

REGIOSELECTIVE AND STEREOSELECTIVE SYNTHESIS OF VINYL-CYCLOPROPANE DERIVATIVES FROM 1,3-DIENES AND A FISCHER CARBENE COMPLEX

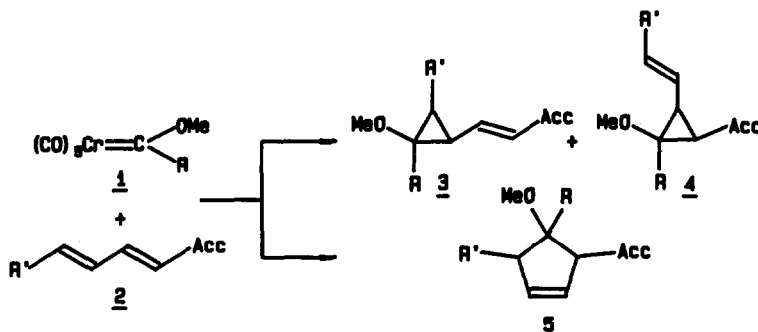
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Summary: Reactions of acceptor-substituted 1,3-dienes with a carbene complex occur with high regioselectivity and stereoselectivity to provide trifunctional cyclopropane derivatives.

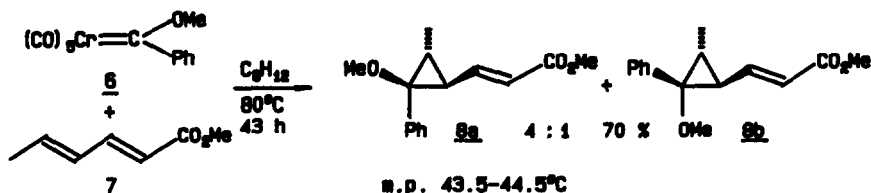
In the preceding letter the conversion of a variety of electron deficient olefins to donor-acceptor-substituted cyclopropanes by means of carbene complexes has been reported.¹⁾ As outlined in Scheme I reactions of 1,3-dienes 2 with carbene sources 1 might have a broader product spectrum, since cyclopentene derivatives 5 might be formed by a [4+1]-process in addition to cyclopropanes 3 or 4. Here we demonstrate that the carbene-transfer to electron deficient 1,3-dienes occurs with high peri-, regio-, and stereoselectivity.

Scheme I



Heating an equimolar mixture of methyl 2,4-hexadienoate 7 and carbene complex 6 in cyclohexane affords a 4:1 mixture of stereoisomeric vinylcyclopropanes 8a and 8b in good yield. Crystallization provides pure 8a in approximately 50% yield (Eq. 1).²⁾

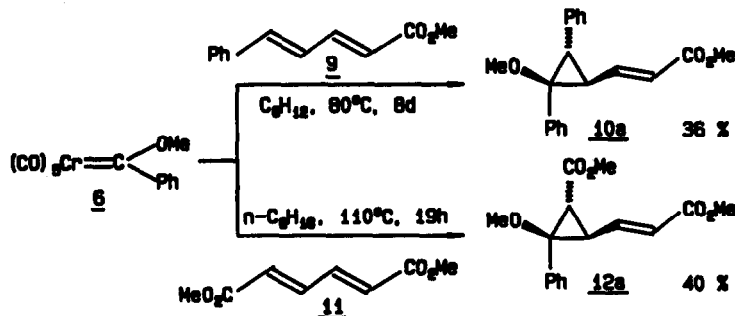
Eq. 1



Similarly, methyl 5-phenyl-2,4-pentadienoate 9 and 6 give 10a (m.p. 98-99°C) in 36% yield, yet, after 8 days at 80°C only 50% of the starting materials have been consumed; ~ 5% of 10b could be detected in crude 10 (Scheme II). Performing this experiment at 110°C (20 h),

small quantities of a regioisomer (2%, type 2) and of a product, which results from cyclopropanation of both double bonds in diene 9, are present in addition to 10.

Scheme II



Muconic acid dimethylester 11 does not react with 6 at 80°C . Heating to 110°C provides the vinylcyclopropane 12a (m.p. $62\text{--}63^\circ\text{C}$) in 40% yield; here again stereoselectivity is in the range of 95:5 in favour of 12a. Pentacarbonyl[methoxy(methyl)carbene]chromium(0) is also capable of transferring its carbene ligand to diene 7. However, double adduct formation could so far not be suppressed even by using 5 equivalents of diene.³⁾

Our preliminary results show that reactions of carbene complex 6 are remarkably slower with electron deficient dienes as compared with other acceptor-substituted olefins.¹⁾ On the other hand, much higher stereoselectivities are attained in the carbene-transfer to dienes, which proceeds regioselectively at the 4,5-double-bond. Although [4+1]-cycloaddition⁴⁾ has not been achieved, cyclopropanes 8, 10, and 12⁵⁾ should be convertible to cyclopentene derivatives by thermolysis.⁶⁾ Also, the three functional groups in these cyclopropanes should be a suitable handle for other useful synthetic transformations.⁷⁾

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References and Notes: 1) A. Wienand, H.-U. Reissig, see preceding letter.- 2) Methyl 2,4-pentadienoate and 6 give only polymers, whereas methyl 3-methyl-2,4-pentadienoate and 6 provide ~20% of a type 3 cyclopropane.- 3) Cyclopropanes of type 3 were isolated in ~40% yield as a mixture of four stereoisomers. The reason for this apparent stereounspecificity has so far not been elucidated.- 4) Cyclopentene formation in very low yield occurs with methyl 2-methoxycarbonyl-2,4-dienoate and 6.- 5) Correct elemental analysis and appropriate spectra have been obtained for 8a, 10a, and 12a, e. g. 8a ^1H NMR (CDCl_3 , 300 MHz) δ = 7.36 (s, Ph), 6.96 (dd, 15.6Hz, 10.3Hz, =CH), 6.07 (d, 15.6Hz, =CH), 3.75 (s, CO_2Me), 3.04 (s, OMe), 1.92 (dd, 10.3Hz, 5.8Hz, CH), 1.75 (dq, 5.8Hz, 6.4Hz, CH), 0.83 (d, 6.4Hz, Me).- 6) For a review on vinylcyclopropane-cyclopentene-rearrangements see: T. Hudlicky, T.M. Kutchan, S.M. Naqvi, in Organic Reactions, (Ed. A.S. Kende), Vol 33, p. 247, Wiley, New York 1985.- 7) H.-U. Reissig, Organic synthesis via cyclopropanes: principles and applications in The Chemistry of the Cyclopropyl Group (Ed. Z. Rappoport), p. 375, Wiley, New York 1987.

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