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PALLADIUM(0)-PROMOTED CROSS-COUPLING OF ALLENYLMETAL COMPOUNDS WITH ARYL AND VINYL IODIDES. A NOVEL ROUTE TO ARYL- AND VINYL-SUBSTITUTED ALLENES

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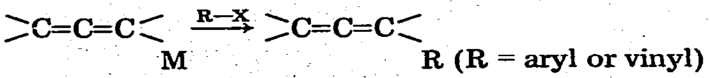
Summary

The reaction of allenylmetal compounds, RR'C=C=CHM (I), with aryl and vinyl iodides, R"I, have been studied. With $Pd(PPh_3)_4$ as catalyst a highly regioselective formation of allenes, RR'C=C=CHR" (II), has been observed for M = MgCl, Cu, $Cu_{1/2}Li_{1/2}$, Ag, $Ag_{1/2}Li_{1/2}$, or ZnCl, but not Li. The reaction of the vinylic iodides proceeds with retention of configuration.

Introduction

Allenes have been the subject of many synthetic and theoretical investigations [1], and several compounds found in nature contain the allene unit as an essential structural feature [1—4]. The present paper describes the synthesis of a number of aryl- and vinyl-allenes. Vinylallenes are of potential interest for prostaglandin synthesis since they can be converted into cyclopentenone derivatives [5]. The insect pheromone of the male dried bean beetle *Acanthoscelides obtectus* also contains the vinylallene structure [6]. Arylallenes have been used to prepare, e.g., indene derivatives [7].

The literature gives several methods of preparing aryl- and vinyl-substituted allenes (cf. ref. 1), but none of these utilizes the following reaction principle:



$$>C{=}C{=}\underset{M}{C}< \xrightarrow{R-X} >C{=}C{=}\underset{R}{C}< \quad (R = \text{aryl or vinyl})$$

Such an approach would be of value because several allenylmetal compounds are readily available. Allenyllithium compounds, for instance, can be obtained by direct lithiation of allenes by alkyllithiums [8,9]. This has opened up easy routes to other allenylmetal compounds, e.g. to allenylcopper [10,11] and allenylsilver compounds [12]. We show below that this approach is indeed of synthetic value, and that several allenylmetal compounds undergo cross-coupling with both aryl and vinyl iodides provided that an effective catalyst is used.

Results and discussion

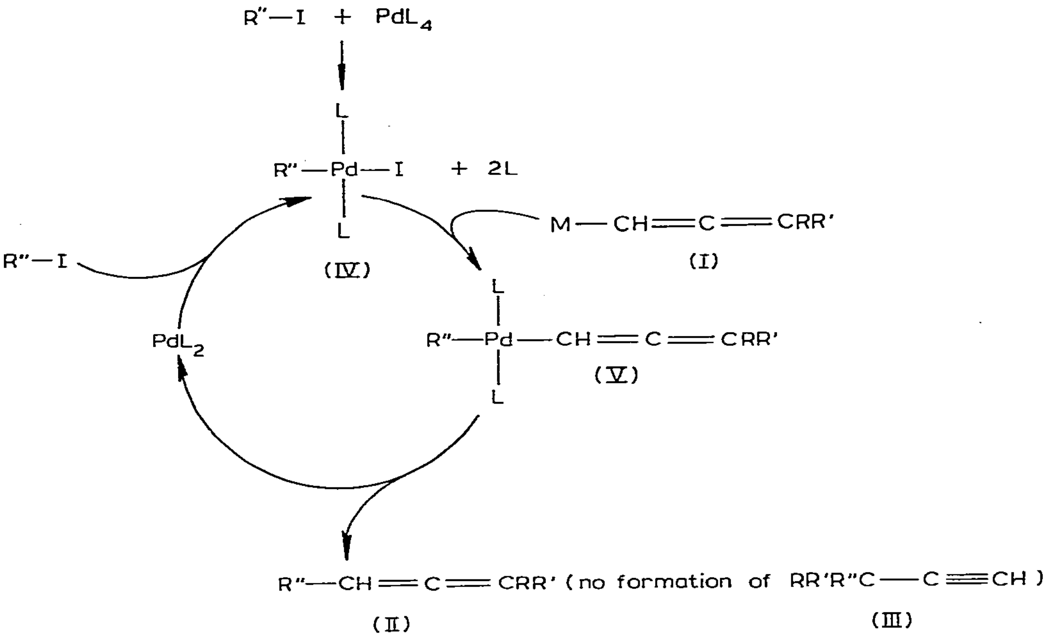
Choice of metal and catalyst. A number of metals M have been investigated in attempts to bring about cross-coupling between RR′C=C=CHM (I) and aryl or vinyl iodides, R″I. Table 1 shows that, except with the highly electropositive lithium, reasonable to excellent cross-coupling reactions are obtained, i.e. for M = MgCl, Cu, $Cu_{1/2}Li_{1/2}$, Ag, $Ag_{1/2}Li_{1/2}$, and ZnCl. For this reaction, which gives only allenes, an effective catalyst is required (see entries 13 and 25). In our case good results were obtained by use of 2—5 mole % of the well-known palladium(0) catalyst $Pd(PPh_3)_4$ [13]. In two experiments the corresponding nickel(0) and platinum(0) complexes were investigated but with less success (see note j in Table 1). All other experiments were therefore carried out using the palladium catalyst.

