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Rhodium Catalysed Decomposition of α-Diazosulfoxides : Formation of α-Oxo Sulfines as Intermediates

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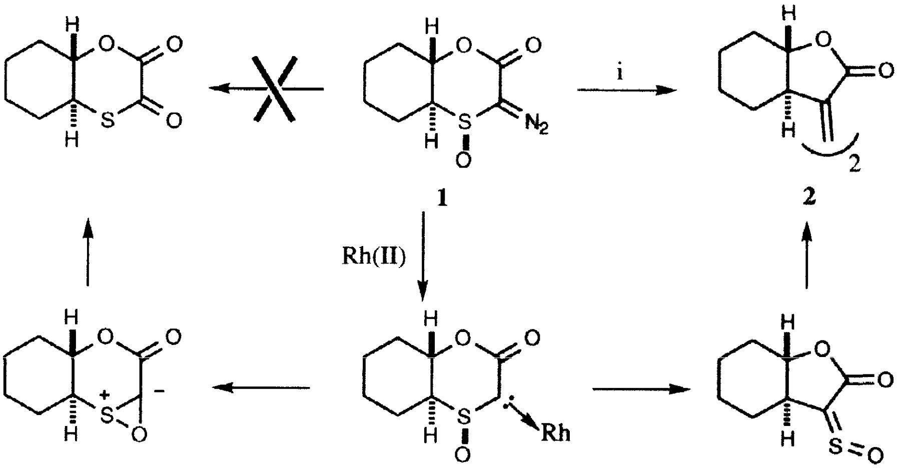
Abstract: Decomposition of α-diazosulfoxides using rhodium carboxylate or carboxamide catalysts proceeds *via* a Wolff type rearrangement to form α-oxo sulfine intermediates, which can be trapped as cycloadducts with dienes. In the absence of a diene trap, dimerisation of the sulfine intermediate is observed.

Transition metal catalysed decomposition of α-diazocarbonyl compounds,[1] and to a lesser extent α-diazosulfonyl and α-diazophosphonyl derivatives,[2] lead to a wide range of synthetically useful transformations. Following our recent report on the synthesis of stable cyclic α-diazo-β-oxo sulfoxides,[3] we describe here their reactivity on treatment with rhodium catalysts. Based on earlier reports[4-6] it was envisaged that on treatment of the α-diazosulfoxides with a transtion metal catalyst oxygen transfer from the sulfoxide to the carbenoid carbon was likely to occur as illustrated in Scheme 1.



i, $Rh_2(OAc)_4$, $Rh_2(pfb)_4$, or $Rh_2(tfacm)_4$ (1 mol %), toluene, RT, 0.25 - 6 h, 14 - 37%; dimer **2** also formed when CH_2Cl_2 or cyclohexene was used as solvent

Scheme 1

On treatment of the diazosulfoxide **1** with a range of rhodium catalysts at RT in toluene, dichloromethane or cyclohexene, decomposition of the diazo derivative proceeded rapidly but there was no evidence of sulfoxide deoxygenation or of carbenoid addition to either toluene or cyclohexene. The only identifiable product isolated from the reactions was the unexpected dimer **2**.[7] Notably this sterically congested dimeric alkene is formed, albeit in low yields, under dilute reaction conditions (typically 0.04M solutions of the diazosulfoxide). While two stereoisomers of the dimeric alkene could be detected in the crude product, **2** was isolated as a single stereoisomer following chromatographic purification and recrystallisation. The stereochemistry of the alkene has been tentatively assigned as *E* but the relative stereochemistry of the ring fusion between the two portions of the dimer has not yet been established. The mechanism which was

