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Rhodium(II) acetate catalysed intramolecular cyclopropanation followed by ring opening of furan toward oxindole incorporated macrocycles

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ABSTRACT

Intramolecular cyclopropanation followed by ring opening of remotely placed furan was demonstrated using rhodium(II) catalysed cyclic diazoamides tethered on furan to produce 12- to 23-membered oxindole incorporated macrocycles. The length of the spacer is an important factor to decide the stereoselectivity of the product.

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1. Introduction

The transition-metal catalysed decomposition of diazo compounds is an effective method for the generation of electrophilic metal carbenes.[1] Rhodium(II) acetate has been the superior catalyst for the generation of transient electrophilic rhodium-carbenoids from α-diazocarbonyl compounds. Subsequently, these undergo an array of reactions which led to a variety of C–C, C–X bond formations that are important for the creation of basic skeleton of the organic structure.[2] Generally, copper or rhodium catalysed reaction of diazocarbonyl compounds with olefins is an efficient method for the preparation of cyclopropane derivatives.[3] The intramolecular cyclopropanation reactions are limited[4] only to simple precursors like acyclic diazo ketones or diazo esters. Generally, transition metal catalysed reaction of diazo compounds with furan was reported[5] to furnish the detectable cyclopropane intermediates which rearrange to a mixture of ring-opened or ring-enlarged products. Interestingly, there is scarcity of report[6] available on the reaction of 3-diazopiperidin-2-one and furan furnishing the corresponding cyclopropane products without ring opening. Doyle and co-workers reported[7] the intramolecular addition of metal carbenes to remotely placed furan to form 13–17 membered macrocyclic lactones/ketones as a mixture of inseparable isomers and then converted into a single isomer using molecular iodine. The intermolecular reaction of diazoamides with furans using rhodium(II) acetate as a catalyst afforded[8] a variety of furan ring opened products **3** in a regio- and stereoselective manner and the stereoselectivity was controlled based on the slow addition of diazoamides (Scheme 1). With a curiosity to extend this reaction with the remotely placed furan ring systems on diazoamides, study of the intramolecular version in the presence of rhodium(II) acetate as a catalyst under the slow addition as well as controlled concentration of diazoamide was planned.

2. Results and discussion

In order to test the intramolecular furan ring opening reactions, we assembled a variety of furan tethered on diazoamides **6a**–**d**. Towards this, the esterification of salicylic acid using furfuryl alcohol in the presence of DCC/DMAP in dichloromethane afforded the corresponding ester **4**. Further, the O-alkylation of **4** using dibromoalkanes in the presence of K_2CO_3/TBAI in DMF afforded the corresponding bromo compounds **5**. Subsequent N-alkylation of 3-diazooxindoles **1** with bromo compounds **5** in the presence of K_2CO_3/TBAI afforded the corresponding furan tethered on diazoamides **6a**–**d** in 80–87% yield (Scheme 2).

