3896 J. Org. Chem. 1985, 50, 3896-3900

The Effect of Added Silver Nitrate on the Palladium-Catalyzed Arylation of Allyltrimethylsilanes

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Received December 6, 1984

The palladium-catalyzed reaction of iodobenzene with allyltrimethylsilane at 120 °C (the Heck arylation) resulted predominantly in arylation at the terminal position giving (*E*)-1-phenyl-3-(trimethylsilyl)-1-propene (**1**) as the major product and considerable amounts of 3-phenyl-1-propene (**6**) and 2-phenyl-1-propene (**7**) as minor products. At 50 °C the reaction gave approximately the same product distribution, but 53% of the iodobenzene remained after 2 days. The addition of silver nitrate at this temperature had a dramatic effect on the reaction. All the starting material was consumed after 2 days. The vinylsilane (*E*)-3-phenyl-1-(trimethylsilyl)-1-propene (**2**) was then the major component, only 3% of **1** was formed, and no desilylation was observed. Thus addition of silver nitrate at low temperature (a) enhances the reaction rate, (b) changes the direction of elimination, and (c) suppresses the desilylation. Arylation of (*E*)-1,3-bis(trimethylsilyl)-1-propene in the presence of silver salts gave almost exclusively the stereospecific product (*Z*)-1,3-bis(trimethylsilyl)-2-phenyl-1-propene (**4**) at 50 °C and 2-phenyl-3-(trimethylsilyl)-1-propene (**3**) at 120 °C. Compound **3** was also formed in the absence of silver nitrate at 120 °C, but then the reaction required a considerably longer reaction time.

Organosilicon compounds have found widespread use in organic synthesis.[1] One reaction that has been intensively studied is the reaction of allylsilanes with different electrophiles.[2] This reaction is of great interest due to the high regioselectivity obtained.

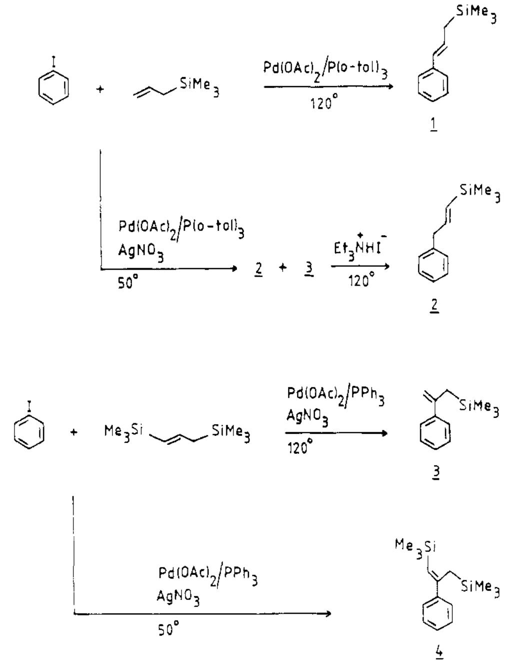
The aim of the present investigation was to explore the possibility of extending the very useful Heck arylation[3] to include allylsilanes.[4]

On the basis of our earlier experience with the arylation of trimethylvinylsilane,[5] where desilylation predominated, leading to styrenes, we expected to obtain analogous compounds in this reaction. In fact, desilylation did occur, but the reaction can be controlled so as to retain the silicon moiety, resulting in compounds such as **1**–**4** in fair isolated yields.