The experiments given in entries 16—24 and 6—12 indicate that allenylzinc chlorides, monoallenylcopper compounds, and diallenyl cuprates are effective in giving aryl- and vinyl-substituted allenes, RR′C=C=CHR″ (II). Interestingly, monoallenylsilver compounds and their "ate"-derivatives can also be used in principle (see entries 14 and 15); the yields of II are somewhat lower than for the other metals, probably because of partial decomposition of the silver reagents. Some cross-coupling reactions involving an allenylmagnesium chloride are also shown in the Table (entries 3—5), and it will be seen an excellent result was obtained for the coupling of this Grignard reagent with (*Z*)-1-iodo-1-hexene (entry 5). Cross-coupling with phenyl iodide is rather slow, however, and the analogous copper, silver, and zinc reagents are superior in this case (compare entries 3 and 4 with 6—10, 14, 15, 18, and 19). It is known that cross-coupling of 1-alkynyl-, aryl-, and benzyl-metal reagents with aryl halides is better with zinc compounds than Grignard derivatives [14—16].

Allenyllithium compounds cannot be utilized in the catalytic reaction (entries 1 and 2). Similar disappointing results were reported with 1-alkynyl- and aryllithium reagents [16]. On the other hand, excellent cross-coupling was observed between vinyl halides and various organolithium compounds using equimolar amounts of $Pd(PPh_3)_4$ [17].

Regio- and stereo-chemistry/mechanism. In none of the experiments of Table 1 were detectable amounts of 1-alkynes, RR′R″C—C≡CH (III, see Scheme 1) formed. The palladium-induced cross-coupling thus proceeds with high regioselectivity (>98%). From the literature is known that the allene/alkyne ratio depends strongly on the nature of the electrophile and of the metal in the allenylmetal compound. For instance, allenyllithium reagents react with n-alkyl halides to a mixture of allene and alkyne [8]; their cuprate derivatives produce only allenes [10]. Allenylsilver compounds are converted into pure allenes by various electrophiles [18]. If carbon disulfide is used, however, the initial product is exclusively the alkyne [12]. In our work the nature of M in I did not influence the regiochemistry of the reaction and this is understandable in terms of the generally assumed oxidative addition—transmetalation—reductive elimination scheme for transition metal-catalysed reactions (cf. ref. 19, see

SCHEME 1



L = PPh_3
M = MgCl, Cu, $Cu_{1/2}Li_{1/2}$, Ag, $Ag_{1/2}Li_{1/2}$, or ZnCl
R = H, Me, or t-Bu
R′ = H or Me
R″ = (*Z*)- or (*E*)-BuCH=CH-, (*Z*)-t-BuCH=CH-, Ph, *p*-ClPh, or *p*-NO_2Ph

Scheme 1). If this mechanism operates in our case, all reactions leading to allenes II will proceed through the palladium(II) intermediates IV and V in the Scheme [20]. On this view the regiochemistry does not depend on the metal M of the allene transferring reagent I, but only on the specificity of the reductive elimination of V. In view of our results the latter must be high.

