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NICKEL(0)-CATALYZED VALENCE ISOMERIZATION OF THE 1,1'-BISHOMOCUBANE SYSTEM[1]

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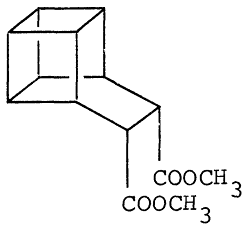
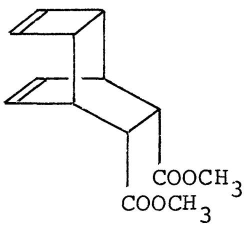
In the presence of nickel(0) complexes *cis*-9,10-dicarbomethoxypentacyclo[4.4.0.$0^{2,5}$.$0^{3,8}$.$0^{4,7}$]decane isomerizes cleanly to give a mixture of *endo*- and *exo*-*cis*-9,10-dicarbomethoxytricyclo[4.2.2.$0^{2,5}$]deca-3,7-dienes.

One of the characteristics of nickel(0) complexes in the reaction involving strained hydrocarbon systems is the ability to effect the *intermolecular* cycloaddition of strained σ bonds across carbon—carbon double bonds.[2-4] Unlike other transition metal catalysts so far investigated, however, nickel(0) complexes have hardly promoted the *intramolecular* rearrangement. For instance, attempted skeletal changes of methylenecyclopropane,[2] bicyclo[1.1.0]butanes,[3] bicyclo[2.1.0]pentane,[4] hexamethyl(Dewar benzene), and [2.2]spiropentane in the absence of olefinic substrate resulted in virtual recovery of the starting hydrocarbons, although a large strain release upon σ bond breakage could be expected. This paper describes an example of isomerization of a strained molecule induced by nickel(0) complexes.

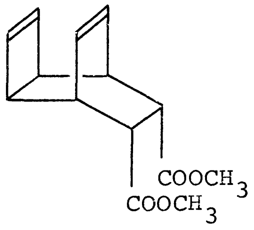
When the 1,1'-bishomocubane I (1 mmol) was treated with bis(1,5-cyclooctadiene)nickel(0) (0.1 mmol) in a mixture of methyl acrylate (1 mmol) and toluene (1.5 ml) at 35°C for 36 hr under a nitrogen atmosphere, the dienes II and III



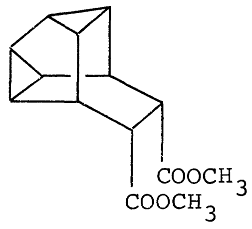
I



II



III



IV

(49:51 ratio) were obtained quantitatively. The possible $[_{\sigma}2 + _{\pi}2]$-type cycloaddition[2,4] between I and the acrylate could not compete with the intramolecular $[_{\sigma}2 + _{\sigma}2]$-type reaction. Bis(acrylonitrile)nickel(0), though was employable with methyl acrylate, could not be used in acrylonitrile because of its insolubility (at 35°C). Bis(1,5-cyclooctadiene)nickel(0) in the absence of acrylate did not cause the valence isomerization of I. Replacement of the acrylate by acrylonitrile destroyed the catalytic activity due to the rapid precipitation of bis(acrylonitrile)nickel(0). Nickel tetracarbonyl (in benzene, 35°C) was ineffective as the catalyst. These findings indicate that the affinity of the saturated compound I for nickel(0) atom is not high enough to displace the cyclooctadiene or carbonyl ligands, and that the production of soluble, coordinatively unsaturated nickel(0) complexes bearing acrylate ligand is the essential sequence for achieving the two-bond cleavage of I.

The metal promoted rearrangements of I are classified into two extreme types, the isomerization leading to the dienes II and III[5] and the bond-switching reaction to give the dicyclopropyl derivative IV.[6] The observed choice of the catalysis mode could be ascribed to the intriguing electronic nature of nickel(0) atom,[3b] and gives further credence to the recent Dauben's postulate[5] that transition metals with the distinct ability of oxidative addition facilitate the cyclobutane—diolefin transformation and, on the other hand, metal ions having great σ electron acceptor ability favor the cyclobutane—dicyclopropyl rearrangement.

NOTES AND REFERENCES

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