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Epoxy-Epimination of Cyclic Conjugated Dienes-VII-

Cycloaddition of Nitroso-Halogenobenzenes to Cyclopentadiene followed by Rearrangement to Epoxy-Epimino- and γ–δ-Epimino-Pentadienal Derivatives via N-O and C-C Bond Breaking.

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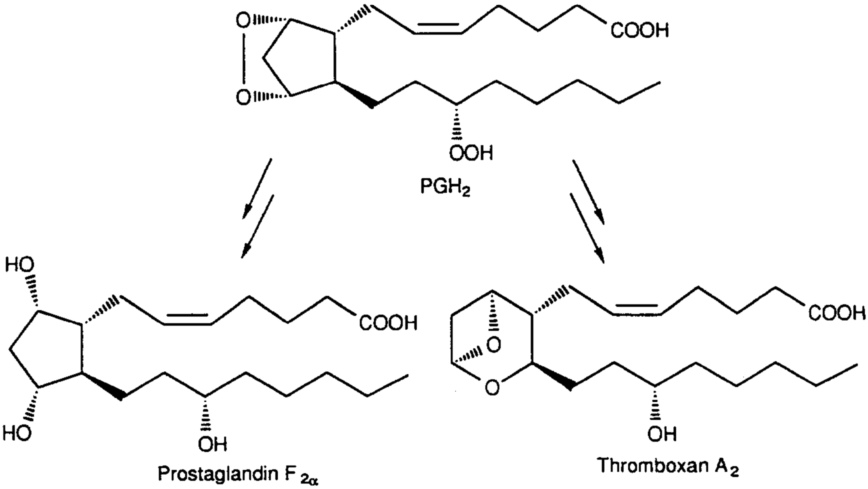
ABSTRACTS : [4+2] Cycloaddition of halogenated nitroso benzenes to cyclopentadiene followed by isomerisation of the intermediate adduct occurs already at room temperature to furnish the epoxy-epimine 1 and the epiminopentadienal 2. The structure proof of 1 is based on X-ray analysis.

Endoperoxides, such as PGH_2, take a central part in fatty acid metabolism producing, for example, prostaglandin $F_{2\alpha}$ and thromboxan A_2 via O-O and, for the latter case, C-C bond rupture[1] (Scheme 1).



Scheme 1

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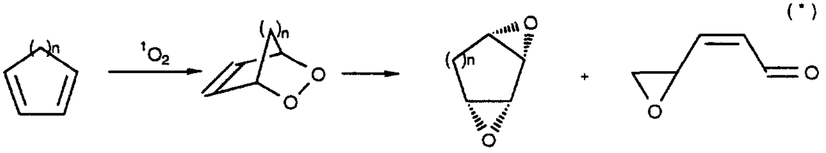
† Presently in the Pharmaceutical Departement of CIBA-GEIGY, CH-4002 Basel.

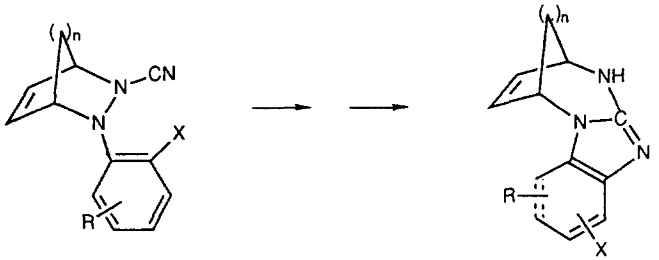
Simple unsaturated bicyclic endoperoxides also undergo thermal homolysis of the weak oxygen-oxygen bond, followed by similar rearrangements. The adduct of singlet oxygen to cyclopentadiene, for example, furnishes thermally both the bisepoxide by addition of the incipient alkoxy radicals to the adjacent double bond and the epoxypentadienal by a C-C bond breaking (Scheme 2). Both products are intermediates in the synthesis of natural products. In the presence of the $RuCl_2(PPh_3)$ complex, the main products are the bisepoxydes[2e].



