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A CONVENIENT SYNTHESIS OF BENZYLMETHYLCHLOROSILANES BY THE PALLADIUM-CATALYZED DECHLORINATIVE SILYLATION OF BENZYLIC CHLORIDES WITH METHYLCHLORODISILANES

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Benzylmethylchlorosilanes were prepared in high yields by the dechlorinative silylation of benzylic chlorides with methylchlorodisilanes $Me_nSi_2Cl_{6-n}$ (n = 2, 3, and 4) in the presence of a catalytic amount of $Pd(PPh_3)_4$.

The Si-Si cleavage reaction of disilanes with organic halides, formally a dehalogenative silylation, constitutes a silicon-carbon bond forming process of quite a new type (eqn. 1). This reaction provides a facile route to functional silicon compounds which are less accessible by the traditional methods involving the Grignard and organolithium reagents.[1-3]

$$\geq Si\text{-}Si\leq + \geq C\text{-}X \longrightarrow \geq Si\text{-}C\leq + \geq Si\text{-}X \qquad (1)$$

Recently, Eaborn and coworkers have reported the synthesis of benzyltrimethylsilanes by the silylation of the corresponding benzyl halides with $Me_3SiSiMe_3$ in the presence of $Pd(PAr_3)_4$.[2] In this instance, however, it has been mentioned that the silylation was, in some cases (e.g., p-$MeC_6H_4CH_2Br$), hampered by the concurrent coupling of benzyl halides themselves.[3] A recent finding, that the reactivity of disilanes toward cleavage reactions is enhanced by the electron-acceptor properties of the Si-Si bonds,[4] has led us to postulate that methylchlorodisilanes of type $Me_nSi_2Cl_{6-n}$ might be efficient reagents for the silylation of benzylic halides.[5] We would like to report that benzylmethylchlorosilanes can be prepared in high yields by the dechlorinative silylation of benzylic chlorides with $Cl_2MeSiSiMeCl_2$, $Cl_2MeSiSiMe_2Cl$, and $ClMe_2SiSiMe_2Cl$ in the presence of $Pd(PPh_3)_4$. Benzylmethylchlorosilanes can be readily converted to many other derivatives such as alkyl-, alkoxy- and hydro-silanes, and also would be useful precursors of organopolysiloxanes.

Typically, a mixture of p-methylbenzyl chloride (7.03 g, 50.0 mmol), $ClMe_2SiSiMe_2Cl$ (18.7 g, 99.8 mmol), the Pd(0) complex (0.46 g, 0.4 mmol), and the mesitylene (5 ml) was heated at 130°C for 3 h in a flask equipped with a magnetic stirrer and a reflux condenser topped with a nitrogen inlet. GLC analysis showed that the reaction had given p-methylbenzyldimethylchlorosilane in 98% yield. The reaction mixture was then diluted with pentanes and filtered. After removal of the low-boling materials, distillation afforded 6.9 g (69% yield) of the benzylsilane: Bp 83°C/3 mmHg; n_D^{20}1.5102; Mass (70 eV) 198 (M^+) and 200 (M^+); IR (neat) 1890(w), 1615(w), 1520(s), 1410(m), and 1260(s) cm^{-1}; Anal. Found: C, 60.64; H, 7.66. Calcd for $C_{10}H_{15}ClSi$: C, 60.43; H, 7.61.

The results of the silylation are summarized in Table 1, and it is seen that $Cl_2MeSiSiMeCl_2$ and $ClMe_2SiSiMe_2Cl$ can be effectively used for the conversion of benzyl chlorides to methyldichlorosilyl and dimethylchlorosilyl derivatives, respectively. Interestingly, the reaction of benzyl chloride with unsymmetrical disilane $Cl_2MeSiSiMe_2Cl$ gives benzylmethyldichlorosilane almost exclusively rather than another possible product, benzyldimethylchlorosilane. Predominant formation of the dichlorosilane is convenient if we want to have difunctional benzylsilanes by the present method. Further, it is worthy to note that our recipe can be readily extended to

Table 1. The Dechlorinative Silylation of Benzylic Chlorides with Methylchlorodisilanes in the Presence of $Pd(PPh_3)_4$[a]

