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NOVEL CYCLODIMERIZATION AND CYCLOTRIMERIZATION OF 3-HEXYNE BY CATIONIC NICKEL HYDRIDE COMPLEX

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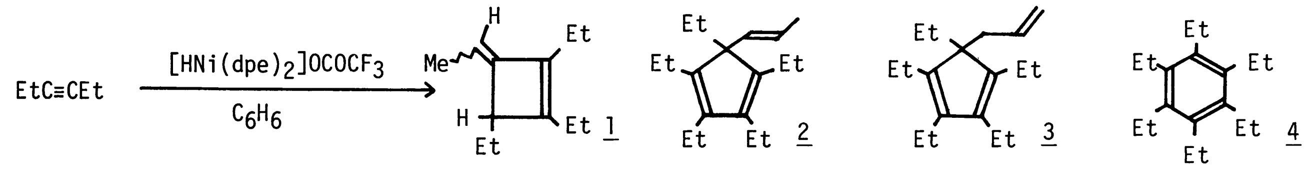
Cationic nickel hydride complex, [HNi(dpe)$_2$]OCOCF$_3$ (dpe=Ph$_2$PCH$_2$-CH$_2$PPh$_2$), catalyzed the novel cyclodimerization and cyclotrimerization of 3-hexyne to afford 1,2,4-triethyl-3-ethylidenecyclobutene 1, pentaethyl-5-propenylcyclopentadiene 2, and pentaethyl-5-allylcyclopentadiene 3.

Previously we reported the reaction of 3-hexyne with CO$_2$ by nickel(0) complexes yielding tetraethyl-2-pyrone accompanied by the formation of novel cyclotrimers, i.e., 2 and 3.$^{1)}$ The formation of these trimers requires the transfer of hydrogen and a certain nickel hydride species has been supposed to be an intermediate. In this paper we describe the results of the reaction of 3-hexyne by a cationic nickel hydride complex, [HNi(dpe)$_2$]OCOCF$_3$.$^{2)}$

When 3-hexyne was allowed to react in the presence of the nickel hydride complex in benzene at 120°C in a glass ampoule, a novel cyclodimer 1$^{3)}$ and three cyclotrimers (2, 3, and hexaethylbenzene 4) were yielded in considerable yields together with a viscous oil.$^{4)}$



Catalytic oligomerization of disubstituted alkyne accompanied by hydrogen transfer has not been hitherto known.$^{5)}$ Results of the reaction are summarized in Table 1.

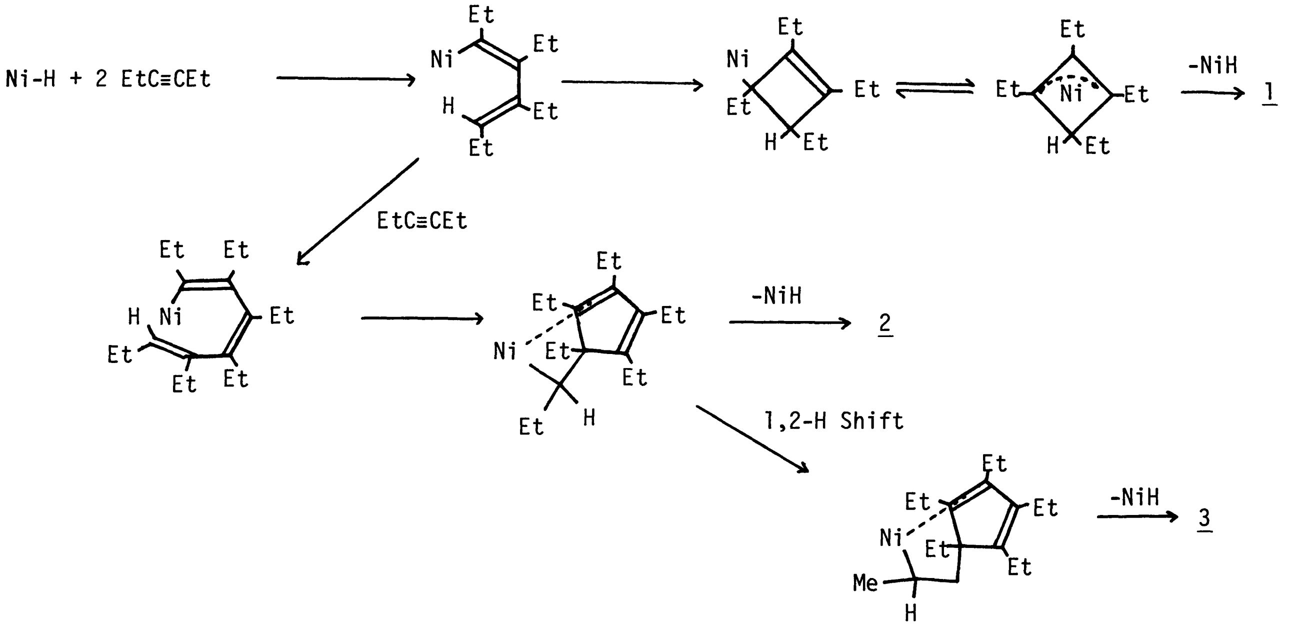
Table 1. Reaction of 3-hexyne by nickel complexes.
3-Hexyne 8.8 mmol, catalyst 0.4 mmol, benzene 5 ml; 120°C, 5 h.

