

TABLE 1. Isotopic Composition of the Methane Obtained in the Reactions (t-BuO)<sub>2</sub>VMe<sub>2</sub>+D<sub>2</sub>O, (t-BuO)<sub>2</sub>V(CD<sub>3</sub>)<sub>2</sub>+D<sub>2</sub>O

Reaction	D <sub>2</sub> O/(I)	CH <sub>4</sub> /(I)	CH <sub>3</sub> D/(I)	Reaction	D <sub>2</sub> O/(II)	CD <sub>3</sub> H/(II)	CD <sub>4</sub> /(II)
(I)+D <sub>2</sub> O	0,05	0,143	0,008	(II)+D <sub>2</sub> O	0,05	0,16	0,007
	0,18	0,06	0,002		0,25	0,08	0,002
	0,45	0,28	0,03		1,7	0,91	0,6
	1,72	0,9	0,63		3,2	0,8	0,7
	2,76	1,08	0,43				

The solubility of water in heptane was found to be  $3.7 \cdot 10^{-6}$  mole/ml. The amount of methane evolved in the reaction was measured chromatographically using a circulatory vacuum apparatus connected to an LKhM-8MD chromatograph (Porapak T column). To determine the isotopic composition of the methane, it was drawn off from the reaction vessel cooled in liquid nitrogen into an ampul, and analyzed in an MI-1305 spectrometer.

### CONCLUSIONS

1. Reaction of (t-BuO)<sub>2</sub>VMe<sub>2</sub> with water occurs by both homolytic and hydrolytic fission of the V-C bond.
2. At low concentrations, water functions as a catalyst for the decomposition of (t-BuO)<sub>2</sub>VMe<sub>2</sub>.

### LITERATURE CITED

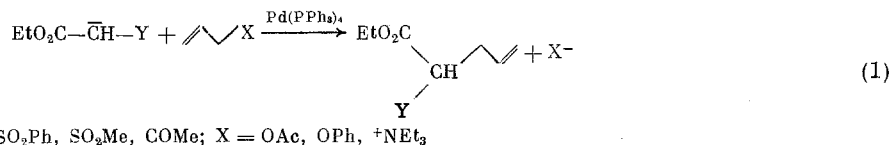
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REACTIONS OF ORGANOMETALLIC COMPOUNDS CATALYZED  
BY COMPLEXES OF TRANSITION METALS  
COMMUNICATION 5. ORGANOMAGNESIUM, -ZINC, -CADMIUM, AND -ALUMINUM  
COMPOUNDS IN ALLYLDOMETALLATION REACTIONS CATALYZED BY  
PALLADIUM COMPLEXES

N. A. Bumagin, A. N. Kasatkin,  
and I. P. Beletskaya

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The allylic alkylation of stable carbanions of type (I) catalyzed by palladium complexes is well known [1, 2].



The application of organotin compounds in reactions (I), which open new vistas for the synthesis of various allylated products, was brought about for the first time in the example of allyl- and enolstannanes in [3, 4] and extended to various aryl, vinyl, and allyl derivatives of tin including stannylated ketones and esters in [5].

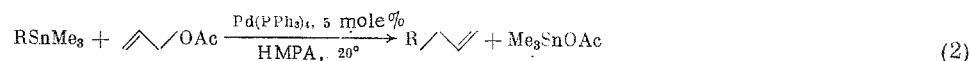
M. V. Lomonosov Moscow State University. L. Ya. Karpov Physical Chemistry Institute, Moscow.  
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TABLE 1. Reactions of Organometallic Compounds PhM with CH<sub>2</sub>=CHCH<sub>2</sub>X Catalyzed by Pd(PPh<sub>3</sub>)<sub>4</sub> (5 mole %) (THF, 20°C, C<sub>RM</sub> = C<sub>CH<sub>2</sub>=CHCH<sub>2</sub>X</sub> = 0.21 mole/liter)

