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THE CATALYZED ADDITION OF MAGNESIUM HYDRIDE TO ISOPRENE AND STYRENE *

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Summary

Addition of magnesium hydride (I), prepared in a homogeneous catalyzed reaction, to isoprene in the presence of various transition metals leads to a mixture of diorganomagnesium compounds having 2,3- (IIa) and 3,3-dimethylallyl groups (IIIa); the proportion IIa/IIIa is to a certain extent dependent on the catalyst. The hydromagnesiation of styrene, in the presence of Cp_2TiCl_2 as catalyst, gives 1-phenylethyl-substituted diorganomagnesium compounds in high selectivity. In both reactions a concomitant oligomerisation of the olefin substrates is observed.

Introduction

The development of a convenient synthesis of a reactive magnesium hydride (I) via catalytic hydrogenation of magnesium [1] and its catalyzed addition to terminal olefins affording primary dialkylmagnesiums [2], prompted us to investigate the reactivity of I towards molecules containing conjugated and activated double bonds. We report here the catalyzed addition of I to isoprene and styrene.

In a preliminary note, a hydromagnesiation of styrene with an active form of magnesium hydride (prepared from NaH and $MgCl_2$) using Cp_2TiCl_2 as a catalyst has been reported [3]. A hydromagnesiation of isoprene and styrene using propylmagnesium bromide as a "HMgBr source" and Cp_2TiCl_2 as a catalyst has also been described previously [4].

Results and discussion

The in situ prepared suspensions of I in THF have been used for the reaction with isoprene or styrene. The transition metal used as the catalyst for the synthesis of I,

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[*] Dedicated to Professor Sei Otsuka on the occasion of his 65th birthday.

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introduced usually as $CrCl_3$, is hence present in the system and in addition further transition metal compounds (vide infra) were added in catalytic amounts to the reaction mixture (compare ref. 2). The reaction of I with isoprene or styrene (molar ratio I/isoprene (styrene)/catalyst = 100/220/1) was carried out under reflux and the progress of the reaction was monitored by removing samples from the suspension and determining the concentration of organomagnesium compounds in the solution after removal of I by centrifugation.

Addition of I to isoprene

The time dependence of the reaction of I with isoprene using different catalysts is shown in Fig. 1. Among the catalysts investigated, Cp_2TiCl_2 and $TiCl_4$ are by far the most efficient catalysts for the hydromagnesiation of isoprene: conversions of 70–75% are achieved within 24 h. Cp_2ZrCl_2, $ZrCl_4$, $HfCl_4$ and $CrCl_3$ show much lower reactivity and conversions are only 15–30% even after longer periods of time. This result is in contrast to those obtained on hydromagnesiation of terminal alkenes [2], where zirconium catalysts proved to be more active than titanium catalysts. Previous work on hydromagnesiation of isoprene using Grignard reagents [4] showed the effectiveness of a titanium catalyst in a similar reaction.

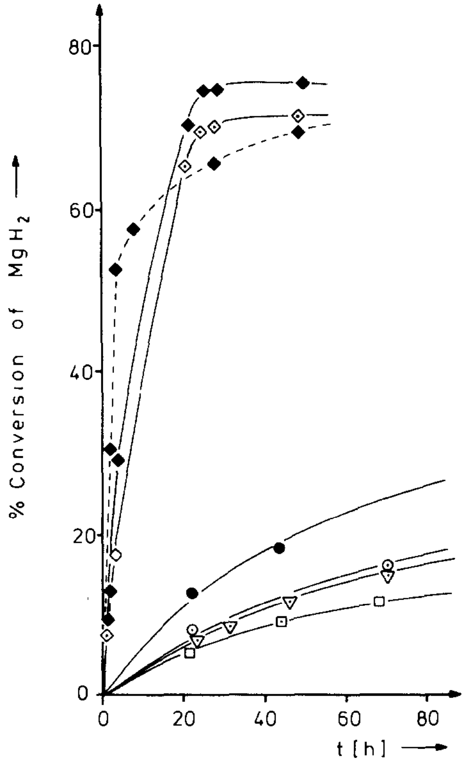

Fig. 1 Time dependence of the reaction of I with isoprene using different catalysts; I/cat./isoprene = 100/1/220 ($CrCl_3$ used as hydrogenation catalyst in all experiments except in the last one); –◆–, Cp_2TiCl_2; –◇–, $TiCl_4$; –●–, Cp_2ZrCl_2; –⊙–, $ZrCl_4$; –▽–, $CrCl_3$; –□–, $HfCl_4$; ---◆---, Cp_2TiCl_2 ($TiCl_4$ as hydrogenation catalyst).

