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STEREOCHEMISTRY OF THE NICKEL(0) CATALYZED REACTION OF BICYCLO[1.1.0]BUTANE AND ELECTRON-DEFICIENT OLEFINS[1]

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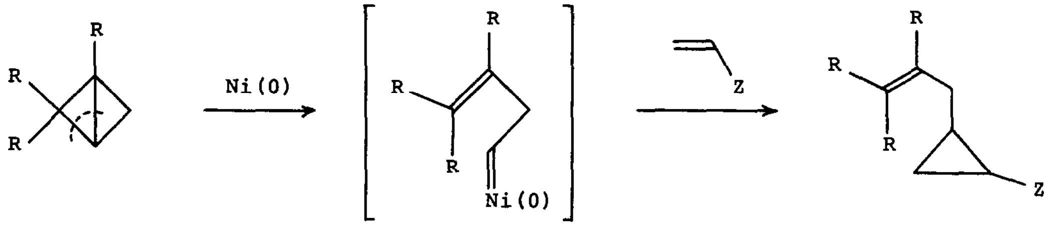
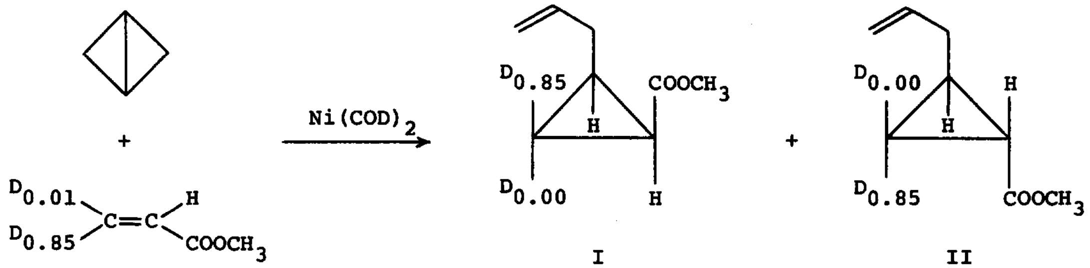
Bicyclo[1.1.0]butanes upon interaction with nickel(0) catalysts undergo the intramolecular retro-carbene addition to produce reactive allylcarbene—nickel(0) intermediates, which in turn cycloadd intermolecularly, in a formal sense, across an electron-poor carbon—carbon double bond giving the cyclopropane adducts.[2] With 1,2-disubstituted olefins such as dimethyl maleate and fumarate, fairly stereospecific cycloadditions were observed. However, the propensity of the maleate for cis—trans isomerization during the catalysis has prevented complete analysis of the stereospecificity. We have reexamined the reaction using deuterium-labeled methyl acrylate as olefinic substrate, and confirmed the stereospecific nature.



R = H or CH_3

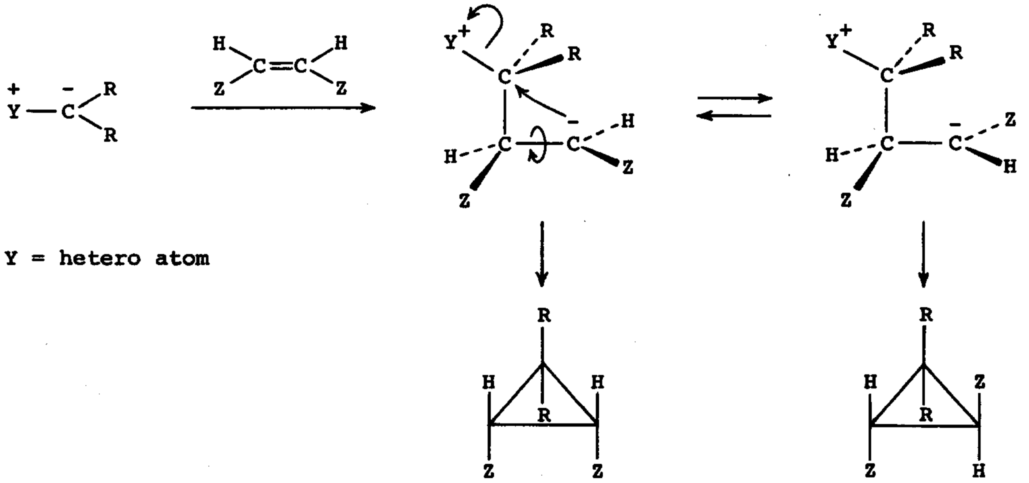
A mixture of bicyclo[1.1.0]butane (3 mmol), methyl cis-β-deuterioacrylate (6 mmol),[3] bis(1,5-cyclooctadiene)nickel(0) (0.8 mmol), and toluene (0.5 ml) was deoxygenated by freeze-pump-thaw cycles and sealed under argon atmosphere. The orange-yellow solution was maintained at 32° for 24 hr to give after distillation a 63:37 mixture of the cycloadducts I and II in 62% yield. Nmr analysis of the recovered acrylate revealed that no detectable isomerization of the starting olefin had took place during the reaction. Although the cyclopropane adducts purified by preparative glpc gave nmr spectra too complicated to analyze directly, their structural assignment could be made readily by examination of the well-resolved spectra taken with the aid of the shift reagent, Eu(fod)$_3$. The result indicates that the overall reaction proceeds with excellent stereospecificity.[4]



