

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

M. ČAPKA and J. HETFLÉŠ

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

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The catalytic effectiveness of $\text{CoX}_2\text{--NaAlH}_2(\text{OCH}_2\text{CH}_2\text{OCH}_3)_2$ systems ($\text{X} = \text{F}, \text{Cl}, \text{Br}, \text{NO}_3, \text{SCN}, \text{CH}_3\text{COO}, \text{CH}_3\text{CH}(\text{OH})\text{COO}, \text{CH}_3\text{C}(\text{--O})=\text{CHCH}(\text{=O})\text{CH}_3$; $\text{X}_2 = \text{OOC--COO}$) was tested on the addition of triethoxysilane and tris(2-methoxyethoxy)silane to the title diene. The systems were effective only at elevated temperatures. The addition of triethoxysilane to 1,3-butadiene was nonselective, giving isomeric 1-silyl-substituted butenes, triethoxysilyl-substituted octadienes, bis(triethoxysilyl)butenes and -butanes. The addition of tris(2-methoxyethoxy)silane produced tris(2-methoxyethoxy)silyl-substituted butanes selectively and in good yields (~85%). The effect of several neutral ligands and solvents of varying polarity on product distribution in the addition of triethoxysilane is reported.

Within the framework of the study of hydrosilylation of conjugated dienes catalysed by Group VIII transition metal complexes (see¹ and references therein) we have recently examined² the catalytic effectiveness of some nickel(II) salts in hydrosilylation of 1,3-butadiene by triethoxy- and trichlorosilane and have found that these salts, although ineffective as such, can be converted into relatively efficient catalysts in the presence of a reducing agent, such as sodium bis(2-methoxyethoxy)aluminium hydride. This interesting possibility which is alternative to the use of alkylaluminium compounds to form hydrosilylation catalysts of Ziegler-Natta type³ led us to test the effectiveness of similar systems based on cobalt(II) salts in hydrosilylation of 1,3-butadiene by triethoxysilane and tris(2-methoxyethoxy)silane. The results of this study are reported in the present work.

EXPERIMENTAL

Compounds Used

Cobalt(II) chloride, bromide, nitrate, thiocyanate and acetylacetonate were commercial products and were used without further purification. Cobalt(II) fluoride, acetate, oxalate, lactate, tartarate

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and citrate were prepared from cobalt(II) carbonate and the appropriate acid in the usual way. Sodium bis(2-methoxyethoxy)aluminium hydride (Synthesia, Kolín) was used as 14% solution in toluene. Tertiary phosphines, arsines and phosphites (Fluka A.G., Buchs) were purified by crystallisation or distillation under argon, except tricyclohexylphosphine which was prepared by reported procedure⁴. 1,3-Butadiene (Kaučuk, Kralupy n/Vlt.) was dried as liquid over a molecular sieve. A mixture of C₄ hydrocarbons (Research Institute for Petrochemistry, Nováky) contained the following substances (in % wt.): isobutane 1.8%, n-butane 7.7%, 1-butene 18.6%, *trans*-2-butene 4.1%, *cis*-2-butene 2.3%, isobutene 30.4%, 1,3-butadiene 32.4%, and an unidentified substance 2.7%. The mixture was dried similarly as the pure diene. Triethoxysilane was prepared by reported procedure⁵.

Tris(2-methoxyethoxy)silane. To a mixture of 700 ml of benzene and 250 g (1.77 mol) of trichlorosilane, 475 g (6.24 mol) of 2-methoxyethanol were added under stirring and introducing nitrogen into the mixture. The reaction mixture was cooled for another 1 h under nitrogen and allowed to warm up to ambient temperature (1 h). The mixture was distilled under a pressure of 10 Torr and the distillate rectified through a 20 TP distillation column to give 250 g (55%) of tris(2-methoxyethoxy)silane, b.p. 120°C/5 Torr. For C₉H₂₂O₆Si₁ (254.4) calculated: 42.50% C, 8.72% H, 11.04% Si; found: 42.32% C, 8.64% H, 11.34% Si. The IR spectrum (liquid, neat): 2220 cm⁻¹ (medium, ν(Si—H)), 1100 cm⁻¹ (very strong, ν(Si—O—C)), no bands at 1105 cm⁻¹ (ν(Si—OH)).