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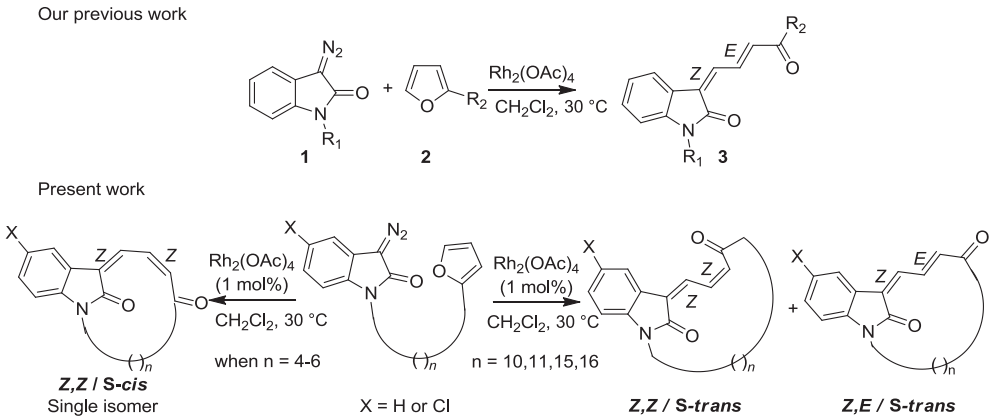
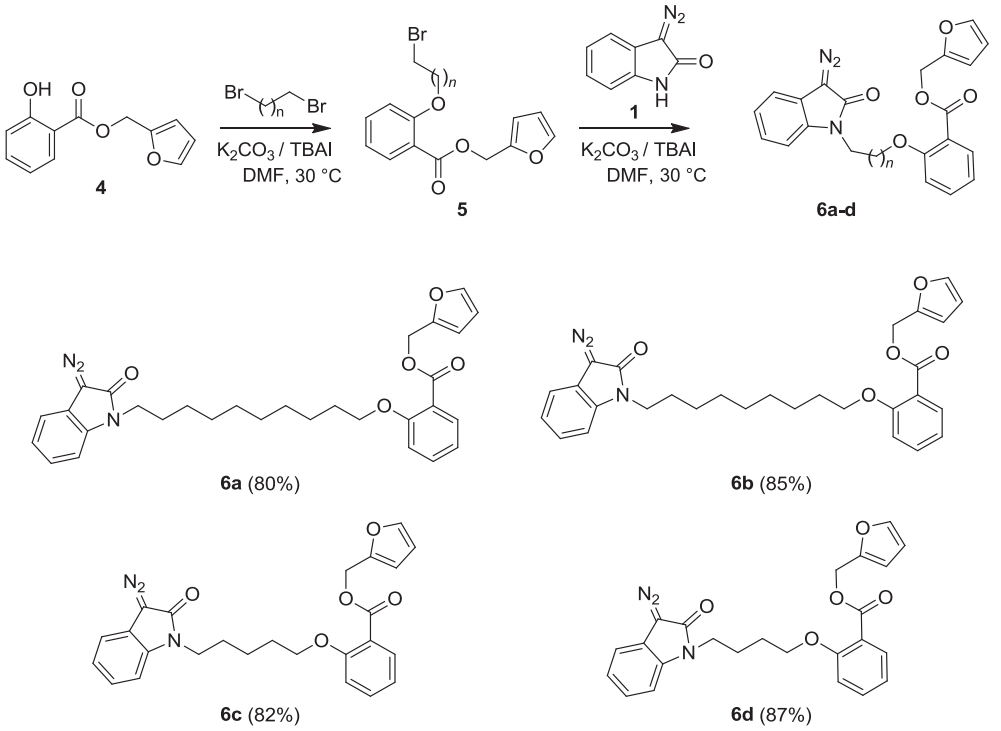


Scheme 1. Ring opening reactions of furan with rhodium(II) carbenoids.



Scheme 2. Synthesis of furan tethered on diazoamides **6a**–**d**.

In our ongoing efforts to construct[9] the functionalized macrocycles, we investigated the metal-catalysed decomposition reactions with slow addition as well as controlled concentration of diazoamides **6** to produce oxaza-macrocycles via intramolecular cyclopropanation followed by the ring opening of furan. Based on our earlier studies,[8] furan tethered on diazoamide **6a** was added with the flow rate of 1.5 mL/h to 1 mol% of rhodium(II) acetate dimer as a catalyst to afford a mixture of products **7a/8a** via intramolecular cyclopropanation followed by the ring opening of furan in 32% yield in the ratio of 50:50. Based on this observation, the flow rate of the diazoamide **6a** was decreased to 1.0 mL/h to give 65% yield of macrocycles **7a/8a**. There is no improvement in the yield as well as ratio of the products **7a/8a** (Table 1) when the flow rate kept as 0.5 mL/h. It was found that CuOTf and $Cu(CH_3CN)_4PF_6$ catalyst was also effective to furnish the ring opened products **7a/8a** but $Cu(acac)_2$ was not suitable for this transformation. The products **7a/8a** were separated by the column chromatography and the ^1H NMR spectra of **7a** and **8a** exhibited a characteristic singlet resonance at δ 4.90 and 5.12 ppm for H_d protons, respectively. The ratio of stereoisomers was determined based on the ^1H NMR spectrum of the crude reaction mixture. The stereochemistry of the product was confirmed based on the coupling constant of the H_b proton in **8a** appeared as a double of doublets at δ 9.14 (J_1=16.0, J_2=11.6 Hz) based on the literature.[8] The H_b proton in **7a** appeared as a non-first order spectral pattern at δ 8.16. To identify the importance of slow addition, the above reaction was performed with the simultaneous addition of diazoamide and catalyst to yield a trace amount of **7a/8a** along with the complex mixture. It indicates that the concentration of the diazoamide in the reaction mixture is important for obtaining the products.

Under these optimized reaction conditions, we next focused our attention on exploring the scope of the reaction for various ring sizes to study using different dibromo compounds. Reaction of **6b** underwent intramolecular cyclopropanation followed by the ring

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