

HYDROSILYLATION OF 1,3-BUTADIENE CATALYSED WITH A NICKEL(II) SALT-SODIUM BIS(2-METHOXYETHOXY)ALUMINIUM HYDRIDE SYSTEM*

M. ČAPKA and J. HETFLIŠ

*Institute of Chemical Process Fundamentals,
Czechoslovak Academy of Sciences, 165 02 Prague 6 - Suchbát*

Received April 15th, 1975

The addition of trichlorosilane and triethoxysilane to 1,3-butadiene catalysed with nickel(II) salt-sodium bis(2-methoxyethoxy)aluminium hydride or nickel(II) salt-tertiary phosphine-sodium bis(2-methoxyethoxy)aluminium hydride system gave 1-silyl-substituted 2-butenes as major products. The systems showed enhanced catalytic activity compared to nickel(II) or nickel(II)-phosphine catalysts and in their efficiency and selectivity were comparable to some zerovalent nickel complexes such as bis(1,5-cyclooctadiene)nickel and tetrakis(triphenylphosphine)nickel.

In previous papers we were concerned with the addition of chloro¹, alkyl-, and alkoxy-silanes² to 1,3-butadiene catalysed with compounds of divalent and zerovalent nickel. On the basis of the results obtained in these studies it was suggested that nickel(II) salts used as catalysts are first reduced by organosilicon hydrides to nickel(0) species, these being common intermediates for both the Ni(II)- and Ni(0)-catalysed additions³.

With the aim of providing further support for this assumption we effected the proposed reduction $\text{Ni(II)} \rightarrow \text{Ni(0)}$ by the addition of the more efficient reducing agent, sodium (2-methoxyethoxy)aluminium hydride (further referred to as the hydride). This hydride was chosen due to its excellent solubility in aromatic hydrocarbons and safe manipulation with it. In the present work we centered on comparison of the catalytic behaviour (activity and selectivity) of a nickel(II) salt-tertiary phosphine-the hydride system with that of some zerovalent nickel complexes, using the earlier studied hydrosilylations of 1,3-butadiene with trichloro- and triethoxysilane as model reactions.

The results presented in Tables I and II show some distinct differences in the course of both reactions and in their sensitivity to the addition of phosphine ligands. For that reason they will be discussed separately.

* Part XXXII in the series Catalysis by Metal Complexes; Part XXXI: This Journal 40, 3020 (1975).

TABLE I

Addition of Trichlorosilane (26 mmol) to 1,3-Butadiene (32 mmol) Catalysed with a Nickel Compound (0.04 mmol)–Triphenylphosphine (0.2 mmol)–Sodium Bis(2-methoxyethoxy)aluminium Hydride (0.1 mmol) System at 40, 70, and 120°C (3 h)

Ni compd. ^a	Temperature °C	Yield, mol.% ^b		
		<i>I</i>	<i>II</i>	<i>III</i>
[Ni(acac) ₂] ^c	40	2	0	0
[Ni(cod) ₂] ^d	40	3	0	0
NiCl ₂	70	54	4	1
NiBr ₂	70	57	3	2
[Ni(acac) ₂] ^c	70	54	4	1
[Ni(cod) ₂] ^d	70	55	5	2
NiBr ₂ ^e	120	47	10	8
[Ni(cod) ₂] ^{d,e}	120	45	13	11

^a With nickel(II) compounds as catalysts, the addition did not take place in the absence of triphenylphosphine. ^b Determined by gas-liquid chromatography and calculated with respect to the silicon hydride. *I* 1-Trichlorosilyl-*cis*-2-butene, *II* 1-trichlorosilyl-*trans*-2-butene, and *III* 4-trichlorosilyl-1-butene. ^c acac = acetylacetonyl. ^d cod = 1,5-cyclooctadiene. In the absence of sodium bis(2-methoxyethoxy)aluminium hydride. ^e Taken from ref.¹

In the reaction of trichlorosilane the addition of sodium bis(2-methoxyethoxy)-aluminium hydride enhances catalytic activity of the system such that hydrosilylation readily proceeds at a temperature by 50°C lower compared to the addition catalysed with the nickel(II) compound itself (Table I). From the inspection of Table I it becomes evident that not only in activity but also in selectivity is this system comparable to the zerovalent nickel complex, bis-(1,5-cyclooctadiene)nickel. Similar to the addition catalysed with nickel(II) compounds at 120°C (ref.¹), also in this case the presence of a stabilizing ligand, preferably triphenylphosphine, is prerequisite. In the absence of such ligand the nickel(II) compounds decomposed to give inactive nickel metal.

