STEREOSPECIFIC PHOTODIMERIZATION OF UNSATURATED COMPOUNDS INDUCED BY NICKEL COMPLEXES

Akira MIYASHITA,[*] Shohgo IKEZU, and Hiroyuki NOHIRA

Department of Applied Chemistry, Faculty of Engineering,

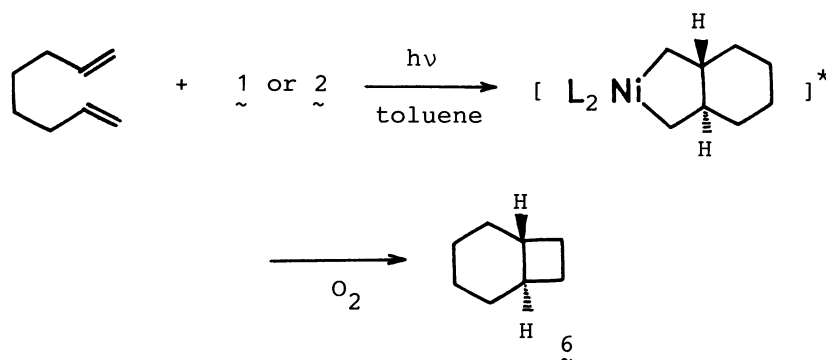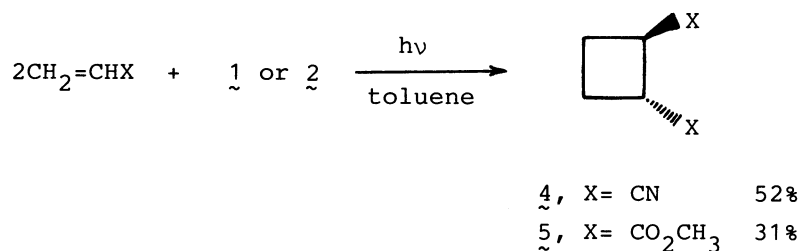Saitama University, Urawa, Saitama 338

Irradiation of (ethylene)bis(triphenylphosphine)nickel (1) or bis(triphenylphosphine)nickelacyclopentane induced stereospecific cyclodimerization of substituted olefins such as acrylonitrile and methylacrylate affording trans-1,2-disubstituted cyclobutanes, while 1,7-octadiene was converted to trans-bicyclo[4.2.0]octane. Ethylene was photochemically dimerized to cyclo- and linear dimers induced by 1.

Metallacyclopentane complexes have been suggested as active intermediates in a number of transition metal-olefin reactions.[1] Of particular interests are regio- and stereospecific cyclodimerization of unstrained unsaturated compounds catalyzed by transition metal complexes. For catalytic cyclodimerization of ethylene and stoichiometric formation of cyclobutane derivatives from unsaturated compounds, 5-co-ordinate tris(triphenylphosphine)nickelacyclopentane (3) is reported to be effective.[2] In these reactions, exchange of olefins in the bis-olefin complexes which are in equilibrium with active nickelacyclopentane intermediates would lead to the formation of new metallacycles, which undergo reductive elimination giving cyclobutane derivatives.[3] However, bis(triphenylphosphine)nickelacyclopentane (2)
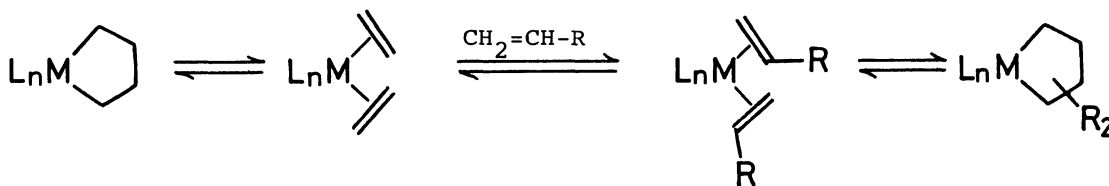
is reported to be virtually inert for cyclodimerization of olefins and proved not to be in equilibrium with the bis-olefin complex.[2,4] Furthermore, 1 is far inactive for cyclodimerization under mild condition. These results may suggest that the bis-olefin complex and active nickelacyclopentane complexes generated from 3 have different configuration from their isolable forms.[4] In order to get more insight into reaction mechanism for cyclodimerization catalyzed by organonickel complexes, we have studied the photochemical reactions of unsaturated compounds with 1 or 2. In this paper we report stereospecific cyclodimerization of substituted olefins and terminal dienes by photochemically activated Ni complexes, and describe linear and cyclodimerization of ethylene.