[(*) when n=1]

Scheme 2

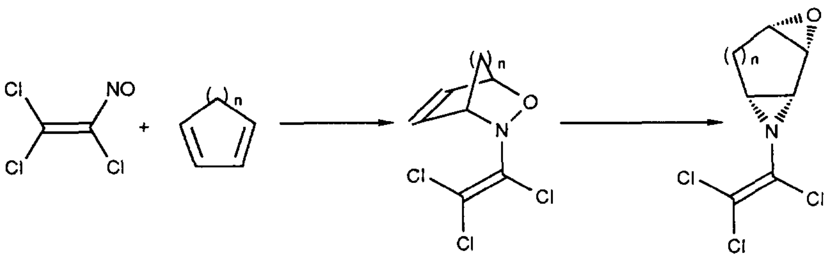
In our laboratory, rearrangements of analogous molecules in which the endoperoxide oxygen is replaced by one or two nitrogen atoms have been studied, showing a large dependance on the N-substituent. The tris-aza-Cope rearrangement of bicyclic N-cyanohydrazines leading to imidazolo-diazepine derivatives[3] is the last reported example (Scheme 3).



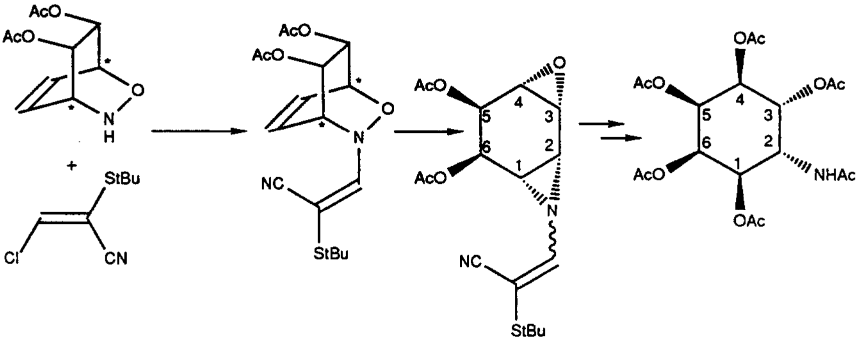
(n = 1 or 2)
(X= H or Cl)

Scheme 3

The first example was encountered, in aza-analogy to the formation of bisepoxydes, when epoxy-epimines were obtained[4] from halogeno-nitrosoethylene adducts to cyclic conjugated dienes (scheme 4). When bicyclic oxazines were N-substituted with a captodative olefin, facile epoxy-epimination occurred (scheme 5). This second method provides an excellent stereochemically controled approach to chiral epoxy-epimines which can be used as precursors for inosamine-streptamine derivatives[4d].



Scheme 4



Scheme 5

Preliminary studies have demonstrated that bicyclic strained oxazines rearrange more easily. Futhermore the nature of the nitrogen substituent is of a determining importance but, so far, only N-vinyl groups with suitable substituents have been reported to render the N-O bond proradical and labile enough to furnish the rearrangement.

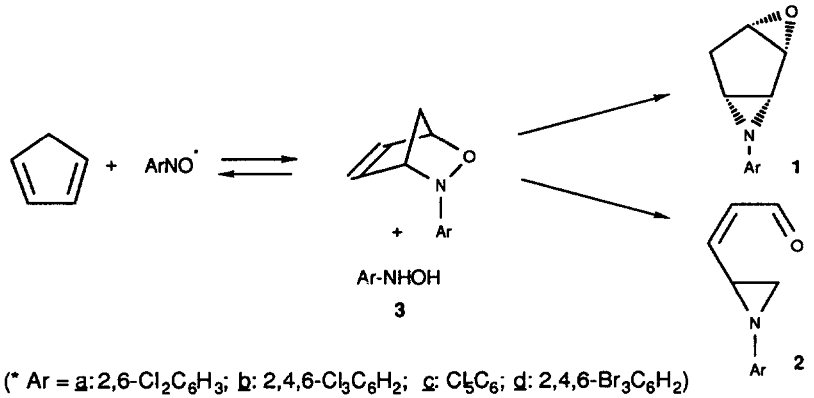
We report herein that various halogenated N-aryl substituents induce the epoxy-epimination reaction: futhermore the epiminopentadienal is formed in aza-analogy to the endoperoxide rearrangement of scheme 1.