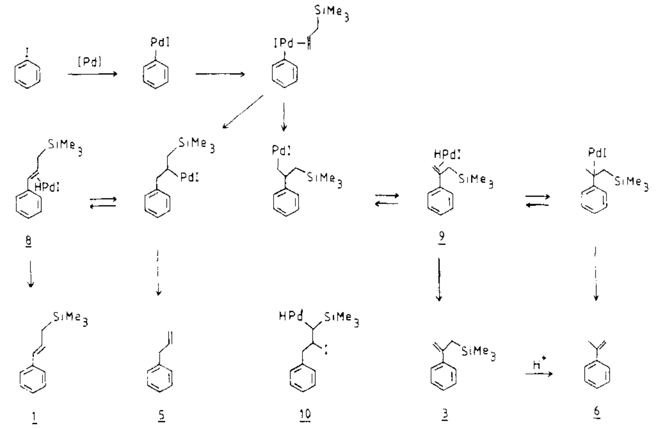
Results

The preparative results of these investigations are summarized in Scheme I. Thus (*E*)-1-phenyl-3-(trimethylsilyl)-1-propene (**1**) was obtained in 32% yield starting from allyltrimethylsilane and iodobenzene by using traditional Heck conditions. However, conducting the reaction at 50 °C in Me_2SO in the presence of silver ions allowed the isolation of the isomer (*E*)-3-phenyl-1-(trimethylsilyl)-1-propene (**2**) in 55% yield. Subjecting (*E*)-1,3-bis(trimethylsilyl)-1-propene and iodobenzene to traditional Heck conditions in the presence of silver nitrate at 120 °C gave 2-phenyl-3-(trimethylsilyl)-1-propene (**3**) in 53% yield. In the absence of silver nitrate at 120 °C the same product is obtained, although the rate of conversion is slower. This reaction involves cleavage of a carbon–silicon bond and is thus related to the palladium-catalyzed arylation of vinylsilanes.[5] In the presence of silver nitrate at 50 °C, this desilylation was completely suppressed, thus resulting in formation of (*Z*)-1,3-bis(trimethylsilyl)-2-phenyl-1-propene (**4**) in 52% yield.

Scheme I



Scheme II



Discussion

The results presented above and in Scheme I were chosen to illustrate some preparative aspects of a thorough study of the Heck arylation of allylsilanes. In Table I a

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[1] For reviews, see: (a) Colvin, E. W.; "Silicon in Organic Synthesis"; Butterworths: London, 1981. (b) Weber, W. P. "Silicon Reagents for Organic Synthesis"; Springer-Verlag: New York, 1983.

[2] Chan, T. H.; Fleming, I. *Synthesis* **1979**, 761 and references cited therein.

[3] For reviews, see: (a) Heck, R. F. *Org. React. (N.Y.)* **1982**, *27*, 345. (b) Heck, R. F. *Acc. Chem. Res.* **1979**, *12*, 146.

[4] (a) Useful π-allylpalladium complexes are formed after attack of palladium(II) at the γ-position of allylsilanes: Hayashi, T.; Konishi, M.; Kumada, M. *J. Chem. Soc., Chem. Commun.* **1983**, 736. (b) For palladium-catalyzed cycloaddition of [2-(acetoxymethyl)-3-allyl]trimethylsilane with electron-deficient olefins, see: Trost, B. M.; Chan, D. M. T. *J. Am. Chem. Soc.* **1983**, *105*, 2326 and references therein.

[5] Hallberg, A.; Westerlund, C. *Chem. Lett.* **1982**, 1993.

0022-3263/85/1950-3896$01.50/0

Table I. Palladium-Catalyzed Arylation of Allyltrimethylsilane

entry[a]		temp, °C	reacn time, h	product distribution,[b] %						
				1	7[e]	2	3	5	6	PhI
1	CH_3CN	120	7	60	1	2	9	9	15	2
2	Me_2SO	120	7	59	3	3	6	13	14	0
3	DMF	120	7	58	1	2	7	17	12	2
4	toluene	120	96	53	3	1	3	20	12	6
5	CH_3CN[c]	100	4	49	1	2	10	6	7	23
6	CH_3CN[c]	100	6	54	1	2	12	6	8	15
7	CH_3CN[c]	100	24	60	1	2	4	7	16	7
8	CH_3CN[c]	100	48	60	1	2	0	7	21	7
9	CH_3CN, Pd/C[d]	120	24	15	1	2	1	25	22	10
10	CH_3CN, Ag^+	120	3	46	1	25	13	7	7	0
11	Me_2SO, Ag^+	120	3	24	1	37	13	20	5	0
12	DMF, Ag^+	120	3	65	1	12	3	7	7	3
13	toluene, Ag^+	120	3	54	0	17	7	10	12	0
14	Me_2SO, Ag^+	100	6	21	1	37	15	20	6	0
15	Me_2SO, Ag^+	80	24	16	1	48	15	16	3	0
16	Me_2SO, Ag^+	50	48	3	0	70	27	0	0	0
17	Me_2SO	50	48	27	2	2	3	5	5	53
18	CH_3CN, Ag^+	100	6	46	1	34	11	3	5	0
19	CH_3CN, Ag^+	80	24	36	2	37	17	2	5	0
20	CH_3CN, Ag^+	50	48	15	3	48	16	0	1	15
21	DMF, Ag^+	80	24	32	3	10	4	9	3	35
22	Me_2SO, Ag^+, no ligand	50	48	2	1	45	16	0	0	35
23	Me_2SO, Ag^+, PPh_3	50	48	2	0	67	29	2	0	0
24	Me_2SO, Ag^+, PEt_3	50	48	0	0	66	24	0	0	10
25	Me_2SO, Ag^+, $PEtPh_2$	50	48	3	0	65	25	0	0	7
26	Me_2SO, Ag^+, $P(OPh)_3$	50	48	2	0	68	28	2	0	0
27	Me_2SO, Ag^+, $Ph_2P(CH_2)_4PPh_2$	50	48	2	0	52	32	2	0	12

