187. Thermal Isomerization of 7,8-Diazabicyclo[4.2.2]deca-2,4,7,9-tetraene *N*-oxide to Benzaldehyde Oxime[1])

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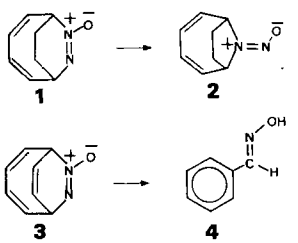
Summary

Thermal transformation of 7,8-diazabicyclo[4.2.2]deca-2,4,7,9-tetraene *N*-oxide (**3**) was observed, (*Z*)-benzaldehyde oxime being the major product, with (*E*)-benzaldehyde oxime as a minor product. *N*-Oxide **3** was labeled with deuterium *α* to the oxidized N-atom. The location of the deuterium label in the thermolysis products fitted one of two reasonable mechanisms.

Introduction. – A recent study of the thermal behaviour of 1,2-diazene *N*-oxide **1** demonstrated that it rearranges *via* a formal [1,2]-sigmatropic shift to furnish the corresponding *N*-nitrosamine **2** [1]. In conjunction with this study we investigated the thermolysis of the closely related 7,8-diazabicyclo[4.2.2]deca-2,4,7,9-tetraene *N*-oxide (**3**) [2]. We now report our investigations on the thermolysis of **3**, which resulted in an unexpected transformation of **3** into **4**.



Results and discussion. – In the absence of light **3** in dioxane is transformed exclusively into a mixture of isomers of benzaldehyde oxime (**4**) [3] and HCN. The major product is the (*Z*)-isomer (72% yield), and the minor is (*E*) (8% yield). The rate of disappearance of **3** – a first-order reaction – was measured at 129.6° in (D_8)-dioxane to be 7.3×10^{-5} s^{-1} corresponding to $\Delta G^{\neq} = 31.4$ kcal/mol.

[1]) Rearrangement of 1,2-diazene *N*-oxides. IV. Part III: *H. Olsen* and *C.L. Pedersen*, Acta Chem. Scand., Ser. B, in press.

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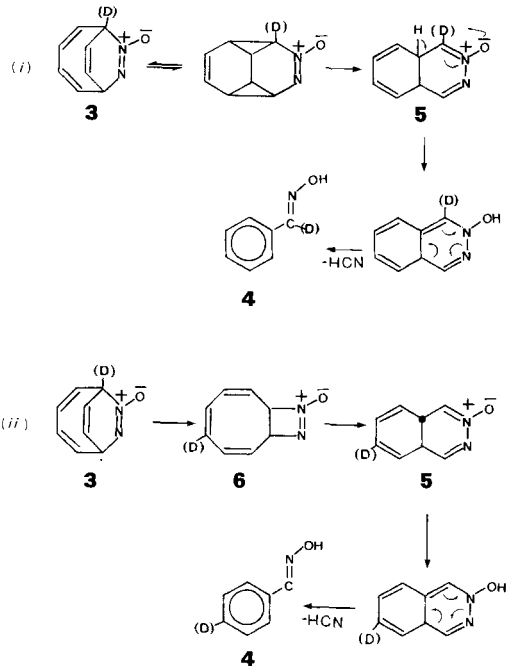
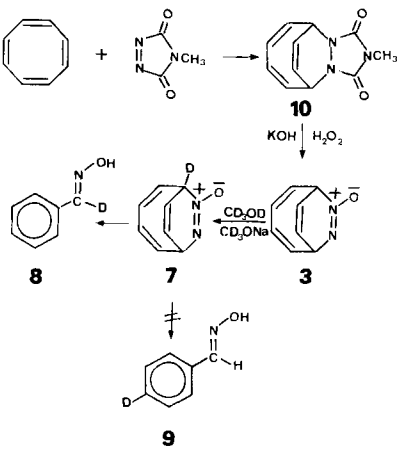
A priori two mechanisms for the transformation of **3** to **4** must be considered (see *Scheme 1*). *(i)* A process initiated by an intramolecular *Diels-Alder* reaction followed by a reverse $[_\pi 4_s + \pi 4_s]$-cycloaddition to give **5**, which rapidly rearranges *via* a [1,4]-sigmatropic shift. Finally expulsion of hydrocyanic acid by a *Alder-Rickert* cleavage provides **4**. The first two steps are an example of the well-known conversion of bicyclo[4.2.2]deca-2,4,7,9-tetraene to 9,10-dihydronaphthalene [4]. The activation parameters for this process were estimated to be $\Delta H^{\neq} = 34$ kcal/mol and $\Delta S^{\neq} = -5$ e.u. [5]; *(ii)* an equally likely process is the conversion of **3** to **6** *via* a [1,5]-sigmatropic shift followed by disrotatory closure and rupture, tautomerization and elimination of hydrocyanic acid to give **4**. The step involving electrocyclic closure and rupture is supported by the finding that bicyclo[6.2.0]deca-2,4,6,9-tetraene smoothly rearranges to *trans*-9,10-dihydronaphthalene with $\Delta H^{\neq} = 24.9$ kcal/mol and $\Delta S^{\neq} = -0.4$ e.u. [6]. Furthermore, X-ray studies of bicyclic azo-*N*-

