Keywords: barium · ligand effects · polymers · solid-state structures · solvent effects

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[2] E. B. Brackett, T. E Brackett, R. L. Sass, *J. Phys. Chem.* **1963**, *67*, 2132-2135.

[3] Crystal structure of **1**: $[BaI_2(\mu_2\text{-}OH_2)_2]_{3/\infty}$, $M_r = 427.17$ g mol^{-1}, monoclinic, space group $C2/c$, $a = 11.042(2)$, $b = 7.574(2)$, $c = 8.622(2)$ Å, $\beta = 113.17(2)$°, $V = 662.9(3)$ Å^3, $Z = 4$, $\rho_{calcd} = 4.280$ Mg m^{-3}, $F(000) = 728$, $\lambda(Mo_{K\alpha}) = 0.71069$ Å, $\mu = 14.292$ mm^{-1}, 1921 reflections of which 800 are independent and 788 observed ($I > 2\sigma I$), 33 parameters, GooF = 1.272, $R1 = 0.0352$, $wR2 = 0.0866$ (against $|F^2|$), Ψ scan. The data for **1** were collected on a STOE four-circle diffractometer at −70 °C under a nitrogen atmosphere. The structure was solved by direct methods with the program SHELXS86 [10] and was refined anisotropically with SHELXL93 [11]. The H atoms of the water molecules were calculated on idealized positions [8b].

[4] Crystal structure of **2**: $[BaI_2(\mu_2)(OC_3H_6)]_{1/\infty}$, $M_r = 467.22$ g mol^{-1}, orthorhombic, space group $Pnnm$, $a = 9.844(2)$, $b = 20.890(4)$, $c = 4.8100(10)$ Å, $V = 989.1$ Å^3, $Z = 4$, $\rho_{calcd} = 3.083$ Mg m^{-3}, $F(000) = 784$, $\lambda(Mo_{K\alpha}) = 0.71069$ Å, $\mu = 9.981$ mm^{-1}, 2608 reflections of which 1326 are independent and 1016 observed ($I > 2\sigma I$), 45 parameters, GooF = 1.137, $R1 = 0.0319$, $wR2 = 0.0759$ (against $|F^2|$), Ψ scan. The data for **2** were collected on an Enraf Nonius CAD4 diffractometer at −70 °C under a nitrogen atmosphere. The structure was solved by direct methods with the program SHELXS86 [10] and refined anisotropically with SHELXL93 [11]. The methyl group of acetone was disordered and the corresponding C atom was only refined isotropically. Thus, the H atoms were neither found nor calculated [8b].

[5] a) D. L. Kepert, A. F. Waters, A. H. White, *Aust. J. Chem.* **1996**, *49*, 117; b) D. L. Kepert, B. W. Skelton, A. F. Waters, A. H. White, *ibid.* **1996**, *49*, 47

[6] Crystal structure of **3**: $[BaI_2(thf)_3]_{1/\infty}$, $M_r = 607.45$ g mol^{-1}, monoclinic, space group $C2/c$, $a = 13.451(3)$, $b = 15.603(3)$, $c = 9.426(2)$ Å, $\beta = 106.38(3)$, $V = 1897.9(7)$ Å^3, $Z = 4$, $\rho_{calcd} = 2.098$ Mg m^{-3}, $F(000) = 1096$, $\mu(Mo_{K\alpha}) = 0.71069$ Å, $\mu = 5.030$ mm^{-1}, 2228 reflections of which 2079 are independent and 2001 are observed ($I > 2\sigma I$), 110 parameters, GooF = 1.061, $R1 = 0.0840$, $wR2 = 0.2494$ (against $|F^2|$). The data for **3** were collected on an Enraf Nonius four-circle diffractometer under a nitrogen atmosphere at −70 °C. The structure was solved by direct methods with the program SHELXS86 [10] and refined with SHELXL93 [11]. One THF molecule was disordered, and split positions were refined for the C atoms. They were described isotropically, the corresponding H atoms were not refined. The positions of the H atoms in the other THF molecule were calculated. This together with the slight dissociation of the crystal during data collection are the reasons for the rather high $R1$ value [8b].

