Tetrahedron Letters,Vol.26,No.7,pp 839-842,1985
Printed in Great Britain

0040-4039/85 $3.00 + .00

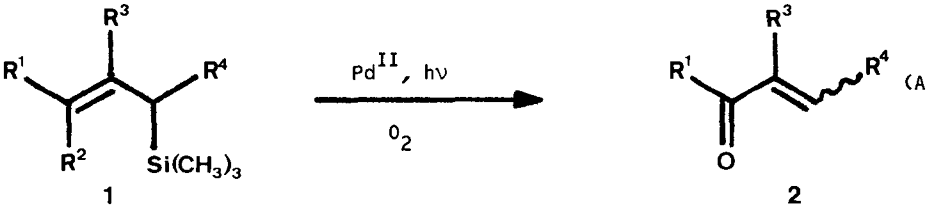
PALLADIUM CATALYZED OXIDATION OF ALLYLSILANES WITH U.V. LIGHT AND MOLECULAR OXYGEN (1)

A. RIAHI, J. COSSY, J. MUZART * and J.P. PETE

Laboratoire de Photochimie, Unité de Recherche Associée au C.N.R.S. n° 459
Université de Champagne-Ardenne, Moulin de la Housse, B.P. 347,
51062 REIMS Cédex, France

Abstract : *Photolysis of oxygenated acetone solutions of allylsilanes containing small amounts of palladium led to α,β-ethylenic alcohols, aldehydes or ketones. Efficient regiospecific oxidation can be observed when the allylsilane was substituted by an arylsulphonyl group.*

The electrophilic substitution of allylsilanes (2) by Pd^{II} salts leads to the splitting of the C-Si bond with formation of η^3-allylpalladium complexes (3-6). We have shown previously that photolysis of oxygenated solutions of such complexes provided the corresponding α,β-ethylenic carbonyl compounds (7,8). Then, it seemed possible to carry out the direct oxidation of allylsilanes (reaction A) ; such a transformation would be useful considering the limitations of the described methods (9).

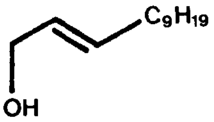


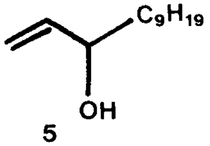
1 2

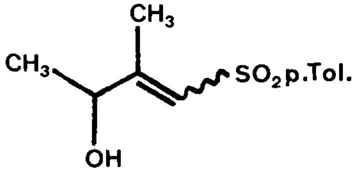
	a	b	c	d	e	f	g	h	i	j	k	l
R^1	H	C_9H_{19}	H	H	CH_3	H	H	CH_3	H	CH_3	SO_2T	SO_2T
R^2	H	H	H	H	H	H	H	H	CH_3	CH_3	CH_3	CH_3
R^3	H	H	H	H	H	CH_3	H	CH_3	CH_3	H	H	CH_3
R^4	H	H	C_9H_{19}	SO_2T	SO_2T	SO_2T	SO_2Ph	SO_2T	SO_2T	SO_2T	H	H

SO_2T = p.Toluenesulphonyl.

To test this hypothesis, photolysis (λ = 366 nm) of an oxygenated solution of the allyltrimethylsilane 1a in acetone-d_6 containing Pd(OCOCF$_3$)$_2$ was carried out in a NMR tube : slow formation of propenal 2a and propenol 3 was observed (table, run 1). Irradiation on a preparative scale of a mixture of monosubstituted allylsilanes 1b and 1c (1b/1c $\sim$ 3) produced alcohols 4 and 5 (4/5 $\sim$ 1)(run 2). In both cases, the reaction was catalytic in palladium.


4


5


6

Recently, we described that allylic photooxidation of alkenes catalyzed by Pd^{II} salts (10) was improved by a sulphonyl substituent at the allylic position (11). For this reason, the oxidation of allylsilanes 1d-1l bearing such a group was investigated (12).