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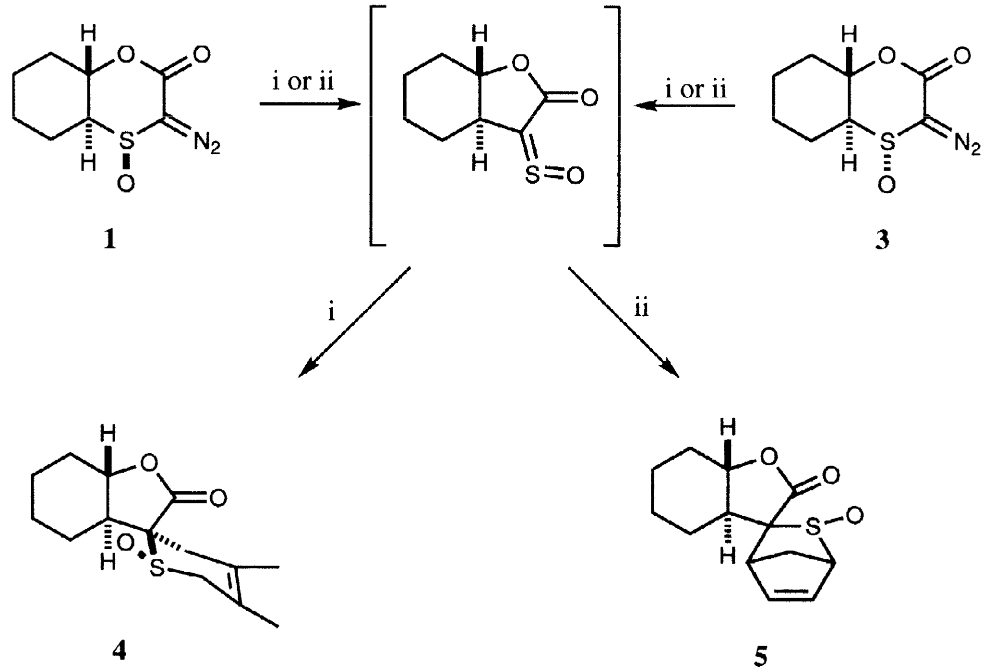
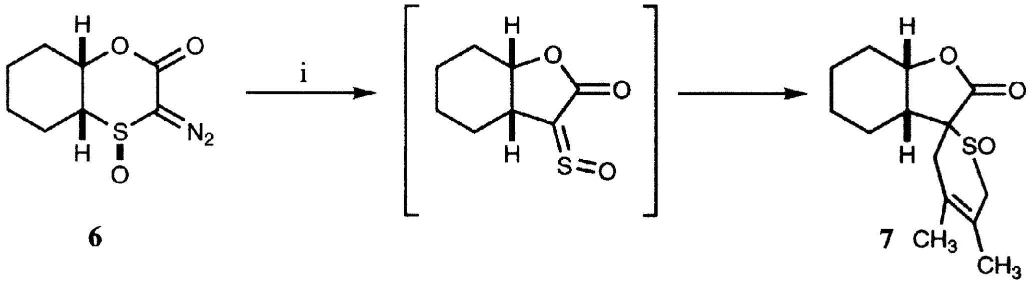


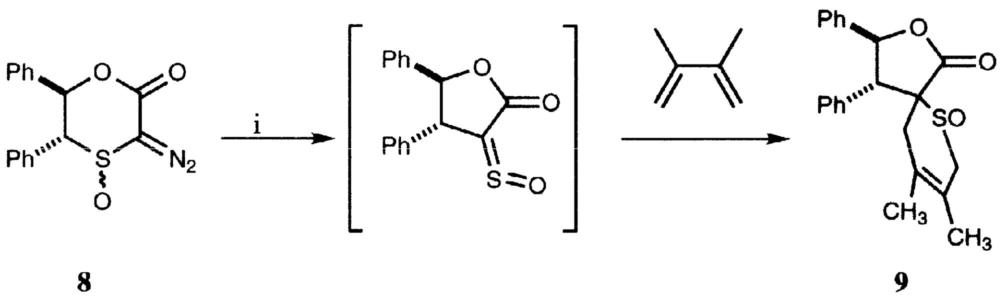
i, 2,3-dimethylbutadiene (10 equiv.), $Rh_2(OAc)_4$ (1 mol %), CH_2Cl_2, < 0.25 h, RT, 44% of **4** from **1** only one diastereomer detected in the crude product, 39% of **4** from **3** a minor diastereomer was detected in the crude product (ratio ~5:1) ; ii, cyclopentadiene (10 equiv.), $Rh_2(OAc)_4$ (1 mol %), CH_2Cl_2, 0.1 - 0.6 h , RT, 35% of **5** from **1**, 14% of **5** from **3**; two diastereomers were detected in the crude product (ratio ~2:1) but **5** was isolated as a single diastereomer in each case.