[7] B. W. Skelton, A. F. Waters, A. H. White, *Aust. J. Chem.* **1996**, *49*, 99.

[8] a) Crystal structure of **4**: $[BaI_2(thf)_5][THF]$, $M_r = 1675.61$ g mol^{-1}, monoclinic, space group $P2_1/c$, $a = 9.469(3)$, $b = 13.323(2)$, $c = 27.664(4)$ Å, $\beta = 92.04(2)$°, $V = 3487.8(13)$ Å^3, $Z = 2$, $\rho_{calcd} = 1.515$ Mg m^3, $F(000) = 1528$, $\lambda(Mo_{K\alpha}) = 0.71069$ Å, $\mu = 2.934$ mm^{-1}, 7118 reflections of which 6119 are independent and 6101 observed ($I > 2\sigma I$), 259 parameters, GooF = 1.189, $R1 = 0.0585$, $wR2 = 0.1307$ (against $|F^2|$), Ψ scan. The data for **4** were collected on a STOE four-circle diffractometer at −70 °C under a nitrogen atmosphere. The structure was solved by direct methods with the program SHELXS86 [10] and refined with SHELXL93 [11]. The positions of H atoms of the THF molecules were calculated. Two free THF molecules in the asymmetric unit were disordered and the atoms were refined on positions with occupation factors of 1/2. b) Further details of the crystal structure investigations may be obtained from the Fachinformationszentrum Karlsruhe, D-76344 Eggenstein-Leopoldshafen (Germany), on quoting the depository numbers CSD-407360 (**1**), CSD-380094 (**2**), CSD-404952 (**3**), and CSD-407359 (**4**).

[9] R. J. Gillespie, E. A. Robinson, *Angew. Chem.* **1996**, *108*, 539; *Angew. Chem. Int. Ed. Engl.* **1996**, *35*, 477.

[10] G. M. Sheldrick, *Acta Crystallogr. Sect. A* **1990**, *46*, 467.

[11] G. M. Sheldrick, *J. Appl. Crystallogr.*, in press.

Rate Enhancement of the Pauson–Khand Reaction by Primary Amines**

Takumichi Sugihara,* Mamiko Yamada, Hitoshi Ban, Masahiko Yamaguchi,* and Chikara Kaneko

The Pauson–Khand reaction is one of the most powerful methods for constructing cyclopentenones[1,2] and has been widely utilized for the synthesis of a variety of natural products.[3] "Hard" ligands, which usually contain an N or O atom, in metal-carbonyl complexes labilize the CO ligands and therefore facilitate the ligand substitution reaction.[4,5] If the "hard" ligands react with $Co_2(CO)_6$(alkyne) complexes in the presence of olefins, the substitution of CO ligands by the olefins might be facilitated. Since the coordinated alkyne is also made reactive by the labilizing effect of the "hard" ligands, the Pauson–Khand reaction might be promoted.[6] To confirm our hypothesis, we first investigated the use of "hard" ligands as solvents to study their effect on the Pauson–Khand reaction. The results are shown in Table 1. In the aprotic solvents usually used in the Pauson–Khand reaction, the desired cyclization did not proceed at 35°C even after three days (Nos. 1–4). Complex **1a** was also recovered almost quantitatively when ethanol or triethylamine, either of which might act as "hard" ligands, was used as solvent (No. 5 and 6). However, whereas the cyclization proceeded slowly in diethylamine (No. 7), it was complete within 5 min in cyclohexylamine to give **2a** in good yield (No. 10).[7,8] Comparison

Table 1. The Pauson–Khand reaction of **1a** in different solvents[a].