Compounds 1d-1g were selectively converted to the corresponding α,β-unsaturated ketones of aldehydes 2d-2g (13,14) while a mixture of 1h and 1i furnished both ketone 2h and alcohol 6. Similar irradiation of 1j-1l led only to their slow degradation.

The regiospecific oxidation of compounds 1d-1i can be attributed to the sulphonyl substituent which induces the oxidation of the allylic position remote from this electron-withdrawing group (8,11).

The substitution of allylsulphones by a trimethylsilane group allows allylic oxidation of internal olefins and increases strongly the efficiency of this reaction. In contrast to 1e, the photolysis of 1-p.tolylsulphonyl-2-butene in the presence of Pd(OCOCF$_3$)$_2$ and O$_2$ led only to a slow degradation of the starting material. Moreover, oxidation under similar conditions of 1-p.tolylsulphonyl-2-propene (11) produced a mixture of 2d and the corresponding unsaturated alcohol with a lower turnover number (T.O. $\sim$ 4).

The efficiency of the oxidation of the allylsilanes depends on the nature of the catalyst (cf table) and we found that Pd(OCOCF$_3$)$_2$and PdCl$_2$(CH$_3$CN)$_2$ were more efficient than Pd(OCOCH$_3$)$_2$. Interestingly, decreasing the amount of the catalyst to 1 mol. % resulted also in a fair yield in the oxidized compound with a high turnover number (run 7). The use of Cu^{II} as cocatalyst did not change greatly the course of the photolysis (run 13). Although Pd° did not generally react with allylsilanes (15) photooxidation of 1d in the presence of Pd(PPh$_3$)$_4$ afforded small amounts of 2d (run 9).

The photoreaction of the allylsilanes described here is very dependent on the employed solvent : in using acetonitrile or chloroform instead of acetone, extensive degradation of the starting material was observed. This might indicate that the irradiation in acetone involves a derivative of the solvent which could contribute to the oxidation of the allyl ligand or (and) to the turnover of the catalyst.

Work is presently in progress to test the efficiency of peroxidic compounds in the palladium catalysed oxidation of allylsilanes.

Table : Irradiation of allylsilanes in acetone (M∿0,01),λ = 366 nm, pO_2 = 1 bar, R.T.

Run	allylsilane	Catalyst (mol. %)	Irradiation time h.	Conversion %	Oxidation product		Turnover number
					yield[a] %	Corrected[b] yield %	
1	1a	$Pd(OCOCF_3)_2(5)$	160	44	2a : 14 3:traces	32	3
2	1b + 1c [c]	$Pd(OCOCF_3)_2(5)$	30	78	4 : 23 5 : 25	29 32	9,5
3		$PdCl_2(CH_3CN)_2(5)$	30	75	4 : 21 5 : 20	28 26	8
4	1d	$Pd(OCOCF_3)_2(5)$	38	100	2d : 95	95	19
5		$Pd\ Cl_2(CH_3CN)_2(5)$	40	95	90	95	18
6		$Pd(OCOCH_3)_3(5)$	40	90	60	66	12
7		$Pd\ Cl_2(CH_3CN)_2(1)$	40	67	58	86	58
8		$Pd\ Cl_2(CH_3CN)_2(1)$[d]	40	87	43	49	43
9		$Pd(PPh_3)_4$ (5)	40	38	32	84	6.5
10	1e	$Pd(OCOCF_3)_2(10)$	94	60	2e : 35	58	3.5
11		$Pd(OCOCF_3)_2(5x2)$[e]	64	83	61	72	6
12		$Pd\ Cl_2(CH_3CN)_2(5)$	64	63	47	74	9.5
13		$Pd(OCOCF_3)_2$ (5) + $Cu(OCOCF_3)_2(50)$	24	36	20	55	4
14	1f	$Pd(OCOCF_3)_2(5)$	40	85	2f : 71	83	14
15		$Pd\ Cl_2(CH_3CN)_2(5)$	40	64	58	90	11.5
16	1g	$Pd(OCOCF_3)_2(5)$	38	100	2g : 95	95	19
17	1h + 1i [f]	$Pd(OCOCF_3)_2(5)$	63	40	2h : 10 6 : 17	25 43	5.5
18		$Pd(OCOCF_3)_2(5)$	236	63	2h : 21 6 : 27	33 43	9.5
19		$Pd\ Cl_2(CH_3CN)_2(5)$	63	29	2h : 8 6 : 17	26 58	5