[a] $Pd(OAc)_26P(o\text{-}tol)_4$ unless otherwise stated. [b] GC yields; less than 3% of unidentified arylpropenylsilane was formed. [c] 50% less solvent than normal. [d] 18% 1,3-diphenylpropene is formed in this reaction. [e] (*Z*)-1-Phenyl-3-(trimethylsilyl)-1-propene.

detailed account of the reactions studied are given. In all cases the starting materials were iodobenzene and allyltrimethylsilane. As is evident from entries 1–4 the complexing ability of the solvent has only minor influence on the product distribution. The main product under standard conditions (entries 1–8) is the 1-arylated product **1**. Thus the same regiochemistry is obtained as in the normal Heck coupling.[3] However, the overall product composition is complicated in our case by the concomitant formation of desilylated products, e.g., **5** and **6**. A possible mechanistic rationale for the formation of the observed products is shown in Scheme II and discussed below.

Consideration of the effects of the reaction time on the product distribution (entries 5–8) seems to indicate that two routes for the desilylation leading to **6** exist. Thus while the amount of **5** seems to be constant after 4 h, this is clearly not the case with **6**, which continues to accumulate with time. Since this increase is accompanied by a nearly identical decrease of the amount of **3**, it seems likely that **3** is converted to **6** under conditions used. This probably occurs via initial protonation of **3**, thus generating a highly stabilized benzylic cation, followed by elimination of trimethylsilyl iodide. In fact, this type of desilylation was used in a preparative manner to facilitate the isolation of **2** (see Scheme I). The formation of both **5** and **6** can also be partially explained by an iodide-promoted, intramolecular, irreversible desilylation reaction. Alternatively, the desilylation may occur from a β-iodo trimethylsilyl intermediate like **10** which is depicted in Scheme II for the case of formation of **5**.[6] The vinylpalladium hydride thereby formed collapses into **5** and palladium(0).

Although it was quite easy to isolate **1** free from isomers with column chromatography, the extent of desilylation in the reactions was unsatisfactory. In the absence of a ligand such as triphenylphosphine the dissociation of hydridopalladium iodide from intermediates **8** and **9** (see Scheme II) would be expected to be rendered more difficult,[7] thus promoting readdition and consequently also desilylation. This effect can be illustrated by comparing entry 1 with entry 9, where Pd/C was used as a catalyst. Since the iodide ion presumably plays an important part in the desilylation reaction, it was argued that the presence of silver ions would possible be advantageous. This assumption proved correct, as was evidenced by the addition of silver nitrate to the reaction mixtures.[8]

As can be seen from entries 10, 12, and 13, not only were the amounts of desilylated products reduced, but also the reaction rates and the direction of elimination were influenced. Thus compound **2** was now formed in good yields, especially when Me_2SO was used as a solvent (entry 11). Using this medium, however, the desilylation reaction was still quite pronounced. This could be completely suppressed by reducing the reaction temperature (entries 11, 14–16). It is evident from entry 17, which shows that ~10% of desilylated products had been formed, even though only ~50% of the iodobenzene had reacted, that the presence of silver ions is a requisite for suppression of the desilylation reaction. At 50 °C in Me_2SO there is a drastic increase in the amount of **2** from 2% to 70% upon addition of silver ions (entries 16, 17). Similar trends as described above, although less pronounced, were also found when acetonitrile was used as a solvent (entries 10, 18–20). In DMF there is still ~35% of unreacted iodobenzene left at 80 °C (entry 21), and in toluene the percentage of

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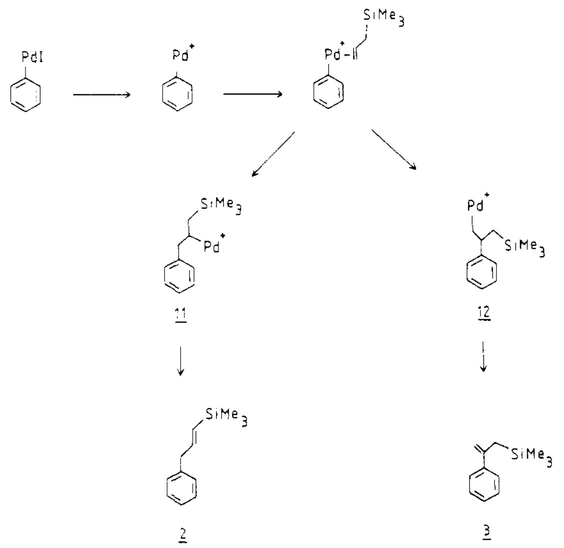
[6] (a) The desilylation involved in the formation of 3-(polyfluoroalkyl)-1-propenes through the $Fe_3(CO)_{12}$- or $Ru_3(CO)_{12}$-catalyzed reaction of polyfluoroalkyl halide with allylsilanes has been suggested to occur via similar intermediates: Fuchikami, T.; Ojima, I. *Tetrahedron Lett.* **1984**, *25*, 307. (b) For cleavage of (*E*)-2-(phenylethenyl)trimethylsilane with palladium chloride, see: Weber, W. P.; Felix, R. A.; Willard, A. K.; Koenig, K. E. *Tetrahedron Lett.* **1971**, 4701.

