

Journal of Organometallic Chemistry, 234 (1982) 367–373
Elsevier Sequoia S.A., Lausanne — Printed in The Netherlands

REDUCTIVE DEHALOGENATION OF α -HALOGENATED CARBONYL AND CYANO COMPOUNDS WITH THE HEXAMETHYLDISILANE/TETRAKIS(TRIPHENYLPHOSPHINE)PALLADIUM SYSTEM

HISAO URATA, HIROHARU SUZUKI ^{*}, YOSHIHIKO MORO-OKA ^{*}, and
TSUNEO IKAWA

*Research Laboratory of Resources Utilization, Tokyo Institute of Technology, 4259
Nagatsuta, Midori-ku, Yokohama 227 (Japan)*

(Received July 1st, 1981; in revised form March 8th, 1982)

Summary

Treatment of α -halogenated carbonyl or cyano compounds with hexamethyldisilane in the presence of catalytic amounts of tetrakis(triphenylphosphine)-palladium gives the corresponding parent carbonyl or cyano compounds in excellent yields via oxy- π -allyl(trimethylsilyl)palladium intermediates.

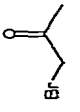
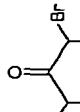
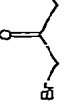
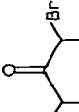
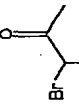
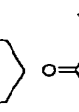
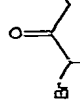
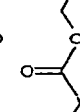
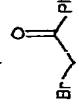
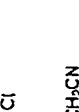
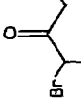
Introduction

The chemistry of disilane has recently been developed by several research groups, and a number of instances of the cleavage of silicon—silicon bonds catalyzed by transition metal complexes of rhodium, nickel, and palladium have been reported [1]. In the course of studies on synthetic applications of hexamethyldisilane, we were encouraged by the results with the reduction of palladium(II) species to palladium(0) by the treatment of Pd(PPh₃)₂Br₂ with hexamethyldisilane to explore an application of hexamethyldisilane/palladium(0) or hexamethyldisilane/palladium(II) system as a reductant for halogenated compounds. Reductive dehalogenation of α -haloketones to the corresponding ketones has also attracted considerable attention and various methods have been developed to bring about such a conversion [2]. This paper describes an effective reductive dehalogenation of α -halogenated carbonyl or cyano compounds by using hexamethyldisilane in the presence of catalytic amounts of palladium(0) complex.

Results and discussion

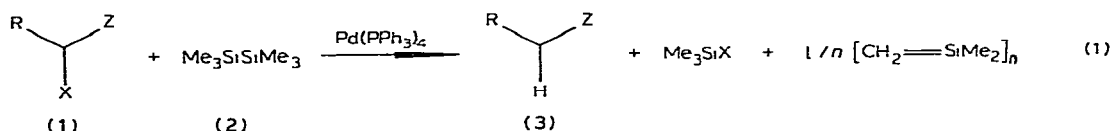
All dehalogenation reactions were conducted in pyrex sealed tubes. Ketones, carboxylic acid esters or cyano compounds having halogen atom in a α -position,

TABLE I
REDUCTIVE DEHALOGENATION OF α -HALOCARBONYL AND α -HALOCYANO COMPOUNDS

Run	1	$\frac{[\text{Cat}]^a}{[\text{I}]}$	Solv.	Temp. para- ture (°C)	Time (h)	Yield ^b of 3 (%)	Run	1	$\frac{[\text{Cat}]^a}{[\text{I}]}$	Solv.	Temp. para- ture (°C)	Time (h)	Yield ^b of 3 (%)
a		1/88	none	140	10	98	g		1/50	none	160	14	100 ^d
b		1/209	none	150	9.5	100	h		1/91	C ₆ H ₆	160	10	96 ^d
c		1/209	none	150	9.5	100	i		1/84	none	150	5	100
d		1/88	none	160	4	100	j		1/45	none	160	12	53 ^e
e		1/119	C ₆ H ₆	100	12	36 ^c	k		1/97	C ₆ H ₆	150	17	50
f		1/52	C ₆ H ₆	170	13	96 ^d							

^a Pd(PPh₃)₄ was used as the catalyst, ^b Yields of dehalogenated compounds 3 were determined by means of NMR, ^c Ph(Me₃SiO)C=CH₂ was obtained as a by-product in a 64% yield, ^d Completely debrominated products were obtained, ^e The product was ClCH₂CO₂C₂H₅.

