Pergamon

Tetrahedron Letters 42 (2001) 4539–4540

TETRAHEDRON LETTERS

t-Butyl *N*,*N*-dibromocarbamate (BBC)—new reagent for aminobromination of terminal alkenes

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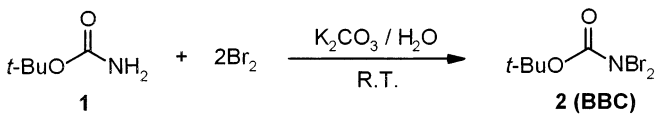
Received 1 March 2001; accepted 19 April 2001

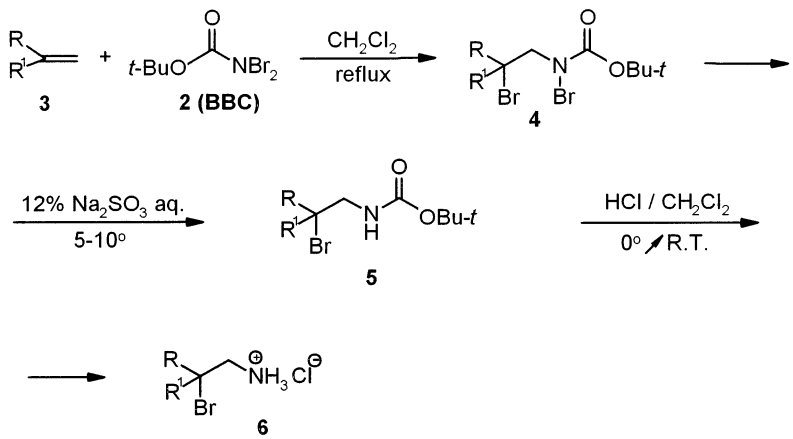
Abstract—*t*-Butyl *N*,*N*-dibromocarbamate, easily obtained by bromination of *t*-butyl carbamate in aqueous potassium carbonate, reacts smoothly with a variety of terminal alkenes to afford the corresponding β-bromo-*N*-Boc-amines upon reduction with aqueous sodium sulphite. Immediate deprotection of *N*-Boc-amines with gaseous HCl yields β-bromoamine hydrochlorides in good yields. © 2001 Elsevier Science Ltd. All rights reserved.

Direct functionalization of a carbon–carbon double bond by free-radical or ionic addition of various pseudohalogens has been the subject of numerous and intensive studies. In a series of our earlier papers[1–4] we have shown that diethyl *N*,*N*-dichlorophosphoramidate (DCPA)[1,2] and its *N*,*N*-dibromoanalogue (DBPA)[3,4] behave as typical pseudohalogens towards alkenes. The latter compound in particular appeared to be a very promising and versatile reagent capable of reacting with alkenes either via a radical-chain mechanism[3] or by an ionic addition pathway,[4] depending upon the reaction conditions. The DBPA–alkene adducts, upon reduction with sodium bisulphite, could subsequently be dephosphorylated to the corresponding β-bromoamine hydrochlorides, useful precursors of aziridines.

As part of our studies aimed at developing a new, phosphorus free reagent for free-radical aminobromination of alkenes, we performed the synthesis of *t*-butyl *N*,*N*-dibromocarbamate (BBC) **2** using *t*-butyl carbamate **1** as a starting material. The bromination of crude **1** using elemental bromine was carried out in aqueous potassium carbonate at room temperature to give **2** in excellent yield (Scheme 1).[5]



Scheme 1.



Scheme 2.

Keywords: *t*-butyl carbamate; free-radical addition; oxazolidinones; Boc-amine deprotection.

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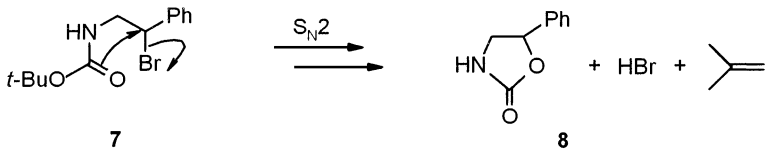
PII: S0040-4039(01)00662-1



7 8

Scheme 3.

