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TANDEM CYCLOPROPANATION/COPE REARRANGEMENT SEQUENCE. STEREOSPECIFIC [3 + 4] CYCLOADDITION REACTION OF VINYLCARBENOIDS WITH CYCLOPENTADIENE

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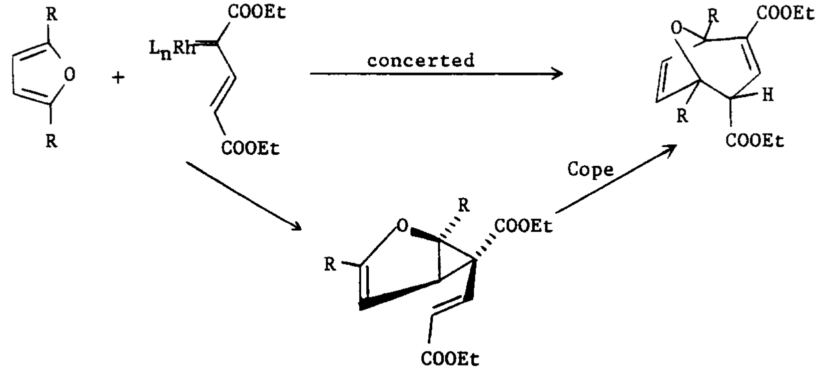
Abstract: Divinylcyclopropane intermediates can be isolated from the [3 + 4] cycloaddition reaction between rhodium(II) acetate-stabilized vinylcarbenoids and cyclopentadiene. This result confirms that the reaction proceeds through a tandem cyclopropanation/Cope rearrangement sequence.

A general and stereoselective synthesis of seven-membered rings might be possible by a formal [3 + 4] cycloaddition reaction between vinylcarbenes and dienes. The successful implementation of such a scheme, however, has been limited,[1] due to the tendency of vinylcarbenes to undergo a variety of rearrangements.[2] We have recently demonstrated[3] that rhodium(II) acetate-stabilized vinylcarbenoids undergo a stereospecific [3 + 4] cycloaddition with a variety of furans (Scheme 1). Two reasonable mechanisms for this reaction can be considered. The first of these is a concerted process with the vinylcarbenoid acting as a delocalized 2π system. A second possibility is a tandem cyclopropanation/Cope rearrangement sequence.

Scheme 1



Based purely on the stereochemical results in the initial study, we favored the two-step process with formation of only the endo furanocyclopropane intermediate. In order to obtain a deeper insight into this reaction, we required further mechanistic evidence, particularly as the related [3 + 4] cycloaddition of methoxy-stabilized vinylcarbenes with dienes has been shown to proceed through a concerted mechanism.[4]

It is well known that the Cope rearrangement of divinylcyclopropanes is very sensitive to steric effects.[5] Therefore, with appropriate choice of substrates, the divinylcyclopropane intermediates should be isolable in these [3 + 4] cycloadditions, if the proposed two step sequence is indeed correct. In this paper we describe our successful attempts to isolate such intermediates by rhodium(II) acetate catalyzed decomposition of sterically congested vinyldiazo compounds in the presence of cyclopentadiene.

A series of progressively more crowded vinyldiazo compounds were prepared according to Scheme 2. Thus, rhodium(II) acetate catalyzed decomposition of 1[3] in the presence of 5 equivalents of methanol resulted in insertion of the carbenoid into the O-H bond to give predominately the E isomer of 2a. Diazotization of 2a with p-acetamidobenzenesulfonyl azide[6] and DBU as base gave exclusively the E isomer of 3a. The ethoxy, isopropoxy and tert-butoxy derivatives 3b-d were also prepared in a similar manner.

Scheme 2

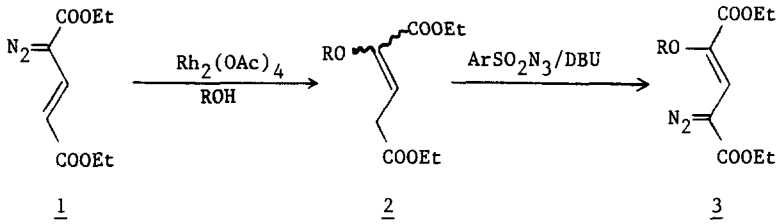
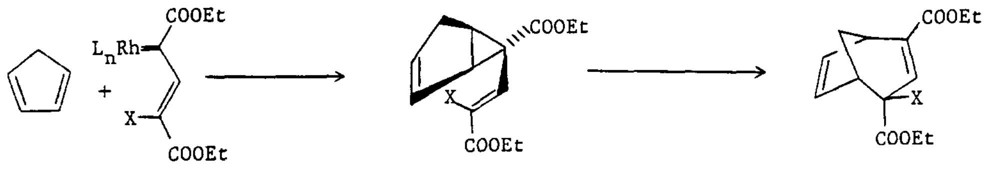


Table 1: Synthesis of Substituted Vinyl Diazo Compounds.