By contrast, in the addition of triethoxysilane good yields of hydrosilylation products were obtained even with the two-component catalysts (Table II). When compared to the reaction of trichlorosilane which produced silyl-substituted butenes as sole products, hydrosilylation of 1,3-butadiene with triethoxysilane was less selective, giving also the coupled products, silyl-substituted octadienes, in relatively small amounts which were somewhat dependent on the nickel(II) component used. The addition of the hydride had again activity-enhancing effect which rendered it possible to carry out the addition already at 40°C. As it is seen from Table II, in the presence of triphenylphosphine the overall yields obtained under otherwise identical

TABLE II

Addition of Triethoxysilane (26 mmol) to 1,3-Butadiene (32 mmol) Catalysed with a Nickel Compound (0.04 mmol)–Sodium Bis(2-methoxyethoxy)aluminium Hydride (0.1 mmol) System in the Presence and Absence of Triphenylphosphine at 40 and 70°C (3 h)

Ni compd.	Temperature °C	Yield, mol.% ^a		Side products ^b	
		<i>IV</i>	<i>V</i>	cod ^c	Si(OC ₂ H ₅) ₄
[Ni(acac) ₂] ^d	40	70	2	1	2
[Ni(cod) ₂] ^{c,e}	40	68	2	0	0
[Ni(acac) ₂] ^d	70	87	8	3 ^f	2
NiBr ₂	70	85	1	0	2
[Ni(cod) ₂] ^{c,e}	70	88	4	0	1
[Ni{P(C ₆ H ₅) ₃ } ₄] ^e	70	91	7	4	1
P(C ₆ H ₅) ₃ (0.2 mmol)					
[Ni(acac) ₂] ^d	40	6	1	1	2
[Ni(cod) ₂] ^{c,e}	40	20	2	0	0
[Ni(acac) ₂] ^d	70	70	9	6 ^f	4
NiBr ₂	70	61	2	2	1
[Ni(cod) ₂] ^{c,e}	70	80	11	5	1
[Ni{P(C ₆ H ₅) ₃ } ₄] ^e	70	79	4	7	1

^a Determined by gas-liquid chromatography and calculated with respect to triethoxysilane. *IV* 1-Triethoxysilyl-*cis*-2-butene, *V* triethoxysilyloctadienes. ^b Per cent by weight determined by gas-liquid chromatography of the reaction mixture after evaporation of compounds boiling below 10°C. ^c cod = 1,5-cyclooctadiene. ^d See footnote^c, Table I. ^e In the absence of sodium bis(2-methoxyethoxy)aluminium hydride. ^f The mixture contained c. 10% wt. butadiene trimers.

conditions are lower, mainly due to the effect of this ligand on 1-triethoxysilyl-*cis*-2-butene formation. Similarly as in the case of the trichlorosilane and 1,3-butadiene reaction also here the activity and selectivity of these catalyst systems is comparable to the catalytic behaviour of zerovalent nickel complexes.

The systems described in this work are of interest also from the synthetic standpoint. Although the enhanced activity of nickel(II) compounds achieved by the addition of the hydride does not make them so efficient catalysts as are Ziegler systems⁴ (*e.g.* Ni(acetylacetonyl)₂ + Al(C₂H₅)₃), this shortcoming is compensated by the fact that here manipulation with such dangerous compounds as *e.g.* triethylaluminium is avoided.

Summarizing, similar activity and selectivity of nickel(II) – the hydride systems and zerovalent nickel complexes established in this study support the assumption that in the hydrosilylation catalysed with nickel(II) compounds one of the reaction steps is reduction of nickel(II) compound to catalytically active zerovalent nickel species, as it was already suggested^{1,2}.

EXPERIMENTAL

All experiments were carried out under argon, using the same reactants, procedure, and analytical methods as in previous works^{1,2}. The products were characterized elsewhere^{1,2}. Sodium bis(2-methoxyethoxy)aluminium hydride was supplied by Synthesia, Kolín, and used as 14% solution in toluene. In preparing reaction mixtures the compounds were introduced to glass tubes in the sequence: nickel compound (together with triphenylphosphine), the hydride, 1,3-butadiene, and organosilicon hydride.

REFERENCES

1. Čapka M., Hetflejš J.: This Journal, in press.
2. Čapka M., Hetflejš J.: This Journal, in press.
3. Kiso Y., Kumada M., Maeda K., Sumitani K., Tamao K.: *J. Organometal. Chem.* 50, 311 (1973).
4. Lappert M. F., Nile T. A., Takahashi S.: *J. Organometal. Chem.* 72, 425 (1974).

Translated by the author (J. H.).