CATALYSIS BY METAL COMPLEXES. X.*
THE ADDITION OF TRIMETHYLSILANOL TO BUTADIENE

M.Čapka, P.Svoboda and J.Hetflejš
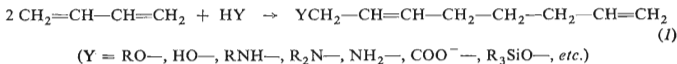
Institute of Chemical Process Fundamentals,
Czechoslovak Academy of Sciences, 165 02 Prague - Suchdol

New catalytic systems, based on Pd(O) and Pd(II) complexes, for preparing 1-trimethylsiloxy-2,7-octadiene by the reaction of trimethylsilanol with butadiene are reported. The results obtained with polymer-supported catalysts are discussed in terms of the earlier proposed mechanism of the reaction.

In the course of our study of selective hydrosilylation of conjugated dienes we found that trichlorosilane reacts with butadiene to give exclusively 1-trichlorosilyl-2-butene[1], while in the reaction of triethoxysilane the corresponding 2-butenyl derivative is accompanied[2] by a considerable amount of 1-triethoxysilyl-2,6-octadiene. These facts, along with the report by Hagihara[3] that the addition of trimethylsilane to butadiene gives almost exclusively 1-trimethylsilyl-2,6-octadiene, show that with increasing hydridic character of the Si—H bond of reactant silane the proportion of the 1 : 1 addition decreases, telomeric product(s) being favoured. In connection with this we were interested in the addition of silanols, which possess an acidic hydrogen in their hydroxyl group.

In last few years several reports have appeared, dealing with reaction of nucleophiles with butadiene catalysed by palladium compounds. A variety of these additions proceed with simultaneous dimerization of butadiene, giving the derivatives of 2,7-octadiene (Eq. (1)),

$$2\ CH_2{=}CH{-}CH{=}CH_2\ +\ HY\ \rightarrow\ YCH_2{-}CH{=}CH{-}CH_2{-}CH_2{-}CH_2{-}CH{=}CH_2$$
$$(1)$$

$$(Y = RO{-},\ HO{-},\ RNH{-},\ R_2N{-},\ NH_2{-},\ COO^-{-},\ R_3SiO{-},\ etc.)$$

and are mostly catalysed by tert-phosphine Pd(O) complexes. Accordingly, methanol and pheno give 1-methoxy-2,7-octadiene[4] and 1-phenoxy-2,7-octadiene[5], respectively. A number of other nucleophiles react similarly: primary and secondary amines[6], carboxylic acids[7], compounds with the active methylene or methine groups[8,9], water[10], ammonia[11], and trimethylsilanol[12]. These reactions are usually accompanied by formation of numerous by-products, the most common being 1,3,7-octatriene and 3-substituted derivatives of 1,7-octadiene. With the excep-

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tion of one report[6], neither the effect of reaction conditions nor the mechanism of these reactions has been studied in detail.

The addition of trimethylsilanol to butadiene has so far been effected in the presence of Pd(O) complexes[12]. As these compounds are usually extremely unstable in air, we sought for more stable systems which could catalyse this reaction and were also interested in its mechanism.

EXPERIMENTAL

All operations were carried out with rigorous exclusion of air oxygen, using an argon or nitrogen atmosphere.

Compounds used. Liquid butadiene was dried over a molecular sieve. Trimethylsilanol was prepared according to the procedure reported by Sommer[13], sodium trimethylsilanolate was obtained by dissolving sodium in trimethylsilanol. Bis(triphenylphosphine)dichloropalladium(II) (ref.[14]), bis(π-allyl)dichlorodipalladium(II) (ref.[15]), tetrakis(triphenylphosphine) palladium(0) (ref.[16]), and bis(benzonitrile)dichloropalladium(II) (ref.[17]) were prepared according to reported procedures. The other compounds were commercial products.

Polymer-supported catalyst I. A solution of 0·9 g of tetrakis(triphenylphosphine)palladium in 40 ml of benzene was poured onto a macroreticular styrene–divinylbenzene copolymer possessing —$CH_2P(C_6H_5)_2$ groups[18]. Immediately after the addition, the yellow solution turned to the dark red. The reaction mixture was stirred at 25°C for 17 h and filtered; the product was washed with four 80 ml portions of benzene and dried *in vacuo* (0·3% Pd).

