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Me_3SiCl-NaI-CH_3CN AS AN EFFICIENT AND PRACTICAL REDUCING AGENT FOR BENZYLIC ALCOHOLS

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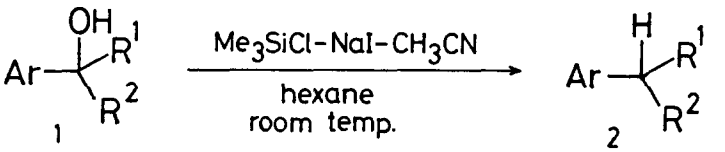
Abstract: Secondary and tertiary benzylic alcohols are reduced conveniently to the corresponding aryl alkanes by using Me_3SiCl-NaI-CH_3CN reagent in hexane. The reaction was successfully applied to a short step synthesis of (±)-arturmerone.

Me_3SiCl-NaI-CH_3CN reagent[1] has been recognized as a Me_3SiI equivalent and widely used as a versatile reagent in organic synthesis.[2] We now wish to report a new entry of its usefulness as an efficient reducing agent of secondary and tertiary benzylic alcohols. Although such transformation can be accomplished conventionally by using many other reagents, such as P_2I_4,[3a] Me_2SiI_2,[3b] $NaBH_4/CF_3CO_2H$,[3c] Me_3SiH-BF_3,[3d] Ph_3P-I_2,[3e] Li/liq. NH_3,[3f] and so on,[3g] the present method has advantages that the reaction can be done conveniently by using the inexpensive and readily available reagent under mild conditions. Clean products can be obtained without special purification process. The reagent does not damage the other functional group in the molecule.



A typical procedure for the present reduction is as follows: To a mixture of Me_3SiCl (1.54 ml, 12 mmol), NaI (1.8 g, 12 mmol), and acetonitrile (0.6 ml, 12 mmol), was added a solution of 1-phenylethanol (1b) (244 mg, 2 mmol) in hexane (2 ml). The mixture was stirred for 24 h at room temperature. Dilution with water, extraction with ether and subsequent isolation process gave ethylbenzene (2b) (158 mg) with sufficient purity in 75% yield.

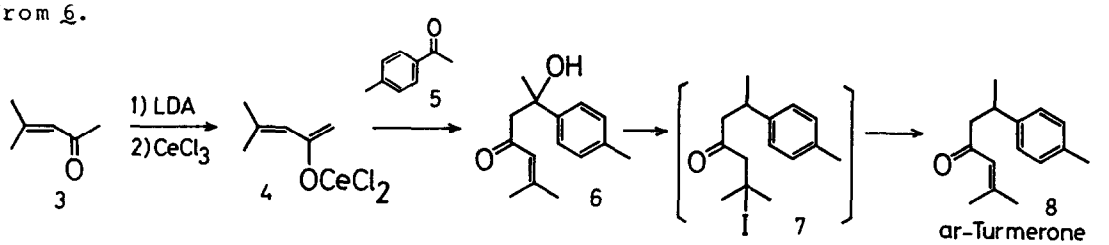
The reaction was applicable to various types of benzylic alcohols as listed in Table 1. Although further investigation is required for the elucidation of the mechanism, the presence of the carbonium ion intermediate stabilized by the aromatic moiety is supported by the fact that optically active 1ℓ[4] (70% e.e.) was converted into racemic 2ℓ. Formation of benzyl iodide in the case of benzylalcohol (1a) may be explained by the difficulty of formation of the primary carbonium ion intermediate.

Table 1. Reduction of Benzylic Alcohols with Me_3SiCl-NaI-CH_3CN Reagent

	Alcohol 1			Product 2[a]		Alcohol 1			Product 2[a]
	Ar	R^1	R^2	Yield (%)[b]		Ar	R^1	R^2	Yield (%)[b]
1a	Ph	H	H	c	1g[d]	Pipe-ronyl-	H	Et	57[d]
1b	Ph	H	Me	75	1h	Ph	Me	Et	76
1c	Ph	H	Et	99	1i	Ph	Me	Pr	82
1d	Ph	H	Pr	75	1j	p-Tolyl	Me	CH_2CO_2Et	91
1e	Ph	H	Bu	74	1k	p-Tolyl	Me	CH_2CO_2H	66
1f	Ph	H	$-CH_2CO_2Et$	91	1l[e]	Ph	Me	CH_2CO_2Me	60

[a]The known compounds were identified by using IR and ^1H NMR spectra. [b]Yields after distillation. [c]Benzyl iodide was obtained in 94% yield. [d]Reference 7. [e]The optical purity was determined to be 70% e.e. by ^1H NMR with $Eu(hfc)_3$.

The combination of the aldol reaction with the present reduction would become a useful synthetic method for the extention of an alkyl chain of aromatic ring. As one of the effective applications of the reaction sequence, (±)-ar-turmerone (8)[5] was conveniently synthesized as shown below. Thus, the aldol reaction of cerium enolate[6] of mesityl oxide (4) (LDA/THF, $CeCl_3$) with p-methylacetophenone (5) gave an alcohol (6)[7] in 54% yield. A similar treatment of 6 with Me_3SiCl-NaI-CH_3CN afforded iodide 7, which without isolation was successfully converted to 8 by the treatment with K_2CO_3/THF in 82% yield from 6.



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6. T. Imamoto, T. Kusumoto, and M. Yokoyama, Tetrahedron Lett., 24, 5233 (1983). Alcohol 6 was obtained in a very low yield without $CeCl_3$.
7. All new compounds showed satisfactory spectral (IR and ^1H NMR) and analytical data.

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