RESULTS AND DISCUSSION

Although the [4+2] addition of aryl-nitroso compounds to cyclic conjugated dienes is well-known to occur as a temperature dependent reversible reaction[5], to the best of our knowledge no isomerisation products have been reported. In the course of our study, various brominated or chlorinated nitrosobenzenes were added to cyclopentadiene. The electron-withdrawing character of these halogen substituents influences favorably the equilibrium of the reversible reaction and helps to promote N-O homolysis of the cycloadducts.

The reactions have been carried out with an excess of cyclopentadiene either at room temperature in solvents such as dichloromethane, tetrachloromethane and benzene, or in refluxing toluene. Whenever the ortho positions of the nitrosoaryl compound are halo-substituted, both the epoxy-epimine **1** and the epiminopentadienal **2** are obtained in low yield together with the hydroxylamine **3** (Scheme 6). With nitrosobenzene, 2,4-dichloronitrosobenzene or 4-bromonitrosobenzene, complex mixtures are obtained.

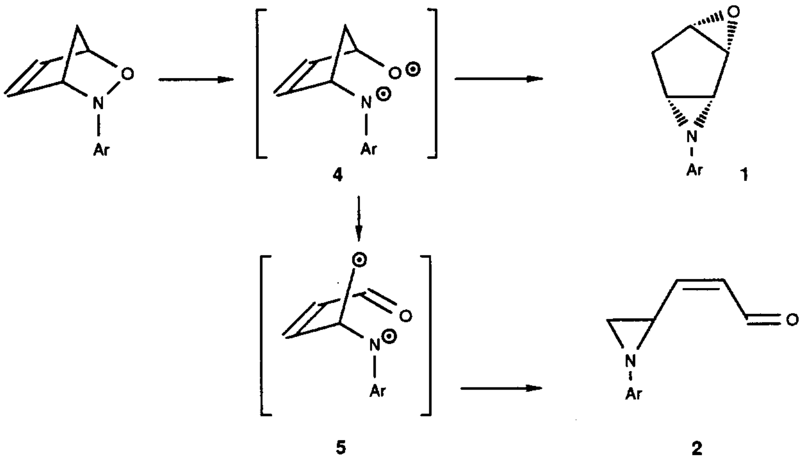
This newly described carbon ring cleavage leading to **2** and accompanying the epoxy-epimine formation is analogous to the already cited endoperoxide rearrangements .



(* Ar = a: 2,6-$Cl_2C_6H_3$; b: 2,4,6-$Cl_3C_6H_2$; c: Cl_5C_6; d: 2,4,6-$Br_3C_6H_2$)

Scheme 6

The steric and electronic substituent effects upon the reaction course are not clear. The formation of the isomers 1 and 2 follows Scheme 7. Depending on the N-substituent, the biradical 4 either collapses to give epoxy-epimine 1 or undergoes β-homolysis of a carbon-carbon bond to generate the biradical 5; its cyclisation produces the epiminopentadienal 2.



(Ar = a: 2,6-$Cl_2C_6H_3$; b: 2,4,6-$Cl_3C_6H_2$; c: Cl_5C_6; d: 2,4,6-$Br_3C_6H_2$)

Scheme 7

Attempts to extend the title reaction to 1,3-cycohexadiene failed because of thermal cycloreversion. Catalytic or photochemical induction remains to be investigated with a double purpose: to render the rearrangement preparatively useful and to understand its mechanism as a model of the prostaglandin and thromboxan chemistry.

The structure of N-(2,6-dichlorophenyl) -1,2-epimino-3,4-epoxycyclopentane 1a has been determined by NMR and X-ray analysis (fig.1). The epoxy-epimine structures 1b-c are deduced from the similarity of their NMR spectral characteristics to those of 1a.. The two three-membered fused rings are cis to each other. The central cyclopentane is planar within experimental error. The tricyclic epoxy-epimine system is very similar in dimension and conformation to N-(2,2-dichlorovinyl)-1,2-epimino-3,4-epoxycyclopentane[6].