The efficiency of transition metal-catalysed cross-coupling of organometal compounds with electrophiles depends greatly on the ease of catalyst recycling during the process. If the process is slow, other reactions such as halogen–metal exchange and thermal decomposition may compete effectively. This is apparently the case when M in I is lithium.

The palladium-induced substitution in the vinylic iodides R″I takes place with retention of configuration in the vinyl unit. This is a common feature for palladium catalysed substitution reactions in vinyl halides [21,22]. This suggests that adduct IV is not formed via free radicals (cf. ref. 17).

Solvent. A mixture of tetrahydrofuran (THF) and hexamethylphosphoric triamide (HMPT) is effective for the cross-coupling reactions. Allenylzinc chlorides, for instance, react with aryl iodides in this mixture faster than in THF alone. Nevertheless, excellent cross-couplings were observed in THF alone (entries 5, 11, 22—24). Interestingly, the parent allenylzinc compound reacts

TABLE 1

FORMATION OF RR′C=C=CHR″ (II) BY REACTION OF RR′C=C=CH-M (I) WITH R″I

Entry	Compound I			R″I	$Pd(PPh_3)_4$ [a] (mole %)	Solvent [b]	Reaction temperature (°C)	Reaction time (min)	Yield [c] of II (%)	Remarks
	R	R′	M							
1	Me	Me	Li	PhI	5.0	THF	25	60	<3	d, e
2	t-Bu	H	Li	PhI	4.0	THF/HMPT	40	30	<3	e, f
3	t-Bu	H	MgCl	PhI	5.0	THF/HMPT	25	60	<3	d, g
4	t-Bu	H	MgCl	PhI	4.0	THF/HMPT	50	60	66	d, g
5	t-Bu	H	MgCl	(*Z*)-BuCH=CHI	4.0	THF	35	120	>98	d, h, i
6	Me	Me	Cu	PhI	4.0	THF/HMPT	40	30	>98	f
7	t-Bu	H	Cu	PhI	4.0	THF/HMPT	25	30	75	f, g
8	t-Bu	H	Cu	PhI	4.0	THF/HMPT	40	30	>98	f
9	t-Bu	H	$Cu_{1/2}Li_{1/2}$	PhI	4.0	THF	25	60	85	d, g
10	t-Bu	H	$Cu_{1/2}Li_{1/2}$	PhI	4.0	THF/HMPT	25	60	>98	d
11	t-Bu	H	Cu	*p*-NO_2PhI	2.0	THF	45	2	>98	f
12	t-Bu	H	Cu	(*Z*)-BuCH=CHI	4.0	THF/HMPT	45	30	>98	f, h, i
13	t-Bu	H	Cu	PhI	0	THF/HMPT	45	30	<3	f, g
14	t-Bu	H	Ag	PhI	4.0	THF/HMPT	45	5	75	f, g
15	t-Bu	H	$Ag_{1/2}Li_{1/2}$	PhI	4.0	THF/HMPT	40	30	70	f, g
16	H	H	ZnCl	PhI	2.0	THF/TMED	25	240	>98	d
17	H	H	ZnCl	*p*-ClPhI	2.0	THF/TMED	25	240	>98	d
18	Me	Me	ZnCl	PhI	2.0	THF/HMPT	25	60	>98	d
19	t-Bu	H	ZnCl	PhI	2.0	THF/HMPT	25	60	>98	d, j
20	t-Bu	H	ZnCl	*p*-ClPhI	2.0	THF/HMPT	25	60	>98	d
21	t-Bu	H	ZnCl	*p*-NO_2PhI	2.0	THF/HMPT	25	60	>98	d
22	t-Bu	H	ZnCl	(*Z*)-BuCH=CH	4.0	THF	45	120	>98	d, h, i
23	t-Bu	H	ZnCl	(*Z*)-t-BuCH=CHI	4.0	THF	50	60	>98	d, h
24	t-Bu	H	ZnCl	(*E*)-BuCH=CHI	4.0	THF	45	120	>98	d, h
25	t-Bu	H	ZnCl	PhI	0	THF/HMPT	25	60	<3	d, g