I II

The observed stereochemical course is to be noted, since the intermediary nickel(0) carbenoids, unlike other carbene complexes generated from diazo alkanes and metals in a high oxidation state,[5] have a considerable ylide character.[6] Certain ylides, particularly those containing a sulfur atom, undergo bimolecular alkylidene transfer reaction with electron-deficient olefins in a nonstereospecific fashion as outlined in Scheme I;[7] the nucleophilic attack of

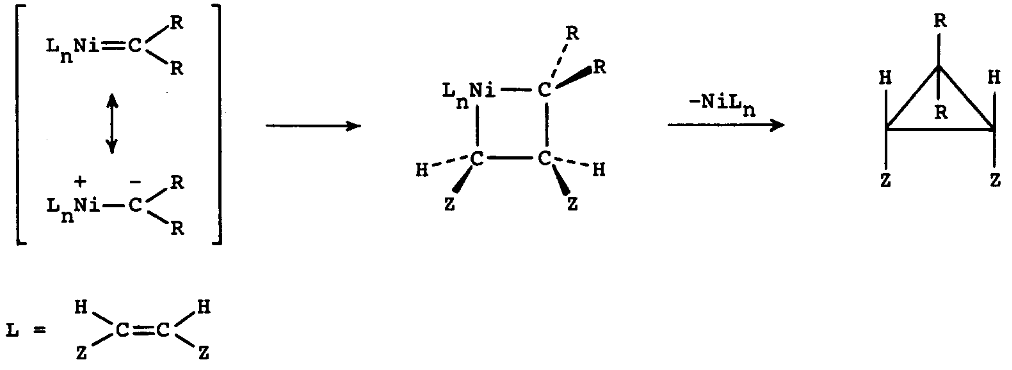
Scheme I



Y = hetero atom

the anionic carbon on the electron-poor double bond followed by cyclization through intramolecular backside displacement gives the cyclopropane adducts. Since electrostatic interaction between the charged moieties in the zwitterionic intermediates is of negligible importance in fixing the conformation, rotation around the $\mathrm{CHZ}—\overset{-}{\mathrm{C}}\mathrm{HZ}$ single bond can take place, leading to the conformational isomer which produces stereoisomeric adduct. On the other hand, the carbenic ligand in the nickel(0) carbenoid could react with the olefinic substrate coordinated to the same metal atom[8] giving the nickelacyclobutane intermediate, which forms the cyclopropane derivative with ejection of the nickel(0) catalyst (Scheme II). The stereospecific cyclopropanation is a result of (1) the presence of a carbon-metal σ bond (or the related interatomic interactions) in the nickelacyclobutane which prevents the inversion of stereochemistry and (2) the operation of concerted mechanism in the reductive elimination step.[9] Reverse process of the final step, cyclopropane → metallacyclobutane transformation, is well documented.[1,10]

Scheme II



Notes and References

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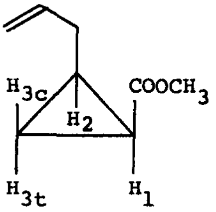
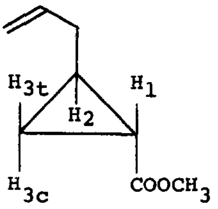
4. Signal integration of the spectra was performed carefully with the samples mixed with varying amounts of the undeuterated substance i or ii (Varian HA-100D spectrometer, 100 MHz, field-sweep mode). Values given in the scheme are means of ten traces. The maximum deviation from the mean observed for each trace was ± 1.4%. Nmr of i (0.20 *M* CCl_4 solution containing 0.23 mol equiv of $Eu(fod)_3$): δ 1.85 (ddd, 1H, H_{3t}), 2.32 (m, 1H, H_2), 2.74 (ddd, 1H, H_{3c}), 3.3—3.7 and 3.9—4.3 (m, 1H each, CH_2=$CHC\underline{H}_2$), 3.85 (ddd, 1H, H_1), 5.2—5.9 (m, 2H, CH=$C\underline{H}_2$), 6.10 (s, 3H, OCH_3), and 6.3—6.8 (m, 1H, $C\underline{H}$=CH_2); J_{1-2} = J_{1-3t} = J_{2-3t} = 8.3 Hz, J_{1-3c} = J_{2-3c} = 7.0 Hz, and J_{3c-3t} = 4.5 Hz. Nmr of ii (0.29 *M* CCl_4 solution containing 0.21 mol equiv of $Eu(fod)_3$): δ 1.02 (ddd, 1H, H_{3t}), 1.5—2.1 (m, 2H, CH_2=$CHC\underline{H}_2$), 3.75 (ddd, 1H, H_{3c}), 4.07 (m, 1H, H_2), 4.20 (ddd, 1H, H_1), 5.1—5.6 (m, 2H, CH=$C\underline{H}_2$), 6.0—6.5 (m, 1H, $C\underline{H}$=CH_2), and 6.80 (s, 3H, OCH_3); J_{1-2} = J_{1-3c} = J_{3c-3t} = 4.5 Hz, J_{1-3t} = J_{2-3c} = 8.5 Hz, and J_{2-3t} = 7.0 Hz.



i



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6. R. Noyori, *Tetrahedron Lett.*, 1691 (1973).
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