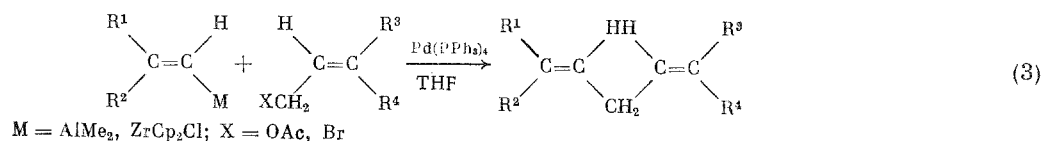
Number according to time	PhM	X	Time, h	Ph	Ph <sub>2</sub>
				%	
1	PhMgBr	Br *	15 min	96	0
2		OPh	1.5	39	60
3	PhZnCl	+NEt <sub>3</sub>	1.5	11	84
4		Br	3.5	100	0
5		OAc	5	100	0
6		OPh	8	98	0
7		+NEt <sub>3</sub>	4	69	25
8		Br	12	71	24
9	PhCdBr	OAc	16	50	46
10		OPh	20	34	60
11		+NEt <sub>3</sub>	20	12	85
12		Br	20	Traces	Traces
13	PhAlCl <sub>2</sub> †	OAc	20	0	»
14		OPh	20	0	»
15		Br	20	37	»

\* In the absence of catalyst 23% allylbenzene was formed after 3 h.

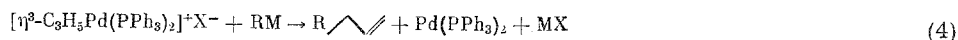
† Reactions were carried out in ether.



More reactive organometallic compounds were introduced in cross combination with CH<sub>2</sub>=CHCH<sub>2</sub>X. These were mainly alkenyl derivatives of aluminum and zirconium [6, 7].



It was suggested in [1] that the intermediate in catalytic processes (1)-(3) was the cationic π-allylpalladium complex [η<sup>3</sup>-C<sub>3</sub>H<sub>5</sub>Pd(PPh<sub>3</sub>)<sub>2</sub>]<sup>+</sup>X<sup>-</sup> which forms the allyldemetallation product on interaction with the organometallic compound RM.

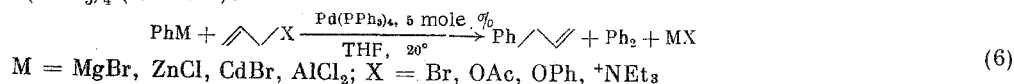


Moreover, the data available in the literature do not permit an answer to the problem how the nature of the metal in RM influences the process of reaction (5) since in the studied reactions of various metal derivatives the nature of the organic radical R, the leaving group X, the palladium catalyst, and also the conditions of carrying out the reaction (solvent, temperature) differ appreciably from one to another.



In the present work we have studied the influence of the nature of M, R, and X on the rate of reaction (5) and on the yield of allyldemetallation product.

With the aim of varying the nature of the metal the reaction was carried out with PhMgBr, PhZnCl, PhCdBr, and PhAlCl<sub>2</sub>, and CH<sub>2</sub>=CHCH<sub>2</sub>X (X = Br, OAc, OPh, +NEt<sub>3</sub>) in tetrahydrofuran (THF) at ~20°C in the presence of 5 mole% Pd(PPh<sub>3</sub>)<sub>4</sub> (Table 1).



As follows from the data of Table 1 the reactivity of organometallic compounds decreases in the following series in reactions with allyl bromide: PhMgBr\* > PhZnCl > PhCdBr >> PhAlCl<sub>2</sub>. Thus, PhMgBr and PhZnCl

\* It should be noted that in the absence of palladium catalyst 23% allylbenzene was formed after 3 h in the reaction of PhMgBr with CH<sub>2</sub>=CHCH<sub>2</sub>Br (THF, 20°C).

TABLE 2. Variation of the Nature of the Palladium Catalyst in Reactions of Organometallic Compounds PhM with Allyl Bromide (THF, 20°C, 5 mole % catalyst,  $C_{RM} = C_{CH_2=CHCH_2Br} = 0.21$  mole/liter)

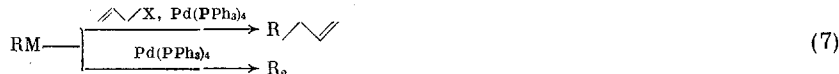
Number according to time	PhM	Catalyst	Time, h	Ph $\backslash$ / $\swarrow$ , %	Ph <sub>2</sub> , %
1	PhMgBr	Pd(PPh <sub>3</sub> ) <sub>4</sub>	15 min	96	0
2		PdCl <sub>2</sub> (PPh <sub>3</sub> ) <sub>2</sub>	15 min	63	35
3	PhZnCl	(η <sup>3</sup> -C <sub>3</sub> H <sub>5</sub> PdCl) <sub>2</sub>	15 min	20	74
4		Pd(PPh <sub>3</sub> ) <sub>4</sub>	3,5	100	0
5	PhAlCl <sub>2</sub> *	(η <sup>3</sup> -C <sub>3</sub> H <sub>5</sub> PdCl) <sub>2</sub>	3	55	40
6		Pd(PPh <sub>3</sub> ) <sub>4</sub>	20	Traces	Traces
7		(η <sup>3</sup> -C <sub>3</sub> H <sub>5</sub> PdCl) <sub>2</sub>	8	94	Traces