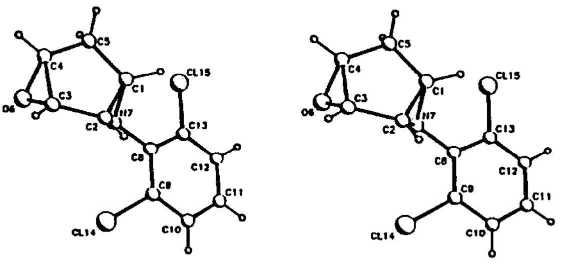
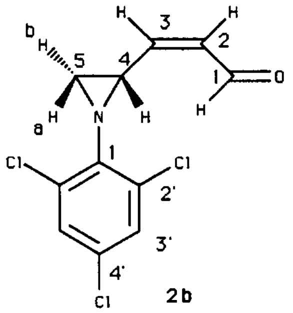


Fig1. Stereopair view of the compound 1a[7]

Compounds 2 have been characterized by spectroscopy . NMR data of **2b** are summarized in table 1 and are comparable with those of the cis-4,5-epoxy-2-pentadienal[8].



2b

Table 1: ^{13}C NMR and ^{1}H NMR data of **2b** (in CDCl3 solution)

Carbon	C d ppm	^{1}JC-H Hz	^{1}H d ppm
5	38.9	^{1}J:178 $^{1'}$J:170	a 2.01 b 2.12
4	38.8	^{1}J:173	3.12
2'	127.8		
4'	128.3		
3'	128.9	^{1}J:171.6	6.90
2	131.7	^{1}J:164.7 ^{2}J:20.6	5.90
1'	144.5		
3	148.6	^{1}J:148.5	5.73
1	189.6	^{1}J:172.6 ^{3}J:12 ^{2}J:1.3	9.96

-The proton-proton coupling constant $^3J_{6-8}$ (11.2Hz) and the carbon-proton coupling constant $^3J_2$ (12Hz) and $^3J_9$ (12Hz) are compatible with a cis configuration.

-The coupling constant $^1J_1$, $^{1'}J_1$,$^1J_2$ in the ^{13}C-NMR spectrum are in agreement with the presence of a small ring

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EXPERIMENTAL SECTION

General

T.l.c. were carried out on silica gel plates (Merck $60F_{254}$) and visualised under U.V. light. Flash chromatographies (FC) were carried out on silica gel (Merck 60; 230-400 Mesh). Melting points were determined on a Buchi (Dr. Tottoli) apparatus. ^1H NMR were recorded in CD_2Cl_2, $CDCl_3$, acetone-d6 or DMSO-d6 using TMS as internal reference at 200MHz on a Varian Gemini or XL 200 spectrometer. Infra-red spectra were obtained on a Perkin Elmer 297 instrument. Mass spectra (MS) were registered on a Varian AMT 44S spectrometer.

Nitrosobenzene (Aldrich Chemical Co.) was recrystallised from ethanol. 1,3-Cyclopentadiene (bp 39-40°C) was prepared by pyrolytic dedimerisation and distillation of the commercially available dicyclopentadiene at atmospheric pressure. 4-Bromonitrosobenzene[9]; 2,6-Dichloronitrosobenzene[10] 2,4,6-Trichloronitrosobenzene[10]; 2,6-Dichloro-nitroso-benzene[10] were synthetised by standard preparative methods, purified by recrystalisation or distillation where appropriate. M.p. and NMR spectra were used to check the purity.

Pentachloronitrosobenzene (m.p.168°C) was synthetised from pentachloroaniline according to the method of Bayer[10] (71%). Anal.Calcd.: C 25.76%, N 5.01%; found: C 25.63%, N 4.72%.

Pentachloroaniline (mp 226°C) was prepared from the corresponding nitro compounds by treatment with $SnCl_2$ according to the method of Bellamy[11]. Anal. Calcd. for $C_6H_2NCl_5$: C 27.12%, H 0.75%, N 5.27%; found: C 26.59%, H 0.70%, N 5.09%.

2,4-Dichloronitrosobenzene (m.p.42°C) was synthetised from 2,4-Dichloronitrobenzene by reduction with palladium according to the method of Entwistle[12]. ^1H NMR ($CDCl_3$) d: 7.81 (s, 1H); 7.22 (d, 2H); 6.21 (d, 2H). ^{13}C NMR: 159.12 (S); 143.26 (Sm, C-Cl); 131.91 (D); 127.32 (D); 109.87 (D).