If $TiCl_4$/Mg-anthracene, instead of the corresponding Cr catalyst, is employed to prepare the suspension of I and additionally Cp_2TiCl_2 added (Fig. 1), the initial reaction rate is somewhat higher but subsequently decreases considerably. This result is presumably associated with the lower reactivity of I prepared using the titanium catalyst [2].

In principle addition of mg–H (mg = 1/2 Mg) to isoprene (Scheme 1) can lead to four species: 1,4-addition (Mg → C(1) or Mg → C(4)) gives rise to organomagnesium compounds having 2,3- (IIa) and 3,3-dimethylallyl groups (IIIa) (these are known to exist, in solution, in equilibrium with the corresponding allyl isomers (IIb and IIIb) *; the equilibrium lying to the side of IIa and IIIa), while the 1,2- (Mg → C(1)) and 3,4- (Mg → C(4)) mg–H additions would afford the organomagnesium compounds IV and V respectively having homoallyl groups.

Hydrolysis of the diorganomagnesium compounds resulting from the hydromagnesiation of isoprene gave a mixture of 2-methyl-1-butene, 2-methyl-2-butene and 3-methyl-1-butene. The four possible addition products cannot, however, be distinguished on the basis of their hydrolysis products (2-methyl-1-butene is the hydrolysis product of both IIa, IIb and V, 2-methyl-2-butene of IIa,IIb and IIIa,IIIb and 3-methyl-1-butene of IIIa,IIIb and IV).

The structure and the composition of the diorganomagnesium compounds (R_2Mg) formed on hydromagnesiation of isoprene was established using the silylation method. The reaction of the R_2Mg compounds with trimethylchlorosilane (TMCS) and the analysis of the resulting mixture of organosilanes by means of GC-MS analysis revealed five isomeric trimethylorganosilanes $C_5H_9Si(CH_3)_3$ (MW 142) in addition to 10–20% of oligomerisation products; four of the five isomers were (partially) separated by means of preparative gas chromatography and identified on the basis of their ^1H NMR spectra. They are *E*- and *Z*-1-trimethylsilyl-2-methyl-2-butene (VIa and VIa′), 2-methyl-3-trimethylsilyl-1-butene (VIb) and 1-trimethylsilyl-3-methyl-2-butene (VII) (Scheme 1). The fifth isomer present only as a minor component has been tentatively assigned as 3-methyl-3-trimethylsilyl-1-butene, i. e. the trimethylsilyl derivative of IIIb **.

On the basis of the structure of the organosilanes VIa, VIa′, VIb and VII it can be concluded that in the catalyzed reaction of I with isoprene only the 1,4-addition of mg–H across the conjugated double bond system occurs, giving rise to mixtures of diorganomagnesium compounds with 2,3- (IIa) and 3,3-dimethylallyl groups IIIa. From the composition of the mixtures of organosilanes $C_5H_9Si(CH_3)_3$ determined by gas chromatography, the proportion of 2,3- versus 3,3-dimethylallyl groups bound to magnesium can be estimated and thus the regioselectivity of the mg–H addition to isoprene using the relationship:

$$\frac{\text{IIa}\ (\%)}{\text{IIIa}\ (\%)} = \frac{\text{VIa}\ (\%) + \text{VIa}'\ (\%) + \text{VIb}\ (\%)}{\text{VII}\ (\%)}$$

The results for various catalysts are shown in Table 1.