\* Reactions were carried out in ether.

react with CH<sub>2</sub>=CHCH<sub>2</sub>Br forming allylbenzene in quantitative yield after 15 min and 3.5 h respectively but in the reaction with PhCdBr 24% diphenyl was obtained together with allylbenzene (71%). Ph<sub>2</sub>AlCl proved to be significantly more reactive than PhAlCl<sub>2</sub>. The latter generally did not react with allyl bromide after 20 h and in the reaction of Ph<sub>2</sub>AlCl with CH<sub>2</sub>=CHCH<sub>2</sub>Br the yield of allylbenzene was 37% after 20 h.

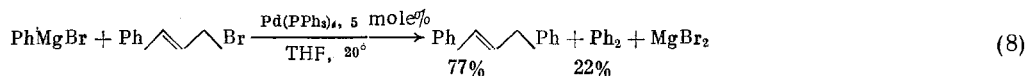
On going over from allyl bromide to allyl acetate, allylphenyl ether, and triethylallylammonium chloride an increase was observed in the amount of Ph<sub>2</sub> formed. Thus, in the reaction of PhCdBr with CH<sub>2</sub>=CHCH<sub>2</sub>Br 24% diphenyl was formed and in reaction with CH<sub>2</sub>=CHCH<sub>2</sub>OAc, CH<sub>2</sub>=CHCH<sub>2</sub>OPh, and (Et<sub>3</sub>NCH<sub>2</sub>CH=CH<sub>2</sub>)Cl the yield of Ph<sub>2</sub> was 46, 60, and 85% respectively. A possible explanation is that the three latter compounds were less reactive than allyl bromide in the oxidative addition to Pd(0) which is one stage of the catalytic cycle [1]. This leads to an increase in the contribution of the side reaction leading to the formation of Ph<sub>2</sub> (reaction 7).

The reason for the formation of diphenyl in reaction (6) is evidently "dimerization" of the organometallic compound which, as in the cross combination is catalyzed by Pd(PPh<sub>3</sub>)<sub>4</sub>.



Independently it was established by experiment that is reality PhMgBr underwent "dimerization" in the presence of 5 mole % Pd(PPh<sub>3</sub>)<sub>4</sub> in THF at ~ 20°C. After 5 h the yield of Ph<sub>2</sub> was 52%. It was shown by us previously in [8] that this process also occurred in the case of the organotin compound RSnMe<sub>3</sub> (R = Ph, PhC≡C, 2-C<sub>4</sub>H<sub>9</sub>S) in hexamethylphosphoramide (HMPA).

Replacement of CH<sub>2</sub>=CHCH<sub>2</sub>Br by cinnamyl bromide in the reaction with PhMgBr catalyzed by Pd(PPh<sub>3</sub>)<sub>4</sub> also led to the formation of a 22% yield of Ph<sub>2</sub> in addition to the cross combination product 1,3-diphenylpropene (77%).



In reactions with allyl acetate (see Table 1, No. 5, 9), allylphenyl ether (No. 2, 6, 10) and triethylallylpalladium chloride (No. 3, 7, 11), PhZnCl proved to be less inclined to the formation of Ph<sub>2</sub> in comparison with PhMgBr and PhCdBr. This fact makes it preferable to use zinc derivatives in the case of X = OAc, OPh, and <sup>+</sup>NET<sub>3</sub>.

Data on the variation of the nature of the palladium catalyst in the reactions of PhMgBr, PhZnCl, and PhAlCl<sub>2</sub> with allyl bromide (THF, 20°C) are shown in Table 2. On going from Pd(PPh<sub>3</sub>)<sub>4</sub> (see Table 2, No. 1) to PdCl<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub> (No. 2) and to (η<sup>3</sup>-C<sub>3</sub>H<sub>5</sub>PdCl)<sub>2</sub> (No. 3) in the reaction of PhMgBr with CH<sub>2</sub>=CHCH<sub>2</sub>Br the yield of allyldemetallation product was reduced but the yield of Ph<sub>2</sub> grew. Replacement of Pd(PPh<sub>3</sub>)<sub>4</sub> with bis-(π-allyl)palladium chloride) in the reaction of PhZnCl with allyl bromide also led to the appearance of significant amounts of "dimerization" products (55% allylbenzene and 40% Ph<sub>2</sub>).

