

t-BuCl–NaI as a Reagent for the Selective Reduction of Olefinic Double Bond of β -Phenyl α,β -Unsaturated Carbonyl Compounds

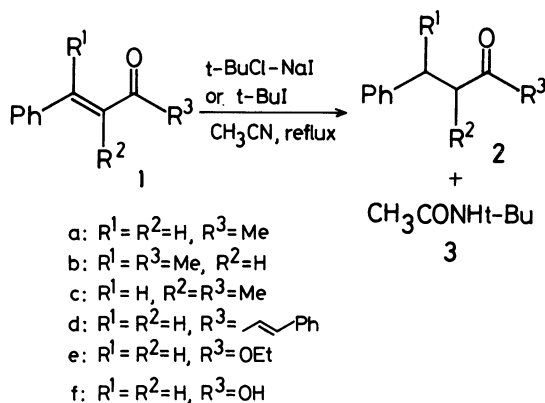
Takashi SAKAI,* Kazuyoshi MIYATA, Kazuomi HONDO, Masanori UTAKA,
and Akira TAKEDA

Department of Synthetic Chemistry, School of Engineering, Okayama University,
Tsushima, Okayama 700

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Synopsis. β -Phenyl α,β -unsaturated carbonyl compounds were conveniently reduced to the corresponding saturated aromatic compounds by heating with *t*-BuCl–NaI in acetonitrile.

We recently disclosed that the Me_3SiCl –NaI–ROH reagent was useful for the selective reduction of olefinic double bond of β -phenyl α,β -unsaturated carbonyl compounds and that the reduction was explained by the 1,4-addition of HI and subsequent attack of an iodide anion to the resulting β -iodo carbonyl intermediate.¹⁾ In this paper, we report that *t*-BuCl–NaI was found to be effective for a similar reduction (Scheme 1). The applicability of the reaction was examined by using the same substrates **1a–f** as those employed in the preceding paper.¹⁾ The present method has advantages that the reagent is readily available and can be handled without a special care to moisture. Yields of the reduction products **2a–f** shown in Table 1 were comparable with those observed for the reaction with Me_3SiCl –NaI–ROH reagent.¹⁾



Scheme 1.

The reaction simply involves heating of the substrates **1a–f** with a six-molar excess of the reagent in acetonitrile for 24 h, giving **2a–f** together with a small amount of *N*-*t*-butylacetamide²⁾ (**3**) in every case. The reaction mixture was colored dark purple gradually due to liberation of iodine. In a typical reduction with **1a**, shortening of the reaction time to 5 h decreased the yield of **2a** and the starting **1a** was recovered in a considerable amount. Unfortunately, the present reaction is not suitable for aliphatic conjugated enones. For example, mesityl oxide was recovered unchanged.

Table 1. Reduction of β -Phenyl α,β -Unsaturated Carbonyl Compounds with *t*-BuCl–NaI Reagent^{a)}

	Substrate 1 ^{c)}			Method ^{b)}	Product 2
	R ¹	R ²	R ³		Yield/% ^{e)}
1a	H	H	Me	A	74 ^{d)}
				A	34 ^{e)}
				B	80 ^{f)}
1b	Me	H	Me	A	74
				B	49
1c	H	Me	Me	A	46
1d	H	H	–CH=CHPh	A	51
1e	H	H	OEt	A	86 ^{g)}
1f	H	H	OH	A	72
				B	59 ^{f)}

a) The reaction was usually done for 24 h under refluxing unless otherwise noted. b) A: *t*-BuCl–NaI in CH_3CN ; B: *t*-BuI in CH_3CN . c) Yield after purification by preparative TLC. d) Reaction time of 12 h. e) Reaction time of 5 h. Thirtytwo per cent of **1a** was recovered. f) Reaction time of 7 h. g) A 65:35 mixture of the ester **2e** and its acid.

The present reduction would be caused by the in situ generated HI in a manner similar to that described previously.¹⁾ The handling of gaseous HI is not easy, because it readily decompose to iodine and hydrogen molecules.³⁾ The *t*-BuCl–NaI reagent is suitable for generation of HI in a reaction vessel. The liberation of isobutene⁴⁾ was detected by GLPC analysis.⁵⁾ The minor by-product **3** may be formed by the reaction of acetonitrile either with isobutene^{2a)} or *t*-BuCl.^{2b)} Furthermore, the applicability of *t*-BuI to the reaction was ascertained, although it is far more expensive than *t*-BuCl.

The present reaction is the first example utilizing *t*-BuCl–NaI as a reagent for the selective reduction of conjugated olefin of β -phenyl α,β -unsaturated carbonyl compounds.

Experimental

General. IR spectra were taken on a JASCO A-102 spectrometer. ¹H NMR spectra (60 MHz) were measured with a JEOL JNM-60 SI spectrometer using Me_4Si as an internal standard. GLPC analysis was done with a Hitachi 163 gas chromatograph.

General Procedure for the Reduction of **1a–f.** Sodium iodide (1.80 g, 12 mmol) was placed in a reaction vessel and the atmosphere is replaced by nitrogen. To this was added a

solution of the substrate **1** (2 mmol) and *t*-butyl chloride (1.11 g, 12 mmol) in acetonitrile (2 ml). The mixture was stirred for the time indicated in Table 1 under refluxing. After addition of water, the ether extract was washed with aqueous sodium thiosulfate to remove liberated iodine and then with water, dried (MgSO₄), and concentrated. The residual oil was purified by preparative TLC (Merck, Kieselgel 60, PF₂₅₄, hexane-ether, 3:1) to give the reduction product **2** and *N*-*t*-butylacetamide²⁰ (60–70 mg).

Reduction of 1a with *t*-BuI. A mixture of **1a** (73 mg, 0.5 mmol), *t*-BuI (0.35 ml, 3.0 mmol), and acetonitrile (1 ml) was heated under reflux for 7 h. The reaction mixture was treated in a similar manner. The yield of **2a** by GLPC analysis of the crude product was 80%.

References

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 - 5) The retention time was compared with that of a commercially available sample (3.0 min, liquid phase thermon-1000, type FFS, 0.25 mm×30 m, oven temperature 70 °C, N₂ 180 ml min⁻¹).
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