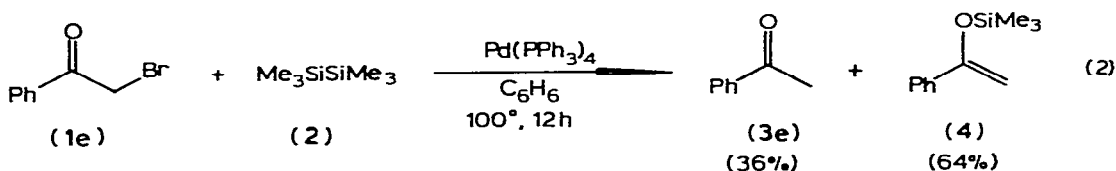
upon treatment with hexamethyldisilane in the presence of catalytic amounts of $\text{Pd}(\text{PPh}_3)_4$ in benzene solution at 100–170°C, afforded the corresponding parent carbonyl or cyano compounds in excellent yields (eq. 1), and selected examples are listed in Table 1.



(X = Br, Cl,
Z = COR, CO₂R, CN)

Experimentally, 2-bromo-3-pentanone (1d) and equimolar amounts of hexamethyldisilane were sealed in the pyrex tube with the catalytic amounts of $\text{Pd}(\text{PPh}_3)_4$ (1.1 mol% based on the bromoketone charged) and the mixture was heated at 160°C for 4 h. Subsequent measurement of ¹H NMR spectrum and GLC analysis showed the presence of a mixture of 3-pentanone (>99% yield), trimethylbromosilane, and unidentified silylated compound. Bromoacetone (1a), 1-bromo-2-butanone (1b), and 3-bromo-2-butanone (1c) were also reduced quantitatively to the parent ketones in a similar manner. Dibromoketones, such as 1,3-dibromo-2-butanone (1f), 2,4-dibromo-3-pentanone (1g), and 2,6-dibromocyclohexanone (1h) were also dehalogenated efficiently to the corresponding ketones with the hexamethyldisilane/ $\text{Pd}(\text{PPh}_3)_4$ system.

This method can be employed effectively for the reductive dehalogenation of not only α-haloalkanones and α-halocycloalkanones but also α-halocarboxylic acid esters (1i and 1j) and an α-halocyano compound (1k) and has an advantage to promote the reaction under neutral conditions without any side reaction. The only exception observed was the reaction of α-bromoacetophenone (1e) in which a silyl enol ether, 4, was formed together with acetophenone (eq. 2).



We propose the following mechanism (Scheme 1) for the reductive dehalogenation of α-halocarbonyl compounds based on the fact that tetrakis(triphenylphosphine)palladium reacts with 2 equiv of α-bromoketone at even ambient temperature to yield dibromobis(triphenylphosphine)palladium, debrominated ketone, and phosphonium ylide [3]. Reduction of $\text{Pd}(\text{PPh}_3)_2\text{Br}_2$, generated by the reaction of $\text{Pd}(\text{PPh}_3)_4$ with α-bromocarbonyl compound, into palladium(0) species with hexamethyldisilane seems to occur at the first stage of the reaction.

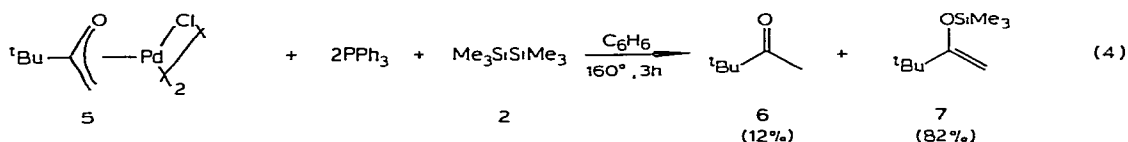
To test the validity of this step, reaction of $\text{Pd}(\text{PPh}_3)_2\text{Br}_2$ with hexamethyldisilane was attempted. Reduction of palladium(II) complex to palladium(0) accompanied with the formation of trimethylbromosilane was observed in the reaction of $\text{Pd}(\text{PPh}_3)_2\text{Br}_2$ with excess amounts of hexamethyldisilane in benzene at 160°C for 8 h. Participation of $\text{Pd}(\text{PPh}_3)_2\text{Br}_2$ in the dehalogenation reaction

even in the absence of solvent and deuterated ketone was not obtained in the reaction using benzene- d_6 as solvent suggests that the source of hydrogen in this reaction is the trimethylsilyl group and may support the reaction path proceeding by way of trimethylsilylpalladium, [B], and palladium hydride intermediates.

Alternatively, oxy- π -allyl(trimethylsilyl)palladium intermediate, [B], may undergo reductive elimination to give trimethylsilyl enol ether and palladium(0) species (path 2).

Direct conversion of silyl enol ether to carbonyl compound was disproved by the following experiment. Namely, treatment of 3-trimethylsiloxy-2-heptene under reaction conditions a–e (a; in C_6H_6 , $160^\circ C$, 37 h, b; in C_6H_6/Me_3SiCl , $160^\circ C$, 37 h, c; in $C_6H_6/Pd(PPh_3)_4$, $170^\circ C$, 18 h, d; in $C_6H_6/Pd(PPh_3)_2Cl_2$, $160^\circ C$, 37 h, e; in $C_6H_6/Me_3SiCl/Pd(PPh_3)_4$, $160^\circ C$, 37 h) resulted in the complete recovery of the starting silyl enol ether without any formation of 3-heptanone.