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[a] Based on amount of I. [b] Ratios are given in the experimental section. [c] In all experiments a slight excess of I was used; yields are based on R″I and refer to undistilled products. [d] The temperature was allowed to rise during 10 min from −60°C to that indicated in the Table, and the mixture was then stirred for the time shown. [e] A mixture of unidentified products was formed, probably arising in part from halogen—metal exchange. [f] The allenylmetal compound was slowly added to a mixture of R″I and the catalyst at the indicated temperature. [g] In addition to II only starting iodide was isolated. [h] The configuration of the double bond was retained during the reaction. [i] Some of the vinylallene underwent [1,5]-sigmatropic hydrogen shift with formation of a mixture of conjugated trienes (cf. ref. 29). [j] In the presence of 2 mole % of $Ni(PPh_3)_4$ or $Pt(PPh_3)_4$ the amount of cross-coupling was less than 5%.

with aryl iodides faster in THF/TMED (tetramethylethylenediamine) than in THF/HMPT while the other allenylzinc compounds gave better results in THF/HMPT.

Conclusion

Our results demonstrate that in the presence of palladium catalysts various allenylmetals can give pure aryl- and vinyl-substituted allenes. Only when the metal is too electropositive, as with Li, is a catalytic amount of the catalyst unsufficient, and probably use of an equimolar amount of Li would be necessary to obtain pure allenes (cf. ref. 17).

Experimental

All experiments were performed under dry nitrogen. Propadiene was prepared from 2,3-dichloro-1-propene and zinc dust [23], 1,1-dimethylallene from 3-bromo-3-methyl-1-butyne and $LiAlH_4$ [12], and t-butylallene from propargyl chloride [24]. The aryl iodides were prepared according to ref. 25 or were commercially available. The vinylic iodides were synthesized according to references 26 and 27. $Pd(PPh_3)_4$ was obtained as described in ref. 28. $ZnCl_2$ was used as a 1.0 *M* solution in THF which was stored over molecular sieves 4 Å. $MgCl_2$ was used as a 0.6 *M* solution in THF.

(a) Preparation of I

M = Li: To a stirred solution of $RR'C{=}C{=}CH_2$ (0.025 mole) in THF (50 ml) at −60°C was added a solution of BuLi (0.025 mole) in hexane (15 ml). The mixture was stirred for 60 min at −60°C. The resulting solution was used for the couplings.

M = MgCl or ZnCl: To the allenyllithium compound (0.025 mole), prepared as indicated above, an equimolar amount of $MgCl_2$ or $ZnCl_2$ was added at −60°C. The resulting solutions were used immediately (see under b).

M = Cu or Ag: To the allenyllithium compound (0.025 mole; see under M = Li) at −60°C was added CuBr (0.025 mole) or a solution of $AgBr(LiBr)_3$ (0.025 mole) in THF (25 ml). The mixture was stirred for 30 min at −20°C prior to use.

$M = Cu_{1/2}Li_{1/2}$ *or* $Ag_{1/2}Li_{1/2}$: The procedure was the same as that described for M = Cu or Ag but using half the amounts of CuBr, AgBr, and LiBr.

