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DIMERIZATION OF 1-CYCLOPROPYL-1,3-BUTADIENE CATALYZED BY NICKEL(0)-TRIPHENYLPHOSPHINE COMPLEX

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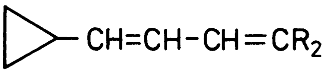
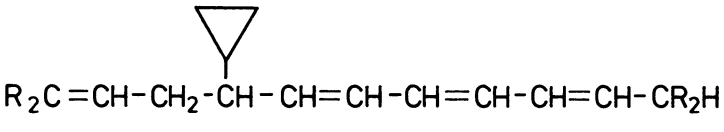
Abstract: Oligomerization of 1-cyclopropyl-1,3-butadiene (1) was accomplished by the catalytic action of nickel(0)-triphenylphosphine. The incorporation of the cyclopropane ring was evident since the dimer 2 isolated in ca. 50% was 4-cyclopropyl-1,5,7,9-undecatetraene. The head-to-head type structure of 2 was proved by the use of 1-cyclopropyl-4,4-dideuterio-1,3-butadiene (1d).

Although the oligomerization of 1,3-butadiene and higher conjugated polyenes are well known,[1] there has been no report describing a similar reaction of vinylcyclopropanes, a homo-1,3-diene. In the presence of nickel(0) catalyst[2] as well as other metal catalysts,[3] vinylcyclopropane derivatives merely undergo isomerization (followed by CO insertion in some cases). Recently, however, we observed that bis(1,5-cyclooctadiene)nickel(0)-triphenylphosphine (1 : 1) catalyzed the oligomerization of 1-cyclopropyl-1,3-butadiene (1).[4] Examinations of the structure of a dimer produced in ca. 50% yield revealed that it was a linear dimer, 4-cyclopropyl-1,5,7,9-undecatetraene (2). Thus, the present result provides the first example of such reactions that a vinylcyclopropane moiety is incorporated in the dimerization catalyzed by the transition metal complexes.

A benzene (15 ml) solution of 1 (17 mmol) was heated in a sealed glass tube at 70°C in the presence of a small amount (0.6 mmol) of Ni(COD)$_2$-P(Ph)$_3$ (1 : 1). After 40 h, 1 was consumed to an extent of 77% of the initial amount. The GLC analysis of the resultant mixture indicated that there were a major component and several minor ones. The major product was isolated by means of distillation (55-58°C (0.03 mm), 60% by weight based on the consumed amount of 1) and prepara-