Scheme 1



oxides indicate that the C,ONN-bond is slightly longer than the C,NNO-bond suggesting that the C,NNO-bond energy is larger than the C,ONN-bond energy [7]. Finally recent studies of the thermal isomerization of 1,2-diazene *N*-oxides have shown that the C,ONN-bond is preferentially cleaved [8]. Experiments with the deuterium-labeled substance **7** permits in principle a distinction between these two mechanisms. Pathway *i* would give product **8** with deuterium bound exclusively to the oxime C-atom, whereas pathway *ii* would afford benzaldehyde oxime with deuterium bound to an aromatic C-atom.

Scheme 2

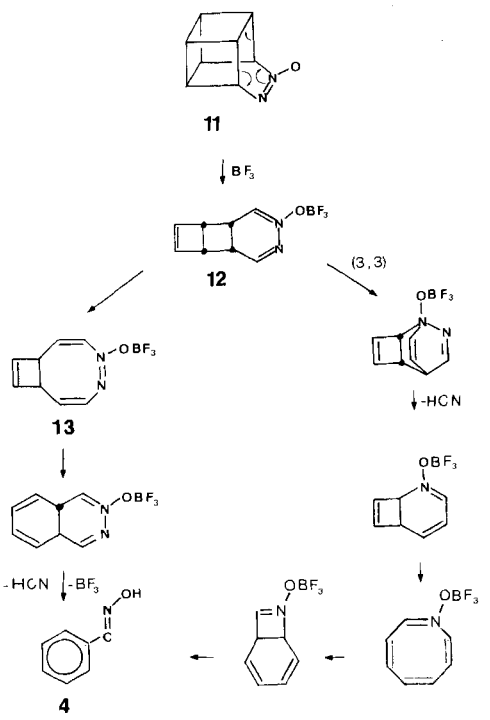


Diazene *N*-oxide **7** was synthesized as outlined in *Scheme 2*. Oxidative hydrolysis [9] of cyclooctatetraene-methyltriazolinedione adduct **10** [10] results in conversion to **3**, which rapidly exchanges the bridgehead proton *a* to oxidized N-atom at RT. to give **7**. The ^{1}H-NMR. spectrum of **3** shows the bridgehead protons *a* to the N-atom at δ 5.37 (*d*×*d*, $J = 7$ and 4 Hz) and at δ 4.87 (br. *s*). The signal at lowest field disappears on treatment with CD_3ONa/CD_3OD. The off-resonance decoupled ^{13}C-NMR. spectrum of **3** displays seven doublets at δ 137.7, 133.9, 128.2, 127.2, 117.9, 71.4 and 57.5. Intensity measurements indicate that the signal resonating at δ 117.9 corresponds to two C-atoms. From the gated-decoupled ^{13}C-NMR. spectrum of *N*-oxide **3**, $^1J(C,H) = 155$ and 148 Hz were observed for the C-atoms resonating at δ 71.4 and 57.5, respectively. The coupling constants indicate a slightly greater degree of *s*-character in the C,H-bond of the bridgehead C-atom resonating at lower field [11]. In the proton-noise-decoupled ^{13}C-NMR. spectrum of **7** the signal at δ 71.4 (of the protio compound) is absent. On the basis of the estimated $^1J(C,H)$ coupling constants of the bridgehead atoms next to the N-atom, exchange experiments in similar systems [12] and ^{13}C-NMR. chemical shift calculations using semi-empirical MO-methods[3]), we conclude that the treatment of diazene N-oxide **3** with CD_3ONa/CD_3OD results in exchange of the proton *a* to the oxidized N-atom. Thus both the proton and C-atom next to the oxygen-bearing N-atom resonate at lower field than the corresponding atoms next to neighbouring N-atom.

