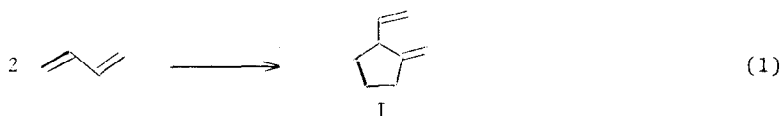


NICKEL-CATALYZED REACTION OF BUTADIENE WITH STRAINED RING OLEFINS.
FORMATION OF FOUR-MEMBERED CYCLIC COMPOUNDS

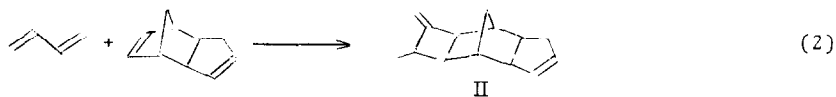
Susumu Yoshikawa, Satoshi Nishimura, Jitsuo Kiji and Junji Furukawa
Department of Synthetic Chemistry, Kyoto University,
Kyoto 606, Japan

(Received in Japan 17 March 1973; received in UK for publication 27 June 1973)

We have recently reported that butadiene is dimerized selectively to 2-methylenevinylcyclopentane (I).¹⁾ On the other hand, highly reactive strained



ring olefins such as norbornene or norbornadiene are catalytically converted into dimers or polymers of various kinds, depending on catalysts used.²⁾ We now report that some strained ring olefins react with butadiene to form the four-membered cyclic compound as expressed by Eq. 2.



In a glass tube was placed $(n\text{-Bu}_3\text{P})_2\text{NiBr}_2$ (1.5 mmol) and NaBH_4 (1.5 mmol) in ethanol (4 ml). Then dicyclopentadiene (20 mmol) was added, followed by liquified butadiene (36 mmol) at -78°C . The tube was sealed with a flame and heated at 80°C . Glpc analysis after 24 hr indicated that the butadiene-dicyclopentadiene coupling product (II) (14.6 mmol) and methylenevinylcyclopentane (I) (2 mmol) were present. The NMR spectrum of II exhibited $=\text{CH}_2$ and $-\text{CH}_3$ protons at 5.4 and 8.9 τ , respectively. When hexadeuterobutadiene, C_4D_6 , instead of butadiene was allowed to react with dicyclopentadiene, the coupling product (II'),

$C_{14}H_{12}D_6$ was obtained. The absorptions due to $=CH_2$ and $-CH_3$ groups are absent from the spectra of II'.

The activities of the catalyst towards the cooligomerization as well as the homoooligomerization by nickel catalysts were summarized in Table 1.

Table 1. Reaction of Butadiene with Dicyclopentadiene^a

Ni Compd.	Products, yield (%)	
	I, (C ₈ H ₁₂) ^b	II, (C ₁₄ H ₁₈) ^c
(n-Bu ₃ P) ₂ NiBr ₂	10.1	73
(n-Bu ₃ P) ₂ NiCl ₂	24.2	15
(n-Bu ₃ P) ₂ Ni(CN) ₂	0	0
(n-Bu ₃ P) ₂ Ni(NO ₃) ₂	6.6	0

^a [Ni] = [NaBH₄] = 1.5 mmol; butadiene, 36 mmol; dicyclopentadiene, 20 mmol; ethanol, 4 ml; 80°C for 24 hr.

^b Based on butadiene used.

^c Based on dicyclopentadiene used.

Catalysts effective for the oligomerization of butadiene are also effective for the cooligomerization (Eq. 2). Therefore, I and II were formed competitively. Strained ring olefins such as norbornene and 5-ethylidene-2-norbornene react with butadiene to give the corresponding coupling products. Reaction 2 is considered to involve a 1,3-shift³⁾ of one hydrogen of butadiene.

References

- 1) J. Kiji, K. Masui and J. Furukawa, Bull. Chem. Soc. Japan, 44, 1956 (1971).
- 2) C. W. Bird, "Transition Metal Intermediates in Organic Synthesis," Academic Press, New York (1967), p. 32.
- 3) D. R. Coulson, J. Org. Chem., 37, 1253 (1972).