Reaction of cyclopentadiene with nitroso-arene dienophiles.

General Procedure:

To a stirred solution of the nitroso-arene (5 mmoles) in CH_2Cl_2 (mode A) or in toluene (300 ml; mode B), freshly distilled cyclopentadiene (50 mmoles) was added. The mixture was stirred at room temperature (mode A) or heated under reflux (mode B). During the reaction the solution becomes gradually dark-coloured. The course of the reaction was monitored by t.l.c. . The solution was then evaporated to near dryness and the reaction products were separated by several flash chromatographies. In each case the pentadienal derivative migrates the fastest, followed by the N-arylhydroxylamine and finally by the N-aryl-epoxy-epimine

Reaction of 2-6-Dichloronitrosobenzene with Cyclopentadiene.

Reaction time: 17 days (mode A) or 40 minutes (mode B).A first F.C. (CCl_4/Et_2O 92/8) was carried out to isolate **1a**. Yield: 133 mg (11%) as a white solid which was recrystallised from CCl_4 (m.p. 169°C). ^1H NMR ($CDCl_3$) d: 7.18 (d, 2H); 6.79(t, 1H); 3.83 (m, 1H); 3.76 (m, 1H); 3.35 (m, 1H); 3.25 (m, 1H); 2.34 (d, 1H); 1.90 (m, 1H).^{13}C NMR ($CDCl_3$) d 145.8 (S, aromatic C-N); 129.2 (D, aromatic m-C-H); 127.3 (S, C-Cl); 127.3 (S, aromatic p-C-H); 66.1 (D); 55.5 (D);54.3 (D); 45.3 (D); 28.8 (T). MS 241 (M^+), 212, 172, 109, 81. Anal Calcd. for $C_{11}H_9Cl_2NO$: C 54.54%, H 3.72%, N 5.79% found: C 53.99%, H 3.49%, N 5.63%. The remaining reaction mixture was separated by a second F.C. (CCl_4/Et_2O 97/3) leading successively to **2a** and **3a**. **2a** yield: 120mg (10%) as a white solid wich was recrystallised in CCl_4 (m.p. 97°C). ^1H NMR (CD_2Cl_2) d 10.21 (d, 1H); 7.29 (d, 2H);6.91 (dd, 1H); 6.35 (m, 1H); 6.18 (m, 1H); 3.76 (m, 1H); 2.73 (m, 2H). ^{13}C NMR (CD_2Cl_2) d 191.0 (Dd, H-C=O); 150.4 (D, olefinic C-H); 146.1 (S, aromatic C-N); 132.2 (Ddm, olefinic C-H); 129.6 (Ddd, aromatic m-C-H); 127.84 (Sm, C-Cl); 124.1 (Dm, aromatic p-C-H); 40.3 (Dd, C-H); 39.7 (DD, CH_2). Anal. Calcd. for $C_{11}H_9Cl_2NO$: C 54.54%, H 3.72%, N 5.79% found: C 54,52%, H 3.73%, N

5.52%. 3a yield: 90 mg (10%) as a white solid wich was recrystallised from benzene (m.p.129°C, lit. 130°C). ^1H NMR (acetone-d6) d 8.14 (s, 1H); 7.39 (d,aromatic 2H); 7.37 (s, 1H);7.11 (dd, aromatic 1H).

Reaction of 2-4-6-Trichloronitrosobenzene with cyclopentadiene.