Table 1. Preparation of β-bromoamine hydrochlorides[a]

Entry	R	R[1]	Yield (%)	Mp[b] (°C)	Lit.[3] mp (°C)
1	H	Ph	83	165–167	158–159
2	Me	Me	78	157–159	151–153
3	Me	Et	80	149–150	133–135
4	H	Bu	54.5	183–185	174–176
5	H	Bn	56	180–182	[c]
6	H	Pr	59	175–177	[c]
7	H	Neo-C_5H_{11}	55	110–112	[c]

[a] All new compounds were fully characterized by MS, IR, and ^{1}H NMR spectra.
[b] Crystallized from ethanol–ether. All compounds decomposed on melting.
[c] Not reported previously.

Crude BBC **2** was found to react smoothly and regioselectively with terminal alkenes **3** in an anti-Markovnikov fashion (which is evident from NMR spectroscopy) yielding the corresponding *N*-bromoadducts **4** which could subsequently be reduced by means of 12% aqueous sodium sulphite at 5–10°C to give β-bromo-*N*-Boc-amines **5** (Scheme 2).

Careful examination of the NMR spectrum of the crude BBC–styrene adduct revealed the presence of ca. 7% of 5-phenyl-oxazolidin-2-one **8** contaminating the expected β-bromo-*N*-Boc-amine **7**. The latter was slowly transformed into **8** on standing in solution even at room temperature. The presence of oxazolidinone **8** in the BBC–styrene adduct can be explained as a result of cyclization of **7** via an intramolecular S_N2 displacement. The analogous conversion of β-mesyloxy-*N*-Boc-amines into oxazolidinones has been reported recently (Scheme 3).[7]

The formation of variable amounts of oxazolidinones was also observed on attempted addition of BBC **2** to other alkenes. In order to minimize this undesired side reaction, the β-bromo-*N*-Boc-amines **5** were not isolated but immediately deprotected just after addition by means of gaseous HCl in CH_2Cl_2 to give β-bromoamine hydrochlorides **6** (Table 1). All BBC additions to terminal alkenes exhibit characteristic features which are indicative of spontaneously initiated free-radical chain reactions.

In summary, we have shown that terminal alkenes can easily be converted into β-bromoamine hydrochlorides **6** utilizing the new aminobrominating reagent **2**. The yields of **6** are higher and their purity is better than reported previously.[3] The use of **2** in other similar synthetic applications is currently under investigation.

References

1. Zwierzak, A.; Koziara, A. *Tetrahedron* **1970**, *26*, 3527–3537.
2. Koziara, A.; Zwierzak, A. *Tetrahedron* **1976**, *32*, 1649–1654.
3. Zawadzki, S.; Zwierzak, A. *Tetrahedron* **1981**, *37*, 2675–2681.
4. Osowska-Pacewicka, K.; Zwierzak, A. *Tetrahedron* **1985**, *41*, 4117–4725.
5. Bromine (35.16 g, 0.22 mol) was added dropwise with stirring for 40 min to a solution of crude *t*-butyl carbamate **1**[6] (prepared in CH_2Cl_2, mp 90–93°C, yield ca. 100%, purity ~90%; 12.9 g, 0.11 mol) and K_2CO_3 (15.2 g, 0.11 mol) in water (200 ml) at ambient temperature. The resulting mixture was stirred for 2 h, CH_2Cl_2 (100 ml) was then added, the organic layer separated, and the aqueous phase was extracted with CH_2Cl_2 (3×30 ml). Combined extracts were washed with water (30 ml), dried, and evaporated to give 24.6 g (90%) of **2** as an orange solid. Crude **2** was contaminated with ca. 9% of *t*-butyl *N*-bromocarbamate. Analytically pure sample **2** (prepared from pure **1**, mp 107–108°C and washed with cold pentane) had mp 93–95°C; ^{1}H NMR (250 MHz, $CDCl_3$): δ (ppm) 1.50 (s, 9H); ^{13}C NMR (63 MHz, $CDCl_3$): δ (ppm) 27.3, 86.2, 156.2; IR (KBr): 2992, 1696, 1368, 1280, 1264, 1248, 1144, 872, 744 cm^{-1}. MS (CI): 274 (M+1, 41%), 276 (M+3, 96%), 278 (M+5, 40%).
6. Loev, B.; Kormendy, M. F. *J. Org. Chem.* **1963**, *28*, 3421–3426.
7. Benedetti, F.; Norbedo, S. *Tetrahedron Lett.* **2000**, *41*, 10071–10074.