Tetrahedron Letters,Vol.27,No.52,pp 6397-6400,1986 0040-4039/86 $3.00 + .00
Printed in Great Britain Pergamon Journals Ltd.

PALLADIUM-CATALYSED REDUCTIVE ADDITION OF ARYL IODIDES TO ARYL AND ALKYLETHYNYLSILANES: A STEREO AND REGIOSELECTIVE ROUTE TO FUNCTIONALIZED 2,2-DISUBSTITUTED VINYLSILANES

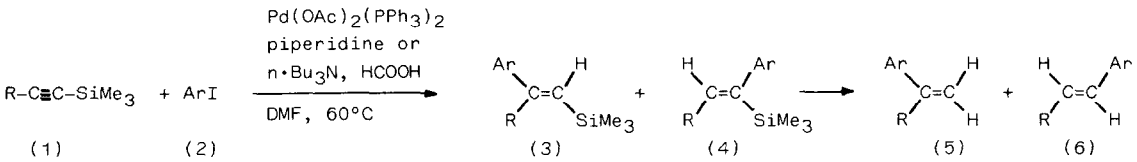
A. Arcadi[a], S. Cacchi[b]*, F. Marinelli[a]

a) Dipartimento di Chimica, Ing. Chimica e Materiali, Via Assergi 4, 67100 L'Aquila (Italy)

b) Istituto di Chimica Organica, Via del Castro Laurenziano 9, 00161 Roma (Italy)

Summary. Aryl and alkylethynylsilanes are converted into 2,2-disubstituted vinylsilanes containing various common functional groups in the presence of aryl iodides, a palladium catalyst, formic acid, and a tertiary or secondary amine with high stereoselectivity and good regioselectivity.

Vinylsilanes are versatile synthetic intermediates: for example, they have been shown to give regioselective and frequently highly stereospecific reactions with electrophiles[1] to produce desilylated vinyl derivatives, saturated carbonyl compounds, and substituted 2-amino-alkylsilanes[2]. We have previously reported that the palladium-catalysed reaction of aryl iodides with propargyl alcohols[3] in the presence of formic acid and tertiary or secondary amines produces γ,γ-disubstituted allylic alcohols. The results obtained suggested that steric factors may have a dominant effect in controlling the regiochemistry of addition of arylpalladium species to the carbon-carbon triple bond and prompted us to investigate the behaviour of the easily available aryl[4] and alkylethynylsilanes[5] (1). Now we report that aryl and alkylethynylsilanes can react with aryl iodides in the presence of the same ammonium formate palladium reagent to give 2,2-disubstituted vinylsilanes (3) in satisfactory yield (see table). Various common functional groups can be tolerated both in the starting ethynylsilane and in the arylating reagent.



R = aryl-, alkyl- Scheme I

Minor amounts of the isomeric 1,2-disubstituted vinylsilanes (4) as well of the desilylated alkenes (5) and (6) were also isolated. The alkenes (5) can be isolated as the main products by

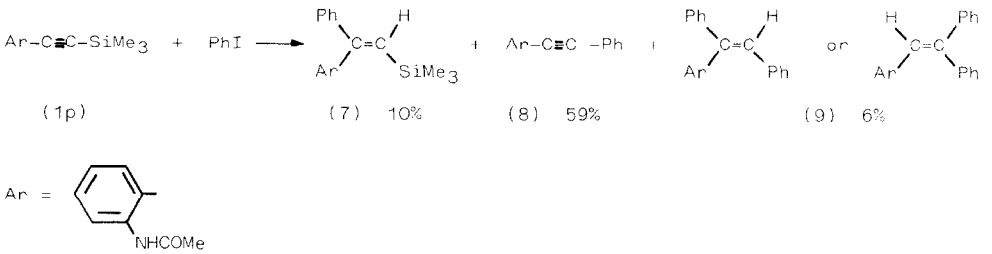
treating the reaction mixture, filtered through a silica gel column, with iodine in benzene/water[6]. The easy of desilylation of the addition derivatives, however, is strongly dependent upon the nature of the substituents. For example, the silyl derivative (3h) was recovered unchanged when the mixture derived from the reaction of 2-methylphenyl, trimethylsilylacetilene with 4-hydroxyphenyl iodide was treated as above (24 h) or with HI in benzene water (room temperature, 24 h). The corresponding 1,1-diarylalkene was obtained in 27% yield by treating the addition intermediate (3h) with iodine in benzene/water at 75°C (48 h).

It is apparent from the results summarized in the table that the bulky trimethylsilyl group is able to control the carbo-palladation step[7] favouring the regioselective formation of (3) in the presence of a variety of functionalities on the aromatic ring bonded to the C-2 of (1). Strongly electron-withdrawing groups seem to affect the reaction worsening the regioselectivity (entry l and m). A slight worsening of the regioselectivity has been also observed with compounds containing an sp^3 carbon atom on the C-2 (entries n and o).