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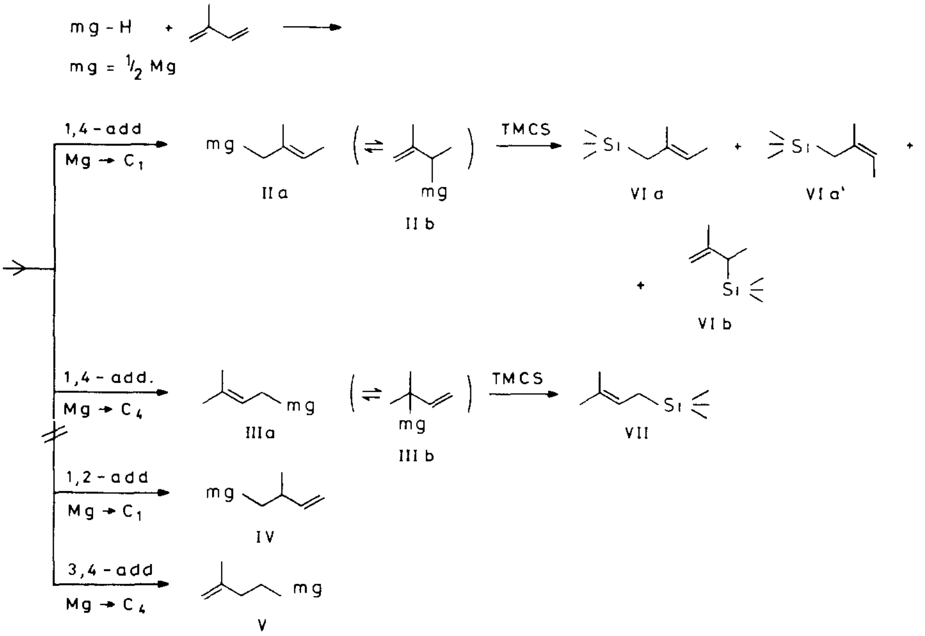
* Due to the equilibria IIa ⇋ IIb and IIIa ⇋ IIIb, the mg–H 1,4-addition (Mg → C(1)) is equivalent to the mg–H 3,4-addition (Mg → C(3)) and the mg–H 1,4-addition (Mg → C(4)) to the mg–H 1,2-addition (Mg → C(2)).

** The possibility that this isomer is a trimethylsilyl derivative of IV or V has not been definitively excluded.



SCHEME 1

As can be seen from the Table, the catalyzed hydromagnesiation of isoprene exhibits in general a low selectivity with respect to the formation of either of the two isomeric species IIa and IIIa. In the presence of Cp_2TiCl_2 or $TiCl_4$ (the chromium hydrogenation catalyst is also present in the system), the formation of IIIa is slightly favoured over IIa (IIIa/IIa = 64–70/36–30). On the other hand, the presence of Cp_2ZrCl_2 leads to a higher yield of the species IIa (IIIa/IIa = 18/82); although in this case the reaction rate and the yield of organomagnesium compounds are low (see Fig. 1). The formation of a mixture of the species IIa and IIIa in the presence of Cp_2TiCl_2 as the catalyst is in contrast to the results of the hydromagnesiation of isoprene with propylmagnesium bromide using the same catalyst: in this case only 2,3-dimethylallylmagnesium bromide (corresponding to IIa) has been observed [4]. It should, however, be stressed that in our case a different hydromagnesiation agent (I) and a different solvent (THF instead of ether) have been employed and that in the reaction two hydromagnesiation steps are involved.