Catalyst II. A macroreticular allyl chloride–divinylbenzene copolymer was reacted with lithium diphenylphosphide, the crude product was thoroughly washed with ethanol and water and dried *in vacuo*. The so prepared support (1.3 g) was added into a solution of 0·45 g of bis(triphenylphosphine)dichloropalladium in 30 ml of chloroform and 15 ml of ethanol. The reaction mixture was heated to 60°C for 6 h, the product was filtered and washed successively with 30 ml chloroform and 15 ml ethanol and dried *in vacuo* (1·8% Pd). *Catalyst* III. A mixture at 2·2 g of a macroreticular styrene–divinylbenzene copolymer substituted with —$CH_2P(C_6H_5)_2$ groups[18], 0·5 g of bis(benzonitrile)dichloropalladium, 25 ml of benzene, and 15 ml of ethanol was heated to 65°C for 10 h. The crude product was washed three times with 35 ml of benzene and 15 ml of ethanol and then dried *in vacuo* (5·9% Pd). *Catalyst* IV. To 1·5 g of the already described styrene–divinylbenzene copolymer, a solution of 0·40 g of bis(π-allyl)dichlorodipalladium in 40 ml of ethanol and 15 ml of benzene was added, and the reaction mixture was heated to 65°C for 10 h. The crude product was washed with three 35 ml portions of ethanol and two 25 ml portions of benzene and then dried *in vacuo* (7·7%Pd). *Catalyst* V. A mixture of 4 g of Amberlyst A 21 (Rohm & Hass) and 20 ml of 5% aqueous palladium chloride was set aside for 24 h. Then the mixture was filtered, the crude product was washed twice with 20 ml of water and once with 20 ml of ethanol and dried *in vacuo* (14·2% Pd). *Catalyst* VI was prepared in the same way as catalyst V, with the exception that a macroreticular styrene–divinylbenzene copolymer containing —CH_2CN groups was used in place of Amberlyst A 21 (3·1% Pd).

Experiments were carried out in sealed ampoules, the reaction components were added under argon and the content of the ampoules was shaken by a vibrator. After the reaction was complete, the ampoules were cooled, unsealed, the unreacted butadiene removed under reduced pressure, and the residual reaction mixture was distilled. The content of 1-trimethylsilyl-2,7-octadiene in the distillate was determined gas chromatographically on Chrom 3 instrument (Laboratorní

přístroje, Prague) provided with flame-ionization detector on a capillary column filled with tributyl phosphate. In the cases where the catalyst was to be re-cycled, unsealing the ampoule, degassing and removal of the liquid phase were carried out under nitrogen, then the catalyst was washed with two 10 ml portions of benzene and dried *in vacuo*. The structure of the product, 1-trimethylsiloxy-2,7-octadiene, was confirmed by elemental analysis, IR and NMR spectra, which all agreed with the literature data[12].

RESULTS AND DISCUSSION

As shown in Table I, the reaction can be catalysed by several other systems based on Pd(O) and Pd(II) complexes than are the already reported tetrakis(triphenyl-phosphine) palladium and its derivatives with dienophiles[12]. On addition of azo-benzene, the catalytic activity of tetrakis(triphenylphosphine)palladium can be increased such that the higher yield of the product can be obtained with half amount of the catalyst. Although several Pd(II) compounds can be used as precursors

TABLE I

Effect of Catalyst and Reaction Conditions on Addition of Trimethylsilanol to Butadiene

The reaction was carried out with a mixture of 72 mmol of butadiene, 27 mmol of trimethyl-silanol and 5 ml of benzene.

Catalyst	mmol	PPh_3 mmol	Base[a] (mmol)	°C	Time h	Yield[b] %
$Pd[P(C_6H_5)_3]_4$	0·05	—	—	65	18	54
$Pd[P(C_6H_5)_3]_4 +$	0·025 +					
$+ C_6H_5N{=}NC_6H_5$	0·053	—	—	60	16	66
$(C_3H_5)_2Pd_2Cl_2$	0·25	0·466	—	60	18	18[c]
$PdCl_2(C_6H_5CN)_2$	0·21	0·397	A (0·575)	60	4·5	3
$PdCl_2(C_6H_5CN)_2$	0·267	0·397	A (1)	60	5	16
$PdCl_2(C_6H_5CN)_2$	0·27	0·387	A (1·25)	60	24	46
$PdCl_2(C_6H_5CN)_2$	0·22	0·397	B (0·267)	80	5	20[d]
$PdCl_2$ (0·26) $+ C_6H_5CN$	0·53	0·397	B (0·267)	50	5	6
$PdCl_2[o{-}C_6H_4(CH_2CN)_2]$	0·109	0·265	B (0·267)	50	5	14
$PdCl_2(C_6H_5CN)_2$	0·23	0·397	B (0·05)	50	4	4
$PdCl_2(C_6H_5CN)_2$	0·23	0·397	B (0·10)	50	4	6
$PdCl_2(C_6H_5CN)_2$	0·23	0·397	B (0·267)	50	4	10
$PdCl_2(C_6H_5CN)_2$	0·23	0·397	B (0·668)	50	4	52
$PdCl_2(C_6H_5CN)_2$	0·23	0·397	B (1·87)	50	4	15[d]
$PdCl_2(C_6H_5CN)_2$	0·23	0·397	B (6·67)	50	4	2[d]