1 : R = H
1d : R = D



2 : R = H
2d : R = D

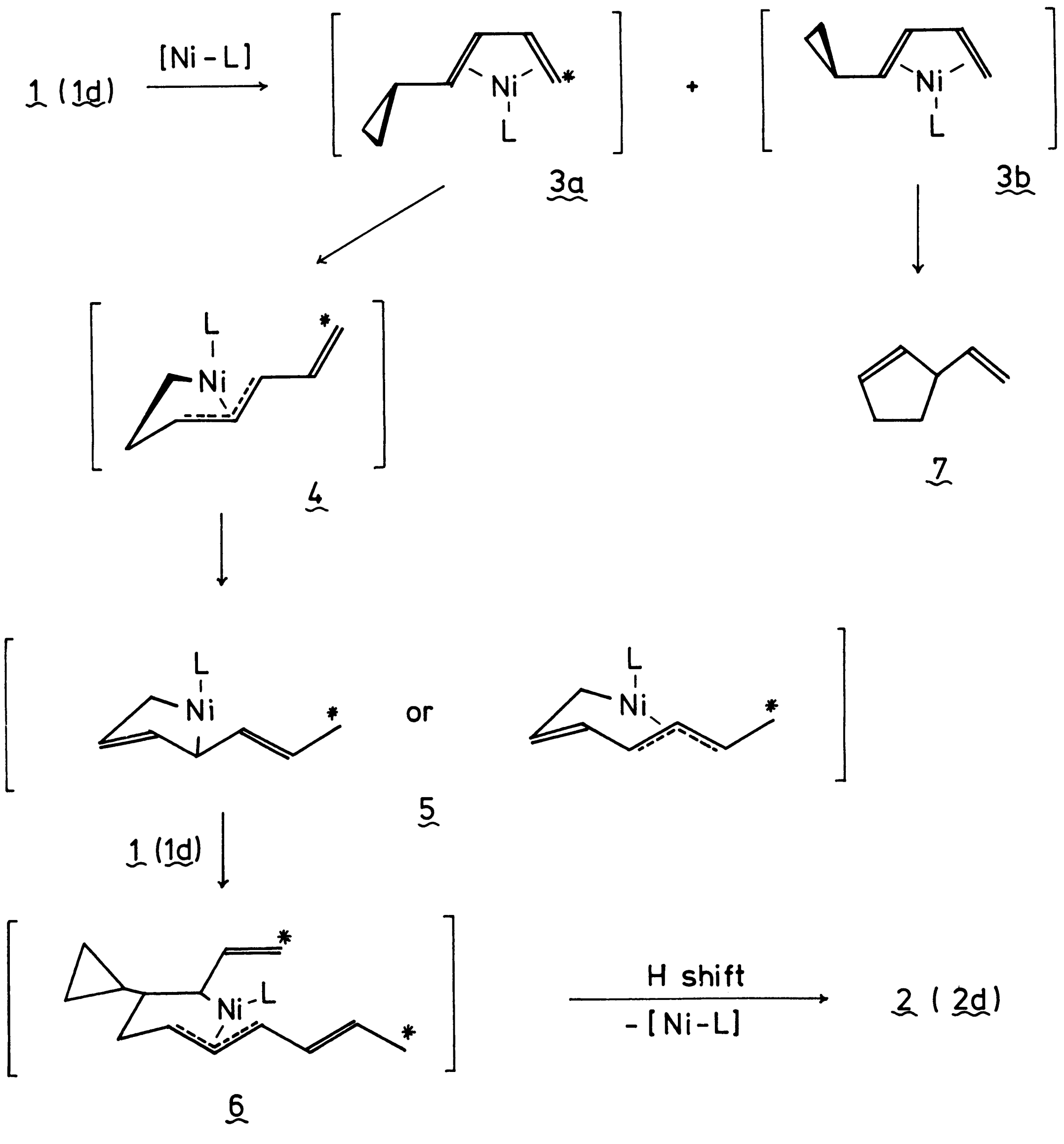
tive GLC (the peak area of the major product being 85% of the total area). The mass spectral analysis showed that the major product was a dimer (m/e 188, M^+ (23)). The base peak was observed at m/e 147 (100), suggesting the presence of an allyl group. The UV spectrum indicates that the product should have a conjugated triene moiety: UV max (ethanol) 261 nm (log ε 4.49), 269 (4.57), and 279 (4.45). The presence of a cyclopropyl, a methyl, and a vinyl group was suggested by the ^{1}H-NMR spectrum: ^{1}H-NMR (C_6D_6) δ -0.1-0.1 (m, 2H), 0.25-0.95 (m, 3H), 1.1-1.6 (m, 1H), 1.68 (d of d, *J* = 7.5 and 2.0 Hz, 3H), 1.95-2.45 (br t, *J* = ca. 6 Hz, 2H), 4.8-5.1 (m, 2H), and 5.3-6.6 (m, 7H). The product gave a satisfactory microanalysis for $C_{14}H_{20}$ and hence the structure **2**[5] was assigned. The ^{13}C-NMR was also consistent with the proposed structure.[6]

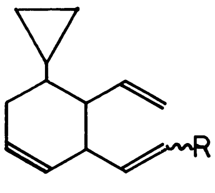
The structure was further confirmed by the following experiments. Ozonolysis of **2**, followed by the silver oxide work-up, gave cyclopropylsuccinic acid, mp 137.0-137.8°C,[7] in 48% yield. Catalytic hydrogenation of **2** over deactivated platinum catalyst yielded 4-cyclopropylundecane (80%), which was identical with an authentic sample prepared from dicyclopropyl ketone.[8]

The fact that **2** is a head-to-head type dimer has been proved by carrying out the reaction with 1-cyclopropyl-4,4-dideuterio-1,3-butadiene (**1d**).[9] The resultant dimer was found as 1,1,11,11-tetradeuterio derivative **2d**: ^{1}H-NMR (C_6D_6) δ 0.0-0.1 (m, 2H), 0.3-0.8 (m, 3H), 1.3-1.6 (m, 1H), 1.6-1.8 (m, 1.3H), 2.13 (t, *J* = 6.5 Hz, 1H), 2.17 (t, *J* = 6.5 Hz, 1H), 5.0-5.2 (m, 0.3H), and 5.4-6.8 (m, 7H). The intensity of the signals due to the terminal methyl and terminal methylene group (underlined) was markedly decreased.

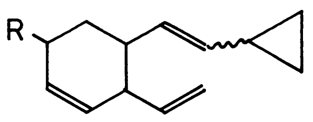
In connection with the results obtained in the reaction of 1-substituted 1-cyclopropyl-1,3-butadienes,[2] the dimerization of **1** to produce **2** may be explained in the following manner. The preferred conformation of a π-complex produced in the reaction of *E*-**1** will most probably be **3a**. The cyclopropane ring cleavage of **3a** should produce a transoid σ,π-allyl complex **4**, which is incapable of producing five membered cyclic products. On the other hand, **3b** can yield vinylcyclopentenes.[2,10] Indeed, the formation of 3-vinylcyclopentene (**7**) was detected in the GLC analysis of the corresponding fraction, although the yield of **7** was less than 10%. Since **1** lacks an additional group at the C-1, the complexation of a second molecule of **1** will be feasible at a certain stage of the reaction and the carbon-carbon bond formation between the previously complexed and ring cleaved **1** and the freshly complexed **1** may occur to yield the intermediate complex **6**.[11] The elimination of the olefinic ligand accompanied by hydrogen shifts will produce **2**.[1,12] The deuterium labeling experiment provided certain informations for the mechanism of the present oligomerization. For example, the cyclopropane cleavage should be accompanied by the 1,6-hydrogen shift. However, the drawing of a detailed picture of the dimerization mechansim should wait until further informations being at hand. A possibility that **1** was at first isomerized to 1,3,5-heptatriene and its subsequent reaction with **1** produced **2** is unlikely because the reaction of **1** in the presence of an equivalent amount of either 1,3,5-hexatriene or 1,3,5-heptatriene resulted in the formation of **8** and **9**,[13] which were not detected in the oligomerization product of **1**.