Addition of I to styrene

From Fig. 2, it can be seen that Cp_2TiCl_2 is the most efficient catalyst investigated for the reaction of I with styrene and gives 90% of soluble organomagnesium compounds within 3 h. The reaction mixtures obtained in the presence of $ZrCl_4$, Cp_2ZrCl_2 or $TiCl_4$ yielded, on hydrolysis, large amounts of styrene oligomers, in addition to the expected ethylbenzene, and were not investigated further. The reaction products formed from I and styrene using Cp_2TiCl_2 as catalyst were characterized by hydrolysis and silylation (TMCS) and the results are shown in Table 2. In addition to the main product, ethylbenzene, lesser amounts of dihydrodimers, dihydrotrimers etc. are found among the hydrolysis products, indicating that

TABLE 1

THE COMPOSITION OF $C_5H_9Si(CH_3)_3$ ISOMERS AND THE PROPORTION OF 2,3- (IIa) VERSUS 3,3-DIMETHYLALLYL GROUPS (IIIa) FOR VARIOUS CATALYSTS

Catalyst [a]		VIa	VIa′	VIb	VII	? [b]	IIa (%)	IIIa (%)
Cp_2TiCl_2	($CrCl_3$)	7.7	20.9	6.9	63.3	1.2	35.5	64.5
$TiCl_4$	($CrCl_3$)	5.0	15.6	9.3	64.1	6.0	29.9	70.1
Cp_2TiCl_2	($TiCl_4$)	11.1	39.5	4.4	44.0	1.0	55.0	45.0
$TiCl_4$	($TiCl_4$)	5.1	14.3	7.5	68.7	4.4	29.9	73.1
$ZrCl_4$	($CrCl_3$)	12.4	35.8	19.7	29.5	2.6	67.9	32.1
Cp_2ZrCl_2	($CrCl_3$)	14.0	44.1	23.4	17.1	1.4	81.5	18.5

[a] The compound in brackets denotes the one used in the preparation of I. [b] It is assumed that this isomer is derived from IIIa,IIIb.

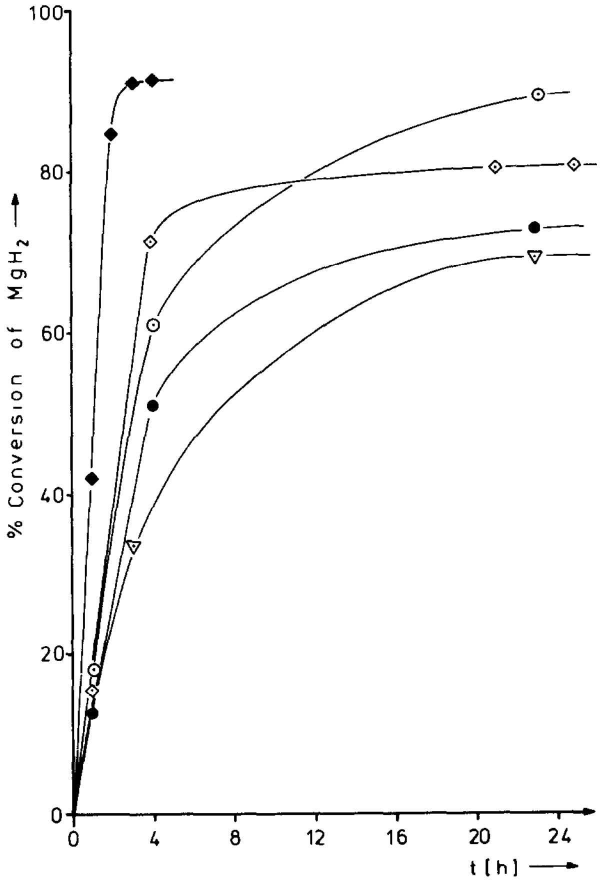


Fig. 2. Time dependence of the reaction of I with styrene using different catalysts; I/cat./styrene = 100/1/220 ($CrCl_3$ as hydrogenation catalyst); -◆-, Cp_2TiCl_2; -◇-, $TiCl_4$; -⊙-, $ZrCl_4$; -●-, Cp_2ZrCl_2; -▽-, no catalyst added.

