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EVIDENCE FOR A TRIMETHYLENEMETHANE COMPLEX INTERMEDIATE IN THE NICKEL(0) CATALYZED REACTION OF METHYLENECYCLOPROPANE[1]

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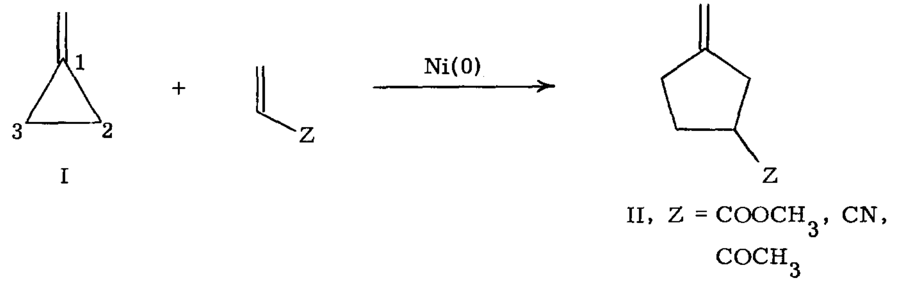
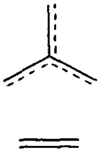
There has been considerable interest in the transition metal promoted reaction of strained cyclic hydrocarbons.[2] Recent studies have indicated that methylenecyclopropanes, when exposed to transition metal complexes, exhibit intriguing behavior[3] and, depending on the reaction conditions, both the carbon to carbon single[3c—e,g,n] and double bonds[3f,i] can participate in the reaction. We have previously demonstrated that Ni(0) complexes promote the rapid cycloaddition of methylenecyclopropane (I) across electron-deficient olefins producing methylenecyclopentane derivative II (eq 1).[3c] It soon became evident by the isotope labeling experiments that the reaction of I and methyl acrylate passes through pathway D; the $_{\sigma}2 + {}_{\pi}2$ type reaction involved cleavage of the vinylic C-1—C-2 bond of I. Other possible mechanisms, A—C, were ruled out.[3d]

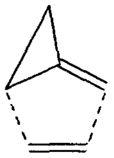


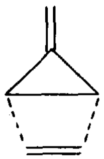
I

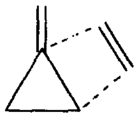
II, Z = $COOCH_3$, CN, $COCH_3$

(1)


A

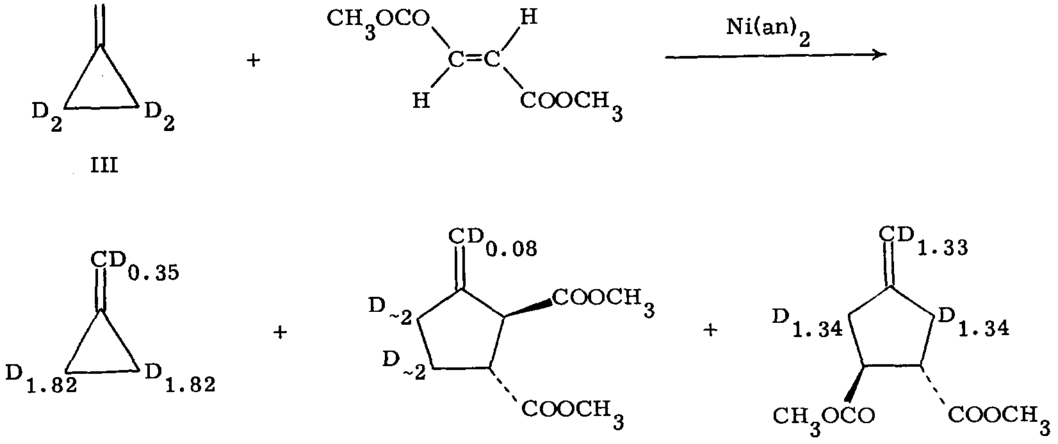

B


C


D

In sharp contrast to such reaction of I and monosubstituted olefins, in the presence of 1,2-disubstituted olefins such as dimethyl fumarate and maleate, I behaved in a different manner to give two kinds of cycloadducts, 2,3- and 3,4-disubstituted methylenecyclopentanes.[3d] The 2,3-isomer can be recognized easily to be the product of mode D combination, but the pathway leading to the 3,4-isomer remained unclarified. This time we have disclosed that the reaction giving the 3,4-isomer proceeds via a trimethylenemethane intermediate (mode A).