Run	Benzylic chloride	Disilane	Conditions	Product	Yield,%[b]
1	$C_6H_5CH_2Cl$	$Cl_2MeSiSiMeCl_2$	80°C, 7 h	$C_6H_5CH_2SiMeCl_2$	97
2		$Cl_2MeSiSiMe_2Cl$	80°C, 2 h	$C_6H_5CH_2SiMeCl_2$[c]	98
3		$ClMe_2SiSiMe_2Cl$	130°C, 2 h	$C_6H_5CH_2SiMe_2Cl$	100
4	$o\text{-}MeC_6H_4CH_2Cl$	$ClMe_2SiSiMe_2Cl$	130°C, 3 h	$o\text{-}MeC_6H_4CH_2SiMe_2Cl$[d]	98
5	$p\text{-}MeC_6H_4CH_2Cl$	$Cl_2MeSiSiMeCl_2$	80°C, 9 h	$p\text{-}MeC_6H_4CH_2SiMeCl_2$	94
6	$o\text{-}ClC_6H_4CH_2Cl$	$ClMe_2SiSiMe_2Cl$	130°C, 2 h	$o\text{-}ClC_6H_4CH_2SiMe_2Cl$[d]	95
7	$m\text{-}ClC_6H_4CH_2Cl$	$Cl_2MeSiSiMeCl_2$	80°C, 3 h	$m\text{-}ClC_6H_4CH_2SiMeCl_2$	94
8	$p\text{-}ClC_6H_4CH_2Cl$	$ClMe_2SiSiMe_2Cl$	130°C, 2 h	$p\text{-}ClC_6H_4CH_2SiMe_2Cl$	86
9	$m\text{-}(ClCH_2)_2C_6H_4$	$ClMe_2SiSiMe_2Cl$	130°C, 5 h	$m\text{-}(ClMe_2SiCH_2)_2C_6H_4$[d]	74
10	$p\text{-}(ClCH_2)_2C_6H_4$	$ClMe_2SiSiMe_2Cl$	130°C, 3 h	$p\text{-}(ClMe_2SiCH_2)_2C_6H_4$	61

[a][Chloride]/[disilane]/[Pd(0)] = 1:2:0.01-1:3:0.01 unless otherwise stated. [b]Yields were determined by GLC. [c]$C_6H_5CH_2SiMe_2Cl$ was also produced in 2% yield. [c]All new compounds gave satisfactory elemental analyses. [d][Chloride]/[disilane]/[Pd(0)] = 1/6/0.01.

the synthesis of bis(dimethylchlorosilyl)xylenes (Run 9 and 10).

Although several methods have been employed for the preparation of benzylchlorosilanes,[6] the aforementioned results indicate that our silylation technique has some synthetic advantages. For instances, the Grignard reaction between $p\text{-}ClC_6H_4CH_2Cl$ and Me_2SiCl_2 resulted in the formation of $p\text{-}ClC_6H_4CH_2SiMe_2Cl$ only in 27% yield.[7] The Friedel-Craft reaction of $Cl_2MeSiCH_2Cl$ with toluene in the presence of $AlCl_3$ gave an isomeric mixture of $MeC_6H_4CH_2SiMeCl_2$.[8] The silylation of α,α'-dichloro-p-xylene with $SiCl_4$ in the presence of methylchlorodisilanes afforded a 70:30 mixture of the mono- and di-silylated products.[5]

Work is in progress to extend the synthetic scope of the present silylation.

References

1) H. Matsumoto, K. Shono, and Y. Nagai, J. Organometal. Chem., 208, 145 (1981) and references cited therein.
2) D. Azarian, S. S. Dua, C. Eaborn, and D. R. M. Walton, J. Organometal. Chem., 117, C55 (1976).
3) K. Yamamoto, S. Suzuki, and J. Tsuji, Tetrahedron Lett., 1980, 1653.
4) K. Tamao, T. Hayashi, and M. Kumada, J. Organometal. Chem., 114, C19 (1976); K. Tamao, S. Okazaki, and M. Kumada, ibid., 146, 87 (1978); H. Matsumoto, T. Yako, S. Nagashima, T. Motegi, and Y. Nagai, ibid., 148, 97 (1978); H. Matsumoto, K. Shono, A. Wada, I. Matsubara, H. Watanabe, and Y. Nagai, ibid., 199, 185 (1980).
5) Recently, Calas and coworkers have reported the synthesis of benzyltrichlorosilanes by the $NiCp_2$-catalyzed reaction of benzylic chlorides with $SiCl_4$ in the presence of $Cl_2MeSiSiMeCl_2$ and/or $Cl_2MeSiSiMe_2Cl$. However, in this particular example, what is acting as a silylating agent is apparently $SiCl_4$ rather than the methylchlorodisilanes that are acting simply as chlorine trapping agents: see, M. Lefort, S. Simmonet, M. Birot, G. Deleris, J. Dunogues, and R. Calas, Tetrahedron Lett., 1980, 1857.
6) For reviews, see, C. Eaborn and R. W. Bott in A. G. MacDiarmid (ed.), "Organometallic Compounds of Group IV Elements", Vol. 1, Part I, Dekker, 1968, Chapt. 2; R. Benkeser, Acc. Chem. Res., 4, 94 (1971); M. Kumada, M. Ishikawa, K. Yamamoto, and K. Tamao, "Yuki Keiso Kagoubutsu no Kagaku", Kagaku Dojin, 1972, Chapt. 1 and 2.
7) J. Včelák, V. Bažant, and V. Chvalovský, Coll. Czech. Chem. Comm., 35, 136 (1970).
8) E. A. Chernyshev, M. E. Dolgaya, and Yu. P. Egorov, Zhur. Obshcheĭ Khim., 27, 267 (1957); Chem. Abstr., 52, 7187 (1958).

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