TABLE 2

HYDROLYSIS AND SILYLATION PRODUCTS OF DIORGANOMAGNESIUM COMPOUNDS FROM Cp_2TiCl_2-CATALYZED ADDITION OF I TO STYRENE

Hydrolysis products (%) [a]		Silylation products (%) [a]
Ethylbenzene	(76)	1-Trimethylsilyl-1-phenylethane (72)
1,3-Diphenylbutane	(14)	1-Trimethylsilyl-2-phenylethane (3.7)
$C_{24}H_{26}$	(5.9)	*E*-1-Trimethylsilyl-2-phenylethylene (9.6)
$C_{32}H_{34}$	(1.4)	1-Trimethylsilyl-1,3-diphenylbutane (11.5) [b]

[a] GC analysis. [b] 1/1 mixture of 2 diastereomers.

the hydromagnesiation reaction of styrene is accompanied by insertion of styrene into the Mg–C bond. In addition to the hydrocarbons, a small amount of hydrogen is evolved on protolysis indicating that organomagnesium hydrides are also present in the mixture of diorganomagnesium compounds.

From the silylation products it can be seen that in the catalyzed hydromagnesiation of styrene (in agreement with preliminary results [3]), the formation of 1-phenylethylmagnesium species is strongly favoured (~ 95/5) over the 2-substituted species. The identification of 1-trimethylsilyl-1,3-diphenylbutane (11.5%) among the silylation products suggests that the 1-phenylethylmagnesium compounds also add to styrene, again in the expected Mg → C(1) sense. The *E*-styrylmagnesium compound, whose silylation product has been detected in 9.6% yield, could have been formed via a transmetallation reaction between styrene and 1-phenylethylmagnesium compounds or alternatively it might be the product of a "catalyzed magnesiation of styrene" by metallic magnesium (possibly present in small amounts in the reaction mixture) similar to the catalyzed lithiation of terminal olefins [6].

Experimental

All experiments were carried out under argon. Isoprene was purified by refluxing over $NaAl(C_2H_5)_4$ and distillation in vacuum and trimethylchlorosilane by distillation at normal pressure. Styrene was dried over $CaCl_2$ and distilled at 40 °C (18 mbar) under argon; the middle fraction was collected and used in the experiments.

The synthesis of MgH_2 (I) has been described elswhere [1,2]. For the present study, I was prepared by hydrogenation of magnesium (70 bar) at room temperature using Cr- or Ti-catalyst (Cr(Ti)/Anthracene/Mg = 1/1/100). Well stirred suspensions of I in THF can be divided into aliquots as a homogeneous solution and such aliquots were used for the reaction with isoprene and styrene. Since the reactivity of I in THF has been found to decrease somewhat after standing (e.g. one month), I was used within one week of its preparation.

Reaction of I with isoprene. In a standard experiment, a suspension of 250 mmol of I in 120 ml THF was syphoned into a three-necked flask fitted with a copper reflux condenser. 2.5 mmol of the transition metal catalyst and 55 ml (550 mmol) of isoprene were added with stirring. The reaction mixture was heated to reflux in an oil bath. At certain intervals, 3.0 ml aliquots of the reaction mixture were pipetted off, centrifuged (30 min) and 1.0 ml of the clear supernatant solution decomposed by water. The hydrolysis product was treated with excess of 0.1 *N* HCl and back-titrated with 0.1 *M* KOH. The percentage conversion of I to soluble R_2Mg compounds was corrected for the volume change by measuring the decrease in the volume of the reaction mixture at the end of the reaction. The conversion of I into R_2Mg with time for different catalysts is shown in Fig. 1.

Silylation of the R_2Mg compounds (Cp_2TiCl_2 as catalyst). After the completion of the reaction with isoprene (24 h), the reaction mixture was separated from excess I by filtration. To 60 ml of the filtrate containing 82 mmol of R_2Mg compounds (acidimetric titration), 23 ml (180 mmol) trimethylchlorosilane were added dropwise with stirring and the mixture refluxed for 10 h. The organosilanes and THF were separated from the catalyst and $MgCl_2$ by vacuum distillation (0.2 mbar, 25–50 °C bath temperature), the distillate treated with saturated NH_4Cl solution and the THF layer separated and dried over $CaCl_2$. THF was distilled off using a fractionating column and the residue distilled in vacuum (0.2 mbar) to yield 19.50 g (84% with respect to R_2Mg) of the organosilane mixture. According to the GC and the GC-MS analysis, the mixture contained five isomeric organosilanes having a molecular weight of 142 in addition to about 20% of oligomerisation products.