Reaction of 2,2,3,3-tetradeuteriomethylenecyclopropane (III)[4] and dimethyl fumarate was carried out in the presence of bis(acrylonitrile)nickel(0) [Ni(an)$_2$] (benzene, 60 °C, 2.5 h) as described previously[3d] (eq 2). The 1:1 cycloadducts IV and V produced in a ratio of 38:62 were separated into each component by a combination of preparative GLC and HLC. The structures of the products were carefully determined by NMR methods (JEOL FX-100 FT NMR): NMR of undeuterated IV ($CDCl_3$) δ 1.5—2.7 (m, 2 CH_2), 3.1—3.8 (m, 2 CH), 3.70 (s, OCH_3), 3.75 (s, OCH_3), and 5.0—5.2 (m, $=CH_2$); NMR of undeuterated V ($CDCl_3$) δ 2.2—2.9 (m, 2 CH_2), 2.9—3.3 (m, 2 CH), 3.71 (s, 2 OCH_3), and 4.8—5.0 (m, $=CH_2$). The analysis revealed that deuterium atoms in the product V are completely statistically scrambled over three carbons.[5] Thus catalytic cleavage of the bisallylic C-2—C-3 bond of I makes the three methylene carbons equivalent (mode A). The isotopic scrambling of III also occur but only slowly under the present reaction conditions, as indicated by analysis of the recovered starting material.[5] This result strongly suggests that a trimethylenemethane—Ni(0) complex of type VI[6] (Scheme I) or the related rapidly equilibrating σ-complex is responsible for the formation of such adducts. Alternative position specific cycloadditions, 2 + 2 + 2 process (mode B)[7] or 2 + 2 process (mode C), are ruled out. By contrast, in the product IV most of the deuterium atoms were located on two of the five-membered ring carbons, which conforms to our earlier



III

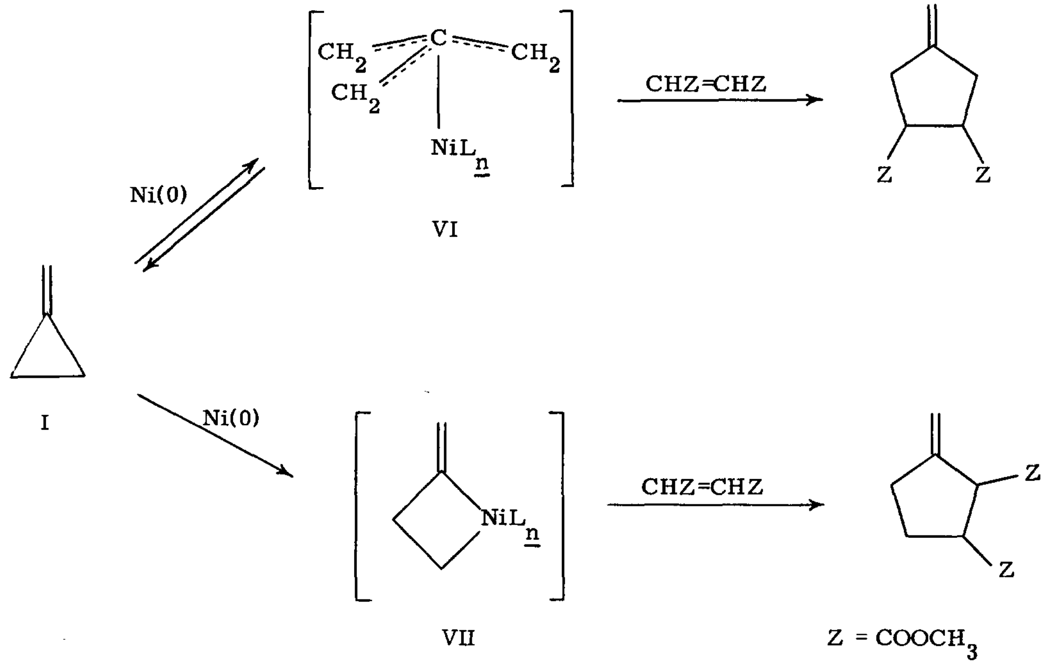
recovered III IV V

(2)

conclusion that this type of compounds arise by way of 2-methylenemetallocyclobutane intermediates of type VII. The slight deuterium incorporation at exocyclic methylene position would be due to the presence of an equilibrium between III and an intermediate of type VI.

Thus, two types of ring opening, mode A and D, proved to occur in the Ni(0) catalyzed reaction of I and electron-deficient olefins depending upon the nature of the olefinic substrates employed. In addition, this observation shows potential utility of trimethylenemethane—transition metal complexes in the synthesis of certain carbocyclic structures.

Scheme I



Z = $COOCH_3$
L = olefinic ligand

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