a) Isolated yield based on the quantity of allylsilane introduced in the reaction medium (except for run 1 where the yield was calculated by NMR). b) Corrected yield is based on allylsilane consumed. c) 1b/1c ∿ 3. d) Me_3SiCl(10 mol.%) was added to the reaction mixture. e) A second batch of catalyst was added after 48h. of irradiation. f) 1h/1i ∿ 1.

References

(1) Part of this work was presented at "Journées de Chimie Organique" in Palaiseau, September 14, 1984.

(2) For reviews on the use of allylsilanes in synthesis, cf :

. E.W. COLVIN, Chem. Soc. Rev., 1978, 7, 15.

. T.H. CHAN and I. FLEMING, Synthesis, 1979, 761.

. H. SAKURAI, Pure Appl. Chem., 1982, 54, 1.

. W.P. WEBER, "Silicon Reagents for Organic Synthesis", Springer-Verlag, 1983.

(3) J.M. KLIEGMAN, J. Organomet. Chem., 1971, 29, 73.

(4) . K. YAMAMOTO, K. SHINOHARA, T. OHUCHI and M. KUMADA, Tetrahedron Lett., 1974, 1153.

. T. HAYASHI, M. KONISHI and K. KUMADA, J. Chem. Soc., Chem. Commun., 1983, 736.

. R.J.P. CORRIU, N. ESCUDIE and C. GUERIN, J. Organomet. Chem., 1984, 271, C7.

(5) K. ITOH, M. FUKUI and Y. KURACHI, J. Chem. Soc., Chem. Commun., 1977, 500.

(6) I.S. AKHREM, N.M. CHISTOVALOVA and M.E. VOL'PIN, Usp. Khim., 1983, 52, 953, translated in Russ. Chem. Rev., 1983, 52, 542.

(7) J. MUZART, P. PALE and J.P. PETE, J. Chem. Soc., Chem. Commun., 1981, 668.

(8) J. MUZART, P. PALE and J.P. PETE, Tetrahedron Lett., 1983, 24, 4567.

(9) . M. OCHIAI and E. FUJITA, Tetrahedron Lett., 1983, 24, 777 and references cited therein

. K. TAMAO and N. ISHIDA, J. Organomet. Chem., 1984, 269, C37.

(10) J. MUZART, P. PALE and J.P. PETE, Tetrahedron Lett., 1982, 23, 3577.

(11) J. MUZART, A. RIAHI and J.P. PETE, J. Organomet. Chem., in press.

(12) These compounds were prepared by treatment of the corresponding allylsulphones by n.butyllithium at - 78°C in THF followed by slow addition of chlorotrimethylsilane.

(13) A mixture of E and Z isomers of ketones was generally observed. Both U.V. light and palladium complexes induce E - Z isomerisation, cf (11).

(14) Control experiment performed under the conditions of run 4 but in the dark did not lead to the aldehyde.

(15) . T. HIRAO, J. ENDA, Y. OSHIRO and T. AGAWA, Tetrahedron Lett., 1981, 22, 3079.

. B.M. TROST, J. YOSHIDA and M. LAUTENS, J. Amer. Chem. Soc., 1983, 105, 4494.

. B.M. TROST and C.R. SELF, J. Amer. Chem. Soc., 1983, 105, 5942.

(Received in France 12 December 1984)