[7] For a discussion of the rate of readdition of the hydridopalladium group in an olefin π-complex intermediate to the double bond relative to its rate of dissociation from the complex, see ref 3a, p 349.

[8] Neither silver tetrafluoroborate nor silver acetate showed any advantages over silver nitrate.

Scheme III



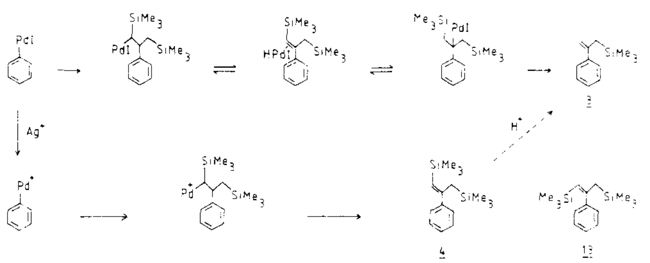
conversion is even lower. A possible mechanistic rationale for the formation of the silyl-containing products **2** and **3** in the presence of silver ions is given in Scheme III and discussed below.

We believe that an initial silver-mediated iodide abstraction from the aryl palladium iodide[9] results in the formation of a tight olefin-palladium complex. The aryl group is transferred from this complex, affording the intermediates **11** and **12**, which in the absence of iodide ions are not prone to desilylate. We have speculatively tried to explain the formation of **2** and **3** from **11** and **12** in the following way. In the case of **11**, preferably the more acidic proton α to the trimethylsilyl group is irreversibly lost, ultimately resulting in the formation of **2**. In the case of **12**, loss of the benzylic proton initiates a similar conversion to **3**. This is in marked contrast to the hydride-based mechanism leading to **1** outlined in Scheme II. Thus, in the latter case the regiochemistry of the elimination is probably determined by thermodynamic control (relative stability), while in the first case it is determined by kinetic control (relative acidity). It is possible in some cases that in the presence of silver ions these reaction routes operate simultaneously. However, it seems that the first one, i.e., the one outlined in Scheme III, is favored at lower temperatures. The possibility that **2** could result from isomerization of **1** seems unlikely since the ratio of **1**/**2** is not influenced by time.[10] Furthermore, no isomerization was detected when **1** was treated with silver nitrate under usual Heck conditions. To further test this hypothesis under conditions, where an active catalyst is certain to have been formed, reaction entry 16 was performed where previously prepared **1** was introduced with the starting reactants. No change in the concentration of **1** was observed.

The relatively high amounts of 3-phenyl-1-propene (**5**) formed at 120 °C in Me_2SO (entry 11) can possibly be explained by assuming the presence of partly dissociated silver iodide at this temperature in this solvent.

The solvating power of the solvent would be expected to influence the balance between the two reaction routes outlined in Scheme II and III. Thus, high cation solvating

Scheme IV



power should favor the latter route. This effect is reflected in the ratio of **1**/**2** at 50 °C in Me_2SO (entry 16, 1/23) vs. acetonitrile (entry 20, 1/3). The presence and nature of ligands used also influenced the product distribution to some extent. Thus, the absence of ligands seems unfavorable and results in low conversion (entry 22). In most cases tri-*o*-tolylphosphine was used as ligand, although triphenylphosphine and triphenyl phosphite gave similar results (entries 23, 26). Triethylphosphine resulted in a somewhat lower conversion (entry 24), although it also completely suppressed the formation of **1**. Bidentate ligands also work quite well in our case (entry 27).[11] The ratio of catalyst/ligand does not seem to be critical, at least not in acetonitrile at 120 °C. The palladium catalyst used throughout this work has been $Pd(OAc)_2$ although $Pd(PPh_3)_4$ gave similar results. The use of Pd/C in the absence of ligands resulted in a lowered conversion. As regards the regiochemistry of the reaction, it was found that the total ratio between terminal and internal arylation (~80/20) was relatively independent of solvent, temperature, catalyst, and ligand in the absence of silver ions. In the presence of such ions, however, this ratio seemed to be more sensitive to the experimental conditions. As is evident from Table I, it proved to be impossible to influence the regiochemistry of the arylation in such a way that compound **3** was obtained as the main product. On the basis of the knowledge that palladium-catalyzed arylation of vinylsilanes results in desilylation,[5] an alternative route to **3** was adopted. Thus, the use of (*E*)-1,3-bis(trimethylsilyl)-1-propene, a compound containing the structural features of both a vinyl- and an allylsilane, as olefin at 120 °C in acetonitrile proved advantageous (see Scheme IV). In this case it was also found that it was possible to suppress the desilylation reaction. Thus at 50 °C in Me_2SO and in the presence of silver nitrate the main product was compound **4** (see Scheme IV). At this temperature the arylation was quite slow, with either $Pd(OAc)_2/PPh_3$ or $Pd(PPh_3)_4$ as catalysts, but it was found that addition of catalytic amounts of trimethylvinylsilane resulted in a marked rate enhancement. The reason for this accelerating effect is not obvious. Addition of allyltrimethylsilane had a similar, although not as pronounced, effect.