A toluene solution of a mixture of acrylonitrile (6.8 mmol) and 1 or 2 (0.34 mmol) was irradiated in a pyrex tube with a high pressure mercury lamp (100 W) for 46 h at 17 °C. After exposing the reaction solution in air, it was found to give trans-1,2-dicyanocyclobutane (4) with 52% yield based on Ni.[5] Methylacrylate was also specifically photodimerized to trans-1,2-cyclobutane dimethylcarboxylate (5) with 31% yield (46 h, 17 °C) accompanied by a trace of cis-isomer.[6] No cyclodimerization took place in the absence of light. These observations are in contrast

$$2CH_2=CHX \quad + \quad 1 \text{ or } 2 \quad \xrightarrow[\text{toluene}]{h\nu}$$

4, X= CN   52%

5, X= CO$_2$CH$_3$ 31%

$$\xrightarrow[\text{toluene}]{h\nu} \quad [\; L_2 Ni \;\;\;\;\;]^*$$

$$\xrightarrow{O_2}$$

6

to the work on cyclodimerization of the substituted olefins promoted by 3 which affords a mixture of trans- and cis-products.[2]

Ni complexes 1 and 2 photochemically induced the intramolecular stereospecific carbon-carbon bond formation of 1,7-octadiene to give trans-bicyclo[4.2.0]octane (6)

in 21% yield (40 °C, 26 h) after exposing in air.[2,7] No cis-isomers were obtained,

but inner-diene isomers of 1,7-octadiene were produced in 23% yield.

On the other hand, ethylene was found to be photochemically dimerized to linear

and cyclo-dimers. A toluene solution of 1 or 2 (0.34 mmol) in the presence of

ethylene (6.1 mmol) was irradiated at several temperature for 5 or 10 h to afford

cyclobutane, butene, methylcyclopropane and butane as summarized in Table 1.

However, no C_4-hydrocarbon product was obtained when these reactions were carried

out in the dark.[2] The yield and selectivity of cyclobutane formation varied with

the reaction conditions employed. The hydrogen source for the formation of butane

was determined by irradiating 7 which has ortho-deuterated triphenylphosphine

(PPh_3-d_6), in the presence of excess ethylene at 25 °C for 12 h. Butane generated

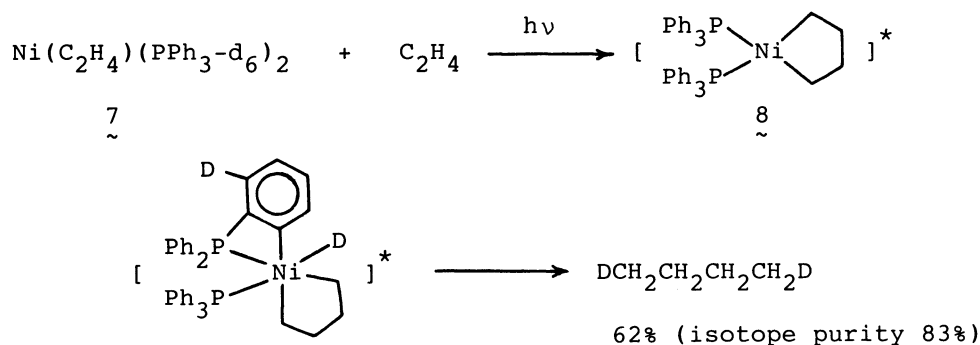from the reaction was collected by preparative GC (Durapak, 2 m, 50 °C) and

Table 1. Photodimerization of C_2H_4 with $Ni(C_2H_4)(PPh_3)_2$[a]