Scheme 2



i, 2,3-dimethylbutadiene (10 eq.), CH_2Cl_2, $Rh_2(tfa)_4$ (0.33 mol %), RT, 31% isolated as a single diastereomer; two diastereomers (ratio ~ 6:1) were detected in the crude product.

Scheme 3



i, 2,3-dimethylbutadiene (10 equiv.) $CHCl_3$, $Rh_2(tfa)_4$ (1 mol %), RT, 0.75 h, 30%, adduct **9** was isolated as a diastereomeric mixture.

Scheme 4

proposed for formation of the dimer **2** is illustrated in Scheme 1. Wolff-type rearrangement of the carbenoid generates a sulfine intermediate which is transformed to the dimer **2**. While Wolff rearrangements are commonly effected photochemically,[1] rhodium acetate catalysed Wolff rearrangements have been reported.[8] Rosati and co-workers reported photochemical ring contraction of 2-diazoceph-3-em oxides to form initially a sulfine intermediate which extrudes sulfur to form an enone;[9,10] however, on treatment with rhodium acetate oxygen transfer was observed rather than Wolff rearrangement.[5] Dimerisation of sulfines to form alkenes has been reported[11] although it is not a major reaction pathway of these labile compounds.[12] Possibly the rhodium catalyst is involved in the sulfine dimerisation *e.g.* by formation of a carbenoid intermediate which reacts with the sulfine to form the alkene **2**.[12,13] When the *cis*-fused diazosulfoxide **6** was treated with rhodium acetate in refluxing toluene for 1h a similar dimeric product was detected in the crude product mixture.

In order to confirm the intermediacy of an α-oxo sulfine,[12] the decomposition of the diazosulfoxide **1** was repeated in the presence of 2,3-dimethyl-1,3-butadiene or cyclopentadiene; the propensity of α-oxo sulfines to undergo cycloadditions with dienes is well-established.[12] As illustrated in Scheme 2 the sulfine was trapped efficiently with 2,3-dimethyl-1,3-butadiene to form cycloadduct **4** as a single diastereomer.[7] The structure and relative stereochemistry of the adduct was established unambiguously by X-ray crystallography (Figure 1).[14] The formation of cycloadduct **4** can be rationalised as proceeding *via* the transition state illustrated in Figure 1, conforming with the general behaviour of sulfines in Diels-Alder reactions.[12] Similarly the epimeric diazosulfoxide **3** formed the same cycloadduct **4**, although in this case a minor diastereomer was observed in the crude product (ratio ~5:1) which was readily removed on chromatographic purification. While a small amount of this minor diastereomer was isolated, its stereochemistry has not yet been determined. Each of the diazosulfoxides **1** and **3** yielded cycloadduct **5** on decomposition in the presence of cyclopentadiene; while additional signals were seen in the ^{1}H NMR spectra of the crude product in each case, believed to indicate the presence of a second diastereomer (ratio ~2:1), the cycloadduct **5** was isolated as a single diastereomer following chromatography.[7]

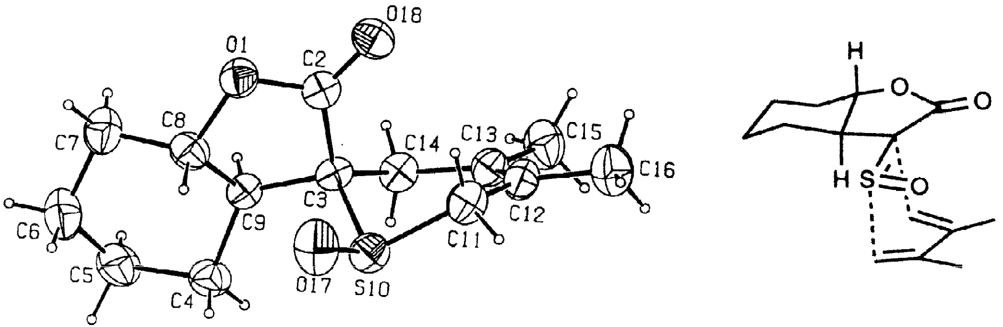


Figure 1 A view of **4** with all non-hydrogen atoms drawn with thermal ellipsoids at the 30% probability level. The hydrogen atoms are drawn as spheres of an arbitrary size for clarity.