No.	Solvent	$CyNH_2$ [equiv][b]	T [°C]	t	Yield [%] **2a**	Yield [%] **1a**
1	*n*-hexane	–	35	3 d	–	99
2	toluene	–	35	3 d	–	98
3	1,2-dichloroethane	–	35	3 d	–	99
4	1,4-dioxane	–	25	4 d	–	98
5	EtOH	–	35	3 d	–	99
6	Et_3N	–	35	3 d	–	99
7	Et_2NH	–	35	3 d	46[c]	23
8	nPrNH$_2$	–	35	5 min	52[c]	–
9	iPrNH$_2$	–	35	5 min	68[c]	–
10	$CyNH_2$[b]	–	35	5 min	72[c]	–
11	tBuNH$_2$	–	35	3 d	54[c]	15
12	1,2-dichloroethane	10	25	10d	46[d]	13
13	1,2-dichloroethane	6	83	5 min	99	–
14	1,2-dichloroethane	3.5	83	5 min	99	–
15	1,2-dichloroethane	3	83	15 min	99	–
16	1,2-dichloroethane	1	83	90 min	94	–
17	1,2-dichloroethane	0	83	10 h	62[c]	–

[a] All reactions were carried out in 0.2 M solution under argon atmosphere. [b] Cy = cyclohexyl. [c] Unidentified polar by-products were also formed. [d] 1-phenyl-6-hepten-1-yne (**3a**) was also formed in 26% yield.

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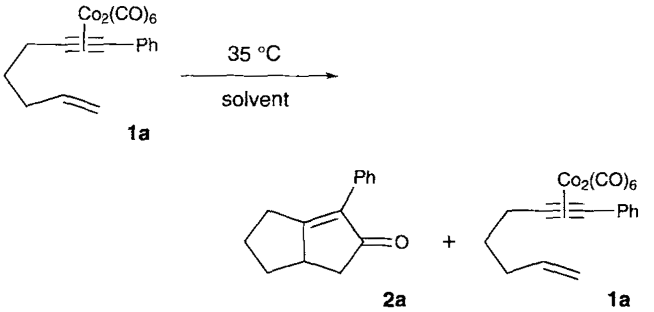


of Nos. 6–11 shows that the use of primary amines as solvents dramatically enhanced the rate of the reaction. The alkyl group on the primary amines also has a great influence on the course of the reaction. The moderately hindered primary amines, such as the ones containing secondary alkyl groups, seem to promote the Pauson–Khand reaction most effectively. The yield of **2a** reduced when an amine with a primary alkyl group was employed (No. 8). The tertiary alkyl substituted amine retarded the reaction (No. 11).

Since cyclohexylamine seemed to be the best promoter for the Pauson–Khand reaction, we varied the amount used to optimize the conditions. The results are also shown in Table 1. When the reaction of **1a** was carried out with 10 equivalents of the amine in 1,2-dichloroethane at 25°C, the desired cyclization was slow and decomplexation reduced the yield of **2a** (No. 12). In contrast, the cyclized product **2a** was produced in quantitative yield at 83°C (No. 13). No. 12–17 shows that more than three equivalents of the amine and the higher reaction temperature were both necessary to perform the desired cyclization in a short time as well as in quantitative yield. Various solvents were examined, such as *n*-hexane, toluene, 1,2-dimethoxyethane, THF, 1,4-dioxane, 2-propanol, acetonitrile, and *N*,*N*-dimethylformamide, but so far 1,2-dichloroethane remains the best solvent to obtain clean reactions and quantitative yields in this reaction system. The present conditions are a new and convenient method to promote the Pauson–Khand reaction without using oxidants.

Since primary amines were effective as promoter, we felt that ammonia should not be an exception. When **1a** was dissolved in 1,4-dioxane that was saturated with ammonia gas at 0°C and stirred in a sealed tube at 30°C for 4.5 days, the desired **2a** was produced along with **3a**. Since the use of a sealed tube is not convenient especially on a large scale, we decided to use a biphasic system[9] in which an aqueous solution of ammonium hydroxide would be the source of ammonia. The results under different conditions are summarized in Table 2. When 16 M aqueous solution of ammonium hydroxide was used as cosolvent, the cyclization proceeded even at 25°C (No. 1), although the enyne **3a** released from the complex was also produced. Comparison of No. 1 with the reaction of **1a** with gaseous ammonia in 1,4-dioxane suggests that water also affects the course of the reaction. Water itself, however, is not an effective promoter, since the reaction did not occur even at 100°C (No. 2 and 3). Moreover, higher temperatures favor cyclization over decomplexation (No. 1, 4, and 5). Even less concentrated solutions of ammonium hydroxide promoted the cyclization reaction (No. 6 and 7)

