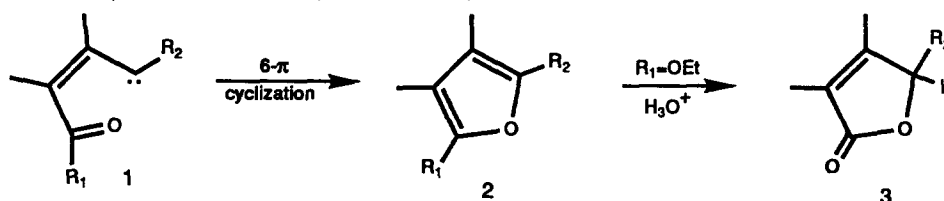


PREPARATION OF OXYGENATED HETEROCYCLES VIA THE CYCLIZATION REACTION OF α -DIAZO SUBSTITUTED ALKYNES

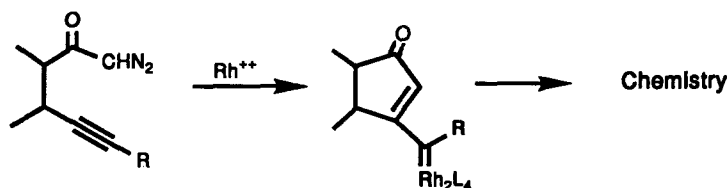
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Abstract: Treatment of a series of α -diazo alkynyl substituted ketones with rhodium (II) carboxylates results in the formation of vinyl rhodium carbenoids. These species undergo further cyclization onto a neighboring carbonyl group to produce furans.

Due to their common occurrence in nature, furans and butenolides are frequent and important targets for synthesis either as final products or as useful synthetic intermediates.¹ One of the approaches to these molecules that has received increasing attention in recent years involves the generation of an alkenone carbene of type 1 and its subsequent intramolecular cyclization.² It should be noted that the production of five-membered rings by 6π -electrocyclization is a well precedented process in heterocyclic chemistry.^{3,4} Several different synthetic approaches to



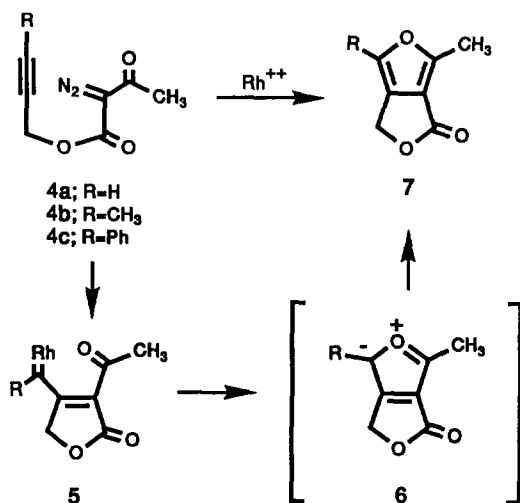
alkenone carbenes have been developed, and they appear to produce intermediates sharing some common trends in their reactivity.⁵⁻⁸ Recently, we have described a method for the formation of alkenone carbenoids which involves a rhodium (II) acetate catalyzed reaction of a α -diazo alkynyl substituted ketone.⁹ The process is believed to proceed by addition of a rhodium-stabilized carbenoid onto the acetylenic π -bond to give the vinyl carbenoid directly or possibly *via* a highly strained cyclopropene derivative. The potential for many diverse chemical pathways exist



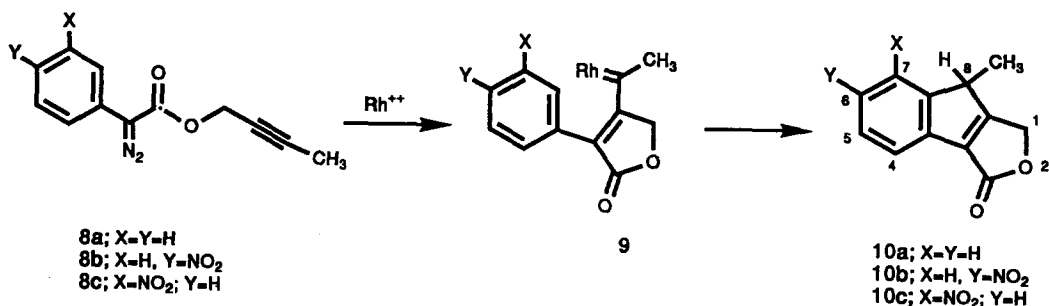
through the generation and further reaction of these rhodium carbenoids. In this communication we report on the scope of the methodology and suggest its application as a means to synthesize a variety of oxygen heterocycles.

Furo[3,4-c]furans 7a-c were produced in high yield (>70%) by treatment of the corresponding alkynyl diazoacetate 4 with a catalytic amount of rhodium (II) acetate at 80°C.¹⁰ The

electrophilic vinyl carbenoid intermediate **5** is attacked by the ketone oxygen to give furan **7** via the intermediacy of carbonyl ylide **6**.