The separation of the individual isomers from the mixture by means of preparative gas chromatography was only partially possible. The following four fractions, whose components have been subsequently identified by ^1H NMR spectroscopy (vide infra), were obtained: 57% VIb and 41% VII; 96% VII and 2.6% VIb; 71% VIa, 25% VIa′, 1.8% VIb and 1.8% VII; 89% VIa′ and 8.7% VIa. It did not prove possible to separate or enrich the fifth isomer due to its low concentration and close proximity to VII in the gas chromatogram. The composition of the mixture of $C_5H_9Si(CH_3)_3$ isomers in experiments with different catalysts is shown in Table 1.

^1H NMR data of $C_5H_9Si(CH_3)_3$ isomers (in THF-d_8, int. standard δ 3.60 ($\mathrm{C}H_2\mathrm{O}$)): VIa, δ 5.03 (q, $=\mathrm{C}H$, J 6 Hz), 1.60 (s, $\mathrm{C}H_2$), 1.5 (m, $\mathrm{C}H_3\text{–}\mathrm{CH}=$, $\mathrm{C}H_3\mathrm{C}\overset{\diagup}{=}$), 0.05 (s, $\mathrm{C}H_3\mathrm{Si}$); VIa′, δ 5.11 (q, $=\mathrm{C}H$, J 7 Hz), 1.67 (m, $\mathrm{C}H\text{–}\mathrm{C}\overset{\diagup}{=}$), 1.53 (s, $\mathrm{C}H_2$), 1.50 (m, $\mathrm{C}H_3\text{–}\mathrm{CH}=$), 0.08 (s, $\mathrm{C}H_3\mathrm{Si}$); VIb, δ 4.66, 4.51 (m, $H_2\mathrm{C}=$), 1.70 (s, $\mathrm{C}H_3\text{–}\mathrm{C}\overset{\diagup}{=}$), 1.12 (d, $\mathrm{C}H_3\text{–}\mathrm{CH}\!<$, J 7 Hz), 0.06 (s, $\mathrm{C}H_3\mathrm{Si}$); VII, δ 5.20 (t, $=\mathrm{C}H$, J 8.5 Hz), 1.69, 1.58 (s, $(\mathrm{C}H_3)_2\mathrm{C}=$), 1.42 (d, $\mathrm{C}H_2$, J 8.5 Hz), 0.04 (s, $\mathrm{C}H_3\mathrm{Si}$).

Reaction of I with styrene (Cp_2TiCl_2 as catalyst). To a suspension of 100 mmol of I in 85 ml THF (prepared using the Cr-catalyst), 0.25 g (1.0 mmol) Cp_2TiCl_2 were added with stirring. The suspension was heated to reflux and 25.3 ml (220 mmol) styrene were added dropwise over 1 h. (The half time of the addition of styrene was taken as the zero time in Fig. 2.) The reaction of I with time was followed in the same way as described above for isoprene. After the reaction was completed (~ 3 h), the reaction mixture was centrifuged (2 h, 4000 rpm) and the clear supernatant solution separated from the precipitate. Photolysis of an aliquot of the solution (EtOH) and MS analysis of the liberated hydrogen indicated about 10% hydride content in R_2Mg compounds. 2.0 ml of the solution (containing 1.65 mmol Mg) were evaporated in vacuum (0.2 mbar) and the residue hydrolyzed (EtOH). The ethanol solution was analyzed by gas chromatography using n-octane as an internal standard. The solution contained a total of 0.39 g of hydrolysis products, whose composition is shown in Table 2.

The silylation of the organomagnesium compounds was performed in an analogous manner to that described for the reaction of I with isoprene with the difference that the silylated products were distilled in high vacuum (bath temperature 25–100 °C). The mixture of organosilanes was analyzed by gas chromatography and the several components of the mixture were separated by means of preparative gas chromatography and identified by ^{1}H NMR spectroscopy. The composition of the mixture of organosilanes is given in Table 2.

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