Catalyst	Conversion (%)	Product(%)$^{a)}$			
		1	2	3	4
Ni(dpe)$_2$ + AcOH (1:1)	9	1	2	2	trace
+ PhOH (1:1)	10	1	3	5	trace
[HNi(dpe)$_2$]OCOCF$_3$	99	36	4	16	3
Ni[P(OMe)$_3$]$_4$ + CF$_3$CO$_2$H (1:1)	19	0	4	3	9

a) Based on the 3-hexyne charged(by GLC). 4-Octyne, after 5 h reaction by [HNi(dpe)$_2$]-OCOCF$_3$ at 90°C, afforded 1,2,4-tripropyl-3-propylidenecyclobutene(18 %), pentapropyl-5-(1-butenyl)cyclopentadiene(4 %), pentapropyl-5-(2-butenyl)cyclopentadiene(9 %), and hexapropylbenzene(trace) as well as viscous oil(conversion 86 %).

Ni(dpe)$_2$ or Ni[P(OMe)$_3$]$_4$ alone showed scarcely any catalytic activity under similar reaction conditions. The data in Table 1 show that the ligand in the nickel complex plays an important part for the dimerization of 3-hexyne.

Although the mechanism remains to be elucidated, the following is suggested as one of the possible routes by analogy with the one proposed by Maitlis on the palladium(II) induced cyclotrimerization of alkynes.$^{5)}$



References and notes

1) Y. Inoue, Y. Itoh, and H. Hashimoto, Chem. Lett., 1978, 633.

2) Schunn reported the formation of the complex but he isolated no solid product; R. A. Schunn, Inorg. Chem., 9, 394(1970). We obtained the complex as orange yellow solids by the addition of an equimolar amount of CF$_3$CO$_2$H to Ni(dpe)$_2$ in benzene. M.p. 140°C in N$_2$(dec.). Anal. Found: C, 66.89; H, 5.09 %. Calcd. for C$_{54}$H$_{49}$O$_2$F$_3$P$_4$Ni: C, 66.04; H, 5.35 %. IR(KBr, cm^{-1}) 1930(νNi-H). PMR(CH$_2$Cl$_2$, δ) -12.95(Ni-H, quintet, J=5.4 Hz).

3) IR(neat, cm^{-1}) 800(-CH=C<). PMR(CD$_3$COCD$_3$, δ) 0.7-1.2(CH$_3$, m, 9H), 1.2-1.7(CH$_2$, m, 2H), 1.59(C$\underline{H}_3$CH=, d, J=7.4 Hz, 3H), 1.8-2.4(CH$_2$, m, 4H), 2.72(CH, t, J=5.7 Hz, 1H), 4.58(CH$_3$$\underline{CH}$=, q, J=7.4 Hz, 1H). CMR(CD$_3$COCD$_3$, δ)152.9(s), 144.0(s), 143.8(s), 102.8(d), 48.5(d), 24.8, 20.7, 20.4, 14.0, 13.7, 12.6, 11.9. UV(n-hexane, nm) λmax 256(ε6500). We could not determine the geometry of the ethylidene moiety. This compound decomposes gradually at ambient temperature and so must be kept below 0°C.

4) The IR spectrum of this oil indicated the existence of CF$_3$CO$_2$- group, but further analysis was not performed.

5) It has been reported that the dimer of this type is formed on the thermal decomposition of a nickel-cyclobutadiene complex; G. Criegee, J. Dekker, W. Engel, P. Ludwig, and K. Noll, Chem. Ber., 96, 2362(1963). Five-membered ring formation from alkynes by palladium compounds has also been reported; T. R. Jack, C. J. May, and J. Powell, J. Am. Chem. Soc., 99, 4707(1977); P. M. Maitlis, Acc. Chem. Res., 9, 93(1976), and references cited therein.

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