Although the stereospecific product **4** was formed almost exclusively, traces (<2%) of the isomer (*E*)-1,3-bis(trimethylsilyl)-2-phenyl-1-propene (**13**) were also formed. By preparative gas chromatography an enrichment of **13** was achieved and a mixture of **4** and **13** in a ratio: of 4:1 was isolated and subsequently analyzed with GC-MS and NMR. The structure assignment of **4** and **13** is based on comparison of the chemical shift of the vinylic proton in the two compounds appearing at δ 5.41 in **4** and at δ 5.23 in **13**.

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(9) An example of chloride abstraction by silver triflate from an arylpalladium chloride derivative giving a binuclear complex containing Pd-H-Pd bonds has recently been reported by: Rimml, H.; Venanzi, L. M. *J. Organomet. Chem.* **1984**, *260*, C52-C54.

(10) Allyltrimethylsilane was isomerized to 1-propenyltrimethylsilane in 20% yield in the presence of palladium(0) at 160 °C for 2 h provided that acetic acid was present, see ref 15d.

(11) Chelating diphosphines, trialkylphosphines, and phosphite esters in general do not produce useful catalytic systems in the Heck reaction, see ref 3b, p 147.

Compound **4** was found to be very sensitive to acids and converted smoothly into **3**. Thus we found that the best way of preparing **3** was by arylation of (*E*)-1,3-bis(trimethylsilyl)-1-propene in the presence of silver nitrate at 120 °C, where the ammonium salt formed is supposed to act as the acid.

Triethylamine has been used as the base throughout this investigation, but we have also tried sodium acetate in DMF.[12] Performing the arylation of allyltrimethylsilane at 50 °C under these conditions resulted in the formation of the same compounds as in entry 17, **1** being the main product. However, the reaction was slow and most of the iodobenzene remained after 2 days. It has recently been reported that a combination of tetrabutylammonium chloride and sodium bicarbonate in DMF is a very efficient combination.[13] Under these conditions no arylation of allyltrimethylsilane occurred even in very concentrated solutions at 50 °C.[14]

In conclusion it seems that the palladium-catalyzed arylation of allylsilanes in the absence or presence of added silver ions is a useful method for obtaining aryl-containing silanes of types **1**–**4**. Due to the simplicity of the experimental procedure, and the expected tolerability of a wide range of substituents in the aryl group, it compares favorably with existing methods[15] for the preparation of compounds of this type.

Experimental Section

Materials. Dimethyl sulfoxide, acetonitrile, dimethylformamide, and toluene were obtained from Janssen Chimica. Palladium acetate, palladium on charcoal, iodobenzene, triphenylphosphine, and triphenyl phosphite were purchased from Fluka AG. Allyltrimethylsilane, triethylamine, and silver nitrate were obtained from Merck; Triethylphosphine, phenyldiethylphosphine, and 1,4-bis(diphenylphosphino)butane were obtained from Ventron. (*E*)-1,3-Bis(trimethylsilyl)-1-propene[16] and tri-*o*-tolylphosphine[17] were prepared by literature methods. All reagents obtained from commercial sources were used as received.

General. ^{1}H NMR spectra were recorded on JEOL PMX 60 and JEOL MH 100 spectrometers in carbon tetrachloride using Me_4Si as internal standard. Mass spectra were obtained on a Finnigan 4021 (Data System Incos 2100) gas chromatograph–mass spectrometer at an ionization potential of 70 eV. Quantitative gas chromatographic analyses were performed on a Varian 1400 instrument equipped with a 3-m column of 3% OV 101 and a Perkin-Elmer 900 instrument using a 2-m column of 5% NPGS. 2-Methylnaphthalene was used as an internal standard. The preparative gas chromatography was performed on a Aerograph equipped with a 3-m column of 15% OV 101 at 120 °C. Flash chromatography was carried out with E. Merck silica gel 60 (230–400 mesh) and light petroleum ether as eluent. Preparative HPLC was performed on an LDC Constra Metric III with LDC UV III monitor equipped with a 250-mm RP18 column using acetonitrile as eluent. All reactions in the temperature range between 80 and 120 °C were run in a 100-mL heavy-walled, thin-necked Pyrex tube, fitted with a Teflon stopcock. Reactions at 50 °C were run in a round-bottomed flask with magnetic stirring.

