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VINYLCYCLOPROPANE-CYCLOPENTENE REARRANGEMENT CATALYZED BY NICKEL(0) COMPLEXES

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Abstract: Bis(1,5-cyclooctadiene)nickel-tributylphosphine (1 : 1) catalyzed the vinylcyclopropane-cyclopentene rearrangement. Only such vinylcyclopropanes as those being capable of complexing with the catalyst (such as 1-substituted 1-cyclopropyl-1,3-butadienes and 1,1-dicyclopropylethylenes) were reactive.

The vinylcyclopropane-cyclopentene rearrangement has attracted much attention not only because of mechanistic interests but also because of a synthetic usefulness of constructing a cyclopentene ring system.[1,2] The rearrangement is usually carried out either by heating the substrate at 300°C or higher[1,2] or by irradiating its chromophore by UV light.[3] We wish to report here that the rearrangement proceeds smoothly in the presence of a catalytic amount of nickel(0)-tributylphosphine complex at relatively low temperature.

It is known that vinylcyclopropanes are sensitive to a catalytic action of transition metals. Thus, 2-methyl-1-vinylcyclopropane and related compounds are reported to produce ring cleaved dienes in their contact with diisobutylaluminum chloride-*trans*-dichlorobis(tributylphosphine)nickel(II) or dicarbonylrhodium(I) chloride dimer.[4] A ring enlargement has been observed in the reaction of some vinylcyclopropanes with iron pentacarbonyl to give CO inserted cyclohexenones.[5] An example has been described for the vinylcyclopropane-cyclopentene rearrangement which takes place on rhodium(I) as the ligand of the complex.[6] However, the catalytic action of the transition metal complexes on the rearrangement is unprecedented.

A typical procedure for the reaction was as follows. A benzene (5 ml) solution of 1,1-dicyclopropyl-1,3-butadiene (1a, 4.3 mmol) was heated at 70°C in the presence of a 1/10 equivalence of Ni(COD)$_2$-PBu$_3$ (1 : 1) in a degassed sealed tube. After 40 h, the tube was opened and the products were isolated by distillation (70% as a mixture). There were two major components in the distillates which were assigned as 2-cyclopropyl-3-vinylcyclopentene (2a, 68%) and 2-cyclopropyl-3-ethylidenecyclopentene (3a, 20%).[7] A control experiment showed that 3a was produced from 2a under the reaction conditions. In a similar manner, several other butadienes (1b-1f) produced 2 and/or 3. The results are summarized in Table I. It should be pointed out that the parent diene, 1-cyclopropyl-1,3-butadiene (1i), produced 2i only in 4% yield, the major product being a dimer.[8] In contrast to these results of the dienes, most of mono-enes, including vinylcyclopropane, 2-

cyclopropylpropene, 1-cyclopropyl-1-phenylethylene, 2-cyclopropyl-1-phenylpropene, and 1-cyclopropyl-1-trimethylsilyloxyethylene, were stable under the reaction conditions.[9] The two exceptional mono-enes were 1,1-dicyclopropylethylene (1g) and 1,1-dicyclopropyl-2-phenylethylene (1h), which produced the corresponding cyclopentene in reasonable yields.

As to the effect of an auxiliary ligand, tributylphosphine was better than triphenylphosphine (run 3). Triphenyl phosphite was detrimental to the reaction (run 2). The addition of tributylphosphine in an amount larger than the equivalence resulted in a suppression of catalytic activity of the complex (run 5).

In the reaction of dienes, it was observed that the complex catalyzed the geometrical isomerization of the substrate, but it seemed to be relatively slow compared to the rearrangement. It should be noted that the diene recovered in run 8, as well as in run 12, was very much rich in one isomer, which had a configuration of the cyclopropyl group being at the Z position to the C-3. This result suggests that the isomer of the cyclopropyl group being at the E position to the C-3 is more reactive than its alternative.[10] This fact may concern with the ability of

Table I. Ni(0)-PR_3 Catalyzed Rearrangement of Vinylcyclopropanes (Benzene, 70°C)

