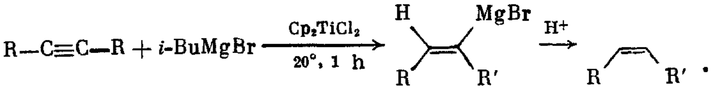
Cp_2TiCl_2-CATALYZED HYDROMAGNATION OF DISUBSTITUTED ACETYLENES AS A STEREOSPECIFIC ROUTE TO Z-ALKENES

U. M. Dzhemilev, O. S. Vostrikova,
R. M. Sultanov, and A. R. Gimaeva

UDC 542.97:547.254.6:547.314:547.313

The catalytic hydromagnation reaction of acetylenes is of significant practical interest as a convenient method for the preparation of otherwise not readily available Z-olefins of high stereopurity [1, 2]:



The reports concerning this reaction have been very limited in scope, however, and the experimental data, in particular, has been uninformative and difficult to reproduce.

In order to develop this reaction into a highly selective and preparatively useful method for the conversion of disubstituted acetylenes to corresponding α-olefins, we have examined in greater detail the principal characteristics of the Cp_2TiCl_2-catalyzed hydromagnation of acetylenes in the presence of i-BuMgBr. In addition, in order to determine the most efficient hydromagnation reagents available, we have also studied other organomagnesium compounds in this context.

In ether solvents (Et_2O, Bu_2O, THF, 1,4-dioxane) in the presence of 5 mole % Cp_2TiCl_2 per mole of organomagnesium compound (at a Mg:acetylene ratio of 1.5:1) hydromagnation is practically complete within 20-30 min. Under these conditions it was found that the conditions used for the formation of the catalytically active complex is the decisive factor which determines the course of the reaction. Thus, in order to obtain reproducibly high yields of alkenylmagnesium compounds, the catalyst sample must be introduced directly into a well-stirred mixture of i-BuMgBr and the corresponding acetylene at a temperature not exceeding 20-25°C (method A). In this event hydromagnation proceeds to completion, even if after the Cp_2TiCl_2 has dissolved the temperature of the reaction mixture is reduced to 0°C. In contrast, when the catalyst is added to the reaction mixture at 0°C, it is inactive, even if the temperature is subsequently raised to 25-30°C or higher.

A second method for the preparation of a highly active catalyst for the hydromagnation of acetylenes involves reduction of Cp_2TiCl_2 in the presence of a ca. 10-fold excess of i-BuMgBr over 5 min in the absence of acetylene; there is no temperature effect under these conditions (method B). The catalyst prepared in this way according to method B is then added to a mixture of acetylene and the residual amount of organomagnesium compound needed. The catalyst prepared in this manner (method B), however, loses its catalytic activity relatively rapidly (ca. 20-30 min).

Unexpectedly, it was found that the catalyst prepared according to method A (in the presence of acetylene) is not an active catalyst for the hydromagnation of 1-octene or isoprene. Based on this data, we conclude that the catalytically active intermediate responsible for the hydromagnation of acetylenes, in contrast to other reactions involving α-olefins [3] or 1,3-dienes [2], is not a simple Ti(III) hydride derivative. In fact, hydrometallation of olefins by a stoichiometric amount of Cp_2TiH (synthesized *in situ* by the reaction of Cp_2TiCl_2 with i-BuMgBr) occurs in the lower yield and less selectively than catalytic hydromagnation. Thus, hydromagnation of 10 mmoles 4-octyne by 12 mmoles Cp_2TiH gives, after hydrolysis, a mixture of 4Z- and 4E-octenes (9:1) in less than 75% yield, based on the amount of octyne converted:

Institute of Chemistry, Bashkir Scientific Center, Ural Branch, Academy of Sciences of the USSR, Ufa. Translated from Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya, No. 9, pp. 2156-2159, September, 1988. Original article submitted March 13, 1987.