(b) Reaction of I with R''I

For reactions in entries 1, 3—5 and 16—25 the catalyst $Pd(PPh_3)_4$ (0.02 *M* solution in THF; see Table 1), R''I (0.024 mole), and, if appropriate (see Table 1), HMPT (10 ml) or TMED (10 ml) were added successively to I at −60°C. The temperature of the mixture was then allowed to rise during 10 min to that indicated in Table 1, and the mixture was stirred for an additional period (see Table 1) at that temperature. The products were isolated by pouring the reaction mixtures into an aqueous solution of NH_4Cl and extracting the aqueous layer with pentane. The extract was washed with water and dried over K_2CO_3. The solvent was then removed in vacuo. In the other experiments the inverse addi-

TABLE 2

PHYSICAL CONSTANTS AND SPECTROSCOPIC DATA FOR ALLENES RR'C=C=CH^{1}R'' (II)

Compound II [a]			B.p. (°C/mmHg)	n_D^{20}	Yield [b] (%)	^{1}H NMR (CCl$_4$, δ(Me$_4$Si) 0 ppm) [c]				
R	R'	R''				δ(H^1)	δ(R)	δ(R')	δ(R'')	^4J(H—C=C=C—H) (Hz)
H	H	Ph	69—70/25	1.5810	95	6.08	5.05	5.05	7.20	6.7
H	H	*p*-ClPh	101—102/12	1.5922	90	6.09	5.12	5.12	7.22	6.8
Me	Me	Ph	93—95/20	1.5623	93	5.89	1.77	1.77	7.15	
t-Bu	H	Ph	108—110/20	1.5380	90	6.11	1.13	5.50	7.19	6.8
t-Bu	H	*p*-ClPh	144—145/12	1.5513	90	6.11	1.11	5.56	7.22	6.6
t-Bu	H	*p*-NO$_2$Ph	110/0.001	[d]	90	6.23	1.18	5.68	7.40/8.18 [e]	6.6
t-Bu	H	(*Z*)-BuCH=CH	— [i]	1.4792	93	6.02	[f]	[f]	[f]	6.0
t-Bu	H	(*Z*)-t-BuCH=CH	84—87/20	1.4754	90	6.23	[g]	[g]	[g]	6.0
t-Bu	H	(*E*)—BuCH=CH	65—67/1	1.4789	95	[h]	1.02	[h]	[h]	[h]

[a] Purity of II: >96% (based on ^{1}H NMR and GLC analysis (conditions: SE 33, 10% on Chromosorb W). All compounds showed interalia an absorption at ≃1950 cm^{-1} ($>C=C=C<$) in the IR-spectrum. [b] Yields refer to distilled compounds. [c] The spectra were recorded on a Varian EM-390 spectrometer. [d] The refractive index was not determined as the compounds melts at 39—40°C. [e] AB pattern; ^3J(H—C=C—H) 9.6 Hz. [f] t-BuCH^2=C=CH^{1}CH^3=CH^4-Bu: δ(H^2 + H^4) 5.12—5.50; δ(H^3) 5.72; δ(t-Bu) 1.04; ^3J(H^1, H^3) ≃ ^3J(H^3, H^4): 11.4 Hz. [g] t-BuCH^2=C=CH^{1}CH^3=CH^4-t-Bu: δ(H^2 + H^4) 5.10—5.30; δ(H^3) 5.54; δ(t-Bu) 1.05, 1.18; ^3J(H^1, H^3) ≃ ^3J(H^3, H^4): 11.7 Hz. [h] The ^{1}H NMR spectrum gives a complicated vinylic pattern. [i] The compound rearranged during distillation; the compound was purified by chromatography (Al$_2$O$_3$/hexane).

tion mode was used in order to prevent decomposition of I. Thus the THF solution of I, diluted with HMPT (10 ml) in entries 6—8, 10, and 12—15, was carefully added to a vigorously stirred mixture of R″I (0.024 mole) and the catalyst (amount of catalyst is given in Table 1) in THF (50 ml) at the temperature shown in Table 1. After the addition of the solution of I the mixture was stirred for the time shown in Table 1. The products were isolated by pouring the mixture into an aqueous solution of NH_4Cl containing NaCN (2 g; not used in experiment 2 of Table 1) and extracting with pentane (see above).

Physical constants, yields, and spectroscopic data for distilled allenes II are given in Table 2.

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