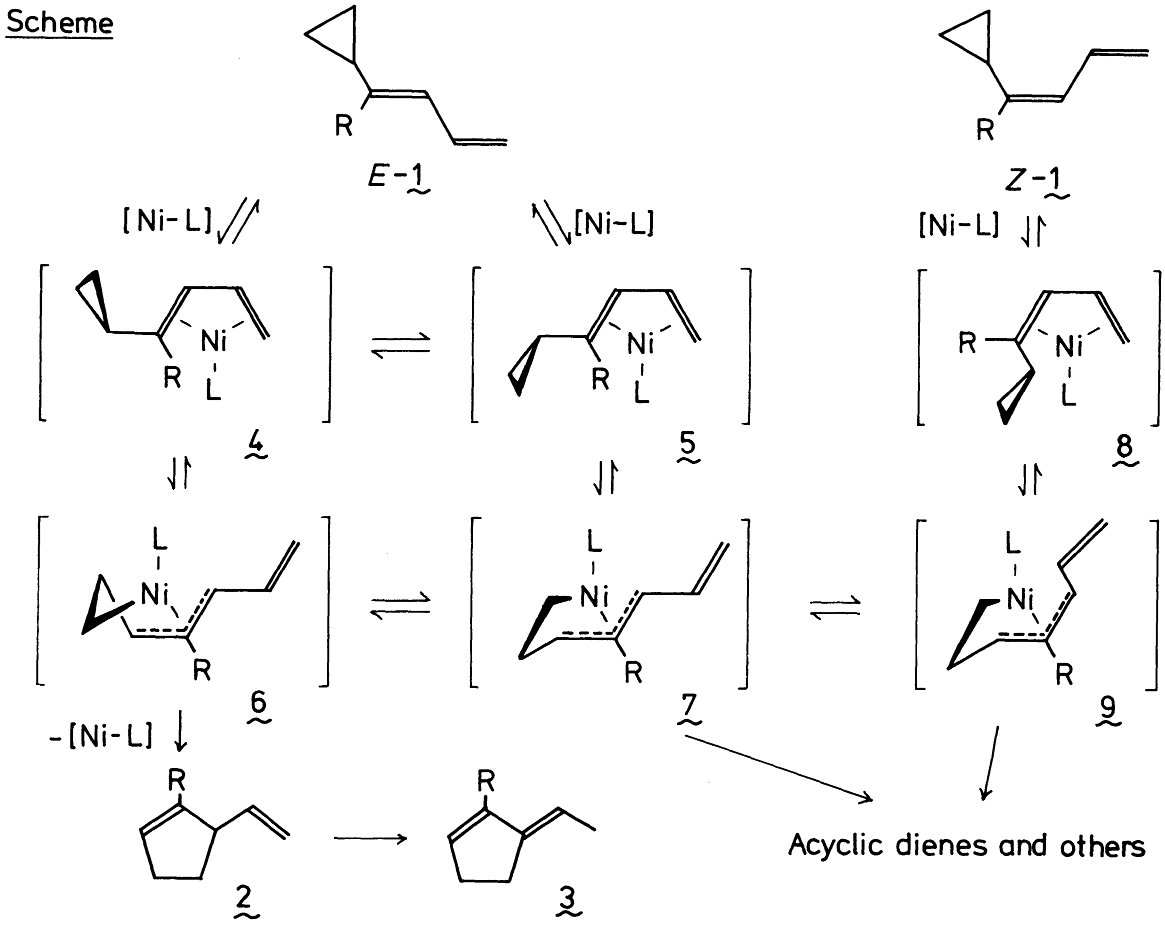
	Olefin: R^1(▷—)C=CH-R^2					Mol Ratio	Conv.[a]	Yield(%)[b]	
Run	1	R^1	R^2	(E/Z)	PR_3	PR_3/Ni	(%)	2	3
1	1a	c-C_3H_5	CH=CH_2		(none)		35	75	--
2	"	"	"		$P(OPh)_3$	0.9	7	50	--
3	"	"	"		$P(Ph)_3$	1.0	72	61	19
4	"	"	"		$P(Bu)_3$	0.9	$>$99	68	20
5	"	"	"		"	3.6	5	22	--
6	1b	CH_3	"	(67/33)	"	1.0	92	57	24
7	1c	C_2H_5	"	(60/40)	"	1.0	95	64	24
8	"	"	"	(99/1)	"	1.0	94[c,d]	79	18
9	"	"	"	(1/99)	"	1.0	38[e]	80	3
10	1d	$(CH_3)_2CH$	"	(ca.1/1)	"	1.0	98	93	6
11	1e	$(CH_3)_3C$	"	($>$99/$<$1)	"	1.0	27	31	--
12	1f	C_6H_5	"	(77/23)	"[f]	1.0	87[g]	75	--
13	1g	c-C_3H_5	H		"	1.0	79	$>$99	--
14	1h	"	C_6H_5		"[f]	1.0	60	77	--
15	1i	H	CH=CH_2	(87/13)	"	1.0	67	4	--[h]