Pyrolysis of a degassed solution of **7** in (D_8)dioxane at 129.6° results as expected in a mixture of benzaldehyde oximes. The proton-noise-decoupled ^{13}C-NMR. spectrum of the crude mixture lacked the signals at $\delta = 149.6$ and 146.4 when compared with the corresponding spectrum of a mixture obtained by thermolysis

[3]) *H. Baumann & H. Olsen*, unpublished results.

Scheme 3



of the protio compound **3**. Since these two signals can be assigned to the oxime C-atoms in the (*Z*)- and (*E*)-benzaldehyde oximes respectively, 1,2-diazene *N*-oxide **3** is probably transformed thermally *via* pathway *i* and not *via* pathway *ii*.

A valence isomer of **3**, namely diazabasketene *N*-oxide **11**, has been reported to rearrange to **4** in the presence of boron trifluoride [13] *(Scheme 3)*. A mechanism consistent with the principles of molecular orbital theory and precedents in the behaviour of basketene and diazabasketene was proposed for this transformation. Coordination of **11** with BF_3 followed by a *Alder-Rickert* cleavage yields intermediate **12**. A [3,3]-sigmatropic shift (*i.e. Cope* rearrangement) followed by irreversible loss of HCN, sequential valence tautomerization and aromatization was proposed to account for the oxime formation. An equally likely thermal process of **11** would be isomerization to **13**, as bicyclo[4.2.0]octa-2,4-diene isomerizes to 1,3,5-cyclooctatriene with $\Delta H^{\neq} = 24.7$ kcal/mol and $\Delta S^{\neq} = 2$ e.u. [14]. That this process is probably involved is suggested by some recent studies of the thermal behaviour of **11**, which we will report later.

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Experimental Part

General. ^{1}H- and ^{13}C-NMR. spectra were recorded on a *Varian XL-100* in $CDCl_3$. Chemical shifts (δ) are given in ppm downfield from internal TMS, coupling constants J are in Hz. IR. spectra (cm^{-1}) were taken on a *Perkin-Elmer* type *125* and *577* spectrophotometer. Melting points (m.p.), taken on a *Büchi 510* in capillary tubes, are uncorrected.

4-Methyl-2,4,6-triazatricyclo[5.4.2.0^{2,6}]trideca-8,10,12-triene-3,5-dione (**10**). A solution of cyclooctatetraene (20.8 g, 200 mmol) in CH_2Cl_2 (110 ml) was added to a solution of 3-methyl-1,2,4-triazoline-3,5-dione (22.6 g, 200 mmol) in dry CH_2Cl_2 (500 ml). After stirring 3 d at RT. the red colour of the dione disappeared completely. The solvent and unreacted cyclooctatetraene were removed under reduced pressure affording a yellow solid which was extracted with ether in a *Soxhlet* apparatus for 24 h. Removal of solvent and recrystallization from ethanol produced white crystals (12.6 g, 58 mmol, 29%); m.p. 138–139°. – IR. ($CHCl_3$): 1755*m*, 1700*s*, 1470*m*. – ^{1}H-NMR.: 6.3–6.0 (*m*, 4 H); 5.93 (*AA'*-part of an *AA'XX'*-pattern, 2 H); 5.07 (*m*, 2 H); 3.07 (*s*, 3 H).