The application of (η<sup>3</sup>-C<sub>3</sub>H<sub>5</sub>PdCl)<sub>2</sub> as catalyst in place of Pd(PPh<sub>3</sub>)<sub>4</sub> proved to be extremely effective in the case of PhAlCl<sub>2</sub>. In the reaction of PhAlCl<sub>2</sub> with allyl bromide catalyzed by Pd(PPh<sub>3</sub>)<sub>4</sub> only traces of allylbenzene were formed after 20 h and in the presence of (η<sup>3</sup>-C<sub>3</sub>H<sub>5</sub>PdCl)<sub>2</sub> the yield of PhCH<sub>2</sub>CH=CH<sub>2</sub> was quantitative after 8 h.

TABLE 3. Yield of Products (RCH<sub>2</sub>CH=CH<sub>2</sub>, %) <sup>a</sup> in Reactions of Organometallic Compounds RM with Allyl Bromide Catalyzed by Pd(PPh<sub>3</sub>)<sub>4</sub> or (η<sup>3</sup>-C<sub>3</sub>H<sub>5</sub>PdCl)<sub>2</sub> (5 mole %) (THF, 20°C, C<sub>RM</sub> = CCH<sub>2</sub> = CHCH<sub>2</sub>Br = 0.21 mole/liter)

Number accord. to time	R	MgBr, Pd(PPh <sub>3</sub> ) <sub>4</sub>	ZnCl, Pd(PPh <sub>3</sub> ) <sub>4</sub>	ZnCl, (η <sup>3</sup> -C <sub>3</sub> H <sub>5</sub> PdCl) <sub>2</sub>	AlCl <sub>3</sub> <sup>b</sup> , (η <sup>3</sup> -C <sub>3</sub> H <sub>5</sub> PdCl) <sub>2</sub>
1	R	96(0), 15 min	100(0), 3,5 h	55(40), 3 h	
2	<i>p</i> -BrC <sub>6</sub> H <sub>4</sub>	92(tr), 15 min			
3	<i>p</i> -MeC <sub>6</sub> H <sub>4</sub>	95(0), 15 min			
4	<i>p</i> -MeOC <sub>6</sub> H <sub>4</sub>	64(32), 15 min	76(19), 5 h		
5	<i>p</i> -Me <sub>2</sub> NC <sub>6</sub> H <sub>4</sub>	53(45), 40 min	65(32), 6,5 h		
6	PhCH <sub>2</sub>	100(tr), 15 min	tr (tr), 20 h	tr (16), 20 h	tr (tr), 20 h
		27(0), 1 h <sup>c</sup>			
7	9-C <sub>13</sub> H <sub>9</sub>	89(tr), 30 min	51(tr), 20h	73(22), 8 h	12(0), 20 h
		19(0), 30 min <sup>c</sup>			
8	2-C <sub>4</sub> H <sub>3</sub> S	100(0), 30 min	32(0), 20 h	45(35), 20 h	36(tr), 20 h
		92(0), 30 min <sup>c</sup>			
9	PhCH=CH	0(100), 30 min	49(47), 3,5h		51(45), 8 h
			25(69), 3,5 h <sup>d</sup>		
10	PhC≡C	0(40), 20h	0(10), 20 h	0(47), 20 h	
		0(94), 20 h <sup>e</sup>			
11	CH <sub>2</sub> CO <sub>2</sub> Et <sup>f</sup>		30(0), 3 h	63(0), 3 h	
			tr (0), 20 h <sup>d</sup>	19(0), 3 h <sup>e</sup>	

a) Yields of R<sub>2</sub> are shown in parentheses (tr indicates trace).

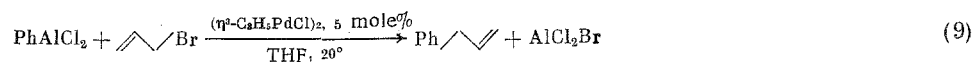
b) Reactions were carried out in ether.

c) Yields of products in the absence of catalyst.

d) CH<sub>2</sub>=CHCH<sub>2</sub>OAc was used.

e) T = 50°C.

