Tetrahedron. Vol. 30, pp. 405 to 407. Pergamon Press 1974. Printed in Great Britain

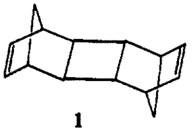
A NOVEL DIMERIZATION OF NORBORNADIENE BY NICKEL CATALYSTS

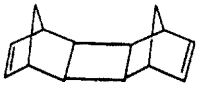
FORMATION OF *exo*-5-(*o*-TOLYL)-2-NORBORNENE

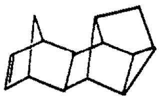
S. Yoshikawa, K. Aoki, J. Kiji and J. Furukawa*
Department of Synthetic Chemistry, Kyoto University, Kyoto 606, Japan

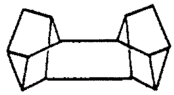
(*Received in Japan* 17 *May* 1973; *Received in the UK for publication* 28 *September* 1973)

Abstract—In amine norbornadiene is converted catalytically into *exo* - 5 - (*o* - tolyl) - 2 - norbornene by $(n\text{-}Bu_3P)_2NiX_2$—$NaBH_4$ (where X is anionic ligand: e.g., Br, Cl, or SCN), the ratio of which is less than 1. Addition of more amount of $NaBH_4$ leads to the formation of [2 + 2] cycloaddition products.


1

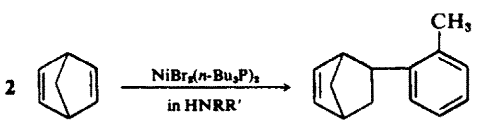

2


3


4

Norbornadiene is converted catalytically into a variety of dimers, depending on the transition metal catalysts used.[1] Transition metal - catalysed reaction is in general delicately influenced by the valence-state of the metal, the presence of either anionic or neutral ligands, or by solvent. It has been reported that the catalyst based on $(n\text{-}Bu_3P)_2NiX_2$ is effective for the reactions of butadiene; e.g., the cyclo-dimerization involving hydrogen transfer to 2-methylenevinylcyclopentane,[2] and the reaction with strained ring olefin[3] or with amine.[4] The authors have proposed that the active species of this catalyst is a zero-valent nickel combined with protonic acid.[5] Now it has been found that this type of catalyst is effective for a novel dimerization of norbornadiene in amines as solvents.

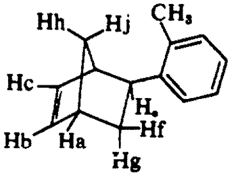
When norbornadiene was allowed to react under the influence of bis (tris - n - butylphosphine) nickel bromide in some amines, *exo*-5-(*o*-tolyl)-2-norbornene was formed selectively. The structure of **5** was established as follows.



5 (1)

The NMR spectrum of **5** has a double doublet at 2·74 ppm due to the proton on the C-5 carbon atom. It is generally accepted that *endo*-proton on the C-5 carbon of the *exo*-substituent has a higher chemical shift than the *exo*-proton of the corresponding *endo*-isomer and that couples to two neighbouring protons on the C-6 carbon atom but not to the proton on the bridge-head,[6] giving a double doublet. The *exo*-proton on the C-5 carbon of *endo*-5-(*p*-tolyl)-2-norbornene, prepared by the Diels–Alder reaction of cyclopentadiene with *p*-tolylstyrene, was observed to appear in low-field at 3·3 ppm. The assignment of the NMR spectrum of **5** is listed in Table 1.

Table 1. NMR data of **5**



Chemical shifts[a] ppm	Assignment	Coupling constants, Hz
7·34 ~ 7·09	aromatic protons	
6·32	H_c	J_{bc}, 5·5; J_{cd}, 2·6;
6·23	H_b	J_{ab}, 3·0
2·98	H_a, H_d	J_{ef}, 9·0; J_{eg}, 5·3;
2·74	H_e	J_{ed}, 1·4
2·29	$-CH_3$	J_{fg}, 11·0; J_{af}, 2·0
1·71	H_f	J_{hi}, 8·0:
1·67	H_h	
1·54	H_i	
1·51	H_g	

[a] Chemical shift in $CDCl_3$ relative to internal TMS.

The hydrogenation product of **5** has the characteristic absorptions of *o*-disubstituted aromatic ring between 1660 and 2000 cm^{-1} and strong absorptions at 730, 750 and 760 cm^{-1} due to C–H out-of-plane vibrations. From all these analytical data dimer **5** was proved to be *exo*-5-(*o*-tolyl)-2-norbornene.

The nickel complexes combined with sodium borohydride showed higher catalytic activities. The effect of the amount of sodium borohydride is graphically shown in Fig 1.

