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A new preparation of BaI_2: application to (*Z*)-enol ether synthesis

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Abstract

A new preparation of BaI_2 is described. Transmetallation of lithium homoenolates with this reagent improved the yield in several chiral *Z*-enol ether syntheses. © 2000 Elsevier Science Ltd. All rights reserved.

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We recently described the preparation of chiral *Z*-enol ethers by isomerisation of the corresponding allyl ethers.[1] This isomerisation can be performed under thermodynamic conditions with *tert*-BuOK in DMSO[2] or under kinetic conditions with *sec*-BuLi in THF as described by Clark Still and Evans.[3] Using the first method generally leads to excellent yields, however attempts to alkylate the potassium homoeneolate intermediate were unsuccessful. In the case of the second method, alkylation of the lithium homoenolate intermediate gave poor yields in several cases depending on the electrophile and on the chiral auxiliary.[1]

Transmetallation of lithium trialkylsilyl homoenolates using anhydrous BaI_2, as described by Yamamoto and co-workers,[4] increases both yield and regioselectivity of γ-alkylations with carbonyl compounds or alkyl halides as electrophiles. The same type of reaction has been recently used by Corey et al.[5] for the stereoselective preparation of tetrasubstituted *Z*-enol silyl ethers. Anhydrous BaI_2 is also a starting material for the preparation of Rieke type barium, a superior reagent for regio- and stereoselective coupling of allylic units.[6] However, in our hands dehydration of the commercially available BaI_2, 2 H_2O proved to be not easily reproducible.[7] An alternative preparation of anhydrous BaI_2 by the reaction of I_2 with Ba pieces in THF has been also reported.[5] In analogy with the preparation of SmI_2,[8] we describe in the present paper a new preparation of anhydrous BaI_2 by reacting Ba with diiodoethane in THF and the use of this reagent for chiral *Z*-enol ether synthesis.[9] The commercialy available anhydrous $Ba(OTf)_2$ has also been used for comparison.

Preparation of BaI_2: A solution of 1,2-diiodoethane (10 mmol, 2.82 g) in ether (20 mL) was washed successively with an aqueous solution of $Na_2S_2O_4$ (10%, 5 mL) and water (10 mL). After decantation, the organic layer was dried over $MgSO_4$, filtered and evaporated under vacuum. The resulting white

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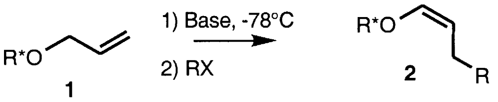
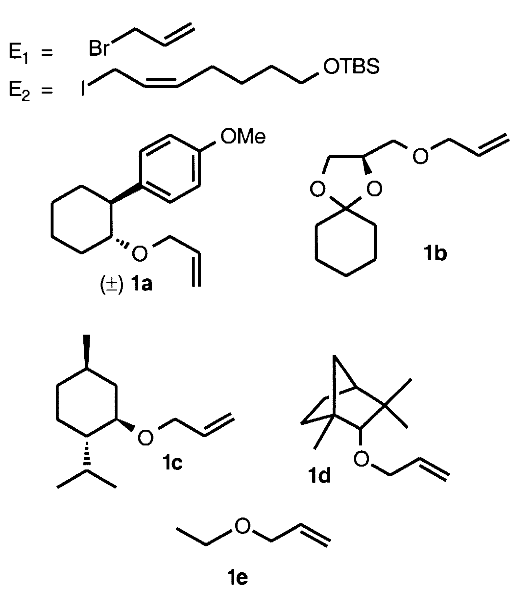
crystalline solid was dried under reduced pressure (1 mm Hg) for 30 min. Barium pieces (14.6 mmol, 2 g) in oil were washed successively with pentane, methanol and pentane and introduced into anhydrous THF (40 mL). The resulting suspension was stirred at −10°C under argon, and a solution of diiodoethane (10 mmol, 2.82 g) in anhydrous THF (10 mL) was added dropwise. The reaction mixture was stirred at the same temperature for 36 h to afford a pale yellow suspension of BaI_2 in THF.[10] This suspension was directly pumped out using a syringe for the transmetallation experiments.[11]

The results of the deprotonation–transmetallation–alkylation sequence of reactions are summarised in Scheme 1. Five allylic ethers **1a**–**1e**,[12] two electrophiles, E_1 and E_2, and three metallation–transmetallation processes, a, b and c, were used in these experiments. In all cases, the γ-alkylation products were obtained as the major isomer in a ratio >95:5. Transmetallation with BaI_2 (condition b) increased the yields in the range of 10 to 35%. By comparison, $Ba(OTf)_2$ (condition c) gave slightly lower yields.[13]



a = *sec*BuLi, THF, HMPA. b = *sec*BuLi, BaI_2, THF. c = *sec*BuLi, $Ba(OTf)_2$, THF

Starting material	Reaction conditions	Electrophile	Product %
1a	a	E_1	**2a** 26
"	b	"	**2a** 65
1b	a	"	**2b** 25
"	b	"	**2b** 38
1c	a	"	**2c** 30
"	b	"	**2c** 50
"	c	"	**2c** 47
1d	a	"	**2d** 50
"	b	"	**2d** 65
1e	a	E_2	**2e** 40
"	b	"	**2e** 60
"	c	"	**2e** 50



Scheme 1.

In conclusion, this paper describes a new method for the preparation of anhydrous BaI_2 and the application of this reagent to the preparation of chiral *Z*-enol ethers. Further uses of these compounds in synthesis are under current development.

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10. The yield of BaI_2 was estimated by bubbling the resulting ethylene in a solution of bromine in excess in CCl_4, followed by back titration of the remaining bromine. The excess of unreacted barium was also weighted at the end of the reaction.
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12. For the preparation of allylic ethers **1a**–**1e** see Ref. 1.
13. Typical experiment: To a 0.2 M solution of *sec*-BuLi (1.1 equivalent) in anhydrous THF at −78°C was addded allylic ether (1 equivalent). After 15 min, a suspension of BaI_2 (1.5 equivalent, 0.2 M in THF) was then introduced in the reaction medium and the resulting pale yellow suspension was stirred at the same temperature for an additional 30 min. The alkyl halide (1.5 equivalent) was in turn introduced and the reaction medium was kept at −78°C for 1 h before being warmed to room temperature. Quenching with an aqueous solution of NH_4Cl was followed by ether extraction and usual work-up.