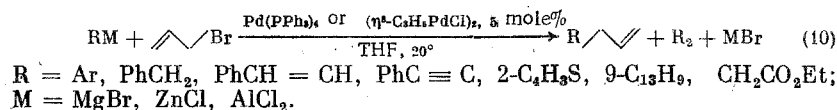
f) THF:HMPA = 1:1, C<sub>RM</sub>:CCH<sub>2</sub>=CHCH<sub>2</sub>Br = 2:1.



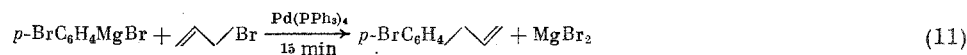
The use of the less active Pd(PPh<sub>3</sub>)<sub>4</sub> proved to be the most convenient for the more reactive organometallic derivatives of magnesium and zinc since it prevented the "dimerization" of RM. In the case of the less reactive organoaluminum compounds the more active "ligand-free" palladium must be used since under these conditions the cross combination proceeds at a greater rate than "dimerization."

The significantly greater catalytic activity of bis-(π-allylpalladium chloride) in comparison with the phosphine complexes of palladium has even been observed previously in cross combination reactions of organotin compounds with aryl and allyl halides in [9].

To clarify the problem as to how the nature of the radical R in the organometallic compound RM influences the rate of the allyldemetallation reaction and the product ratio of RCH<sub>2</sub>CH=CH<sub>2</sub> and R<sub>2</sub>, we studied the reactions of RMgBr, RZnCl, and RAlCl<sub>2</sub> with allyl bromide in THF at ~ 20°C, which are catalyzed by Pd complexes. Results are shown in Table 3.



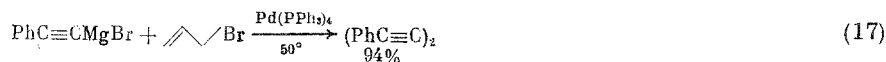
As follows from the data of Table 3 the introduction of electron donating groups into the aromatic ring in a series of aryl organomagnesium compounds led to a reduction in the yield of allyldemetallation products and an increase in the yield of the corresponding diaryls. Thus *p*-tolylmagnesium bromide and *p*-bromophenylmagnesium bromide like phenylmagnesium bromide reacted with allyl bromide in the presence of Pd(PPh<sub>3</sub>)<sub>4</sub> forming the corresponding *p*-methylallylbenzene and *p*-bromoallylbenzene in quantitative yield.



In the absence of palladium catalyst reaction (11) proceeds significantly more slowly and less selectively [10].



Phenylethynylmagnesium bromide proved to be significantly less reactive in comparison with the remaining organomagnesium compounds in the reaction with allyl bromide catalyzed by Pd(PPh<sub>3</sub>)<sub>4</sub>. After 20 h reaction not even traces of cross combination product were formed and bis(phenylethynyl) was formed in 40% yield. An increase of temperature (50°C) led to an increase in the yield of (PhC≡C)<sub>2</sub> to 94%.

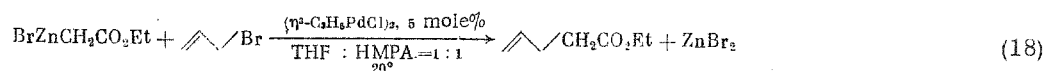


The reaction of PhC≡CZnCl with allyl bromide catalyzed by both Pd(PPh<sub>3</sub>)<sub>4</sub> and by (η<sup>3</sup>-C<sub>3</sub>H<sub>5</sub>PdCl)<sub>2</sub> also did not lead to the preparation of PhC≡CCH<sub>2</sub>CH=CH<sub>2</sub> (see Table 3, No. 10).

In accordance with the proposed mechanism (reaction 4) for establishing the reasons for the low reactivity of PhC≡CMgBr a stoichiometric reaction was carried out of the complex [η<sup>3</sup>-C<sub>3</sub>H<sub>5</sub>Pd(PPh<sub>3</sub>)<sub>2</sub>]<sup>+</sup>Cl<sup>-</sup>, obtained in situ from (η<sup>3</sup>-C<sub>3</sub>H<sub>5</sub>PdCl)<sub>2</sub> and 2 equiv. PPh<sub>3</sub> (calculated on Pd), with PhC≡CMgBr in THF at ~20°C. It was established that under the indicated conditions PhC≡CCH<sub>2</sub>CH=CH<sub>2</sub> was not formed even after 30 h. In addition an intense spot (R<sub>f</sub> 0.7) luminous in UV light was detected on a chromatogram of the reaction mixture (silufol, chloroform) corresponding seemingly to a new palladium complex the structure of which was not investigated specially. On heating the chromatogram (150-160°C) the mentioned spot blackened as a result of the separation of metallic palladium. It is possible that the formation of such a complex not undergoing further conversion is also a reason for the low reactivity of PhC≡CMgBr in the catalytic reaction with CH<sub>2</sub>=CHCH<sub>2</sub>Br.