$C_{11}H_{11}N_2O_2$ Calc. C 60.8 H 5.1 N 19.3% Found C 60.9 H 5.2 N 19.5%

7,8-Diazabicyclo[4.2.2]deca-2,4,7,9-tetraene N-*oxide* (**3**). To a mixture of adduct **10** (4.35 g, 20 mmol), ethylene glycol (60 ml) and 30% H_2O_2-solution (140 ml) was added dropwise a solution of KOH (98.0 g, 1750 mmol) in distilled water (98 ml) at 40–55° over a period of 25 min. The mixture was then heated to 60° for an additional 30 min. The cooled mixture was extracted with $CHCl_3$ (3 × 100 ml), the extracts were dried ($MgSO_4$) and the solvent was stripped *in vacuo* to afford a white solid (0.54 g, 3.6 mmol, 18%), identical with an analytical sample of **3** (^{1}H-NMR.). The aqueous phase was neutralized with conc. HCl-solution, extracted with $CHCl_3$ (3 × 100 ml), dried ($MgSO_4$) and concentrated under reduced pressure to afford a brown oil (2.16 g). The oil was purified by column chromatography on silica gel with ether to give a white crystalline solid (1.09 g, 7.4 mmol, 37%), identical with an analytical sample of **3** (^{1}H-NMR.). Recrystallization of **3** from ether afforded white crystals; m.p. 82–83°. – IR. ($CHCl_3$): 1501*s*, 1298*m*, 1283*m*. – ^{1}H-NMR.: 6.6–5.7 (*m*, 6 H); 5.37 (*d* × *d*, J = 7 and 4, 1 H); 4.87 (br. *s*, 1 H). – ^{13}C-NMR.: 137.7 (*d*), 133.9 (*d*), 128.2 (*d*), 127.2 (*d*), 117.9 (*d*), 71.4 (*d*), 57.5 (*d*).

$C_8H_8N_2O$ Calc. C 64.9 H 5.4 N 18.9% Found C 64.7 H 5.5 N 18.8%

[6-$^2H_1$]-7,8-Diazabicyclo[4.2.2]deca-2,4,7,9-tetraene-7 N-*oxide* (**7**). *N*-oxide **3** (150 mg) was dissolved in a mixture of CD_3ONa/CD_3OD in an NMR. tube at RT. The disappearance of the signal of the bridgehead proton at δ 5.37 was followed by ^{1}H-NMR. spectroscopy. After complete exchange, the solution was neutralized using conc. DCl-solution and then extracted with $CHCl_3$ (3 × 50 ml). The combined extracts were dried ($CaCl_2$). Removal of the solvent *in vacuo* produced a crystalline solid (120 mg, 80%); m.p. 82–84°.

Thermolysis of **3**. A solution of **3** in (D_8)dioxane in an NMR. tube was degassed and sealed *in vacuo*. The *N*-oxide was heated at 129.6 ± 0.1° over several half-lives and periodically monitored at RT. by integration of the bridgehead protons against the methylene protons of dioxane. Unimolecular rate constants were calculated by least-squares analysis of ln(*N*-oxide integral/dioxane integral) *vs.* time. Product identity was established by comparison of TLC., IR., ^{1}H- and ^{13}C-NMR. spectra, and MS. with independently prepared samples of benzaldehyde oxime [3]. ^{13}C-NMR. spectrum of the reaction mixture: 149.5, 134.0, 129.9, 129.2 and 127.3 corresponding to the major isomer of **4**; 146.1, 131.3, 130.1 and 128.9 corresponding to the minor isomer of **4**.

Thermolysis of **7**. A solution of **7** in (D_8) dioxane in an NMR. tube was degassed and sealed *in vacuo*. The proton noise-decoupled ^{13}C-NMR. spectrum showed signals at δ 137.5, 133.5, 126.7, 125.8, 117.4, 117.0 and 56.3. The sample was heated at 129.6 ± 0.1° for 500 min. The off-resonance decoupled ^{13}C-NMR. spectrum of the reaction mixture revealed signals at δ 134.0 (*s*), 129.9 (*d*), 129.2 (*d*), 127.3 (*d*) corresponding to the major isomer of **8** and at δ 131.3 (*d*), 130.1 (*d*), 128.9 (*d*) corresponding to the minor isomer of **8**.

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