Scheme[14]





8 R= H or Me



9 R = H or Me

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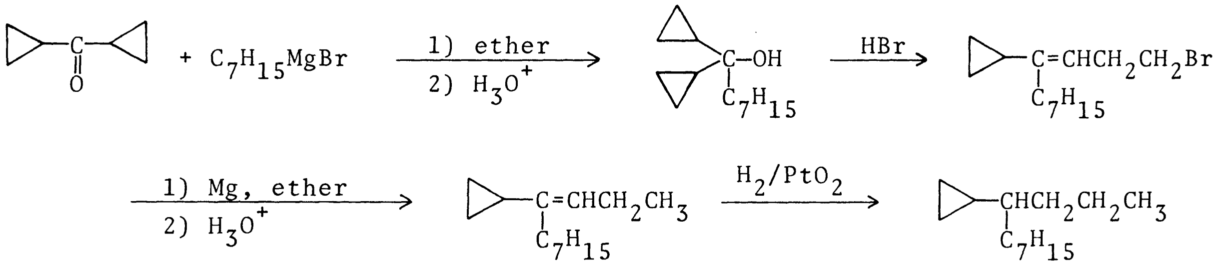
REFERENCES AND NOTES

1) P. W. Jolly and G. Wilke, "The Organic Chemistry of Nickel," Vol. 2, Academic Press, New York, N. Y. (1975).
2) M. Murakami and S. Nishida, Chem. Lett., **1979**, 0000: the preceding paper.
3) R. G. Salomon, M. F. Salomon, and J. L. C. Kachinski, J. Am. Chem. Soc., **99**, 1043 (1977); V. Aris, J. M. Brown, J. A. Conneely, B. T. Golding, and D. H. Williamson, J. Chem. Soc., Perkin Trans. **2**, **1975**, 4; S. Sarel, Acc. Chem. Res., **11**, 204 (1978); and references cited therein.
4) Prepared from 4-bromo-1-cyclopropyl-1-butene by dehydrobromination with potassium *t*-butoxide in *t*-butyl alcohol, *E* : *Z* = 87 : 13 (M. Hanack and H. Eggensperger, Justus Liebigs Ann. Chem., **663**, 31 (1963)).
5) Presumably the all trans isomer, although the geometry around the double bonds has not been fully established.
6) ^{13}C-NMR ($CDCl_3$): δ 3.62 (t), 4.33 (t), 13.24 (d), 15.70 (q), 39.94 (t), 47.61 (d), 115.77 (t), 122.66 (d), 124.80 (d), 125.19 (d), 126.75 (d), 137.08 (d), and 138.71 (d).
7) ^{1}H-NMR (acetone-d_6) δ 0.1-0.7 (m, 4H), 0.72-1.16 (m, 1H), 2.08 (m, 1H), 2.62 (d of d, *J* = 16 and 5.5 Hz, 1H), 2.73 (d of d, *J* = 16 and 9 Hz, 1H). *Anal*. Calcd for $C_7H_{10}O_4$: C, 53.17; H, 6.37. Found: C, 53.02; H, 6.34.
8) Prepared according to the following sequence:



9) Labeled to an extent of 89% (^{1}H-NMR).
10) For related discussions, see ref. 2.
11) The fact that nickel(0) catalyzed the ring cleavage was proved by carrying out the reaction in ethanol. 1,3,5-Heptatriene was produced in ca. 30% yield after 40 h at 70°C.
12) The process is similar to those proposed in the oligomerization of 1,3-butadiene (P. Heimbach, Angew. Chem., Int. Ed. Engl., **12**, 975 (1973); G. Henrici-Olivé and S. Olivé, "Coordination and Catalysis," Verlag Chemie, Weinheim (1977)).
13) A complex mixture of oligomers was actually produced. For example, the reaction of **1** and 1,3,5-hexatriene (1 : 1) in the presence of 1/10 equivalence of the catalyst gave a dimer fraction (40%), which was mainly composed of **2**, **8**, and **9** in ca. 1 : 1 : 1 ratio (GLC).
14) The position whish is labeled by deuterium is marked by an asterisk.

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