[a] A = NaOH, B = $(CH_3)_3SiONa$; [b] the yield of 1-trimethylsiloxy-2,7-octadiene is calculated with respect to trimethylsilanol; [c] 1-trimethylsiloxy-2,7-octadiene was contaminated by several by-products; [d] the reaction mixture consisted of higher butadiene oligomers.

of catalytically active intermediates, bis(benzonitrile)dichloropalladium turned out to be most advantageous. The addition of triphenylphosphine is necessary for preventing the catalyst to decompose, and the addition of alkalies aids in increasing nucleophility of the addent particle. Of these, the best were sodium hydroxide and sodium silanolate. In the presence of other phosphorus-containing ligands, such as tributylphosphine or triphenylphosphite, the reaction did not take place. The reaction is further very sensitive to the relative proportions of the catalyst, ligand, and alkalies and it is also strongly dependent on the reaction temperature. So, for instance, while it does not proceed at the low concentration of the alkaline component, its overdosing results in a greater proportion of the competitive polymerization of butadiene. A high temperature has a similar effect. The choice of the suitable and economical catalyst is not superficial, since until the work by Atkins[12], the preparation of 1-siloxy-2,7-octadiene, followed by its hydrogenation and alkaline solvolysis (or its hydrolysis and subsequent hydrogenation) appeared to be one of the most promising ways for preparing 1-octanol[12]. We were therefore interested in the synthesis of the polymer-supported catalysts[18,19] which would enable to recycle the catalyst and to obtain further information concerning the mechanism of this reaction. The addition of protonic substances to butadiene has been assumed by Hagihara and co-workers[6,12,20] to proceed *via* formation of an intermediate *B*, suggested earlier by Wilke[21] for a nickel-catalysed cyclooligomerization of butadiene; the 1,6-addition of the substance ROH to complex *B* leads to $ROCH_2CH=CH-CH_2CH_2CH_2CH=CH_2$; Do is a donor, M is Ni or Pd.

A   *B*
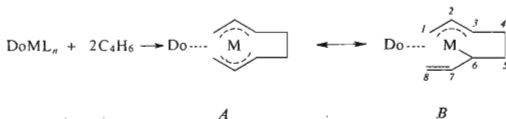
Intermediates *A* and *B* thus contain unsaturated C_8-chain, which, when coordinated as bis-allyl, would occupy nearly the whole coordination sphere of the palladium and would have also great steric demands. On using the palladium compounds fixed to the ligands bonded to a polymer skeleton, it can be expected that, if the above mechanism were operative, due to steric and electronic requirements of the intermediate, the fixation of the transition metal to the polymer should be loosened and the palladium complex could come to the solution. As the result, the content of the palladium in the polymer would be lower and this catalyst would not be probably active. The results summarized in Table II do confirm the above assumptions. The content of the metal on the polymers was always considerably smaller than in fresh catalysts (especially for the catalysts with a high content of the metal and a relatively high activity) and in no case could the catalyst be re-cycled.

The metal could, of course, be cleaved from the catalyst also by the exchange of the polymeric ligand for the triphenylphosphine present in excess in the reaction mixture. In order to check this possibility we heated the catalyst V under the conditions given in Table II in the presence of all the reaction components but butadiene; the content of the metal in the catalyst decreased to 4·7 per cent, while in the presence of butadiene the recovered catalyst contained only 0·7% Pd. The conversion of the palladium complex to a soluble form is thus necessary for effecting the reaction. These results support the mechanism suggested by Hagihara and coworkers[12]. They also show that the use of polymer-supported catalysts might not be so promising in cases where reaction components completely or nearly completely occupy the coordination sphere of the reaction intermediate (*e.g.* in cyclooligomerization of butadiene).

TABLE II

Addition of Trimethylsilanol to Butadiene Catalysed by Polymer-Supported Catalysts

A mixture of the catalyst, 4 ml of benzene, 0·265 mmol of $P(C_6H_5)_3$, 0·267 mmol of $(CH_3)_3$.SiONa, 27 mmol of $(CH_3)_3SiOH$, and 72 mmol of butadiene was heated to 67°C for 5 h.

Catalyst[a]	Pd, mmol[b]	Pd, %[c]	Pd, %[d]	Yield, %[e]
I	0·055	0·3	0·2	2
II	0·051	1·8	0·1	2
III	0·06	5·9	1·1	4
IV	0·119	7·7	1·8	46
V	0·146	14·2	0·7[f]	36
VI	0·048	3·1	0·2	6

[a] See Experimental; [b] calculated from the weighted amount of the catalyst; [c] in fresh catalyst; [d] in once-used catalyst; [e] the yield of 1-trimethylsiloxy-2,7-octadiene obtained with fresh catalysts and calculated with respect to trimethylsilanol; once-used catalysts all were inactive. [f] In the absence of the butadiene the recovered catalyst contained 4·7% Pd.

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