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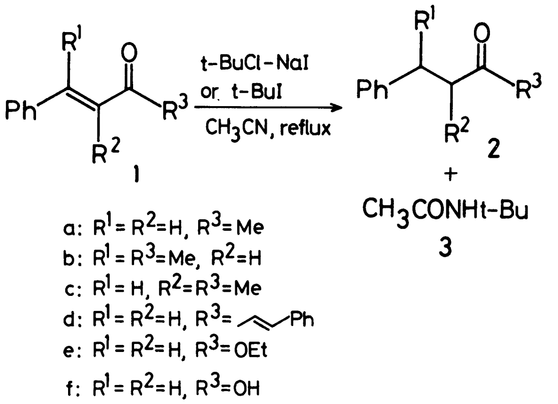
Synopsis. β-Phenyl α,β-unsaturated carbonyl compounds were conveniently reduced to the corresponding saturated aromatic compounds by heating with *t*-BuCl–NaI in acetonitrile.

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 preceeding 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 Reagenta)

	Substrate **1**			Methodb)	Product **2**
	R^1	R^2	R^3		Yield/%c)
1a	H	H	Me	A	74d)
				A	34e)
				B	80f)
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	86g)
1f	H	H	OH	A	72
				B	59f)

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 isobutene2a) 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 ($MgSO_4$), and concentrated. The residual oil was purified by preparative TLC (Merck, Kieselgel 60, PF_{254}, hexane–ether, 3:1) to give the reduction product **2** and *N*-*t*-butylacetamide[2] (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%.

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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, N_2 180 ml min^{-1}).