To test the preceding mechanistic proposal, the reaction of hexamethyldisilane with oxy- π -allylpalladium complex, **5**, derived from 3,3-dimethyl-2-trimethylsiloxy-1-butene and $Pd(PhCN)_2Cl_2$ [4] was examined. As expected, the products obtained from the reaction of **5** with hexamethyldisilane in the presence of 2 equiv of triphenylphosphine at $160^\circ C$ were a mixture of pinacolone (**6**) (12%) and 3,3-dimethyl-2-trimethylsiloxy-1-butene (**7**) (82%) (eq. 4).



In addition, **5** reacted with 2 equiv of trimethylsilyllithium in tetrahydrofuran at room temperature to give pinacolone (**6**) in a 24% yield. These results are consistent with a reaction which occurs by initial oxidative addition of the α -halocarbonyl compound to palladium(0) species to form an oxy- π -allylpalladium intermediate, which undergoes nucleophilic attack of hexamethyldisilane to yield the dehalogenated carbonyl compound.

Experimental

Benzene and diethyl ether were distilled from sodium benzophenone ketyl. Methanol was distilled from magnesium turnings prior to use. Methyl bromoacetate, bromoacetophenone, and chloroacetonitrile were obtained from commercial suppliers and were distilled before use. Ethyl dichloroacetate was prepared by esterification of dichloroacetic acid. Other bromo ketones were prepared from corresponding ketones and bromine. Hexamethyldisilane was prepared from disilane residue by methylation with methylmagnesium bromide. Tetrakis(triphenylphosphine)palladium [5] and dibromobis(triphenylphosphine)palladium [6] were prepared by standard procedures. Oxy- π -allylpalladium complex, **5**, was prepared according to the literature direction [4]. Identification of the reaction products and determination of the yields were performed by means of 1H NMR and GLC. 1H NMR spectra were determined on a Hitachi High Resolution NMR Spectrometer R-24B. Chemical shifts were expressed in

parts per million (ppm) downfield from internal tetramethylsilane. Gas-liquid partition chromatography (GLC) was done with Shimadzu GC-6A chromatograph.

Reaction of halocarbonyl and halocyano compounds with hexamethyldisilane

All reactions of halocarbonyl and halocyano compounds with hexamethyldisilane were carried out under nitrogen at temperature of 100–170°C in a sealed pyrex tube. Typical examples are described below.

(a) *Reaction of 2-bromo-3-pentanone (1d) with hexamethyldisilane in the presence of Pd(PPh₃)₄.* Tetrakis(triphenylphosphine)palladium, Pd(PPh₃)₄, (66.5 mg, 0.057 mmol) was placed in a pyrex tube equipped with three-way stopcock. Then the atmosphere was replaced with dry nitrogen. 2-Bromo-3-pentanone (827 mg, 5.01 mmol) was added via syringe and after hexamethyldisilane (754 mg, 5.15 mmol) was added, the reaction vessel was sealed and heated at 160°C for 4 h. ¹H NMR spectrum and GLC analysis of the resulting mixture disclosed the production of 3-pentanone (quant.), trimethylbromosilane (quant.), and unidentified silylated compound (¹H NMR(CCl₄/TMS) δ 0.04) with a quantitative conversion.

(b) *Reaction of bromoacetophenone (1e) with hexamethyldisilane in the presence of Pd(PPh₃)₄.* Tetrakis(triphenylphosphine)palladium (53.4 mg, 0.046 mmol) was introduced into a pyrex tube equipped with three-way stopcock. After bromoacetophenone (974 mg, 4.89 mmol), hexamethyldisilane (763 mg, 5.21 mmol), and 1 ml of dry benzene were added, the reaction vessel was sealed and heated at 100°C for 12 h. GLC analysis and determination of ¹H NMR spectrum of resulting mixture showed the production of acetophenone (36%), α-trimethylsilyloxystyrene (64%), trimethylbromosilane (quant.), and unidentified silylated compound (¹H NMR(CCl₄/TMS) δ 0.04) with a quantitative conversion. The mixture was then diluted with petroleum ether and the precipitated catalyst was filtered off. Concentration of the filtrate followed by the purification with column chromatography on silica gel afforded acetophenone in a 71% yield. The reaction was also carried out using benzene-d₆ as solvent. Incorporation of deuterium in the product was not observed at all by ¹H NMR and GC-mass spectrum of acetophenone produced in the reaction.