Organozinc compounds obtained by the introduction of α-bromo derivatives of esters with zinc dust (Reformatsky reagent) react (according to [11, 12]) with aryl and vinyl halides in the presence of palladium complexes forming the corresponding cross combination products (α-aryl and α-vinyl substituted esters) in high yield. With the aim of extending the given reaction to allyl halides we studied the reaction of BrZnCH<sub>2</sub>CO<sub>2</sub>Et with allyl bromide in the presence of Pd(PPh<sub>3</sub>)<sub>4</sub> and (η<sup>3</sup>-C<sub>3</sub>H<sub>5</sub>PdCl)<sub>2</sub>.

On using bis-(π-allylpalladium chloride) as catalyst and a 1:1 mixture of THF and HMPA as solvent the ethyl ester of allylacetic acid was obtained in 63% yield after 3 h.



Replacement of (η<sup>3</sup>-C<sub>3</sub>H<sub>5</sub>PdCl)<sub>2</sub> by Pd(PPh<sub>3</sub>)<sub>4</sub> and also increasing the temperature led to a reduction in the yield of product (see Table 3, No. 11), in pure THF only traces of CH<sub>2</sub>=CHCH<sub>2</sub>CH<sub>2</sub>CO<sub>2</sub>Et were formed after 20 h.

Reaction (18) was a convenient method of introducing an allyl group into the α-position of esters.

## EXPERIMENTAL

Organomagnesium compounds (as 1.5 M solutions), palladium complexes, and the necessary standard compounds were synthesized by known procedures. Organozinc, cadmium, and aluminum compounds were obtained in situ by reaction of the corresponding organomagnesium compounds with anhydrous ZnCl<sub>2</sub>, CdBr<sub>2</sub>, and AlCl<sub>3</sub> in THF.

Chromatographic analysis was carried out on a "Tsvet-110" chromatograph with a flame ionization detector in a flow of helium (60 ml/min); column 2 m × 3 mm, 3% SE-30 on Chromaton N super. TLC was carried out on "Silufol UV-254" plates with visualization in UV light or iodine vapor. UV spectra were described on a Hitachi-124 spectrophotometer in quartz cuvettes.

Reaction of PhMg with CH<sub>2</sub>=CHCH<sub>2</sub>X in the Presence of Palladium Complexes. THF (2 ml), 1.5 M solution (0.36 ml:0.55 mmole) of PhMgBr in ether, and allyl bromide (0.061 g:0.5 mmole) were placed, in a stream of argon, in a flask fitted with a magnetic stirrer and Pd(PPh<sub>3</sub>)<sub>4</sub> (0.029 g:0.025 mmole) was added with stirring to the solution. The yield of allylbenzene was determined after 15 min by GLC using an internal standard (n-decane). Yield of PhCH<sub>2</sub>CH=CH<sub>2</sub> was 96%. The same reaction in the absence of catalyst led to the preparation of allylbenzene in 23% yield after 3 h.

The reactions of PhMgBr, PhZnCl, PhCdBr, PhAlCl<sub>2</sub>, and Ph<sub>2</sub>AlCl with CH<sub>2</sub>=CHCH<sub>2</sub>X (X = Br, OAc, OPh, <sup>+</sup>NEt<sub>3</sub>) in the presence of Pd(PPh<sub>3</sub>)<sub>4</sub>, PdCl<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub>, and (η<sup>3</sup>-C<sub>3</sub>H<sub>5</sub>PdCl)<sub>2</sub> were carried out in a similar manner. The yield of Ph<sub>2</sub> was determined by TLC and UV spectroscopy. Data are shown in Tables 1 and 2.

"Dimerization" of PhMgBr in the Presence of Pd(PPh<sub>3</sub>)<sub>4</sub>. In a stream of Ar, THF (2 ml) and a 1.5 M solution (0.36 ml:0.55 mmole) of PhMgBr in ether were placed in a flask which had been blown through with

Ar, and Pd(PPh<sub>3</sub>)<sub>4</sub> (0.029 g:0.025 mmole) was added with stirring to the obtained solution. The yield of Ph<sub>2</sub> was determined after 5 h by TLC and UV spectroscopy and amounted to 52%.

