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Unusual Dirhodium Tetraacetate Catalyzed Intramolecular Cyclization of Isoquinoline Diazoamides

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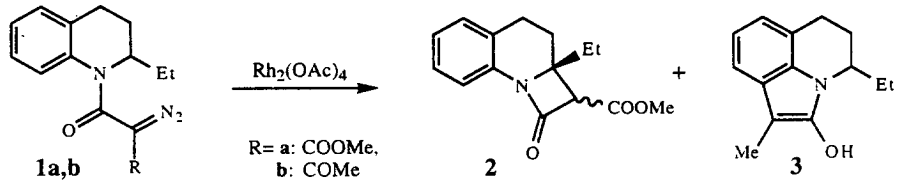
Abstract: The dirhodium(II) tetraacetate catalyzed decomposition of an isoquinoline diazoamide leads to the unexpected formation of a 1,3-oxazin-4-one ring which is consistent with a rare example of an intramolecular metal-carbene hydride-abstraction mechanism.

The intramolecular carbon-hydrogen insertion (C-H) of metal-carbenes, generated from α-diazocarbonyl compounds, in heterocyclic and carbocyclic ring formation, is a well documented process.[1] A synthetically valuable reaction is the rhodium(II) carboxylate-catalysed decomposition of diazo amides, which leads to the construction of β- or γ-lactam rings.[1] In this context, the rhodium(II) acetate catalyzed reaction of the tetrahydroquinoline diazoamides **1a,b** has been reported (Scheme 1) to give the β-lactam **2** from **1a** and the aromatic C-H insertion compound **3** from **1b**.[2] In other words, the α-substituent on the rhodium carbenoid has been found to control the chemoselectivity of the C-H insertion reaction.



Scheme 1

Following our interest in intramolecular metal carbenoid mediated C-H insertion reactions,[3] we now report that, while investigating a potential dirhodium(II)-catalyzed C-H insertion of tetrahydroisoquinoline diazoamides **5a,b** (Scheme 2), we came across a surprising transformation which did not lead to any of the expected β-lactams arising from C-H insertion at the *N*-substituents, but to an unexpected compound. Tetrahydroisoquinoline diazoamides **5a,b** were prepared in a convenient yield by a diazotransfer reaction performed on the corresponding amides **4a,b** ($TosN_3$, TEA, MeCN) which were obtained by acylation of the tetrahydroisoquinoline with α-carbethoxyacetylchloride and 2,2,6-trimethyl-4*H*-3-dioxin-4-one, respectively. Treatment of **5a** with rhodium(II) acetate in refluxing toluene led to an intractable mixture of compounds. In contrast, the decomposition of the acetyl-substituted diazo compound **5b** gave the 2-methyl-7,11b-dihydro-4*H*,6*H*-[1,3]oxazino[2,3-a]isoquinolin-4-one **9**[4] (72% yield) as the only detectable product. The structure of this compound was substantiated by ^{1}H-NMR, ^{13}C-NMR, COSY, TOCSY,

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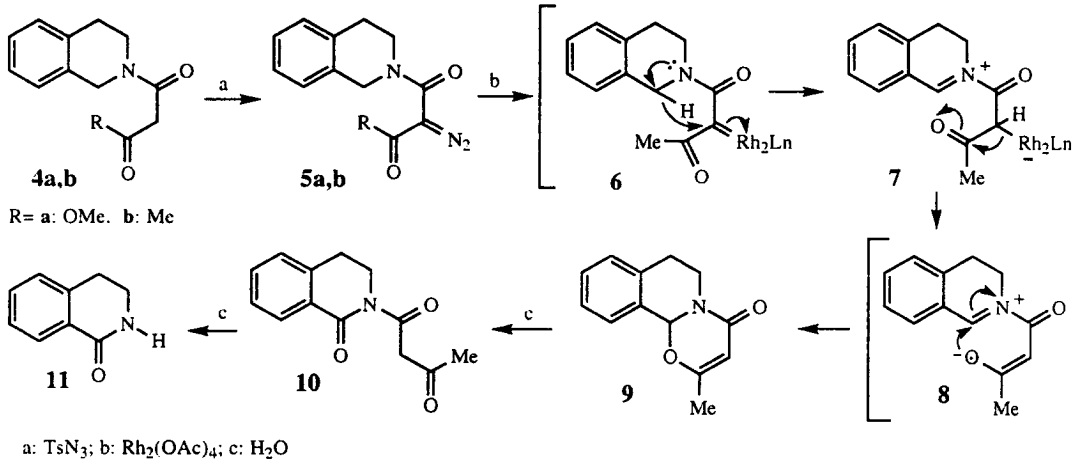
HETCOR, long range HETCOR and NOESY spectra and indirectly confirmed by isolation of compounds **10** and **11** arising from slow hydrolysis - oxidation.



Scheme 2

The formation of **9** is envisaged to occur *via* a mechanism which involves an intramolecular hydride shift from the *N*-benzyl carbon to the rhodium-carbene carbon to give the transient ylide-type intermediate **7**. This undergoes electron rearrangement to produce the zwitterion **8** which finally cyclizes to the six-membered ring **9**.

In conclusion we have reported that the dirhodium(II) tetraacetate catalyzed decomposition of an isoquinoline diazoamide leads to the unexpected formation of a 1,3-oxazin-4-one ring which is consistent with a rare example of intramolecular metal-carbene hydride-abstraction mechanism.[5]

References and Notes

1. Review : Ye, Tao ; McKervey, M. A. *Chem. Rev.* **1994**, *94*, 1091. Doyle, M. P.; McKervey, M. A.: Ye, T. *Modern Catalytic Methods for Organic Synthesis with Diazo Compounds*; John Wiley & Sons: New York, **1997**.
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3. Chelucci, G.; Saba, A. *Angew. Chem. Int. Ed. Engl.* **1995**, *34*, 78. Chelucci, G.; Saba, A. *Tetrahedron Lett.* **1995**, *36*, 4673. Chelucci, G.; Saba, A.; Valle, G. *Tetrahedron: Asymmetry* **1995**, *6*, 807. Chelucci, G.; Saba, A. *Tetrahedron: Asymmetry* **1997**, *8*, 699.
4. Selected data for **9**: white crystals; mp 69-71 °C; IR (nujol): 1655, 1617, 1412, 1363, 1294, 988 cm^{-1}; ^{1}H-NMR ($CDCl_3$) δ: 7.50-7.21 (m, 4H); 6.09 (s, 1H), 5.39 (s, 1H), 4.33-4.26 (m, 1H), 3.32-3.23 (m, 1H), 3.07-2.96 (m, 1H), 2.80 (dt, 1H, J=15.8, 3.8 Hz), 2.04 (s, 3H); ^{13}C-NMR ($CDCl_3$) δ: 167.4, 164.6, 136.3, 132.4, 131.8, 131.3, 130.9, 130.3, 100.6, 84.3, 37.3, 28.4, 19.3. Anal. Calcd. for $C_{13}H_{13}NO_2$ C, 72.12; H, 6.27; N, 6.30. Found: C, 72.34; H, 6.09; N, 6.51.
5. To our knowledge only two examples of this mechanism have been reported so far : Doyle, M. P.; Dyatkin, A.B.; Autry, C. L. *J. Chem. Soc., Perkin Trans 1* **1995**, 619. Zaragoza, F.; Zahn, G.; *J. Prakt. Chem./ Chem.-Ztg.* **1995**, *337*, 292.