CYCLO-CODIMERIZATION OF 1,3-BUTADIENE DERIVATIVES WITH NON-ACTIVATED TERMINAL ACETYLENES CATALYZED BY CATIONIC RHODIUM(I) COMPLEX

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Summary: An efficient cyclo-codimerization between 1,3-diene and non-activated terminal acetylene has been attained by the catalysis of  $[Rh(COD)(DPPB)]PF_6$  to give 1,4-disubstituted cyclohexa-1,3-dienes under mild conditions.

Although transition metal catalyzed cyclo-codimerization<sup>1</sup> and linear codimerization<sup>2</sup> of 1,3-diene with acetylene have recently attracted considerable interest, there are limited examples<sup>3</sup> to give cyclohexadiene from 1,3-diene and non-activated acetylene. Especially it is difficult to use terminal acetylenes as a component of cyclo-codimerization because of the susceptibility for the homooligomerization<sup>1</sup> in the presence of transition metal catalysis. We now report here a facile route to form cyclohexa-1,3-diene by rhodium catalyzed cyclo-codimerization of 2-substituted 1,3-butadiene and terminal acetylene.

Reaction of phenylacetylene with an equivalent of isoprene in a CH<sub>2</sub>Cl<sub>2</sub> solution at 100 °C for 2 h in the presence of [Rh(COD)(DPPB)]PF6 as catalyst afforded a mixture of cyclo-codimerized products 3a, 5a, and 6a with the concomitant dehydrogenated product 7a in 75 % yield (3a:5a:6a:7a = 93:2:3:2) after bulb-to-bulb distillation. Although rhodium catalyzed homopolymerization of acetylene or 1,3-diene and homodimerization of terminal acetylene<sup>4</sup>, small amount of polymerized phenylacetylene was detected as the side products in the present reaction. It should be stressed that the direction of coupling can be controlled strictly to give 1,4- or 2,5-disubstituted products<sup>5</sup>. Some other combinations of 1 and 2 proceeded similarly at near room temperature to give cyclic codimers and the relative position between two substituents in the products was retained at 1,4-positions<sup>5</sup> in the case of 2-substituted-1,3-butadienes. When 1,3-butadiene itself was used, relatively large excess of diene was necessary in order to suppress homopolymerization of acetylenes and major product changed to <u>6</u>. The results are summarized in



In contrast with terminal acetylene, internal one, 1-phenylpropyne, Table 1. gave neither codimer nor homopolymer under analogous conditions. This point is quite different from cyclo-codimerization catalyzed by Fe(0) complex in which  $\eta^2$ -type coordination of acetylene plays an important role.<sup>3a</sup>

Reaction conditions					Cyclo-codimerization products <sup>6</sup>								
Entry	Mole ratio	Temp.	Time		Substituents		Yield	Selectivity <sup>ii)</sup>					
	1/2	(°C)	(h)		R <sup>1</sup>	$R^2$	(	3	4	5	é	7	
1	1.3	41	144	a	СН3	с <sub>6</sub> н <sub>5</sub>	85 <sup>iii)</sup>	93	0	2	3	2	
2	1.0	43	43	b	СНЗ	n-C <sub>3</sub> H <sub>7</sub>	65	94	1	1	3	1	
3	1.4	25	145	с	СНЗ	$n - C_5 H_{11}$	74	88	2	1	4	4	
4	6	25	120	d	CH <sub>3</sub>	Me3SiCH2	44	100	0	0	0	0	
5	1.4	25	168	е	$\gamma \sim \gamma$	с <sub>6</sub> н <sub>5</sub>	75	78	3	4	7	8	
6	1.3	25	72	f	$\gamma \gamma \gamma$	n-C <sub>3</sub> H <sub>7</sub>	83	89	3 <sup>iv)</sup>	2 <sup>iv)</sup>	4	2	
7	10	25	144	g	Н	C <sub>6</sub> H <sub>5</sub>	69	40	0	8	42	10	
8	6	25	144	h	Н	n-C5 <sup>H</sup> 11	58	8	0	2	78	12	

Table 1. Cyclo-codimerization of 1,3-dienes and terminal acetylenes catalyzed by [Rh(COD)(DPPB)]PF<sub>6</sub>.<sup>i)</sup>

i) The reaction (5 mmole scale in  $CH_2Cl_2$ ) was conducted in a sealed tube under argon atmosphere using 1 - 5 mole % of [Rh(COD)(DPPB)]PF6.

ii) Determined by GLC analyses (OV 101 50 m column).

- iii) When 0.2 mole % of catalyst was used, turnover number of Rh attained to 446 within 166 h.
- iv) The data is tentative, because GLC signals of these compounds are ambiguous.

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## References and notes

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  R.S. Dickson, "Homogeneous Catalysis with Compounds of Rhodium and Intervented and Publiching Co. Dependence (1985).

- Iridium", Chapter 7, D. Reidel Publishing Co., Dordrecht, (1985). 5. Relative position between two substituents was determined by proton NMR and GLC analyses of the aromatic products which were directly derived from
- a mixed primary products 3 7 by the interaction of trityl perchlorate. 6. Compounds 4b, 4c, 5c, and 5f were assigned tentatively. The rest were identified by proton NMR and elemental analyses or by the comparison of GLC data with those of authentic samples.

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