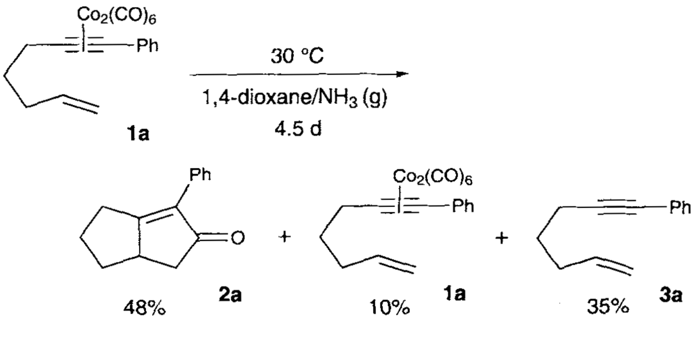
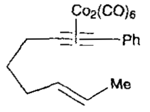


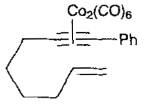
Table 2. The Pauson–Khand reaction of **1a** in a biphasic system under different conditions [a].

No.	Aqueous solvent	T[°C]	t	Yield [%] **2a**	**1a**	**3a**
1	16 M NH_4OH	25	2 d	72	–	25
2	H_2O	25	4 d	–	97	–
3	H_2O	100	30 min	–	91	–
4	16 M NH_4OH	70	15 min	83	–	16
5	16 M NH_4OH	100	15 min	95	–	4
6	4 M NH_4OH	100	15 min	91	–	9
7	2 M NH_4OH	100	15 min	93	–	7
8	1 M NH_4OH	100	45 min	96	–	–
9	5 M NaOH	100	15 min	38 [b]	–	–
10	4.7 M NH_4Cl	100	15 min	22	62	–

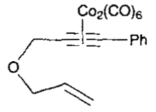
[a] All reactions were carried out in 0.1 M solution of 1,4-dioxane/aqueous solvent (1:3 v/v). [b] Unidentified polar by-products were also formed.



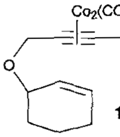
1b



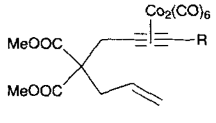
1c



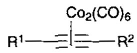
1d



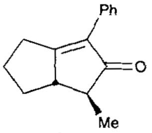
1e



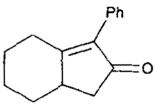
1f R = H
1g R = Ph



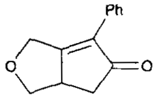
1h R^1 = Ph, R^2 = H
1i R^1 = *n*Bu, R^2 = H
1j R^1 = *n*Pr, R^2 = *n*Pr



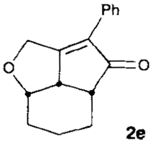
2b



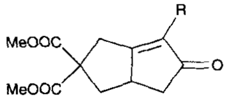
2c



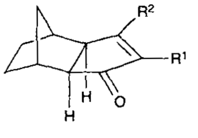
2d



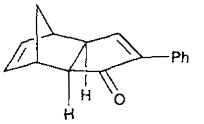
2e



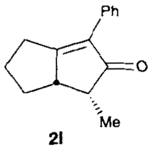
2f R = H
2g R = Ph



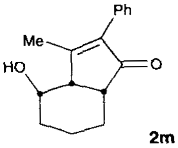
2h R^1 = Ph, R^2 = H
2j R^1 = *n*Bu, R^2 = H
2k R^1 = *n*Pr, R^2 = *n*Pr