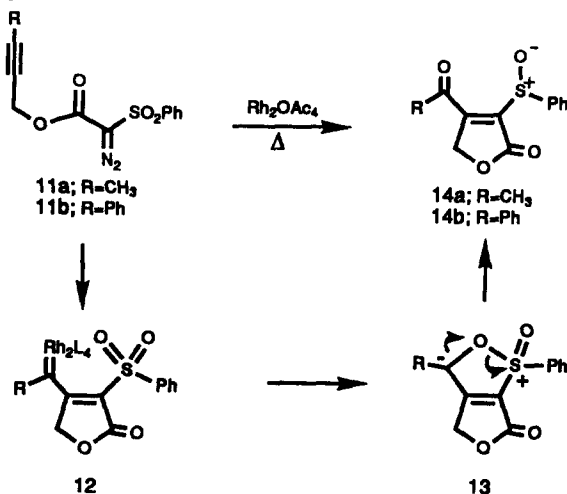


Likewise, indeno[1,2-*c*]furans **10a-c** were produced in 45-60% yield from the diazo precursors **8a-c**. Here the initial vinyl carbenoid **9** undergoes aromatic C-H insertion. The diazo precursors **8b** and **8c** were prepared in order to evaluate the role of an electron withdrawing group on the C-H insertion process. Interestingly, there seemed to be little effect displayed by the substituent group and indeno[1,2-*c*]furans **10b** and **10c** were isolated as the exclusive products. The fact that insertion occurs *ortho* to the nitro group (i.e. **8c**→**10c**) rather than producing a mixture of *ortho* and *para* isomers, suggests that subtle factors play a role in this process.¹¹

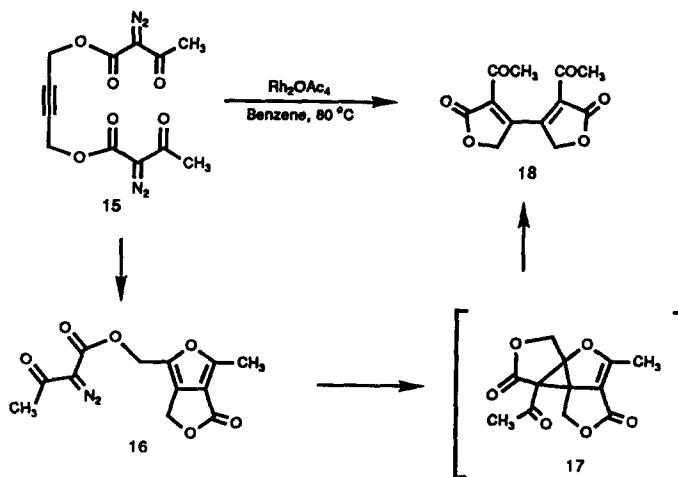


α -Diazosulfones have previously been used for carbene mediated C-H insertion and cyclopropanation reactions.¹²⁻¹⁴ In order to appraise the role of this substituent group on the cyclization process, we prepared diazo alkyne sulfones **11a** and **11b**. Treatment of these compounds with Rh_2OAc_4 at 80°C gave sulfoxides **14a** and **14b** in 60 and 90% yield, respectively. This novel oxygen transfer reaction can be rationalized by sulfone oxygen attack onto

the vinyl carbenoid (12) producing the dipolar species 13. Subsequent collapse of this transient affords the ring opened butenolides 14a and 14b.¹⁵



Very few examples of the chemistry of *bis*(diazoesters) have been reported.¹⁶ This is not surprising when one considers the number of possible complications that may arise from the combination of two reactive carbenoid centers in the same molecule. However, should the rhodium-catalyzed carbenoid formation occur one step at a time, then a single product might result from such a process. With this in mind, the symmetrical bis(diazoester) 15 was prepared in the normal manner. Heating a benzene solution of 15 with Rh₂OAc₄ at reflux gave rise to a 90% yield of *bis*(butenolide) 18. The mechanism of this reaction requires that one diazoester group react with the alkyne to generate a vinyl carbenoid which subsequently cyclizes to produce furan 16. Further reaction of 16 with rhodium generates a second carbenoid which undergoes an intramolecular cyclopropanation onto the furan ring.¹⁷ The resulting cycloadduct 17 then undergoes a typical cyclopropanated furan fragmentation reaction to give the symmetrical product 18.¹⁸



The above results are demonstrative of the wealth of chemical processes that can arise from the controlled reactions of vinyl carbenoids. The nature of substituents that flank the diazomethylene group not only controls the formation of the vinyl carbenoid but also the products that result from the interaction of that substituent with the adjacent reactive center. We are continuing to explore the scope and mechanistic details of these cyclization reactions and will report additional findings at a later date.

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