0568-5230/88/3709-1936$12.50
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TABLE 1. Effect of the Nature and Structure of Organomagnesium Reagents on the Yield and Stereopurity of 4-Octyne Hydromagnation Products in the Presence of Cp_2TiCl_2*

Experiment No.	RMgX	Ratio of reagents †	Conversion of 4-octyne	Stereopurity of 4Z-octene after hydrolysis
			% (GLC)	
1	*n*-PrMgBr	A	98	98
2	*n*-Pr_2Mg	C	100	98
3	*n*-BuMgBr	A	90	95
4	*i*-Bu_2Mg	C	100	97
5	*i*-BuMgCl	B	90	99
6	*i*-BuMgBr	B	85	98
7	*i*-BuMgI	B	50	97
8	*s*-BuMgBr	A	10	95
9	*t*-BuMgBr	A	0	–
10	*n*-$C_5H_{11}MgBr$	A	75	97
11	*n*-$C_6H_{13}MgBr$	A	60	97
12	*n*-$C_7H_{15}MgBr$	A	50	98
13	*n*-$C_9H_{19}MgBr$	A	20	97
14	cyclo- $C_6H_{11}MgBr$	A	45	96
15	C_3H_5MgBr	A	0	–
16	»	A	0	–

*Experimental conditions: 25°C, 30 min, ether, $[C]_{RMgX}$ = 1.7 moles/liter.

†Reagent ratios RMgX:acetylene:Cp_2TiCl_2 = 150:100:5 (A); 150:100:3 (B); 65:100:3 (C).

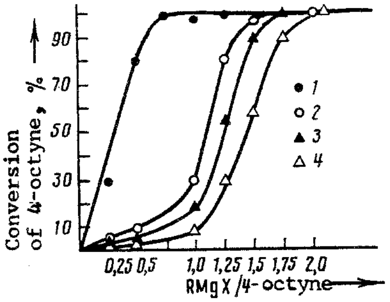


Fig. 1

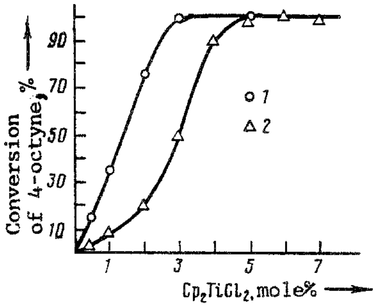
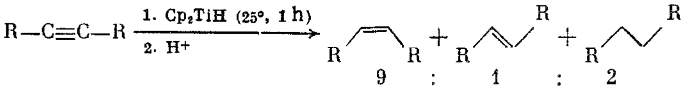


Fig. 2

Fig. 1. Relationship between the conversion of 4-octyne and the RMgX:4-octyne ratio and the nature of X. Reaction conditions: [R-Mg]:Cp_2TiCl_2 = 100:3, 25°C, ether, 0.5 h $[C]_{RMgX}$ = 1.7 mmoles/ml. X = R = n-Bu (1); X = Cl, R = n-Bu (2); X = Br, R = n-Bu (3); X = I, R = n-Bu (4).

Fig. 2. Relationship between the conversion of 4-octyne and the concentration of catalyst. Reaction conditions: [R-Mg]:4-octyne = 100:150, 0.5 h, 25°C, ether, $[C]_{RMgX}$ = 1.7 mmoles/ml. X = R = i-Bu (1), X = Br, R = i-Bu (2).



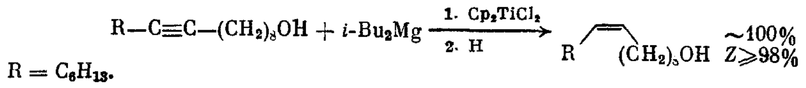
R = C_3H_7.

The observed results indicate that the catalytically active intermediate in the hydromagnation reaction of acetylenes has a complex structure and is, apparently, a bimetallic complex which contains an acetylene ligand in its coordination sphere.

These optimum reaction conditions were then used to carry out the reactions of 4-octyne with alkyl-, allyl-, and vinylmagnesium halides, as well as with magnesium alkyls. It was found that, in addition to i-BuMgBr, other organomagnesium compounds which can participate in this reaction are those containing normal-alkyl radicals, beginning with C_3H_7, although the acetylene conversion decreases with increasing length of the hydrocarbon chain (Table 1). Organomagnesium compounds containing secondary or cycloalkyl radicals are less active, while those with tertiary, allyl, and vinyl alkyl groups do not undergo hydromagnation.