However, only with arylethynylsilanes bearing 2-hydroxy and 2-acetamido substituents on the aromatic ring some anomalies in the general trend of the reaction were observed.

In the reaction of 2-hydroxyphenyl,trimethylsilylacetilene with 4-methoxyphenyl iodide (entry c) the olefinic derivative (6c) was isolated as the main product proving that in this case the inverse regiochemistry of addition of arylpalladium intermediate to the carbon-carbon triple bond is favoured. This may be the consequence of an hydroxyl coordination of the approaching palladium atom[3,8]. Steric factors should not be involved as in the presence of 2-methyl group (entry h) the usual trend was observed. The isolation of only olefinic derivatives could be dependent on an easy desilylation of the corresponding vinylsilanes promoted by the 2-hydroxy group.

In the reaction of 2-acetamidophenyl,trimethylsilylacetilene (1p) with phenyl iodide (scheme 2), 2-acetamidophenyl,phenylacetilene (8) was isolated as the main product, very likely through the desilylation of the starting arylethynylsilane and subsequent palladium-catalysed coupling with phenyl iodide.



Scheme II

Control experiments revealed that (1p) desilylates easily in the presence of piperidine and formic acid to give 2-acetamidophenylacetilene (78% yield, 8 h, 60°C). The addition of bis(triphenylphosphine)palladium diacetate to (1p), piperidine, and formic acid (60 °C, 3 h) resulted in the disappearance of the starting ethynylsilane and in the isolation of only 7% of

2(2-acetamidophenyl)-1-trimethylsilylethylene and 20% of 2-acetamido-1-ethylbenzene. The formation of polymer[9] could account for this result. Apparently, under usual conditions, the palladium-catalysed coupling of the in situ formed 2-acetamidophenylacetilene with phenyl iodide is faster than any other reaction pathway.

The regiochemistry of the silyl derivatives (3), isolated as single stereoisomers, was assigned on the basis of ^{1}H-NMR analysis and confirmed by their desilylation to the corresponding 1,1-disubstituted alkenes or to 2,2-disubstituted acetaldehydes[10]. The syn-stereochemistry of addition was assumed on mechanistic grounds, literature data[9], and the unambiguous result of the X-ray analysis of 1,2,3-triphenylprop-2-en-1-ol derived from the related palladium-catalysed reductive addition of phenyl iodide to 1,3-diphenylprop-2-yn--1-ol[11].

Table - Pd-Catalysed Reductive Addition of Aryl Iodides to Aryl and Alkylethylnylsilanes[a]

Entry	Procedure	Starting material (1), R[b]	Aryl iodide (2), Ar	Reaction time (h)[c]	Vinylsilane, % (3)	(4)	Alkene, % (5)	(6)
a	A	4-H_2N-C_6H_4 (94)	4-MeO-C_6H_4	6	48	--	23	--
	B	" "	" "	5 (1)	--	--	71	--
b	A	4-HO-C_6H_4 (83)	" "	5	60	--	15	--
	B	" "	" "	5 (8)	--	--	76	--
c	A	2-HO-C_6H_4	" "	7	--	--	13	43
d	A	4-Cl-C_6H_4 (84)	4-HO-C_6H_4	8	56	11	--	--
	B	" "	" "	7 (6)	--	--	63	--
e	A	3-MeOOC-C_6H_4 (70)	" "	6	60	11	5	--
f	A	4-MeCONH-C_6H_4 (80)	C_6H_5	8	50	10	--	--
g	A	3-H_2N-C_6H_4 (88)	3-Me-C_6H_4	36	41	--	--	--
h	A	2-Me-C_6H_4 (97)	4-HO-C_6H_4	7	71	--	--	--
i	A	4-MeO-C_6H_4 (96)	4-MeO-C_6H_4	12	55	--	--	--
l	A	4-MeOOC-C_6H_4 (64)	4-HO-C_6H_4	8	47	18	8	--
m	A	4-MeCO-C_6H_4 (92)	4-MeO-C_6H_4	8	44	10	6	--
n	A	Me[d]	" "	8	43	12	--	--
o[e]	A	$CH_3(CH_2)_5$ (66)	4-HO-C_6H_4	8	23	20	19	--

a) Yields are given on isolated products, are calculated on the starting ethynylsilanes (1), and refer to single not optimized runs. b) Figures in parentheses refer to the isolated yield of (1), prepared from aryl halides according to the reference (7), except (1o), prepared from 1-octyne according to the reference (5). c) Figures in parentheses refer to the time of the desilylation step. d) Commmercially available and used without further purification. e) Substitution of t-Bu,Ph_2Si- group for the less bulky Me_3Si- group allowed the isolation of the corresponding 2,2-disubstituted vinylsilane in 58% yield.