Hydrosilylation Procedure and Products

Experiments were carried out under argon or nitrogen in the way reported earlier². A mixture of 1-triethoxysilyl-*cis*-2-butene (*I*), 1-triethoxysilyl-*trans*-2-butene (*II*) and 4-triethoxysilyl-1-butene (*III*) formed by addition of triethoxysilane to 1,3-butadiene was not possible to separate to individual isomers by distillation; the product distribution was determined as follows. Isomeric trichlorosilylbutenes obtained and identified by reported methods⁶ were converted by the action of ethanol in the presence of pyridine to the corresponding triethoxysilyl derivatives (see below). The IR analysis of the compounds confirmed^{6,7} that the butenes are not isomerized under these conditions. The above mixtures with the known isomer distribution were then used in gas chromatographic analyses of reaction mixtures to assign chromatographic peaks to individual isomers *I—III*.

In a typical example, to a solution of 20 mmol of 1-trichlorosilyl-*trans*-2-butene and 5 mmol of 1-trichlorosilyl-*cis*-2-butene in 20 ml of diethyl ether, a mixture of 5.25 ml (90 mmol) of ethanol and 7.2 ml (90 mmol) of pyridine was added dropwise under stirring. After completion of the addition, the mixture was refluxed for 2 h and cooled, the precipitate pyridine hydrochloride was filtered off and the liquid layer was rectified to give a mixture of 1-triethoxysilyl-*cis*- and -*trans*-2-butenes containing both isomers in the ratio corresponding to the *cis* to *trans* ratio of the starting trichlorosilylbutenes.

Tris(2-methoxyethoxy)silylbutene. A pressure vessel was charged with 0.1 g (0.39 mmol) of cobalt(II) acetylacetonate cooled to -50°C and then 13 ml (156 mmol) of liquid 1,3-butadiene, 2 ml of 14% toluene solution of sodium bis(2-methoxyethoxy)aluminium hydride and 22 g (86.5 mmol) of tris(2-methoxyethoxy)silane were successively added, the reaction vessel sealed and the mixture heated at 120°C for 5 h. The resulting reaction mixture was fractionated, giving 22.7 g (85%) of tris(2-methoxyethoxy)silylbutene, b.p. 125°C/2 Torr. For C₁₃H₂₈O₆Si₁ (308.5) calculated: 50.62% C, 9.15% H, 9.11% Si; found: 50.33% C, 8.96% H, 9.30% Si. The IR spectrum (liquid, neat): two bands in the 3100—3000 cm⁻¹ region (3020 cm⁻¹, medium; 3080 cm⁻¹, weak) confirm =C—H present mainly as the terminal C=C bond, a pair of weak bands located

in the $1700\text{--}1600\text{ cm}^{-1}$ indicates the presence of at least two isomers, a medium band at 705 cm^{-1} can be assigned to the $\text{C}=\text{C}$ bond with the *cis* configuration. Very broad and strong band at 970 cm^{-1} ($\text{C}-\text{C}$ vibrations of the $\text{O}-\text{CH}_2\text{CH}_2-\text{O}$) does not allow to detect the presence of the *trans* isomer. According to the analysis, the *cis*-2-butene to 1-butene derivative ratio is approximately 1 : 1.

A mixture of triethoxysilyloctadienes (*IV*) obtained in the addition of triethoxysilane to 1,3-butadiene was identified by comparison with an authentic sample prepared earlier⁷. A mixture of bis(triethoxysilyl)butenes and -butanes was analysed by mass spectrometry combined with gas chromatography (LKM 9000 GLC-Mass Spectrometer, Sweden) and by comparing the retention time of the product with that of 1,4-bis(triethoxysilyl)-2-butene⁸. Products from the triethoxysilane and butadiene reaction were analysed on a Chrom III chromatograph equipped with a 1.6 m-column filled with Silicone Elastomer E 302 (11.5%) on Chromosorb W 30/60 (50–90°C at 5°C/min rate), except isomers *I–III* which under these conditions were not well separated. Their distribution was determined using a capillary column (50 m) filled with tricresyl phosphate (110°C, 1 at nitrogen).

RESULTS AND DISCUSSION

As shown in Table I, the systems tested were catalytically active in the addition of triethoxysilane to 1,3-butadiene only at elevated temperatures. The main products were in general silylsubstituted 1 : 1 adducts, 1-triethoxysilyl-*cis*-2-butene (*I*) and 1-triethoxysilyl-*trans*-2-butenes (*II*), indicating that the reaction proceeds predominantly *via* the 1,4-addition of the silicon hydride to the conjugated double bond system. The isomer with terminal double bond, 4-triethoxysilyl-1-butene was produced in only small amounts, with one exception which will be discussed later. In addition to these products, the reaction mixtures contained in some cases also triethoxysilyloctadienes of unidentified isomerism, bis(triethoxysilyl)butanes and -butenes. The reaction was accompanied by formation of tetraethoxysilane resulting presumably from disproportionation of the starting triethoxysilane.

