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Generation and reactivity of polyanions derived from 1-[1-(benzotriazol-1-yl)alkyl]-1*H*-benzotriazoles

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Abstract—1-[1-(Benzotriazol-1-yl)alkyl]-1*H*-benzotriazoles undergo deprotonation with *n*-BuLi at the α-position of the *N*-substituent and at the 7-position of benzotriazole to afford polyanions. Treatment of these polyanions with electrophiles allows the preparation of highly functionalized benzotriazole derivatives.

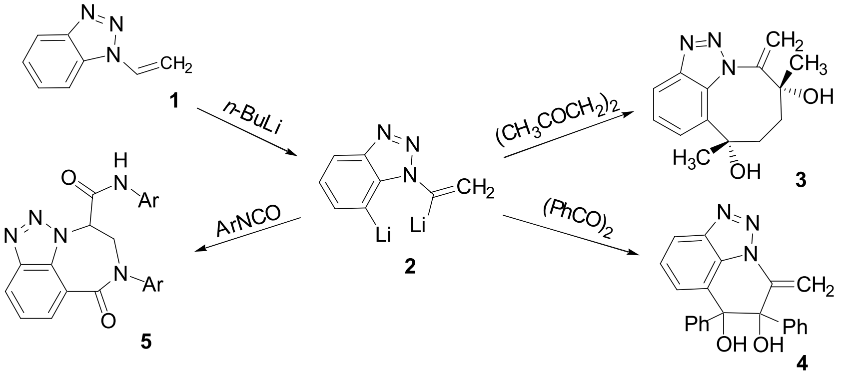
1. Introduction

Reactions of di- and polyanions with electrophiles are of great importance in synthetic organic chemistry. Although such reactions frequently involve only the most nucleophilic center of the polyanion, reactions of dianions as dinucleophiles with electrophiles have also been studied.[1] Previously, we[2] and Knight et al.[3] reported that certain N-substituted benzotriazoles can be dilithiated by deprotonation both at the α-position of *N*-substituent and at the 7-position of benzotriazole. Recently, we studied the reactions of dianion of the 1-vinylbenzotriazole **1** with electrophiles, which gave the new heterocyclic ring systems **3**, **4** and **5** (Scheme 1).[4]

Continuing our efforts to develop new routes to heterocycles and to investigate the reactivity of polyanions toward electrophiles, we have now studied the generation of polyanions **7** and **15** from dibenzotriazolylmethane **6** and 1,1-dibenzotriazolylethane **14**, respectively, and their reactions with a variety of mono-, di- and trielectrophiles (Schemes 2 and 3). Upon reactions with electrophiles, we found that the formation of **7** and **15** occurs giving the corresponding products of addition or substitution. In one case, the heterocyclization took place to give product **20**.

2. Results and discussion

Compound **6** was treated with excess of *n*-BuLi (4.1 equiv) in THF at −78 °C for a period of 12 h to give polyanion **7**, which was treated with 4 equiv of methyl iodide at the same



Scheme 1.

Keywords: Polyanions; Functionalization; Benzotriazole; Deprotonation; Electrophiles.