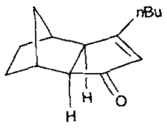
2i



2l

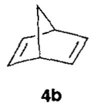


2m



2n


4a


4b

until a threshold dilution of about 1 M at which the reaction slowed down (No. 8). Moderate concentrations of ammonium hydroxide are apparently important. In addition, when an aqueous solution of sodium hydroxide was used instead of ammonium hydroxide, the desired cyclization did not proceed cleanly but afforded a complex reaction mixture (No. 9). Furthermore, aqueous ammonium chloride slowed down the reaction (No. 10). Therefore, neither hydroxide anions nor ammonium cations but ammonia itself is essential to enhance the rate of the Pauson-Khand reaction in this biphasic system. It is worth pointing out that aqueous ammonium hydroxide is the cheapest and the most convenient promoter for the Pauson-Khand reaction and that a simple extraction workup gave the spectroscopically pure samples of the product in the present system.[10] To our knowledge, this method is the first report of the Pauson-Khand type cyclization[1,2,11] in the presence of water.[12]

Two sets of conditions to promote the Pauson-Khand reaction, namely, 3.5 equivalents of cyclohexylamine in 1,2-dichloroethane at 83°C (conditions A) and a 1:3 mixture (v/v) of 1,4-dioxane and 2 M aqueous solution of ammonium hydroxide at 100°C (conditions B), were applied to various substrates. The results are summarized in Table 3. In all cases the reaction was complete in short times and afforded the desired cyclopentenones in good yield. The two methods gave comparable results in terms of the rates and yields.

Table 3. The Pauson-Khand reaction of **1b**-**j** under different conditions

No.	Starting material		Product	Conditions A [a]		Conditions B [b]	
	1	**4**	**2**	*t* [min]	Yield [%]	*t* [min]	Yield [%]
1	**b**		**b**	10	89 [c]	30	92
2	**c**		**c**	30	90 [d]	30	90
3	**d**		**d**	10	60	10	78
4	e		**e**	30	71 [e]	45	75 [f]
5	**f**		**f**	10	62	30	67
6	**g**		**g**	20	89	30	90
7	**h**	**a** [g]	**h**	10	98 [h]	10	100 [h]
8	**h**	**b** [g]	**i**	10	83 [h]	30	50 [h,i]
9	**i**	**a** [g]	**j**	15	94 [h]	10	92 [j]
10	**j**	**a** [g]	**k**	10	45 [h]	135	42 [h]

[a] Reactions were carried out in 0.2 M solution of 1,2-dichloroethane at 83°C in the presence of 3.5 equiv of cyclohexylamine under argon atmosphere. [b] Reactions were carried out in 0.1 M solution of 1,4-dioxane/2 M aqueous solution of NH_4OH (1:3 v/v) at 100°C under argon atmosphere. [c] Cyclopentenones **2c** and **2l** were also produced in 5 % and 5 % yield, respectively. [d] Cyclopentenones **2b** and **2l** were also produced in 5 % and 2 % yield, respectively. [e] Cyclopentenone **2m** was also produced in 14 % yield. [f] Cyclopentenones **2m** was also produced in 12 % yield. [g] A 1.5 equiv of **4a** or **4b** was used. [h] No regio- or stereoisomer was detected. [i] The reaction of **1h** with **4b** (10 equiv) for 30 min under conditions B gave **2i** in 91 % yield. [j] Cyclopentenone **2n** was also produced in 4 % yield.

In conclusion, convenient and economical promoters for the Pauson-Khand reaction have been developed. We are now trying to clarify the reaction mechanism and studying the reaction of the $Co_2(CO)_6$(alkyne) complexes with primary amines in more detail.

