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Chromium(II)-Mediated Synthesis of 1,1-Bis(trimethylsilyl)alkenes from Aldehydes and $(Me_3Si)_2CBr_2$

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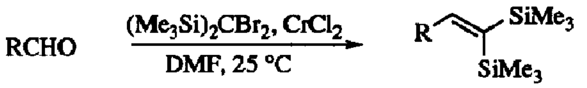
***Abstract:** The synthesis of 1,1-bis(trimethylsilyl)alkenes from aldehydes and $(Me_3Si)_2CBr_2$ using $CrCl_2$ is described.*

The utility of 1-trimethylsilylalkenes in organic synthesis is well-established.[1] In contrast, 1,1-bis(trimethylsilyl)alkenes are a relatively unexplored class of materials.[2] A deterrent to investigating their chemistry is the lack of methods available for their preparation, particularly under mild conditions. One potentially attractive method would be *via* alkylidenation of aldehydes. However, Peterson reaction using $LiC(SiMe_3)_3$ is essentially restricted to nonenolisable aldehydes,[3] as is reaction with $Li_2C(SiMe_3)_2$[4] or $(MgBr)_2C(SiMe_3)_2$.[5] In connection with our interest in the development and application of organochromium reagents in organic synthesis,[6] we communicate here our preliminary results concerning the synthesis of 1,1-bis(trimethylsilyl)alkenes by one-carbon homologation of aldehydes using $(Me_3Si)_2CBr_2$[5b] and $CrCl_2$ (Eq. 1).[7]

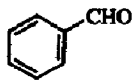
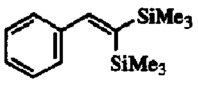
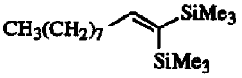
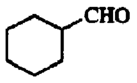
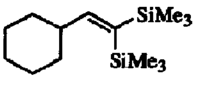
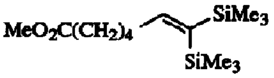
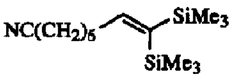
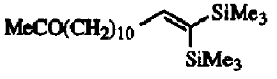
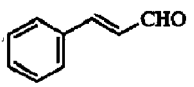
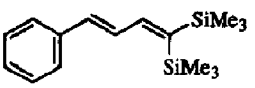
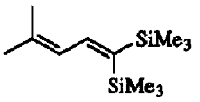


(1)

Initial experiments with aldehydes indicated that $(Me_3Si)_2CBr_2$ was not reduced effectively by $CrCl_2$ in neat THF, even in the presence of LiI,[6b] and addition of DMF as a cosolvent was required before successful reaction was observed. The use of neat DMF as solvent led to rapid reduction of $(Me_3Si)_2CBr_2$ and gave improved yields of the desired 1,1-bis(trimethylsilyl)alkenes. The reaction was found to be applicable to a range of aldehydes (Table 1), and the chemistry of the products is currently under investigation. The following 1,1-bis(trimethylsilyl)alkene synthetic procedure is representative:

A solution of cinnamaldehyde (0.133 g, 1 mmol) and $(Me_3Si)_2CBr_2$ (0.64 g, 2.1 mmol) in dry, deoxygenated DMF (5 ml) was added dropwise to a well-stirred solution of $CrCl_2$ (1.03 g, Aldrich 95% w/w pure, 8 mmol) in dry, deoxygenated DMF (9 ml) under argon at 25 °C. After 24 h at 25 °C water (40 ml) was added and the mixture was extracted with diethyl ether (3 x 40 ml). The combined organic extracts were washed with 1*M* aqueous $CuSO_4$ solution (40 ml), water (40 ml), brine (40 ml), dried ($MgSO_4$), and evaporated under reduced pressure. Purification of the residue by column chromatography (SiO_2, pentane) gave a colourless oil, 4-phenyl-1,1-bis(trimethylsilyl)-1,3-butadiene[3c] (0.233 g, 84 %).[9]

Table 1. Synthesis of 1,1-Bis(trimethylsilyl)alkenes

Entry	Aldehyde^8	1,1-Bis(trimethylsilyl)alkene	Yield,^{9} %
1.			84
2.	$CH_3(CH_2)_7CHO$		78
3,			79
4.	$MeO_2C(CH_2)_4CHO$		64
5	$NC(CH_2)_6CHO$		70
6.	$MeCO(CH_2)_{10}CHO$		58
7			84
8			73

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REFERENCES AND NOTES

1. Fleming, I.; Dunoguès, J.; Smithers, R. *Org. React.* **1989**, *39*, 57-575.
2. For references containing isolated examples of reactions of simple 1,1-bis(trimethylsilyl)alkenes which indicate some of their synthetic potential see: Hudrlik, P. F.; Hudrlik, A. M. α,β-Epoxysilanes. In *Advances in Silicon Chemistry*; Larson, G. L. Ed.; JAI Press Inc.: Greenwich. Vol. 2; 1993; pp. 1-89. Negishi, E.; Boardman, L. D.; Sawada, H.; Bagheri, V.; Stoll, T. A.; Tour, J. M.; Rand, C. L. *J. Am. Chem. Soc.*, **1988**, *110*, 5383-5396. Seebach, D.; Bürstinghaus, R.; Gröbel, B.-T.; Kolb, M. *Liebigs Ann. Chem.* **1977**, 830-845. Gröbel, B.-T.; Seebach, D. *Chem. Ber.* **1977**, *110*, 867-877.
3. (a) Ager, D. J. *Org. React.* **1990**, *38*, 1-223. (b) Fleming, I.; Floyd, C. D. *J. Chem. Soc., Perkin Trans. I* **1981**, 969-976. (c) Gröbel, B.-T.; Seebach, D. *Chem. Ber.* **1977**, *110*, 852-866.
4. van Eikema Hommes, N. J. R.; Bickelhaupt, F.; Klumpp, G. W. *Tetrahedron Lett.* **1988**, *29*, 5237-5240.
5. (a) Bickelhaupt, F. *J. Organomet. Chem.*, **1994**, *475*, 1-15. (b) Hogenbirk, M.; van Eikema Hommes, N. J. R.; Schat, G.; Akkerman, O. S.; Bickelhaupt, F.; Klumpp, G. W. *Tetrahedron Lett.* **1989**, *30*, 6195-6198.
6. (a) Hodgson, D. M.; Comina, P. J. *Synlett* **1994**, 663-664. (b) Review: Hodgson, D. M. *J. Organomet. Chem.* **1994**, *476*, 1-5.
7. For the homologation of aldehydes to *E*-alkenylsilanes using $Me_3SiCHBr_2$ and $CrCl_2$ see: Takai, K.; Kataoka, Y.; Okazoe, T.; Utimoto, K. *Tetrahedron Lett.* **1987**, *28*, 1443-1446.
8. Prepared according to: Bosone, E.; Farina, P.; Guazzi, G.; Innocenti, S.; Marotta, V. *Synthesis* **1983**, 942-944 (entry 4). Ohno, M.; Naruse, N.; Terasawa, I. *Org. Synth., Coll. Vol. V* **1973**, 266-269 (entry 5). Büchi, G.; Wüest, H. *Helv. Chim. Acta* **1979**, *62*, 2661-2672 (entry 6).
9. Isolated total yields of chromatographically homogeneous, spectroscopically pure products.

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