

A NOVEL CYCLODIMERIZATION OF BUTADIENE BY NICKEL CATALYSTS.

SYNTHESIS OF 1-VINYL-2-METHYLENECYCLOPENTANE

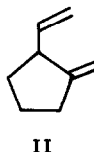
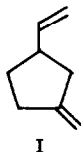
Jitsuo Kiji, Kazuo Masui, and Junji Furukawa

Department of Synthetic Chemistry, Faculty of Engineering,

Kyoto University, Kyoto, Japan

(Received in Japan 16 March 1970; received in UK for publication 26 May 1970)

Dimerizations of butadiene in the presence of transition metals to cyclic or linear products have been studied extensively by many workers (1). The principal products are isomeric n-octatrienes, methylheptatrienes, vinylcyclohexene, and cyclooctadiene. Until present, however, no effective catalysts have been reported to convert butadiene into a five-membered cyclic dimer, 1-vinyl-3-methylenecyclopentane [I] or 1-vinyl-2-methylenecyclopentane [II], except for the work of Müller (2), who isolated the five-membered cyclic dimer [I] of butadiene as a by-product.



We have found that a new five-membered cyclic dimer of butadiene, 1-vinyl-2-methylenecyclopentane [II], is obtained selectively by some nickel catalysts, which are used with a considerable amount of alcohols.

The following illustrates a typical example. In a glass tube, bis(tributylphosphine)-dichloronickel (3 mmole) was allowed to react with o-lithio-N,N-dimethylbenzylamine [III] (3) (3 mmole) in benzene (15 ml) under argon atmosphere with shaking for about 30 min. Methanol (3 ml) and subsequently liquefied butadiene (9 g) were added. The tube was sealed and the deep red solution was heated at 60 — 65° for 50 hr. The product was separated by distillation and a colorless liquid (6.3 g, b.p. 121 — 122°, n_D^{24} 1.4553*) was obtained. The gas


chromatogram showed one peak free from significant by-products. The molecular weight measured by mass spectrometry agreed with the formula, C_8H_{12} . Infrared absorption bands at 910 and 990 cm^{-1} and a band at 880 cm^{-1} indicated the presence of a vinyl group and a group of the type $>C=CH_2$, respectively. The absorption band at 1370 cm^{-1} for methyl group was absent in the spectrum. One mole of the sample absorbed 2 moles of hydrogen to give trans-1-methyl-2-ethylcyclopentane as the main product. The above facts lead to a conclusion that the original dimer is 1-vinyl-2-methylenecyclopentane [II].

Several examples of the cyclodimerization with some nickel catalysts are summarized in Table 1. Butyllithium as well as III is available as the organolithium component.

Table 1. Cyclodimerization of Butadiene^{a)}

No.	Catalyst		Amount (mmole)		C_4H_6 (mmole)	CH_3OH (mmole)	Product	Yield (%)
	Ni	Li	Ni	Li				
1	$(Bu_3P)_2NiCl_2$	III ^{b)}	1.0	1.0	100	25	II	70
2	$(Bu_3P)_2NiBr_2$	BuLi	1.0	1.0	100	25	II	90
3	$(Bu_3P)_2NiCl_2$	BuLi	1.4	0.7	80	40	II	50
4	$(Bu_3P)_2NiCl_2$	BuLi	1.3	5.1	70	40	II	50
5 ^{c)}	$(\pi-C_3H_5NiBr)_2$	(Bu_3P)	1.0	(4.0) ^{d)}	70	50	II	50

a) In benzene (5 ml), at 60 — 70° for 40 — 44 hr.

b)  $-CH_2-N(CH_3)_2$

c) Without adding organolithium compound.

d) Tributylphosphine.

π -Allylnickel bromide coordinated with tributylphosphine is also effective without adding the organolithium compounds. No significant dimerization was observed at room temperature.

One of the most important factors in this cyclodimerization seems to be the addition of a considerable amount of alcohols, as shown in Table 2. Without alcohol II was not formed but 4-vinyl-1-cyclohexene and 1,5-cyclooctadiene were obtained in low yields. On the other hand, addition of a large amount of alcohol resulted in the formation of higher boiling products. Benzylalcohol was also available as an active hydrogen compound, but acetic acid decomposed the nickel catalysts. Triphenylphosphine complexes were not applicable, because they were poorly soluble.

Table 2. Effect of Alcohols on the Cyclodimerization^{a)}

No.	Catalyst ^{b)}		Alcohol		Product	Yield (%)
	(mmole)		(mmole)			
1	1.5	CH ₃ OH	2.5	COD, ^{c)} VCH ^{d)}	trace	
2	1.5	CH ₃ OH	25	II	70	
3	1.5	CH ₃ OH	75	II	45 ^{e)}	
4	1.5	C ₆ H ₅ CH ₂ OH	5	dimers	n.d.	
5	1.5	C ₆ H ₅ CH ₂ OH	20	II	70	

a) In benzene (2.3 ml), at 60 — 70° for 40 hr. Butadiene, 80 — 110 mmole.

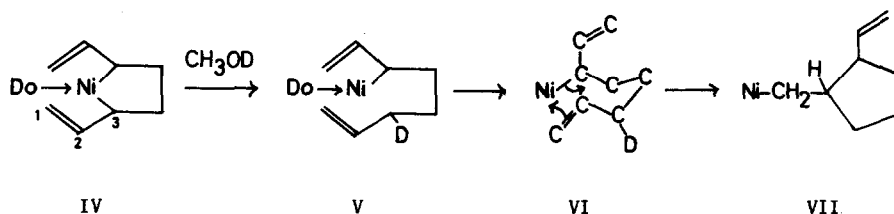
b) (Bu₃P)₂NiCl₂ : III = 1.5 : 1.5.

c) 1,5-Cyclooctadiene.

d) 4-Vinyl-1-cyclohexene.

e) Formation of higher boiling products was confirmed by gas chromatography.

In connection with a mechanism of the cyclodimerization, the experiment using CH₃OD is interesting to note. When the experiment (No. 1 in Table 1) was duplicated with exception that CH₃OD was used in place of CH₃OH, the product was found by mass spectrometry to be C₈H₁₁D of 50 % isotopic purity. The nmr spectrum showed deuterium labelling at the 3-carbon atom. This fact suggests that the complexation with nickel atom occurs at the 3-carbon atom. The cyclodimerization may be explained by the following intermediates IV — VII.



σ -Complex [IV] is formed by coordination of strong donor molecule, i.e., tributylphosphine, followed by alcoholysis. The terminal double bond in VI participates in an insertion between nickel-carbon bond to form cyclopentane ring. The ring closure like VI by intramolecular insertion to form a five-membered ring has been postulated for the reactions of organo-aluminum (4, 5) and -nickel (6) compounds.

REFERENCES

1. C. W. Bird, "Transition Metal Intermediates in Organic Synthesis," Academic Press, New York, 1967, p. 30.
2. H. Müller, D. Wittenberg, H. Seibt, and E. Scharf, Angew. Chem., International Ed., 4, 327 (1965).
3. A. Kasahara and T. Izumi, Bull. Chem. Soc. Japan, 42, 1765 (1969).
4. K. Ziegler, "Organometallic Chemistry," H. Zeiss, Ed., Reinhold Publishing Corp., New York, N. Y., 1960, p. 194.
5. G. Hata and A. Miyake, J. Org. Chem., 28, 3237 (1963).
6. G. P. Chiusoli and L. Cassar, Angew. Chem., 79, 177 (1967).

* W. D. Huntsman and R. P. Hall, J. Org. Chem., 27, 1988 (1962), reported n_D^{27} 1.4557 for II.