General Procedure for Small-Scale Experiments. A mixture consisting of 0.05 mmol (11.2 mg) of palladium acetate, 0.10 or 0.30 mmol of phosphine, 1.0 mmol (170 mg) of silver nitrate (when present), 1.0 mmol (204 mg) of iodobenzene, 1.2 mmol (121 mg) of triethylamine, 2.5 mmol (285 mg) of allyltrimethylsilane, and 25 mL of the solvent was placed in a Pyrex tube or in a 50-mL round-bottomed flask equipped with magnetic stirring. After heating in an oil bath for the appropriate time and cooling to room temperature, the mixture was added to 25 mL of water and extracted twice with 15 mL of ether. The organic phase was then analyzed by gas chromatography.

Preparative Runs. (*E*)-1-Phenyl-3-(trimethylsilyl)-1-propene (1). A mixture of 0.224 g (1.0 mmol) of palladium acetate, 1.82 g (6.0 mmol) of tri-*o*-tolylphosphine, 4.08 g (20 mmol) of iodobenzene, 5.70 g (50 mmol) of allyltrimethylsilane, 2.42 g (24 mmol) of triethylamine, and 30 mL of acetonitrile was introduced into a Pyrex tube. The solution was heated in an oil bath at 120 °C for 3 days. The reaction mixture was then poured into 200 mL of water and extracted with ether (4 × 50 mL). The combined organic phases were washed with 50 mL of water and dried ($MgSO_4$). The crude product obtained was then purified by flash chromatography to give 1.20 g (32%) of the title compound **1**[15b] as a colorless oil, with a purity of >98%.

(*E*)-3-Phenyl-1-(trimethylsilyl)-1-propene (2). A 500-mL round-bottomed reaction flask containing a magnetic stirring bar was charged with 250 mL of Me_2SO. In the following order, 67 mg (0.3 mmol) of palladium acetate, 547 mg (1.8 mmol) of tri-*o*-tolylphosphine, 1.70 g (10 mmol) of silver nitrate, 2.04 g (10 mmol) of iodobenzene, 1.21 g (12 mmol) of triethylamine, and 2.85 g (25 mmol) of allyltrimethylsilane were then added, and the mixture was heated at 50 °C with stirring for 2 days. The reaction mixture was then poured into 250 mL of water and worked up as above. After concentration the crude residue (a mixture of (*E*)-3-phenyl-1-(trimethylsilyl)-1-propene (**2**) and 2-phenyl-3-(trimethylsilyl)-1-propene (**3**)) was placed in a Pyrex tube containing 10 mL of acetonitrile and 0.57 g (2.5 mmol) of triethylammonium iodide and heated in an oil bath at 100 °C overnight. After ethereal workup as above, the crude product was then subjected to chromatography yielding 1.05 g (55%) of the title compound **2**[18] with a purity of >95%.

2-Phenyl-3-(trimethylsilyl)-1-propene (3). A Pyrex tube containing 35 mL of acetonitrile, 22.4 mg (0.10 mmol) of palladium acetate, 157 mg (0.6 mmol) of triphenylphosphine, 0.85 g (5.0 mmol) of silver nitrate, 1.02 g (5.0 mmol) of iodobenzene, 0.6 g (6.0 mmol) of triethylamine, and 1.12 g (6.0 mmol) of (*E*)-1,3-bis(trimethylsilyl)-1-propene was heated in an oil bath at 120 °C for 2 h. After cooling to room temperature, 22.4 mg (0.10 mmol) of palladium acetate and 0.20 g (1.2 mmol) of silver nitrate was added to the reaction mixture, which was then heated for a further hour at 120 °C. The reaction mixture was allowed to reach room temperature and poured into 50 mL of water. After workup as above, the crude product was purified by flash chromatography, giving 0.50 g (53%) of the title compound **3**,[15g] with a purity of >98%.

(*Z*)-1,3-Bis(trimethylsilyl)-2-phenyl-1-propene (4). Into a 500-mL round-bottomed reaction flask charged with 250 mL of Me_2SO were added, in the following order, 35.9 mg (0.16 mmol) of palladium acetate, 252 mg (0.96 mmol) of triphenylphosphine, 1.36 g (8.0 mmol) of silver nitrate, 1.63 g (8.0 mmol) of iodo-

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[12] Spencer, A. *J. Organomet. Chem.* **1983**, *258*, 101.

[13] Jeffrey, T. *J. Chem. Soc., Chem. Commun.* **1984**, 1287.

[14] The efficacy of the procedure was checked by using methyl acrylate as the olefin, which afforded methyl cinnamate as expected (cf. ref 13).