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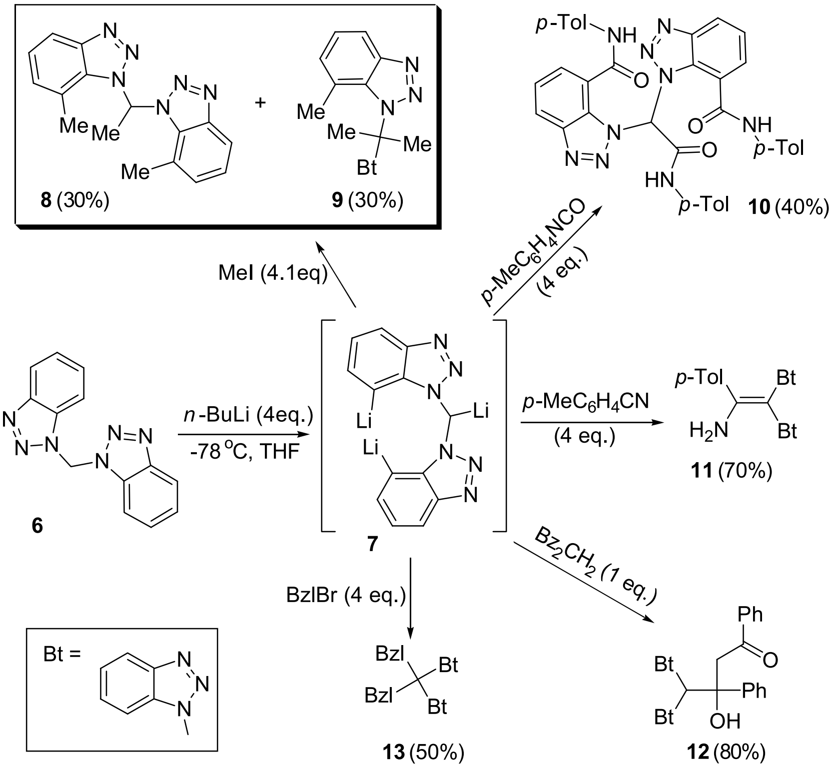
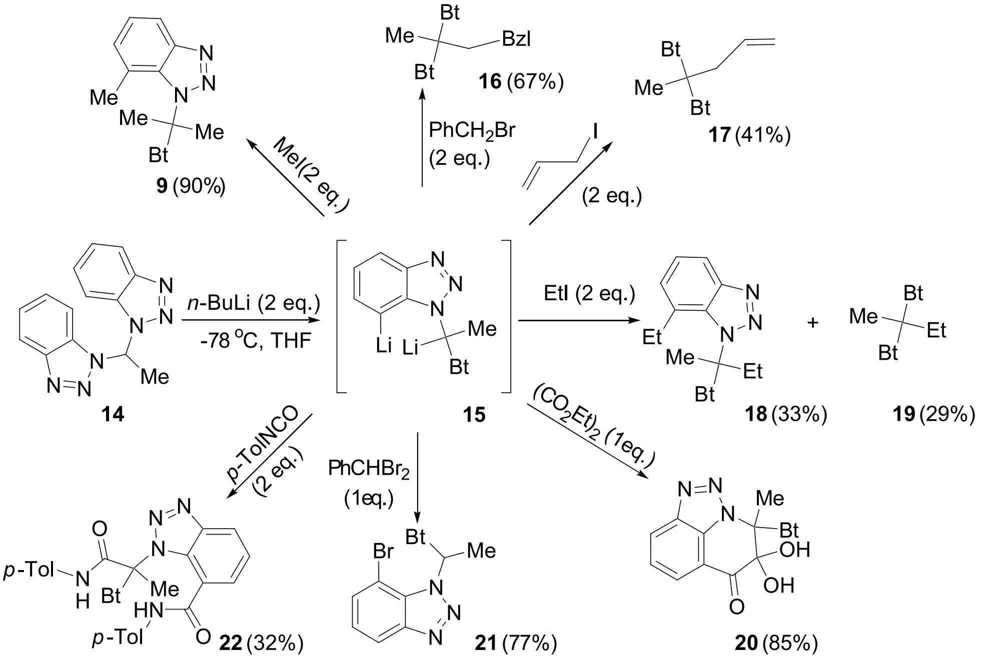


Scheme 2.

temperature for 1 h to furnish products **8** and **9** (Scheme 2). The reaction of **7** with *p*-tolyl isocyanate (4 equiv) gave the corresponding amide **10** in 40% yield. Treatment of polyanion **7** with 4-methylbenzonitrile (4 equiv) gave only enamine **11** in 70% yield as a result of single addition–tautomerization.[5] Reaction of **7** with dibenzoylmethane gave only the product of single addition **12** in 80% yield probably due to the high acidity of the methylene protons of the diketone. Unlike the reaction of **7** with methyl iodide, treatment with benzyl bromide produced a single product **13**; no products involving the reaction of the 7-position of the benzotriazole rings in **7** were observed. Attempts to trap polyanion **7** with di- and tri-electrophiles, such as benzotrichloride, diethyl oxalate, diphenylethanedione, hexachloroethane and 1,2-diiodoethane gave complex mixtures of products.

To determine the threshold of lithiation, compound **14** was



Scheme 3.