Run	Temp	Time	Product (%/Ni)[b]			
	°C	h	□	C_4H_8	$n-C_4H_{10}$	△
1	0	5	4	1	43	0
2	8	5	9	33	50	0
3	23	10	22	10	83	1
4	62	5	31	99	68	9
5[c]	23	10	0	0	0	0

a) In toluene, C_2H_4/Ni = 15, 450 W high pressure mercury lamp, in quartz

tube. b) All products were identified by the comparison of mass, NMR

spectra, and retention time of GC with these of authentic samples.

c) In the dark.

determined by mass spectroscopy to be 1,4-dideuterobutane with 83% isotopic purity.

This result suggests that the nickelacyclopentane intermediate (8) derived from

photochemical reaction of (7) with ethylene is apparently involved in the reaction,

$Ni(C_2H_4)(PPh_3-d_6)_2$ + C_2H_4 $\xrightarrow{h\nu}$ $[Ph_3P\diagdown Ni\diagup \bigcirc]^*$

7   8

$[Ph_2P\diagdown Ni\diagup^D \bigcirc]^* \longrightarrow DCH_2CH_2CH_2CH_2D$

62% (isotope purity 83%)

followed by deuterium migration from the ortho-position on the phenyl group of PPh_3-d_6 leading to reductive elimination of 1,4-dideuterobutane. The experimental fact that unsaturated compounds do not cyclodimerize without light, is compatible with the hypothesis that the photochemically activated bis-olefin nickel complex is formed in these reactions and plays an important role in the following cyclodimerization. These photo-induced facile and stereospecific carbon-carbon bond formation reactions of unsaturated compounds may be ascribed to the formation of nickelacyclopentane complexes as plausible intermediates. Further detailed kinetic and mechanistic studies are now in progress.

References

1) R.Noyori, Y.Kumagai, and H.Takaya, J. Am. Chem. Soc.,96, 634 (1974); P.Binger, Angew. Chem.,Int. Ed. Engl.,11, 609 (1972).

2) R.H.Grubbs and A.Miyashita, J. Am. Chem. Soc.,100, 7416 (1978); 99, 3863 (1977); J. Chem. Soc., Chem. Commun.,1977, 864.

3) R.H.Grubbs and A.Miyashita, J. Am. Chem. Soc.,100, 1300 (1978).

4) R.H.Grubbs and A.Miyashita, " Fundamental Research in Homogeneous Catalysis," ed by M.Tsutsui, Plenum Press, New York (1979), p.51 ; R.J.McKinney, D.L.Thorn, R.Hoffmann and A.Stockis, J. Am. Chem. Soc.,103, 2595 (1981); A.Miyashita, unpublished results.

5) trans-1,2-Dicyanocyclobutane: ^1H NMR ($CDCl_3$) δ 2.37 (m, 4H), 3.44 ppm (m, 2H), ^{13}C NMR ($CDCl_3$) δ 24.8 (t,CH_2), 26.7 (d, CH), 118.4 ppm (s, CN), Mass spectrum (EI, 75 ev) 106 (M^+), 88 ($C_4H_2N_2^+$), 53 ($C_3H_3N^+$), 28 ($C_2H_4^+$). W.L.Lehn and G.Raymond, U.S.Pat. 3265723 (1966).

6) trans-1,2-Cyclobutane dimethylcarboxylate: ^1H NMR ($CDCl_3$) δ 2.15 (m, 4H), 3.4 (m, 2H), 3.7 (s, 6H), ^{13}C NMR ($CDCl_3$) δ 22.0 (t, CH_2), 40.3 (d, CH), 51.8 (q, CH_3), 173.9 (s, CO), Mass spectrum (EI, 75 eV) 172 (M^+), 144 ($C_6H_8O_4^+$), 86 ($C_4H_6O_2^+$), 28 ($C_2H_4^+$). These are identical with the authentic sample prepared by the treatment of trans-1,2-cyclobutanecarboxylic acid chloride, obtained from the Aldrich Chemical Co., with methanol.

7) R.H.Grubbs and A.Miyashita, J. Organomet. Chem., 161, 371 (1978).