It was also established that the nature of the alkyl substituent, as well as the conditions used to carry out the hydromagnation reactions, have practically no effect on the selectivity of hydromagnation or the stereopurity of the resulting Z-alkenes, which in all experiments was 95-98% (see Table 1). The nature of the second group attached to the Mg atom does exert a substantial effect on the activity of a hydromagnation reagents. Thus, in the series i-BuMgI < i-BuMgBr < i-BuMgCl < i-Bu_2Mg the yield of 4Z-octene from 4-octyne increases from 50 to 100%, under otherwise identical reaction conditions (Experiments 4-7, Table 1). The most active hydromagnation reagent is clearly $(i\text{-Bu})_2$Mg, in which both radicals can be replaced by vinyl groups, although the conversion of i-BuMgHal under these conditions was found to be incomplete (Fig. 1). Furthermore, a lower amount of catalyst is required to carry out hydromagnation reactions using i-Bu_2Mg (Fig. 2).

The feasibility of using this catalytic hydromagnation reaction for the conversion of acetylenic alcohols to Z-alkenols was demonstrated on the basis of the stereoselective reduction of the acetylenic bond in 9-hexadecyn-1-ol to a Z-double bond:



Catalytic hydromagnation thus represents a convenient method for the conversion of disubstituted acetylenes to Z-olefins or Z-alkenylmagnesium compounds, which may be further used in organic synthesis.

EXPERIMENTAL

All of the experiments were carried out under an atmosphere of dry Ar. The hydrocarbons used had purities of greater than 99%; they were distilled over Na immediately prior to use. The ether solvents were treated with KOH, refluxed over Na wire, and then distilled under Ar over $LiAlH_4$. Grignard reagents were prepared in a conventional manner [4]; R_2Mg were prepared by disproportionation of RMgBr according to [5].

The hydrocarbon mixtures were analyzed on a Chrom-5 gas chromatograph equipped with a flame-ionization detector, using a 3.7 m × 3 mm column filled with 10% polyethylene glycol-succinate on GN-AW-DMCS Chromosorb (0.2-0.25 mm), which was modified with 2% $AgNO_3$; the temperature was 120°C; the carrier gas was helium.

General Method for the Hydromagnation of Disubstituted Acetylenes. Method A. To a solution of 6.5 mmoles $(i\text{-Bu})_2$Mg or 15 mmoles alkylmagnesium halide and 10 mmoles disubstituted acetylene at 20-25°C was added the required amount of Cp_2TiCl_2, while maintaining constant stirring; the reaction mixture was maintained for 20-30 min at 20°C, then cooled to 0°C, and the catalyst was hydrolyzed with a saturated solution of NH_4Cl. The organic layer was separated, dried over $MgSO_4$, and analyzed by comparison with authentic samples [6, 7]. For the hydromagnation of alkynols, to a solution of 12 mmoles i-Bu_2Mg cooled to −20°C was added dropwise 10 mmoles of alkynol; the temperature was then raised to ca. 20°C and then the catalyst was introduced.

Method B. To a solution of 2 mmoles i-BuMgBr in 2 ml Et_2O was added 50 mg (0.2 mmole) Cp_2TiCl_2; the mixture was stirred until a homogeneous solution was formed and the required amounts of disubstituted acetylene and organomagnesium compound were then added. Further workup was the same as described above for method A.

CONCLUSIONS

The hydromagnation reaction of disubstituted acetylenes has been systematically studied in the presence of catalytic quantities of Cp_2TiCl_2. It was found that the conditions used to form the catalytic complex exerted the decisive effect on the course of the reaction, and that the most active hydromagnation reagents were n-Pr_2Mg and i-Bu_2Mg.

The hydrotitanation of disubstituted acetylenes using Cp_2TiH was also demonstrated.