[15] Selected methods for preparation of **1** and related compunds were from the following. (a) From aldehydes and [2-(trimethylsilyl)-ethylidine]triphenylphosphorane: Seyferth, D.; Wursthorn, K. R.; Lim, T. F. O.; Sepelak, D. J. *J. Organomet. Chem.* **1979**, *181*, 293. (b) From aldehydes and 1-(phenylsulfonyl)-2-(trimethylsilyl)ethane: Hsiao, C.-N.; Shechter, H. *Tetrahedron Lett.* **1982**, *23*, 1963. (c) From propiophenone or phenylacetone and their (phenylsulfonyl)hydrazones, butyllithium, and trimethylsilyl chloride: Fristad, W. E.; Han, Y.-K.; Paquette, L. A. *J. Organomet. Chem.* **1979**, *174*, 27. (d) From allylic esters, hexamethyldisilane, and catalytic amounts of palladium(0) or rhodium(I) complex: Urata, H.; Suzuki, H.; Moro-oka, Y.; Ikawa, T. *Bull. Chem. Soc. Jpn.* **1984**, *57*, 607. (e) From bromostyrene and (trimethylsilyl)methylmagnesium chloride in the presence of nickel(II) complex: Hayashi, T.; Kabeta, K.; Hamachi, I.; Kumada, M. *Tetrahedron Lett.* **1983**, *24*, 2865 and references cited therein. For preparation of **2**, i.e., (f) from alkanesulfonyl chloride and (trimethylsilyl)diazomethane: Aoyama, T.; Toyama, S.; Tamaki, N.; Shioiri, T. *Chem. Pharm. Bull.* **1983**, *31*, 2957. For preparation of **3** and related compounds, see the following. (g) From esters and (trimethylsilyl)methylmagnesium chloride: Fleming, I.; Pearce, A. *J. Chem. Soc., Perkin Trans. 1* **1981**, 251. (h) From silyl enol ethers and (trimethylsilyl)methylmagnesium chloride in the presence of nickel catalyst: Hayashi, T.; Katsuro, Y.; Kumada, M. *Tetrahedron Lett.* **1980**, *21*, 3915. (i) From enol phosphates and (trimethylsilyl)methylmagnesium halide in the presence of nickel or palladium catalysts: Hayashi, T.; Fujiwa, T.; Okamoto, Y.; Katsuro, Y.; Kumada, M. *Synthesis* **1981**, 1001.

[16] Dunoguès, J.; Calas, R.; Ardoin, N.; Biran, C. *J. Organomet. Chem.* **1971**, *32*, C31–C34.

[17] Ziegler, C. B.; Heck, R. F. *J. Org. Chem.* **1978**, *43*, 2941.

[18] Carey, F. A.; Toler, J. R. *J. Org. Chem.* **1976**, *41*, 1966.

benzene, 0.91 g (9.0 mmol) of triethylamine 1.86 g (10.0 mmol) of (*E*)-1,3-bis(trimethylsilyl)-1-propene, and a trace of trimethylvinylsilane. The mixture was heated with stirring at 50 °C for 15 h, and 35.9 mg (0.16 mmol) of palladium acetate, 0.34 g (2.0 mmol) of silver nitrate, and a trace of trimethylvinylsilane were thereafter added to the reaction mixture, which was then heated for an additional 3 h at 50 °C. (The addition of fresh reagents reduced the time necessary for completion.) The crude product was worked up and purified by flash chromatography as above, yielding 1.10 g (52%) of the title compound as a colorless oil: ^{1}H NMR (CCl$_4$) δ −0.18 (s, 9 H), 0.16 (s, 9 H), 2.15 (s, 2 H), 5.41 (s, 1 H), 7.20 (m, 5 H); mass spectrum, *m/e* 262 (M$^+$). Anal. Calcd for $C_{15}H_{26}Si_2$: C, 68.62; H, 9.98; Si, 21.40. Found: C, 68.67; H, 9.95; Si, 21.36.

Minor amounts of (*E*)-1,3-bis(trimethylsilyl)-2-phenyl-1-propene **13** (<2%) and a small amount of an unidentified isomer were present in the purified material. Enrichment of **13**, by preparative gas chromatography resulted in the isolation of a mixture of **4** and **13** in a ratio of 4:1. These isomers were separable by analytical GC–MS, and both isomers gave identical mass spectra. The signals from the vinylic and allylic protons in **13** appeared at δ 5.23 (s, 1 H) and 1.97 (s, 2 H), respectively. Compound **4** was obtained as a single compound by purification by HPLC.

Acknowledgment. We gratefully acknowledge the support of A.H. through grants from the Swedish Natural Science Research Council and of Mr. T. Klingstedt for stimulating discussions.