Reaction time: 8 days (mode A) or 15 minutes (mode B).A first F.C. (CH_2Cl_2) was carried out to isolate 1b. Yield: 278 mg (20%) as a white solid which was recrystallised from CCl_4 (m.p. 130°C). ^1H NMR ($CDCl_3$) d: 7.11 (s, 2H); 3.74 (m, 1H); 3.68 (m, 1H); 3.26 (m, 1H); 3.16 (m, 1H); 2.24 (d, 1H); 1.83 (m, 1H). ^{13}C NMR ($CDCl_3$) d 144.4 (S, aromatic C-N); 128.5 (D, aromatic C-H); 127.2 (S, o-C-Cl) ;126.7 (S, p-C-Cl); 65.7 (D); 55.1 (D); 53.9 (D, C-H); 45.1 (D, C-H); 28.4 (T). MS 275 (M^+), 248, 246, 206, 143, 109, 81. Anal Calcd. for $C_{11}H_8Cl_3NO$: C 47.74%, H 2.89%, N 5.06%; found: C 47.52%, H 2.57%, N 5.02%. The remaining reaction mixture was separated by a second F.C. (CH_2Cl_2/petroleum ether 95/5) leading successively to 2b and 3b. 2b yield: 195mg (14%) as a white solid which was recrystallised in CCl_4 (m.p. 93°C). ^1H NMR (C_6D_6) d 9.96 (d, 1H); 6.90 (s, 2H); 5.90 (dd, 1H); 5.73 (dd, 1H); 3.12 (m, 1H); 2.12 (d, 1H); 2.01 (d, 1H). ^{13}C NMR (C_6D_6) d 189.4 (Ddd, H-C=O); 148.6 (D, olefinic C-H); 144.5 (S, aromatic C-N); 131.7 (Ddm, olefinic C-H); 128.9 (Dd, aromatic C-H); 128.3 (Sm, p-C-Cl); 127.8 (Sm, o-C-Cl); 39.8 (Dd, C-H); 39.0 (DD, CH_2). MS 275 (M^+) 246, 240, 207, 149, 109, 81. Anal. Calcd. for $C_{11}H_8Cl_3NO$: C 47.74%, H 2.89%, N 5.06%; found: C 48,00%, H 2.95%, N 5.15%. 3b yield: 169 mg (16%) as a white solid which was recrystallised from benzene (m.p.119°C, lit. 119-121°C). ^1H NMR (DMSO) d 8.96 (s, 1H); 7.70 (s, 1H); 7.60 (s, 2H).

Reaction of Pentachloronitrosobenzene with cyclopentadiene

Reaction time: 7 weeks (mode A) or 1 day (mode B).A first F.C. (CCl_4/CH_2Cl_2 50/50) was carried out to isolate 1c. Yield: 309.6 mg (18%) as a white solid which was recrystallised from CCl_4 (m.p. 177°C). ^1H NMR ($CDCl_3$) d: 3.85 (m, 1H); 3.79 (m, 1H); 3.40 (m, 1H); 3.29 (dd, 1H); 2.29 (d, 1H); 1.95 (dm, 1H).^{13}C NMR ($CDCl_3$) d 148.3 (S, aromatic C-N); 131.9 (S); 125.9 (S); 124.5 (S); 65.7 (D); 58.2 (D); 54.0(D); 46.2 (D); 28.5 (T). MS 343 (M^+), 314, 274, 245, 81. Anal Calcd. for $C_{11}H_6Cl_5NO$: C 38.21%, H 1.74%, N 4.05% found: C 38.09%, H 1.63%, N 4.00%. The remaining reaction mixture was separated by a second F.C. (CCl_4/CH_2Cl_2 75/25) leading successively to 2c and 3c. 2c yield: 172mg (8%) as a white solid which was recrystallised in CCl_4 (m.p. 101°C). ^1H NMR (C_6D_6) d 9.87 (d, 1H); 5.84 (dd, 1H); 5.62 (dd, 1H); 3.13 (m, 1H); 2.09 (d, 1H); 2.93 (d, 1H). ^{13}C NMR (CD_2Cl_2) d 189.3 (Ddd, H-C=O); 147.4 (Dm, olefinic C-H); 146.5 (Sm, aromatic C-N); 132.1 (S); 131.6 (Ddm, olefinic C-H); 128.7 (S); 127.1 (S); 40.7 (Dd, C-H); 39.5 (DD, CH_2). MS 342 (M^+) 274, 239, 204, 141, 81. Anal. Calcd. for $C_{11}H_6Cl_5NO$: C 38.21%, H 1.74%, N 4.05%; found: C 37.91%, H 1.79%, N 3.97%. 3c yield: 140 mg (10%) as a white solid which was recrystallised from benzene (m.p.154°C, lit. 154°C). MS 279(M^+), 262, 235, 192, 166, 86. Anal. Calcd. for $C_6H_2Cl_5NO$: C 25.58%, H 0.71, N 4.97%; found: C 25.69%, H 0.64%, N 4.69%.