[a] After 40 h. [b] Based on the consumed amount of 1; determined by GLC. [c] Recovered diene was practically pure Z isomer. [d] After 20 h, the conversion was 80%: 2c : 3c = 92 : 8. Recovered diene was a mixture of E and Z in 57 : 43 ratio. [e] Recovered diene was a mixture of E and Z in 4 : 96 ratio. [f] With triphenylphosphine, no rearrangement took place. [g] Recovered diene was practically pure E isomer. [h] The major product was a dimer. A better result was obtained with triphenylphosphine in the dimer formation.[8]

the diene to achieve a suitable orientation to undergo the catalytic rearrangement. The mechanism of the present reaction is thus deduced as follows.

The first step of the reaction will be the formation of a butadiene-nickel(0) complex.[11,12] The complexation of another molecule of the diene will be difficult because of the steric hindrance caused by the two groups at the C-1. This will be the reason why dimerization of the diene has not been the major course of the reaction, except for **1i**, although the complex utilized is an effective catalyst for the butadiene oligomerization.[11] Now, in the reaction of *E* dienes (*Z* dienes in **1e** and **1f**), the complex will exist as either **4** or **5**, if the bisected conformation is assumed for the vinylcyclopropane moiety in the ligand. When the second group (R) at the C-1 is bulky, as is indeed the case in most of the dienes, **4** will be more favorable than **5**. The complex **4** will open its three membered ring in such a way to produce a cisoid σ,π-allyl complex **6**,[13] which is a requisite for the cyclopentene ring formation. In contrast, **5** should produce a transoid complex **7**. Since **7** is incapable of forming a five membered ring, it will recyclize back to **5** or give ring cleaved dienes after hydride shifts. The *Z* dienes (*E* dienes in **1e** and **1f**) may produce **8**, in which the cyclopropane ring is pushed away from the ligand on the nickel atom. Thus, **8** is in a situation similar to that of **5** and hence the resultant **9** will not be able to give **2**. The *Z* dienes will, therefore, isomerize to the *E* isomer via **9** and **7**,[14] and then **2** may be produced. Since the geometrical isomerization is relatively slow, the conversion of the *Z* dienes was somewhat low.

Scheme



The scheme accounts for the all other observations made in the present study. For example, the low reactivity of 1e will be due to the poor coordination ability of the diene caused by the steric hindrance of the bulky t-butyl group. The effectiveness of tributylphosphine as the auxiliary ligand may be explained by the σ-donating ability of such phosphines, which results in the stabilization of the high oxidation state of the nickel in 6. The fact that vinylcyclopropane and 2-cyclopropylpropene failed to rearrange should be ascribed to the poor ability of these olefins to donate electron density to the nickel atom. The lack of the reactivity in silyl enol ether may be the result of preferred complexation of n electrons with the catalyst. Similarly, complexation of the aromatic π electrons with the complex will account for the relatively low reactivities of phenyl substituted substrates such as 1f and 1h. The transformation of 4 to 6 may be envisioned as a [4n+2] electron process,[6,15] because it may involve the coordinative interaction of the vinylcyclopropane moiety with nickel (4 electrons from the ligand and 2 electrons from the metal). The ring closure of 6 to 2 may also be a [4n+2] electron process (4 electrons from the allylic moiety and 2 electrons from the Ni-C bond).

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