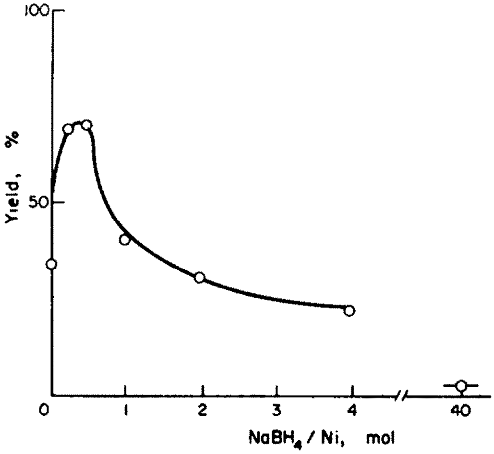


Fig 1. Dependence of yield on the amount of NaBH$_4$ at 80° for 16 h; 0·32 mM-(n-Bu$_3$P)$_2$NiBr$_2$, 1 ml-iso-propylamine with 7·3 mM-norbornadiene.

In morpholine or piperidine the reaction proceeded smoothly without using sodium borohydride. In this case the nickel complexes are reduced by the amine to a low-valent active species. Previously it was pointed out that the phosphine complexes of nickel salt are reduced to $L_2Ni + HX$ by the addition of less than 1 mole of the reducing agent such as sodium borohydride or sodium alkoxide, giving a precursor of the active species for the cyclodimerization of butadiene to 2 - methylene - vinylcyclopentane.[2,5] Catalysts of the same composition were also effective for this dimerization of norbornadiene. The addition of more amount of sodium borohydride increased the formation of dimers **1** and **2** due to the cycloaddition, which is presumably catalyzed by zero-valent nickel.[7,8]

Among nickel complexes studied, n-butylphosphine complexes of chloride and bromide were the best catalysts for the dimerization into **5**, while the corresponding nitrate favored the formation of **1** and **2**. Table 2 summarizes the catalytic efficiencies of the different nickel complexes.

In this reaction the amine plays an important role and seems to act as a weak electron donor molecule and to participate in the stabilization of the reaction intermediate. The IR spectrum of the recovered nickel complex shows that it is converted into an amine complex after the reaction. Actually, after the reaction in piperidine brown crystals of a nickel complex were recovered. The IR spectrum in Nujol null shows a strong absorption at 3180 cm^{-1}, which is 120 cm^{-1} lower than that of pipieridine. A considerable amount of **1** and **2** was formed in primary amines such as i-propylamine or n-butylamine. This is attributed to the formation of zero-valent nickel by the reduction with such amines. Dimer **5** was also formed in pyridine. Therefore, the hydrogen on the N atom is not always necessary during this reaction. Pyrrole, benzylamine, and pyrolidone led to the polymerization of norbornadiene. There is no relationship between pK_b of amine and the yield of **5** (Fig 2).

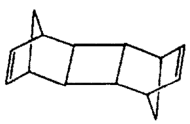
Table 2. Dimerization of norbornadiene at 80°C[a]

Catalyst	Yield (%) 1	2	5	Total yield
$NiCl_2(PBu_3)_2$	1·7	8·7	60·4	70·8
$NiCl_2(PBu_3)_2$[b]	0·4	2·3	10·7	13·4
$NiBr_2(PBu_3)_2$		0·9	69·2	70·1
$Ni(NO_3)_2(PBu_3)_2$	11·8	50·2	19·5	81·5
$NiBr_2(PPh_3)_2$	0·3	6·0	15·4	21·7
$Ni(SCN)_2(PBu_3)_2$	0·3	2·8	11·6	14·7

[a] In 1 ml of i-propylamine for 18 h. Ni, 0·5 mmol; NaBH$_4$, 0·25 mmol; norbornadiene, 14 mmol.

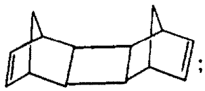
[b] Without using NaBH$_4$.

1



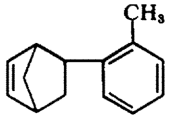
;

2



;

5



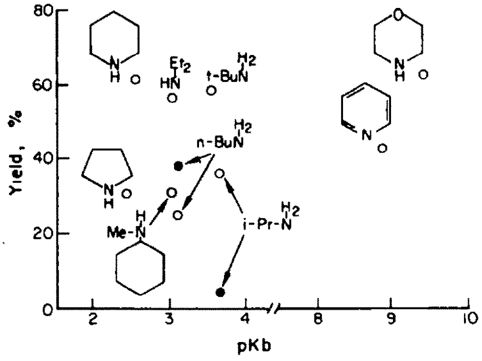
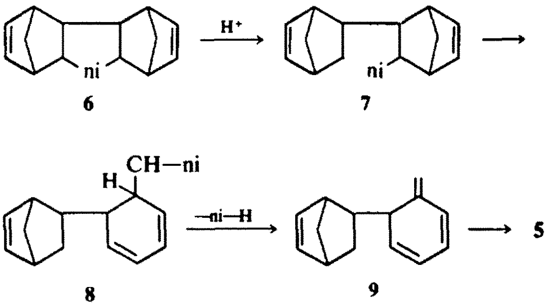


Fig. 2. Dependence of yield on amine at 80°C for 24 h (**5** (○), **1** + **2** (●)); 0·32 mM-(n-Bu$_3$P)$_2$NiBr$_2$, 0·30 mM-NaBH$_4$, 1 ml-iso-propylamine with 7·3 mM-norbornadiene.