Experimental Section

For conditions A: Synthesis of **2a**: Under an argon atmosphere, a solution of **1a** (456 mg, 1.00 mmol) and cyclohexylamine (0.395 mL, 3.49 mmol) in 1,2-dichloroethane (5 mL) was stirred at 83°C for 5 min. After cooling, Et_2O was added, and the resulting suspension was filtered. The filtrate was washed successively with 5 % aqueous HCl, H_2O, and saturated aqueous $NaHCO_3$, dried over $MgSO_4$, and concentrated in vacuo. Purification by silica gel column chromatography (Et_2O/*n*-hexane 15/85) gave 197 mg (99 %) of **2a**. M.p. 65°C (Et_2O/*n*-hexane); IR (neat): $\tilde{\nu} = 1693, 740, 700\ cm^{-1}$; ^1H NMR (300 MHz, $CDCl_3$, 25°C, TMS): $\delta = 1.0-1.25$ (m, 1 H), 2.0-2.15 (m, 2 H), 2.15-2.35 (m, 2 H), 2.55-2.75 (m, 1 H), 2.75-3.0 (m, 3 H), 7.2-7.35 (m, 1 H), 7.35-7.45 (m, 2 H), 7.55-7.65 (m, 2 H); ^{13}C NMR (75 MHz, $CDCl_3$, 25°C): $\delta = 25.57$, 26.98, 30.61, 42.61, 44.29, 127.50, 128.05, 128.08, 131.66, 134.14, 185.50, 208.58; C,H analysis (%) calcd. for $C_{14}H_{14}O$ (198.26): C 84.81, H 7.12; found: C 84.53, H 7.12.

For conditions B: Synthesis of **2h**: Under an argon atmosphere, a solution of **1h** (440 mg, 1.13 mmol) and norbornene (**4a**; 160 mg, 1.70 mmol) in 1,4-dioxane (3.0 mL) and 2 M aqueous solution of NH_4OH (9.0 mL) was stirred at 100°C for 10 min. After cooling, Et_2O was added, and the resulting suspension was filtered. The filtrate was washed successively with H_2O, 5 % aqueous HCl, and saturated aqueous $NaHCO_3$, dried over $MgSO_4$, and concentrated in vacuo. Purification by silica gel column chromatography (Et_2O/*n*-hexane 15/85) gave 253 mg (100 %) of **2h**. M.p. 95°C (Et_2O/*n*-hexane); IR (neat): $\tilde{\nu} = 1693\ cm^{-1}$; ^1H NMR (300 MHz, $CDCl_3$, 25°C, TMS): $\delta = 0.95-1.05$ (m, 1 H), 1.05-1.2 (m, 1 H), 1.25-1.45 (m, 2 H), 1.55-1.8 (m, 2 H), 2.28 (br. d, $J = 3.8$ Hz, 1 H), 2.37 (d, $J = 5.2$ Hz, 1 H), 2.50 (br. d, $J = 3.8$ Hz, 1 H), 2.65-2.75 (m, 1 H), 7.25-7.45 (m, 3 H), 7.64 (d, $J = 2.7$ Hz, 1 H), 7.65-7.75 (m, 2 H); ^{13}C NMR (75 MHz, $CDCl_3$, 25°C): $\delta = 28.24$, 28.99, 31.13, 38.22, 39.33, 39.52, 47.59, 54.83, 127.06, 128.40, 131.57, 146.07, 160.31, 209.12; C,H analysis (%) calcd. for $C_{16}H_{16}O$ (198.26): C 86.45, H 6.35; found: C 86.33, H 6.55.

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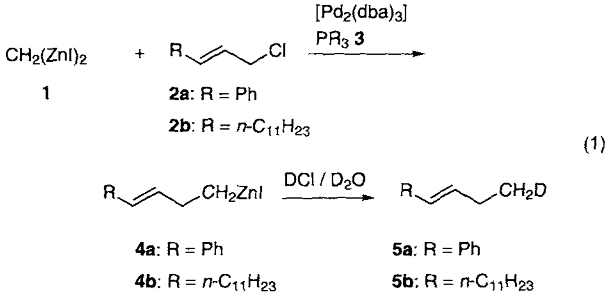
Stepwise Reaction of Bis(iodozincio)methane with Two Different Electrophiles**

Kiitiro Utimoto,* Narihiro Toda, Takeshi Mizuno, Masami Kobata, and Seijiro Matsubara

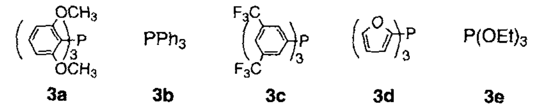
Geminal dimetallic reagents have attracted considerable attention as versatile reagents in organic synthesis,[1] and consequently their preparation has been extensively studied.[2] Application of the reagents has focused on regioselective olefination of carbonyl compounds[3] and coupling with two different electrophilic building blocks.[4] We have developed a method for preparing *gem*-bis(halozincio)alkanes from the corresponding dihalides and have used the organozinc compounds for the olefination of aldehydes and ketones.[5] We have also observed that one of the two C–Zn bonds of bis(iodozincio)methane is much more reactive than the other in the reaction with water or iodine.[5b] These results suggested that the two C–Zn bonds could be used separately. We describe here a stepwise reaction of *gem*-dizinc compounds with two different electrophiles under palladium catalysis.