Reactions of RMgBr, RZnCl, and AlCl<sub>3</sub> with Allyl Bromide in the Presence of Palladium Complexes.

1) In a stream of Ar, THF (20 ml), 1.5 M solution (3.6 ml:5.5 mmole) of p-MeC<sub>6</sub>H<sub>4</sub>MgBr in ether, and allyl bromide (0.61 g:5 mmole) were placed in a flask which had been blown through with Ar, and Pd(PPh<sub>3</sub>)<sub>4</sub> (0.29 g:0.25 mmole) was added with stirring to the obtained solution. After 15 min the reaction mixture was diluted with hexane and passed through a short column of silica gel to remove palladium complexes. By fractional distillation p-MeC<sub>6</sub>H<sub>4</sub>CH<sub>2</sub>CH=CH<sub>2</sub> [13] was isolated having bp 70°C (12 mm).

The following RMgBr were reacted with allyl bromide catalyzed by Pd(PPh<sub>3</sub>)<sub>4</sub> under analogous conditions.

2) p-BrC<sub>6</sub>H<sub>4</sub>MgBr. p-BrC<sub>6</sub>H<sub>4</sub>CH<sub>2</sub>CH=CH<sub>2</sub> (0.91 g:92%) was isolated after 15 min and had bp 92°C (8 mm) [10]. 3) p-MeOC<sub>6</sub>H<sub>4</sub>MgBr. p-MeOC<sub>6</sub>H<sub>4</sub>CH<sub>2</sub>CH=CH<sub>2</sub> (0.47 g:64%) was isolated after 15 min and had bp 96°C (12 mm) [13]. In addition (p-MeOC<sub>6</sub>H<sub>4</sub>)<sub>2</sub> (32%) was formed (TLC, UV spectroscopy). 4) p-Me<sub>2</sub>NC<sub>6</sub>H<sub>4</sub>MgBr. After 30 min, yield 0.43 g (53%) p-Me<sub>2</sub>NC<sub>6</sub>H<sub>4</sub>CH<sub>2</sub>CH=CH<sub>2</sub> [14], bp 87°C (3 mm). In addition (p-Me<sub>2</sub>NC<sub>6</sub>H<sub>4</sub>)<sub>2</sub> (45%) was formed (TLC, UV spectroscopy). 5) PhCH<sub>2</sub>MgBr. PhCH<sub>2</sub>CH<sub>2</sub>CH=CH<sub>2</sub> (0.66 g:100%) was isolated after 15 min and had bp 64°C (10 mm) [15]. 6) (2-C<sub>4</sub>H<sub>9</sub>S)MgBr. (2-C<sub>4</sub>H<sub>9</sub>S)CH<sub>2</sub>CH=CH<sub>2</sub> (0.62 g:100%) was isolated after 30 min and had bp 157-159°C [16]. 7) (9-C<sub>13</sub>H<sub>9</sub>)MgBr. 9-Allylfluorene (0.92 g:89%) was isolated after 30 min by TLC on silica gel (hexane:ether = 3:1) [17]. 8) PhCH=CHMgBr. (PhCH)<sub>2</sub> (100%) was formed after 30 min (TLC, UV spectroscopy). 9) PhC≡CMgBr. (PhC≡C)<sub>2</sub> (40%) was formed after 20 h (TLC, UV spectroscopy). The same reaction at 50°C led to the formation of (PhC≡C)<sub>2</sub> in 94% yield after 20 h.

The reactions of RZnCl and AlCl<sub>3</sub> with allyl bromide in the presence of Pd(PPh<sub>3</sub>)<sub>4</sub> and (η<sup>3</sup>-C<sub>3</sub>H<sub>5</sub>PdCl)<sub>2</sub> were carried out by a similar procedure. Yields of RCH<sub>2</sub>CH=CH<sub>2</sub> were determined by GLC using an internal standard (n-decane), yields of R<sub>2</sub> were determined by TLC and UV spectroscopy. Results are shown in Table 3.