Chemoselectivity in Palladium-Catalyzed Reactions of 2-Bromoallyl Esters

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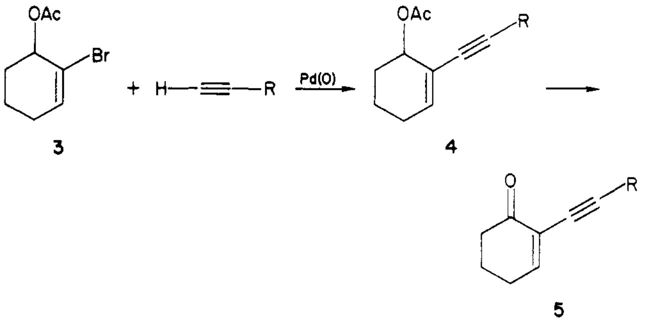
Received January 9, 1985

The chemoselectivity of palladium-catalyzed reactions of 2-bromoallyl esters has been established. With compatible carbon nucleophiles, 2-bromoallyl esters gave products of coupling to the vinyl bromide moiety instead of nucleophilic allylic substitution. Products from reactions with nitrogen nucleophiles and in the absence of added nucleophiles are also consistent with the absence or minor importance of the (π-allyl)palladium complex formation as a competing pathway. These results illustrate an unusual influence of the 2-bromo substituent on the usual ease of fission of the allylic C–O bond.

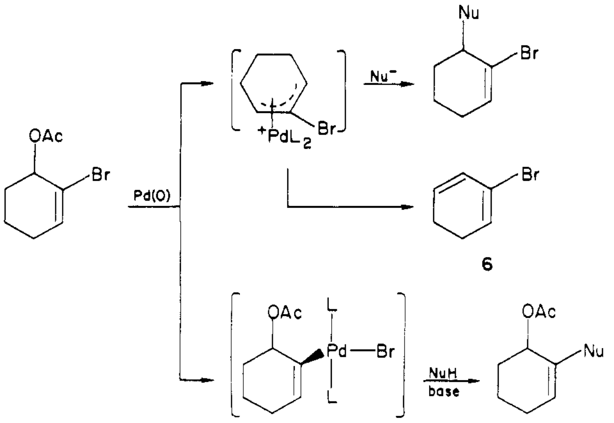
Two types of palladium-catalyzed reactions that find frequent use in organic syntheses are the coupling reactions of vinyl or aryl halides[2–8] and the nucleophilic substitution of allyl esters.[9] The mechanisms of these two types of palladium-catalyzed reactions have received good attention,[3,9] but selectivity between them in the same molecule has so far attracted only cursory examination. Recently, examples of selectivity between different ester groups situated allylic to the same double bond were reported and rates of nucleophilic allylic substitution of different ester groups in different molecules were also compared.[10,11] But in general, the influence of substituents on the vinyl carbons on the reactivity of the allylic C–O bond has not been addressed.

Our interest in the chemoselectivity of palladium-catalyzed reactions of 2-bromoallyl esters arose from difficulties in attempts[12] to ethynylate, with the help of various palladium catalysts, the ethylene glycol ketal of 2-bromo-

Scheme I



Scheme II



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[1] Present address: Department of Chemistry, Virginia Polytechnic Institute and State University, Blacksburg, VA 24061.

[2] Cassar, L. *J. Organomet. Chem.* **1975**, *93*, 253. Sekiya, A.; Ishikawa, N. *Ibid.* **1976**, *118*, 349. Dieck, H. A.; Heck, F. R. *Ibid.* **1975**, *93*, 259.

[3] Sonogashira, K.; Tohda, Y.; Hagihara, N. *Tetrahedron Lett.* **1975**, 4467. Fitton, J.; Rick, E. A. *J. Organomet. Chem.* **1971**, *28*, 287.

[4] Takahashi, S.; Kuroyama, Y.; Sonogashira, K.; Hagihara, N. *Synthesis* **1980**, 627.

[5] Minato, A.; Suzuki, K.; Tamao, K.; Kumada, M. *Tetrahedron Lett.* **1984**, *25*, 83.

[6] Dang, H. P.; Linstrumelle, G. *Tetrahedron Lett.* **1978**, 191.

[7] Ratovelomanana, V.; Linstrumelle, G. *Tetrahedron Lett.* **1981**, *22*, 315.

[8] Rossi, R.; Carpita, A.; Quirici, M. G.; Gaudenzi, M. L. *Tetrahedron* **1982**, *38*, 631.

[9] Trost, B. M. *Acc. Chem. Res.* **1980**, *13*, 635, and references therein.

[10] Tsuji, J.; Shimizu, I.; Minami, I.; Ohashi, Y. *Tetrahedron Lett.* **1982**, *23*, 4809.

[11] Tanigawa, Y.; Nishimura, K.; Kawasaki, A.; Murahashi, S.-I. *Tetrahedron Lett.* **1982**, *23*, 5549.

0022-3263/85/1950-3900$01.50/0