Tetrahedron Letters,Vol.26,No.46,pp 5659-5662,1985 0040-4039/85 $3.00 + .00
Printed in Great Britain

[3 + 4] CYCLOADDITION REACTIONS OF VINYL CARBENOIDS WITH FURANS

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Abstract: The rhodium(II) acetate catalyzed decomposition of diethyl 4-diazopent-2-enedioate in the presence of furans results in the formation of products derived from a [3 + 4] cycloaddition.

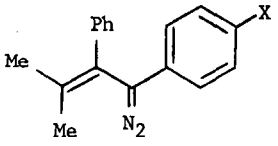
The [3 + 4] cycloaddition of allyl cations with dienes[1,2] has become a very useful method for the synthesis of seven-membered rings. The yields from these cycloadditions, however, tend to be moderate because competing electrophilic additions and carbocation rearrangements often occur. Moreover, as the reactions are not always concerted,[1] high stereoselectivity is not assured. Conceptually, the reaction of vinyl carbenoids with dienes could also lead to highly functionalized cycloheptadienes (Scheme 1). The initial phase of our studies into the feasibility of such a reaction using furans as dienes is reported here.

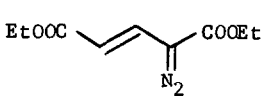
Scheme 1

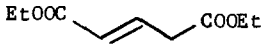
The chemistry of vinyl carbenes is dominated by their propensity for intramolecular reactions. When appropriately functionalized, they can undergo rearrangements to cyclopropenes,[3-6] allenes[7,8] acetylenes[8,9] and dienes[9,10] insertion onto C-H,[9] O-H[9] and C=C[11,12] bonds, and electrocyclization to furans,[6,13] indenes[8,9,14] and cyclopentadienes.[9] Consequently, even though some vinyl carbenes can be efficiently

trapped by dienes, competing side reactions generally occur.[15-17] The reactivity of vinyl carbenes might be quite different if they were generated by metal catalyzed decomposition of vinyl diazo compounds. Under these conditions the intermediate would be a metal carbenoid complex which should be more stable than the free carbene. Undesirable intramolecular reactions, therefore, should be more controllable.

In view of the intense current interest in vinyl carbenes, it is rather surprising that very few metal catalyzed decompositions of vinyl diazo compounds have been reported.[11] This is presumably because of the general instability of vinyl diazo compounds, which tend to rearrange spontaneously to 3H-pyrazoles.[4,18] A detailed examination[4] of the reaction kinetics of this electrocyclization showed that electron withdrawing groups, especially on the alpha carbon, inhibit this reaction. For example,[4] 1a undergoes cyclization at 78.6°C an order of magnitude slower than 1b. We reasoned, therefore, that the vinyl diazo compound 2 would be an ideal substrate for our initial studies. The two carboethoxy groups should greatly inhibit 3H-pyrazole formation and 2 should be readily prepared by diazotization of commercially available diethyl glutaconate (3). Indeed, treatment of 3 with p-(n-dodecyl)benzenesulfonyl azide[19] in the presence of triethylamine as base results in the formation of 2 in 94% yield. Moreover, 2 appears to be indefinitely stable at 25°C. Even though commercial diethyl glutaconate consists of a mixture of cis and trans isomers, the trans form of 2 is exclusively formed indicating that equilibration occurs under the reaction conditions.







1a X = CN
1b X = OMe

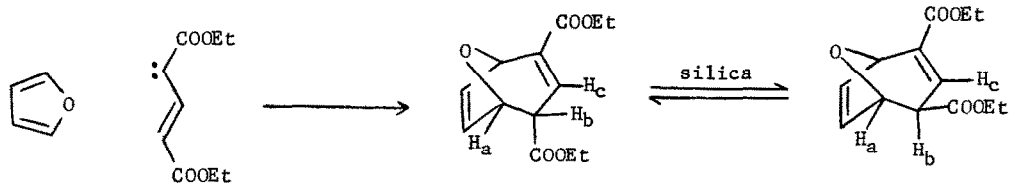
2

3

Rhodium(II) acetate catalyzed decomposition of 2 in the presence of furan forms the desired cycloadduct 4a in 45% yield after distillation (Scheme 2). The stereochemistry of 4a was readily determined by comparison of the NMR data with related compounds such as 5a and 5b.[20] In the exo isomer 5a, J_{HaHb} = 0 Hz, while in the endo isomer 5b, JH_aH_b = 5 Hz. In the proton NMR of the product 4a, J_{HaHb} = 5.8 Hz which suggests it is the endo product. Some decomposition was observed during the distillation of 4a and therefore, the product was also purified by chromatography. Even though a similar yield of cycloadduct was obtained, the exposure to silica resulted in partial isomerization of 4a to 4b. In the proton NMR of 4b there is no coupling between H_a and H_b which is the

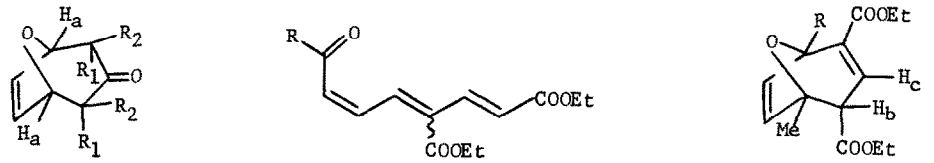
expected value for the exo isomer.[20] Also, H_b of the exo isomer appears at higher field (δ 2.81) than that of the endo isomer (δ 3.79) which is due to the shielding effect of the double bond derived from the furan. It should also be noted that for the endo isomer 4a, J_{HbHc} = 2.8 Hz while for the exo isomer 4b, J_{HbHc} = 4.0 Hz. During the chromatographic purification of 4, the triene 6a (14% yield) was also isolated. This product is presumably formed through rearrangement of an unstable cyclopropane intermediate.[17,21]

Scheme 2



4a 4b

The reaction of 2 was further examined with other furan derivatives as trapping agents. With 2-methylfuran, cycloadduct 7a and triene 6b are formed in 28% and 44% yield, respectively. An examination of the NMR spectrum of 7a shows that the endo product is exclusively formed (H_b, δ 3.49, J_{HbHc} = 2.9 Hz). A very clean reaction also occurs between 2 and 2,5-dimethylfuran which results in the exclusive formation of the endo cycloadduct 7b (H_b, δ 3.48, J_{HbHc} = 2.7 Hz) in 80% yield.



5a $R_1 = H_b$, R_2 = Me
5b R_1 = Me, $R_2 = H_b$

6a R = H
6b R = Me

7a R = H
7b R = Me

In summary, these initial studies clearly demonstrate that a stereospecific [3 + 4] cycloaddition between vinyl carbenoids and dienes is indeed feasible. The reaction may proceed either concertedly or via divinylcyclopropane intermediates; further studies are in progress to distinguish between these possibilities.

Acknowledgement: Financial support of this work by a William and Flora Hewlett Grant of Research Corporation and by the Petroleum Research Fund is gratefully acknowledged.

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(Received in USA 10 July 1985)