- and -CHN- protons at *ca.* δ 5.5 and the olefinic protons at *ca.* δ 6.5.

Table. Proton (300 MHz) and Carbon (75 MHz) Shifts Assignement of Adduct (4) (δ, ppm, $CDCl_3$).

	-CH=CH-	-CHO-	-CHN-	$-CH_2-$	Aromatic Ring[a]
^{1}H-nmr	6.14(s,br,4H)	4.28(m,2H)	4.88(m,1H) 4.91(m,1H)	2.80(m,4H)	7.02(m,2H) 7.12(m,2H)
^{13}C-nmr	113.09 134.36	72.82 73.26	62.00 62.12	38.17	123.24, 123.35 129.24, 129.42

[a]*The four quaternary sp^2 carbon signals did not appear clearly.*

The reverse regioisomeric structure (the double bond of the cyclopentene rings close to the -CHO- group) should be rather excluded, since the proton -CHO- signals in that case are expected to appear downfield (*ca.* δ 5.5) and the -CHN- protons upfield.[6,8,9] Although the complete stereochemistry of this compound can not be unequivocally deduced from the available experimental data, it is apparent from the nmr spectra that a diastereomeric mixture of a couple of enantiomers and the *meso* compound is present, the cyclopentene



rings being in *trans* and *cis* positions, respectively.

The second fraction, isolated as colorless gum with R_f 0.5 (in ethyl acetate) in 21%

yield, was also an adduct of cyclopentadiene to **1** in ratio 2:1, as shown by the microanalysis and the mass spectrum. However, both ^{1}H- and ^{13}C-nmr spectra indicated that this was a mixture, which we were unable to analyse and purify by the conventional methods while, furthermore, we found that it is relatively unstable, decomposing in attempted crystallization or further chromatographic separation. The nmr spectra of the mixture, however, show that the main component of this fraction is, most likely, the bis-epoxyepimine (**5**)[8] in the form of mixture of diastereomers. The multiplets at δ 3.3-3.8 and δ 2.0 could be assighed to the oxirane/aziridine and methylene protons, respectively, while the groups of carbon peaks appeared at δ 29, 48, 54, 55 and 67 are the expected ones for the epoxyepimine systems.[10] It should be noted here that other dienes, such as 2,3-dimethylbutadiene, did not give analogous reaction with **1**, the products precipitated being unmelted solids of polymeric nature.

The fate of simple bicyclic oxazines prepared from hetero-Diels-Alder reactions of nitroso compounds with cyclopentadiene has been extensively studied last years, their stability being strongly dependent on the nature of the N-linking group. They can undergo retro-Diels-Alder reaction[11] or homolytic breaking[12] of the N-O bond towards epoxyepimines[8,10] or γ,δ-epiminopentadienal derivatives,[10] while in the cases of the adducts of C-nitrosocarbonyl compounds to cyclopentadiene, a [3,3]-Cope rearrangement often appears.[6,13]

It is apparent in the present case, that the cyclopentadiene is added to the two nitroso groups of **2** and the resulting bis-adduct (**3**), being unstable, either isomerises to **4** *via* a bis-Aza-Cope metathesis or rearranges to **5** through a biradical N-O cleavage. An alternative reaction pathway for the formation of **4**, involving a direct double hetero-Diels-Alder addition of cyclopentadiene to species (**2**), the former acting as dienophile,[6] does not seem likely, since simple alkenes react with **1** in a different manner.[14] In both cases, however, the reaction proceeds through the 2,3-dinitrosoquinoxaline (**2**), demonstrating thus chemically the existence of furoxans dinitroso equivalent. Further studies on the reaction of furazan *N*-oxides with dienes are in progress.

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