In a typical preparation of 2,2-disubstituted silanes (entry b, procedure A), to a stirred solution of 4-methoxyphenyl iodide (1.062 g, 4.54 mmol), piperidine (0.64 ml, 6.43 mmol) and DMF (2 ml) were added 4-hydroxyphenyl,trimethylsilylacetilene (0.36 g, 1.89 mmol) and $Pd(OAc)_2(PPh_3)_2$ (0.071 g, 0.094 mmol). The mixture was gently purged with nitrogen, and formic acid (0.19 ml, 4.99 mmol) was added all at once. The mixture was stirred at 60°C under a nitrogen atmosphere for 5 h, AcOEt and water were added, and the organic layer was separated, washed with water, dried ($MgSO_4$), and concentrated at reduced pressure. The residue (1.1 g) was purified by flash-chromatography. Elution with a 91/9 n-hexane/AcOEt mixture gave the silyl derivative (3b) (0.337 g, 60% yield) and the corresponding 1,1-diarylethylene (5b) (0.065 g, 15% yield). For (3b): mp 74-81°C (dec); IR (KBr) 3420, 1610, 1590, 1245, 1030, 835 cm^{-1} ; ^1H-NMR ($CDCl_3$, Me_3Si- group as internal standard) δ 7.53-6.80 (m, 8H), 6.26 (s, 1H), 5.27 (s, 1H, exchange with D_2O), 3.90 (s, 3H). For (5b): mp 107-108°C; IR (KBr) 3360, 1610, 1250, 1030, 845 cm^{-1}; ^1H-NMR ($CDCl_3$) δ 7.47-6.70 (m, 8H), 5.30 (s, 2H), 4.83 (s, 1H, exchange with D_2O), 3.82 (s, 3H); MS (m/e) = 226 (M^+).

In a typical preparation of 1,1-disubstituted alkenes (entry b, procedure B), 4-hydroxyphenyl,trimethylsilylacetilene (0,31 g, 1.62 mmol) was reacted with 4-methoxyphenyl iodide (0.91 g, 3.88 mmol) as described in the procedure A. After 5 h the reaction mixture was filtered through a column of silica gel (60 g, 70-230 mesh) eluting with diethyl ether (350 ml). The solution was concentrated at reduced pressure and the residue was added of benzene (10 ml), water (5 ml), and iodine (0,041 g, 0,016 mmol). The mixture was stirred at 75°C for 7.5 h. Then diethyl ether and $Na_2S_2O_3$ 20% were added, the organic layer was separated, washed with water, dried ($MgSO_4$), and concentrated at reduced pressure. The residue (0.64 g) was purified by flash chromatography. Elution with a 90/10 n-hexane/AcOEt mixture gave pure (5b) (0.28 g, 76% yield).

Aknowledgment - The research was supported by a grant from Ministero della Pubblica Istruzione.

References

1) T.H. Chan, Acc. Chem. Res. 10, 442 (1977); T.H. Chan, I. Fleming, Synthesis, 761 (1979); E. Negishi, Organo-Metallics in Organic Synthesis, Vol. 1, Wiley-Interscience, 1980; W.P. Weber, Silicon Reagents for Organic Synthesis, Springer-Verlag, Berlin, 1983; D.J. Ager, Synthesis, 384 (1984).
2) J. Barluenga, C. Jiménez, C. Najera, M. Yus, Synthesis, 414 (1982)
3) A. Arcadi, S. Cacchi, F. Marinelli, Tetrahedron, 41, 5121 (1985)
4) S. Takahashi, Y. Kuroyama, K. Sonogashira, N. Hagihara, Synthesis 627 (1980)
5) C. Eaborn, D.R.M. Walton, J. Organomet. Chem. 2, 95 (1964)
6) K. Utimoto, M. Kitai, H. Nozaki, Tetrahedron Lett. 2825 (1975)
7) S. Cacchi, M. Felici, B. Pietroni, Tetrahedron Lett. 3137 (1984)
8) R.F. Heck, Org. React. 27, 345 (1982)
9) N.A. Cortese, R.F. Heck, J. Org. Chem. 43, 3985 (1978); J.R. Weir, B.A. Patel, R.F. Heck, J. Org. Chem., 45, 4926 (1980)
10) R.K. Boeckman, Jr., K.J. Bruza, Tetrahedron Lett., 3365 (1974)
11) A. Arcadi, S. Cacchi, S. Ianelli, F. Marinelli, M. Nardelli, Gazz. Chim. Ital., in press

(Received in UK 20 October 1986)