The results show that in contrast to related nickel(II) catalysts², the activity and selectivity of the cobalt salts is affected by the nature of anionic ligand (Table I). The unexpected and relatively high activity and selectivity of the catalyst formed from cobalt(II) nitrate is at present difficult to rationalize. Comparable in activity but inferior in selectivity turned out to be the cobalt(II) acetylacetonate catalyst (Table I). The addition may be effected also in the presence of solvents (Table II) whose decreasing polarity seems to slightly increase the *II* to *I* isomer ratio and suppress formation of *IV*. Changes in relative amounts of the other products are less clear-cut or are irregular. In majority of the solvents used the catalyst showed similar activity, except tetrachloromethane and dimethyl sulphoxide. Low overall yields obtained in the latter solvents may, along with inactivation of the catalyst system, be also due to consumption of triethoxysilane by reactions with these solvents (hydrogenative dehalogenation of tetrachloromethane to trichloromethane and reduction of dimethyl sulphoxide to dimethyl sulphide⁹).

TABLE I

The Catalytic Activity of Cobalt(II) Salt (0.04 mmol)–Sodium Bis(2-methoxyethoxy)aluminium Hydride (0.15 mmol) Systems in the Addition of Triethoxysilane (26 mmol) to 1,3-Butadiene (32 mmol) (120°C, 3 h)

Co(II) salt ^a	<i>I</i>	<i>II</i>	<i>III</i>	<i>IV</i>	<i>V</i>	Si(OC ₂ H ₅) ₄
CoF ₂	4 (3)	2 (2)	1 (1)	0 (0)	0 (0)	15 (3)
CoCl ₂	24 (21)	22 (14)	2 (2)	0 (0)	8 (4)	20 (7)
CoBr ₂	20 (10)	19 (8)	2 (1)	0 (0)	9 (3)	21 (7)
Co(NO ₃) ₂	72 (21)	4 (9)	2 (4)	2 (2)	6 (3)	9 (5)
Co(SCN) ₂	3 (3)	2 (2)	1 (1)	0 (0)	0 (0)	19 (5)
Co(OOCCH ₃) ₂	10 (2)	3 (1)	2 (0)	0 (0)	0 (0)	19 (5)
Co(OOCCOO)	7 (10)	6 (3)	2 (1)	0 (0)	0 (0)	10 (13)
Co(OOCC(OH)CH ₃) ₂ ^b	9 (8)	2 (2)	3 (1)	0 (0)	0 (0)	6 (5)
[Co(acac) ₂]	30 (24)	20 (23)	5 (3)	5 (6)	20 (21)	11 (11)
[Co(acac) ₂] ^c	31 (17)	23 (12)	11 (6)	5 (3)	20 (16)	11 (11)

^a The yields of the products *I*–*V* and Si(OC₂H₅)₄ are given in mol.% with respect to triethoxysilane, those given in parentheses were obtained with added triphenylphosphine (0.2 mmol); *I* 1-triethoxysilyl-*cis*-2-butene, *II* 1-triethoxysilyl-*trans*-2-butene, *III* 4-triethoxysilyl-1-butene, *IV* a mixture of triethoxysilyloctadienes, *V* a mixture of bis(triethoxysilyl)butenes and -butanes; ^b the citrate and tartarate were inactive; ^c 150°C, 2 h (80°C, 5 h: *I* 16, *II* 19, *III* 2, *IV* 5, *V* 14, Si(OC₂H₅)₄ 3 mol.%).

TABLE II

The Effect of Solvents (6 ml) on Hydrosilylation of 1,3-Butadiene (32 mmol) by Triethoxysilane (26 mmol) Catalysed with Cobalt(II) Acetylacetonate (0.04 mmol)–Sodium Bis(2-methoxyethoxy)aluminium Hydride (0.15 mmol) (120°C, 3 h)

Solvent ^a	<i>I</i>	<i>II</i>	<i>III</i>	<i>IV</i>	<i>V</i>	Si(OC ₂ H ₅) ₄
None	30	20	5	5	20	11
n-C ₇ H ₁₆	23	26	6	5	21	9
CCl ₄	2	1	0	2	7	14
C ₆ H ₆	23	27	3	3	17	13
DMSO ^b	7	2	3	2	3	17
THF ^c	24	15	9	— ^d	17	14
HMPT ^e	30	20	11	— ^d	16	11

^a The yields of the products *I*–*V* (for numbering see Table I) and tetraethoxysilane were determined by gas-liquid chromatography with respect to triethoxysilane and are given in mol.%; ^b DMSO dimethyl sulphoxide; ^c THF tetrahydrofuran; ^d traces; ^e HMPT hexamethylphosphor-triamide.