Reaction of BrZnCH<sub>2</sub>CO<sub>2</sub>Et with Allyl Bromide Catalyzed by (η<sup>3</sup>-C<sub>3</sub>H<sub>5</sub>PdCl)<sub>2</sub>. In a stream of Ar, a 1-M solution (10 ml:10 mmole) of BrZnCH<sub>2</sub>CO<sub>2</sub>Et in THF (obtained by the reaction of BrCH<sub>2</sub>CO<sub>2</sub>Et with zinc dust), HMPA (10 ml), and allyl bromide (0.61 g:5 mmole) were placed in a flask which had been swept out with Ar, and (η<sup>3</sup>-C<sub>3</sub>H<sub>5</sub>PdCl)<sub>2</sub> (0.046 g:0.25 mmole) was added with stirring to the obtained solution. The reaction mixture was stored for 3 h at ~20°C, CH<sub>2</sub>=CHCH<sub>2</sub>CH<sub>2</sub>CO<sub>2</sub>Et (0.40 g:63%) was isolated by fractional distillation, and had bp 144-146°C [18].

Stoichiometric Reaction of [η<sup>3</sup>-C<sub>3</sub>H<sub>5</sub>Pd(PPh<sub>3</sub>)<sub>2</sub>]<sup>+</sup>Cl<sup>-</sup> with PhC≡CMgBr. In a current of Ar, THF (3 ml), (η<sup>3</sup>-C<sub>3</sub>H<sub>5</sub>PdCl)<sub>2</sub> (0.045 g:0.125 mmole), and PPh<sub>3</sub> (0.131 g:0.5 mmole) were placed in a flask fitted with a magnetic stirrer which had been swept out with Ar. After stirring for 20 min spots of (η<sup>3</sup>-C<sub>3</sub>H<sub>5</sub>PdCl)<sub>2</sub> and PPh<sub>3</sub> had disappeared from a chromatogram (heptane, visualization with I<sub>2</sub>). A 1.5 M solution (0.17 ml:0.25 mmole) of PhC≡CMgBr in ether was added to the reaction mixture. The homogeneous solution was kept at ~20°C for 30 h. Analysis of the reaction mixture showed the absence of PhC≡CCH<sub>2</sub>CH=CH<sub>2</sub> (GLC) and the presence of a new palladium complex of unknown structure (TLC, CHCl<sub>3</sub>, R<sub>f</sub> 0.7). The spot with R<sub>f</sub> 0.7, evidently corresponding to this complex, was intensely colored in UV light and on heating to 150-160°C became dark as a result of the separation of metallic palladium. In addition (PhC≡C)<sub>2</sub> was formed in 15% yield (TLC, UV spectroscopy).

## CONCLUSIONS

1. Reactions of organometallic compounds RM (R = Ph, p-MeC<sub>6</sub>H<sub>4</sub>, p-BrC<sub>6</sub>H<sub>4</sub>, p-MeOC<sub>6</sub>H<sub>4</sub>, p-Me<sub>2</sub>NC<sub>6</sub>H<sub>4</sub>, PhCH<sub>2</sub>, PhCH=CH, 9-fluorenyl, 2-thienyl, PhC≡C; M = MgBr, ZnCl, CdBr, AlCl<sub>3</sub>) with CH<sub>2</sub>=CHCH<sub>2</sub>X (X = Br, OAc, OPh, <sup>+</sup>NEt<sub>3</sub>) catalyzed by Pd(PPh<sub>3</sub>)<sub>4</sub> and (η<sup>3</sup>-C<sub>3</sub>H<sub>5</sub>PdCl)<sub>2</sub> in THF have been studied. The influence has been investigated of the nature of metal M, of the organic radical R, and of the leaving group X on the rate of allyldemetallation and on the yield of products RCH<sub>2</sub>CH=CH<sub>2</sub> and R<sub>2</sub>.

2. The reactions of RMgBr (R = Ph, p-MeC<sub>6</sub>H<sub>4</sub>, p-BrC<sub>6</sub>H<sub>4</sub>, PhCH<sub>2</sub>, 9-fluorenyl, 2-thienyl) with CH<sub>2</sub>=CHCH<sub>2</sub>Br catalyzed by Pd(PPh<sub>3</sub>)<sub>4</sub> proceeded significantly more rapidly and selectively than in the absence of palladium catalyst which made it possible to obtain the corresponding products of allyldemetallation under mild conditions and in high yield.

3. The main possibility of allyldemetallation of Reformatsky reagents has been shown for the first time in the example of the reaction of BrZnCH<sub>2</sub>CO<sub>2</sub>Et with CH<sub>2</sub>=CHCH<sub>2</sub>Br catalyzed by (η<sup>3</sup>-C<sub>3</sub>H<sub>5</sub>PdCl)<sub>2</sub> and leading to the preparation of CH<sub>2</sub>=CHCH<sub>2</sub>CO<sub>2</sub>Et. The reaction is a convenient method for introducing the allyl group into the α-position of esters.

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