Reaction of oxy-π-allylpalladium complex, (5), with hexamethyldisilane

μ,μ'-Dichlorobis(η³-2-tert-butyl-oxyallyl)dipalladium, (5), (480 mg, 1.0 mmol) and triphenylphosphine (530 mg, 2.0 mmol) were placed in a pyrex tube equipped with three-way stopcock. After 5 ml of dry tetrahydrofuran and hexamethyldisilane (300 mg, 2.0 mmol) were added via syringe, the reaction vessel was sealed and heated at 160°C for 3 h. ¹H NMR and IR spectra, and GLC analysis of the resulting reaction mixture disclosed the production of pinacolone (12%) and 3,3-dimethyl-2-trimethylsiloxy-1-butene (82%) with a quantitative conversion.

Reaction of oxy-π-allylpalladium complex, (5), with trimethylsilyllithium

μ,μ'-Dichlorobis(η³-2-tert-butyl-oxyallyl)dipalladium, (5), (720 mg, 1.5 mmol) and triphenylphosphine (790 mg, 3.0 mmol) were placed in a 50 ml, round-bottomed flask and atmosphere was replaced with dry nitrogen. Then

15 ml of dry tetrahydrofuran was syringed into the flask. While being stirred at -30°C 5 ml of trimethylsilyllithium (0.6 *N* in tetrahydrofuran) was added. The reaction mixture was stirred for 3 h at -30°C , allowed to warm up to room temperature, and kept at room temperature for 30 min. To the resulting brown solution was added 100 ml of *n*-hexane and precipitates were filtered off. IR spectrum and GLC analysis of the filtrate disclosed the production of pinacolone (24%).

Acknowledgement

The authors are grateful to the Toshiba Silicon Co. Ltd. for a generous gift of disilane residue in the direct synthesis.

References

- 1 For example,
 - (a) H. Sakurai, Y. Kamiyama and Y. Nakadaira, *J. Organometal. Chem.*, **131** (1977) 147; (b) K. Tamao, S. Okazaki and M. Kumada, *J. Organometal. Chem.*, **146** (1978) 87; (c) H. Matsumoto, T. Yako, S. Nagashima, T. Motegi and Y. Nagai, *J. Organometal. Chem.*, **148** (1978) 97; (d) H. Matsumoto, S. Nagashima, T. Kato and Y. Nagai, *Angew. Chem. Int. Ed. Eng.*, **17** (1978) 279; (e) K. Yamamoto, S. Suzuki and J. Tsuji, *Tetrahedron Lett.*, **21** (1980) 1653; (f) H. Watanabe, M. Kobayashi, H. Higuchi and Y. Nagai, *J. Organometal. Chem.*, **186** (1980) 51; (g) M. Lefort, C. Simmonet, M. Birot, G. Deleris, J. Dunogues and R. Calas, *Tetrahedron Lett.*, **21** (1980) 1857.
- 2 (a) T. Goto and Y. Kishi, *Tetrahedron Lett.*, (1961) 513; (b) I.J. Borowitz and L.I. Crossman, *Tetrahedron Lett.*, (1963) 471; (c) H.G. Kuivila and L.W. Menapace, *J. Org. Chem.*, **28** (1963) 2165; (d) I.J. Borowitz, K.C. Kirby, Jr., P.E. Rusek and E. Lord, *J. Org. Chem.*, **34** (1969) 2687; (e) R.R. Sauer and C.K. Hu, *J. Org. Chem.*, **36** (1971) 1153; (f) M. Oki, W. Funakoshi and A. Nakamura, *Bull. Chem. Soc. Jpn.*, **44** (1971) 828; (g) J.M. Townsend and T.A. Spencer, *Tetrahedron Lett.*, (1971) 137; (h) T.L. Ho and C.M. Wong, *Synth. Commun.*, **3** (1973) 237; (i) T.L. Ho and G.A. Olah, *Synthesis*, (1976) 807; (j) H. Alper, K.D. Logbo and H. des Abbayeo, *Tetrahedron Lett.*, (1977) 2861; (k) G.A. Olah, Y.D. Vankar and A.P. Fung, *Synthesis*, (1979) 59; (l) G.A. Olah, M.A. Arvanaghi and Y.D. Vankar, *J. Org. Chem.*, **45** (1980) 3531.
- 3 J.P. Collman and L.S. Hegedus, *Principles and Applications of Organotransition Metal Chemistry*, University Science Books, Mill Valley, CA, 1980, pp. 191.
- 4 (a) Y. Ito, T. Hirao and T. Saegusa, *J. Org. Chem.*, **43** (1978) 1011; (b) Y. Ito, H. Aoyama, T. Hirao, A. Moriguchi and T. Saegusa, *J. Am. Chem. Soc.*, **101** (1979) 494.
- 5 D.R. Coulson, *Inorg. Syn.*, **13** (1972) 121.
- 6 J.M. Jenkins and B.L. Shaw, *J. Chem. Soc. A*, (1966) 770.