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TRANSITION METAL σ-COMPLEXES IN ORGANIC SYNTHESIS.

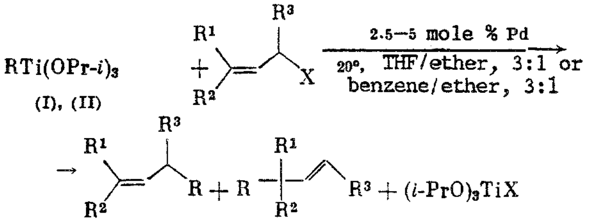
4. CROSS COUPLING OF ALLYL ESTERS AND ALLYL ARYL SULFONES WITH ORGANOTITANIUM COMPOUNDS IN THE PRESENCE OF PALLADIUM COMPLEXES

A. N. Kasatkin, A. N. Kulak,
G. A. Tolstikov, and S. I. Lomakina

UDC 542.97:547.292'361:
547.258.2

We have previously reported the Pd-complex-catalyzed reaction of organotitanium compounds (OTC) $RTi(OR')_3$ and $RTi(NEt_2)_3$ (R = Ar, Me, alkenyl; R' = Alk, Ph) with allyl halides, which gives allyldemetallation products [1-3]. In the present paper we have examined the cross-coupling reactions of allyl acetates, allyl phenyl ethers, allyl aryl sulfones, and allyl tosylates and mesylates with OTC. The OTC starting materials were $PhTi(OPr\text{-}i)_3$ (I) and $MeTi(OPr\text{-}i)_3$ (II), which were prepared *in situ* by the reaction of PhLi or MeLi with $(i\text{-}PrO)_3TiCl$ [4]:

$$RLi + (i\text{-}PrO)_3TiCl \xrightarrow[20°,\ 1\ h]{ether} \underset{(I),\ (II)}{RTi(OPr\text{-}i)_3} + LiCl$$



(1)

$R^1, R^3 = H$, Alk; $R^2 = H$, Alk, Ph: X = OAc, OPh, SO_2Ph, $SO_2C_6H_4Cl\text{-}p$, OTs, OMs;
Pd = $Pd(PPh_3)_4$(A), $(\eta^3\text{-}C_3H_5PdCl)_2$(B).

Reaction of (I) with allyl acetates, allyl phenyl ethers, allyl phenyl and allyl p-chlorophenyl sulfones in THF/ether (3:1) solution in the presence of 5 mole % tetrakis(triphenylphosphine)palladium (A) at 20°C gave the cross-coupling products (III-VIII) in 60-100% yields (Table 1). For the series of compounds $CH_2{=}CHCH_2X$ the reactivity [with respect to reaction (I)] increases in the following order: X = SO_2Ph < X = OAc < X = OPh; in the series of compounds $CH_2{=}CH(CH_2)_3CH{=}CHCH_2X$ the reactivity increases in the transition from X = SO_2Ph to X = OAc and further to X = $SO_2C_6H_4Cl$-p. It is noteworthy that allyl p-chlorophenyl sulfones are substantially more reactive in this regard than allyl phenyl sulfones. Thus, for the reaction of (I) with $CH_2{=}CH(CH_2)_3CH{=}CHCH_2SO_2C_6H_4Cl$-p in the presence of (A), the overall yield of regioisomeric phenyloctadienes (Va, b) after 58 h was 76%; in contrast, reaction of (I) with $CH_2{=}CH(CH_2)_3CH{=}CHCH_2SO_2Ph$ gave only traces of allyl demetallation products after 100 h. The small decrease noted in the rate of cross coupling in the transition from allyl phenyl ethers and allyl p-chlorophenyl sulfones to the corresponding allyl acetates can, apparently, be attributed to transesterification side reactions of the latter to give isopropyl acetates in the presence of organotitanium reagents [5]:

Institute of Chemistry, Bashkir Scientific Center, Ural Branch, Academy of Sciences of the USSR, Ufa. Translated from Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya, No. 9, pp. 2159-2166, September, 1988. Original article submitted January 6, 1987.

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