The *cis* fused diazosulfoxide derivative **6** yielded a cycloadduct **7** on decomposition with rhodium trifluoroacetate in the presence of 2,3-dimethyl-1,3-butadiene.[7] Rhodium catalysed decomposition of **6** was noticeably slower than that of either of the *trans* fused derivatives **1** or **3**; indeed no reaction was observed with rhodium acetate as catalyst after 24 h at room temperature, and even with rhodium trifluoroacetate the decomposition required several hours at room temperature. Again, while signals corresponding to a minor diastereomer could be detected in the ^{1}H NMR spectrum of the crude product (ratio ~6:1), the cycloadduct was diastereomerically pure following purification. Rhodium catalysed decomposition of the monocyclic diazosulfoxide **8** in the presence of 2,3-dimethyl-1,3-butadiene led to the cycloadduct **9** as a diastereomeric mixture which was less readily separated than the previous adducts.[7] One major diastereomer and two or three minor diastereomers could be detected in the ^{1}H NMR spectra.

Thus, rhodium carboxylate catalysed decomposition of the diazosulfoxides **1**, **3**, **6** and **8** in the presence of dienes leads to the cycloadducts, which were readily isolated diastereomerically pure in the case of the bicyclic systems **1**, **3** and **6**. Furthermore, in the crude product mixture of each of the cycloadducts one diastereomer predominated in each case. While the geometrical configuration of sulfines is usually retained in cycloadducts,[12] the yields obtained in these cycloadditions were moderate and, therefore, no definite conclusion can be made at this stage about the stereochemistry of the sulfine formed in the rearrangement.

Isolation of the cycloadducts from the decomposition of the diazosulfoxides in the presence of the dienes confirms the intermediacy of α-oxo sulfines formed by rhodium-catalysed Wolff-type ring contraction. Rhodium-catalysed decomposition of diazosulfoxides provides a very mild route to these labile intermediates and allows access to new α-oxo sulfine derviatives;[12] notably, while there have been some reports of sulfines bearing carboxylic acid and ester substituents, most of the work has been conducted with ketone derivatives, and, to the best of our knowledge, this is the first report of a lactone derivative. Further work is underway to investigate the reactivity of α-diazo-β-oxo sulfoxides, including the sulfine cycloaddition and dimerisation pathways, and to explore their synthetic utility especially in stereoselective synthesis.

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14. Crystals of **4** are triclinic, space group $P\bar{1}$ with two molecules of $C_{14}H_{20}O_3S$ in a unit cell of dimensions, a = 6.076(2), b = 11.304(4), c = 11.609(3) Å, α = 62.71(2)°, β = 78.99(2)°, γ = 75.80(2)°,V = 684.1(4) $Å^3$, F(000) = 288, μ(Mo–Kα) = 0.24 mm^{-1}, $R(F_o)$ = 0.049 for 1498 observed reflections with I > 2σ(I), $wR_2(F^2)$ = 0.114 for all 2402 unique reflections. Data in the θ range 2 -25° were collected on a Nonius MACH3 diffractometer using monochromatic radiation and corrected for Lorentz and polarization effects. The structure was solved by direct methods and refined by full-matrix least-squares methods using SHELXL-93 and all F^2 data. All non-H atoms were allowed anisotropic motion. The H atoms were placed in calculated positions and allowed to ride on the parent atom. Full details of molecular dimensions, fractional coordinates, thermal parameters and structure factor listings are available from the authors and have been deposited with the Cambridge Crystallographic Data Centre.