Reaction of 2-4-6-Bromonitrosobenzene with cyclopentadiene

Reaction time: 1 hour (mode B, longer reactions times produce very complexes mixtures).A first F.C. (CH_2Cl_2) was carried out to isolate the starting nitroso compound (50%) and 1d. Yield: 121 mg (6%) as a white solid which was recrystallised from CCl_4 (m.p. 167°C). ^1H NMR ($CDCl_3$) d: 7.58 (s, 2H); 3.87 (m, 1H); 3.79 (m, 1H); 3.40 (m, 1H); 3.25 (m, 1H); 2.40 (d, 1H); 1.98 (m, 1H). ^{13}C NMR ($CDCl_3$) d 147.0 (S, aromatic C-N); 135.0 (D, aromatic C-H); 116.3 (S, o-C-Cl) ;114.2 (S, p-C-Cl); 65.4 (D); 56.5 (D); 54.1 (D, C-H); 46.4 (D, C-H); 28.7 (T). MS 409 (M^+), 380, 340, 330, 301, 220, 153, 81. Anal Calcd. for $C_{11}H_8Br_3NO$: C 32.20%, H 1.95%, N 3.41%; found: C 32.14%, H 1.95%, N 3.37%. The remaining reaction mixture was separated by a second F.C. (CH_2Cl_2/petroleum ether 95/5) to 2d. yield: 141 mg (7%) as a white solid wich was recrystallised in CCl_4 (m.p. 114°C). ^1H NMR (CD_2Cl_2) d 10.23 (d, 1H); 7.69 (s, 2H); 6.29 (m, 2H); 3.81 (m, 1H); 2.86 (d, 1H); 2.76 (d, 1H). ^{13}C NMR (CD_2Cl_2) d 190.6 (Dd, H-C=O); 149.7 (D, olefinic C-H); 147.4 (S, aromatic C-N); 135.5 (Dd, aromatic C-H); 131.86 (Dd, olefinic C-H); 117.1 (Sm, o-C-Cl); 115.4 (Sm, o-C-Cl); 41.6 (Dd, C-H); 40.7 (DD, CH_2). MS 409 (M^+) 380, 340, 328, 221, 140, 81. Anal. Calcd. for $C_{11}H_8Br_3NO$: C 32.20%, H 1.95%, N 3.41% found: C 31,43%, H 1.80%, N 3.56%. No hydroxylamine 3d , although observed by t.l.c, could be isolated.

X-Ray analysis of 1a

The crystallographic data are as follows : $C_{11}H_9NOCl_2$, Mr = 242.1, monoclinic, $P2_1/a$, a = 11.703(5), b = 6.737(3), c = 13.425(4) Å, β = 99.09(3)°, V = 1045.2(7) $Å^3$, Dx = 1.54 $g.cm^{-3}$ for Z = 4. Mokα, λ = 0.71069 Å, μ = 5.9 cm^{-1}, F(000) = 496, T = 291 K, R = 0.039 for 1576 observed reflections. The intensities of 6087 reflections were collected on a Syntex P2$_1$ four circle diffractometer using MoKα graphite monochromatized radiation. 2057 independent reflections (Rmerg = 0.027) with sin $\theta/\lambda \leq 0.62$ Å^{-1}; 1576 with $I \geq 2.5\ \sigma(I)$ were used in the refinement. The structure was solved by direct methods using SHELXS-86[13] and refined by anisotropic least squares on F values using SHELX-76[14]. All H atoms were located from a difference Fourier synthesis and included in the refinement with a common isotropic temperature factor (B = 3.8 Å^2). Two positions, labelled 06 and 06', were refined for the epoxy oxygen atom. At the end of the refinement their occupation factors converge to 63 and 37% respectively. W= $1/(\sigma^2 + 0.00014\ F^2)$, R= 0.0039, RW= 0.036, S= 1.66 for 1576 observed reflections. The list of atomic coordinates and molecular dimensions has been deposited with the Cambridge Qata center.

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