In alcohol the rapid polymerization occurred, and in thiol the addition of thiol to the olefinic double bond was the major reaction.

Dimers **1** and **2** were stable toward the catalyst under the reaction conditions. When 211 mg of a mixture of **1** and **2** (1:3) were allowed to react under the influence of 161 mg of NiBr$_2$(n-Bu$_3$P)$_2$ and 3 mg of NaBH$_4$ in 0·6 ml of morpholine at 80° for 18 h, 61 and 82% of **1** and **2**, respectively, were recovered unchanged. No dimer other than **1** and **2** was detected. Only a small amount of polymeric product was formed.

Insufficient information is in hand to reasonably define the reaction mechanism for this catalytic reaction. However, by analogies with the dimerization of butadiene[5] and with the isolation of metallocyclic intermediate of [2 + 2] cycloaddition reactions,[9] it is proposed in the present case that the reaction is an acid-promoted dimerization on zero-valent nickel. The following mechanism of homolytic coupling on zero-valent nickel followed by protonolysis seems to be plausible:



where ni means the active source of the catalyst. Amine participates in the stabilization of intermediates **6–8** through the coordination to the Ni atom. The moderately stabilized intermediate (**6**) is hydrolysed to **7**, which is converted into **5** via **8** and **9**.

Driving forces of the isomerization are the strain energy of C1—C7 bond and the stabilization energy of the aromatization. This type of the β-fission of a strained ring bond catalysed by Ni has been observed on the skeletal isomerization of vinylcyclopropane to 1,3-diene.[10]

EXPERIMENTAL

Commercially available norbornadiene was dried over Molecular Sieve 3A. Solvents were purified by the conventional method and used under an atmosphere of N$_2$. Phosphine complexes of Ni salts were prepared by the method as described earlier.[2]

The NMR spectra were determined on Varian 220 MH$_z$ spectrometer Model HR220 of Department of Hydrocarbon Chemistry, Kyoto University, using TMS as an internal standard.

Dimerization of norbornadiene. The nickel phosphine complex and NaBH$_4$ were placed in a glass tube (20 mm in dia). The tube was immediately fitted with a 3-way stopcock. The atmosphere of the tube was replaced with N$_2$ by repeating evacuation and introduction of N$_2$. Solvent and norbornadiene were added in this order, and then the tube was sealed with a flame and heated. The mixture was subject to distillation without separating the catalyst. Distillation gave colorless liquid, b.p. 78° (3 mm), molecular weight, 184 (mass spectrometry). The reaction conditions are summarized in Table 2. The yields of the products were determined by gas chromatography using tetraline as an internal standard.

REFERENCES

[1] C. W. Bird, *Transition Metal Intermediates in Organic Synthesis* p. 32, and Refs cited. Academic Press, New York (1967)

[2] J. Kiji, K. Masui and J. Furukawa, *Bull. Chem. Soc. Japan* **44**, 1956 (1971)

[3] S. Yoshikawa, J. Kiji, S. Nishimura and J. Furukawa, *The 20th Symposium on Organometallic Chemistry*, Kyoto (1972)

[4] J. Furukawa, J. Kiji, S. Mitani, S. Yoshikawa, K. Yamamoto and E. Sasakawa, *Chemistry Letters* 1211 (1972)

[5] J. Kiji, K. Yamamoto, S. Mitani, S. Yoshikawa and J. Furukawa, *Bull. Chem. Soc. Japan* **46**, 1791 (1973)

[6] P. Laszlo and P. von R. Schleyer, *J. Am. Chem. Soc.* **86**, 1171 (1964)

[7] G. N. Schrauzer and S. Eichler, *Chem. Ber.* **95**, 2764 (1962)

[8] D. R. Arnold, D. J. Trecker and E. B. Whipple, *J. Am. Chem. Soc.* **87**, 2596 (1965)

[9] A. R. Fraser, P. H. Bird, S. A. Bezman, J. R. Shapley, R. White and J. A. Osborn, *Ibid.* **95**, 597 (1973)

[10] R. G. Miller and P. A. Pinke, *Ibid.* **90**, 4500 (1968)