(1)

We initially examined the Pd-catalyzed coupling of bis(iodozincio)methane (**1**) with allyl chlorides. As shown in Equation (1), an allyl chloride **2** (1.0 mmol) was treated with **1** (1.0 mmol) in the presence of $[Pd_2(dba)_3]\cdot CHCl_3$ (0.025 mmol) and a phosphane **3** (0.1 mmol) as a ligand in THF (dba = dibenzylideneacetone). After 30 min the resulting mixture was quenched with $DCl–D_2O$ to give the deuterated product **5**. Combinations of allyl chlorides and ligands, as well as yields of coupling products **5** are summarized in Table 1. Excellent results were obtained by ligand tuning; phosphane ligands with electron-withdrawing groups such as tris[3,5-bis(trifluoromethyl)phenyl]phosphane (**3c**) and tris(2-furanyl)phosphane (**3d**) afforded the coupling products in good-to-excellent yields. Quantitative formation of iodozinciomethylated products **4a** was confirmed by ^1H NMR spectroscopy in $[D_8]THF$; the spectra showed the exclusive formation of (*E*)-4-phenyl-3-butenylzinc iodide when **3d** is employed as a ligand.

Table 1. Yields [%] of the products **5** obtained by Pd-catalyzed coupling of **1** with allyl chlorides **2** depending on the phosphane **3**.



	3a	**3b**	**3c**	**3d**	**3e**
2a[a]	< 1	16	88	97	14
2b[a]	< 1	< 1	82	91	< 1

[a] Reaction mixture was treated with $DCl–D_2O$. The D contents of the products were determined by ^1H NMR spectroscopy (> 95%).

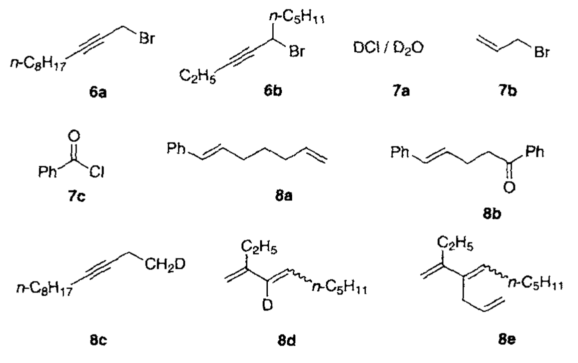
The intermediary organozinc compounds **4a** and **4b** reacted with other electrophiles such as allyl or acyl halides under the same palladium catalysis as shown in Equation (1).[6,7] This reaction permits a sequential coupling of bis(iodozincio)methane with two different electrophiles [Eq. (2)]

$$\underset{\mathbf{1}}{CH_2(ZnI)_2} + RX \xrightarrow[\text{2) EX }\mathbf{7}]{\text{1) }[Pd_2(dba)_3]/\mathbf{3d}} \underset{\mathbf{8}}{RCH_2E} \qquad (2)$$

2/6

to give the three-component-coupling products in excellent yields. The results of such sequential reactions are shown in Table 2. The formation of **8d** and **8e** can be explained by Equation (3).

Table 2. Stepwise reaction of bis(iodozincio)methane with two electrophiles.



Entry	RX	EX	Product	Yield [%][a]
1	**2a**	**7b**	**8a**	87
2	**2a**	**7c**	**8b**	78
3	**6a**	**7a**	**8c**	55[b]
4	**6b**	**7a**	**8d**	80[b,c]
5	**6b**	**7b**	**8e**	70[c]

[a] Yield of isolated product. [b] >95% D. [c] Isolated as a diastereomeric mixture.

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