	R	yield of 2, %	yield of 3, %
a	CH_3	91	76
b	CH_2CH_3	84	86
c	$CH(CH_3)_2$	87	86
d	$C(CH_3)_3$	72	77

The rhodium(II) acetate catalyzed decomposition of 1 and 3 in the presence of cyclopentadiene resulted in extremely clean reactions. Reaction with 1 gave the expected cycloadduct 5a in 98% yield after distillation. Even though the NMR of the crude reaction mixture showed the *endo* cycloadduct[7,8] was exclusively formed, partial isomerization to the *exo* isomer[8] readily occurred on chromatography and on excessive heating during distillation. Similar decomposition of the more sterically crowded vinyl diazo compounds 3a-d failed to generate the [3 + 4] cycloadducts directly. Instead the *endo* divinylcyclopropanes 4b-e were readily isolable.[9] Even though 4b-e were stable for days at room temperature, heating solutions of 4b-e in toluene for 12 h, resulted in essentially quantitative rearrangements to 5b-e.

Scheme 3



4 5

Table 2: Rhodium(II) Acetate Catalyzed Decomposition of 1, 3 in the Presence of Cyclopentadiene.

Substrate	Product	Yield, %
1	5a X=H	98
3a	4b X=OCH_3	89
3b	4c X=OCH_2CH_3	77
3c	4d X=$OCH(CH_3)_2$	80
3d	4e X=$OC(CH_3)_3$	86

These results give further evidence that the [3 + 4] cycloaddition reaction between rhodium(II) acetate stabilized vinylcarbenoids and dienes does proceed by a tandem cyclopropanation/Cope rearrangement mechanism. This confirms that the reactivity of these metal stabilized vinylcarbenoids is quite different from that of methoxy stabilized vinylcarbenes.[4] Two remarkable features of this reaction are that the *endo* divinylcyclopropane intermediates are exclusively formed,[10] and due to the stereochemical constraints of the Cope rearrangement, the overall transformations are stereospecific.

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References

1. (a) Franck-Neumann, M.; Miesch, M. Tetrahedron Lett. 1984, 25, 2909; (b) Franck-Neumann, M.; Dietrich-Buchecker, C. Tetrahedron 1978, 34, 2797; (c) Franck-Neumann, M.; Lohmann, J. J. Angew. Chem. Int. Ed. Engl. 1977, 16, 323.

2. (a) Price, J. D.; Johnson, R. P. J. Am. Chem. Soc. 1985, 107, 2187; (b) Pincock, J. A.; Murray, K. P. Can. J. Chem. 1979, 57, 1403; (c) Pincock, J. A.; Mathur, N. C. J. Org. Chem. 1982, 47, 3699; (d) Pincock, J. A.; Moutsokapas, A. A. Can. J. Chem. 1977, 55, 979; (e) Padwa, A.; Kennedy, G. D. J. Org. Chem. 1984, 49, 4344; (f) Steinmetz, M. G.; Mayes, R. T. J. Am. Chem. Soc. 1985, 107, 2111; (g) Padwa, A. Acc. Chem. Res. 1979, 12, 310; (h) Perez, J. D.; Yranzo, G. I. J. Org. Chem. 1982, 47, 2221; (i) Buchi, G.; White, J. D. J. Am. Chem. Soc. 1964, 86, 2884; (j) Mandai, T.; Hara, K.; Kawada, M.; Nokami, J. Tetrahedron Lett. 1983, 24, 1517; (k) Hendrick, M. E. J. Am. Chem. Soc. 1971, 93, 6337; (l) Zimmerman, H. E.; Hovey, M. C. J. Org. Chem. 1979, 44, 2331.

3. Davies, H. M. L.; Clark, D. M.; Smith, T. K. Tetrahedron Lett. 1985, 26, 5659.

4. (a) Boger, D. L.; Brotherton, C. E. J. Org. Chem. 1985, 50, 3425; (b) Boger, D. L.; Brotherton, C. E. Tetrahedron 1986, 42, 2777; (c) Boger, D. L.; Brotherton, C. E. J. Am. Chem. Soc. 1986 108, 6695; (d) Boger, D. L.; Brotherton, C. E. J. Am. Chem. Soc. 1986, 108, 6713.

5. Schneider, M. P.; Rau, A. J. Am. Chem. Soc. 1979, 101, 4426.

6. Hatch, C. E.; Baum, J. S.; Takashima, T.; Kondo, K. J. Org. Chem. 1980, 45, 3281.

7. Satisfactory spectroscopic data (^{1}H NMR and IR) were obtained for all new compounds. Molecular composition was established by combustion analysis or high resolution MS, except for compounds 3a-d which have limited stability.

8. Stereochemical assignments were based on proton coupling to the bridgehead position, as described previously in ref. 3. For the endo isomer, $J_{H4H5} = 5$ Hz, and for the exo isomer, $J_{H4H5} = 0$ Hz.

9. Stereochemical assignments were based on strong nOe enhancements between the vinylic hydrogens.

10. Preference for the endo divinylcyclopropane has been reported previously: See (a) ref 4; (b) Baird, M.S.; Nethercott, W. Tetrahedron Lett. 1983, 24, 605 and references cited therein.

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