Generally low selectivity of the cobalt catalysts compared to analogous nickel compounds led us to investigate the effect of some neutral ligands on product distribution. With most systems, the addition of triphenylphosphine suppressed formation of tetraethoxysilane and bis(triethoxysilyl)-substituted derivative *V*, in the case of relatively effective catalysts (cobalt(II) chloride, bromide, nitrate, acetylacetonate) usually in the expense of their catalytic activity (Table I). The results obtained with the so modified cobalt(II) acetylacetonate catalyst are summarized in Table III. Of interest is the presence of terminal silyl-substituted butene *III* among reaction products. To our knowledge, formation of a product of 1,2-addition during hydrosilylation of 1,3-butadiene has been observed only in additions of trimethylsilane catalysed by $[\text{Co}_2(\text{CO})_8]$ (ref.¹¹) and some palladium(II) complexes¹², of diethoxypropyl- and ethoxydipropylsilane catalysed by palladium(II) compounds¹⁰ and of trichlorosilane catalysed by nickel compounds⁸. The fact that here the reaction of triethoxysilane with 1,3-butadiene leads as a rule also to the product of 1,2-addition *III* differentiates the cobalt compounds from other transition metal hydrosilylation catalysts. Thus, for example, we have found that the addition of triethoxysilane to this diene catalysed by rhodium(I) (ref.¹), nickel(0) and nickel(II) complexes⁷ produces selectively the *cis*-isomer *I* and the addition catalysed by palladium(II) compounds¹⁰ affords a mixture of *I* and *II*. Markedly increased amount of *III* obtained upon addition of tricyclohexylphosphine is analogous to the effect of this

TABLE III

The Effect of Neutral Ligands (0.2 mmol) on Hydrosilylation of 1,3-Butadiene (32 mmol) by Triethoxysilane (26 mmol) Catalysed with Cobalt(II) Acetylacetonate (0.04 mmol)–Sodium Bis(2-methoxyethoxy)aluminium Hydride (0.25 mmol) (120°C, 3 h)

Ligand ^d	<i>I</i>	<i>II</i>	<i>III</i>	<i>IV</i>	<i>V</i>	Si(OC ₂ H ₅) ₄
None ^{b,c}	26	23	4	3	18	12
As(C ₆ H ₅) ₃	30	20	3	3	23	17
P(OC ₆ H ₅) ₃	1	0	1	0	0	23
P(OC ₄ H ₉ - <i>n</i>) ₃	3	2	2	0	0	35
P(C ₆ H ₅) ₃	24	23	3	6	21	11
P(C ₆ H ₅) ₃ ^b	19	20	4	3	15	13
P(<i>n</i> -C ₄ H ₉) ₃	10	7	33	0	14	14
P(cyclo-C ₆ H ₁₁) ₃	24	15	14	3	24	14
Diphos ^d	6	2	1	0	0	35

^a The yields of the products *I*–*V* (for numbering see Table I) and tetraethoxysilane are given in mol.% (cf. note^a in Table II); ^b the results for a C₄ fraction (for composition see Experimental);

^c the data for the pure butadiene are recorded in Table II; ^d diphos 1,2-bis(diphenylphosphino)ethane (0.1 mmol).

ligand in the nickel-catalysed hydrosilylation of 1,3-butadiene with trichlorosilane ($III/(I + II)$ ratio increased⁸ in the order $P(C_6H_5)_3 < P(n-C_4H_9)_3 < P(\text{cyclo-}C_6H_{11})_3$) and indicates that formation of III is not controlled only by electronic effects of the ligands but also by their steric demands (compare the results for $P(n-C_4H_9)_3$ and $P(\text{cyclo-}C_6H_{11})_3$). It should be noted that relative amounts of III increase also with increasing reaction temperature (Table I).

Experiments with a mixture of C_4 hydrocarbons containing about 31% of 1,3-butadiene showed that under the conditions used triethoxysilane does not react with the alkenes present and the product distribution is nearly the same as that achieved with the pure diene (Table III). A similar exclusive transformation of conjugated dienes in the presence of alkenes has so far been reported only for some palladium complexes¹³.

Although the cobalt catalysts show rather low selectivity in the addition of triethoxysilane to 1,3-butadiene and are thus here of limited value from the synthetic viewpoint, they might prove useful for some other additions. For example, under essentially identical conditions with those used in the addition of triethoxysilane, tris(2-methoxyethoxy)silane adds to 1,3-butadiene to give 1-tris(2-methoxyethoxy)silyl-*cis*-2-butene and 4-tris(2-methoxyethoxy)silyl-1-butene (1 : 1, by IR spectroscopy) in 85% overall yield (83% yield with added triphenylphosphine). This interesting application is being investigated in more detail.

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