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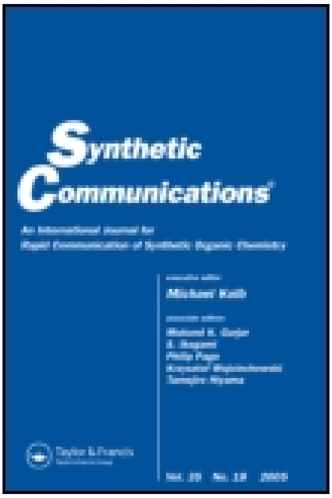

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Facile and Efficient Method for the Debromination of vic-Dibromides to Alkenes with $BiCl_3$/Ga System

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FACILE AND EFFICIENT METHOD FOR THE DEBROMINATION OF *vic*-DIBROMIDES TO ALKENES WITH BiCl$_3$/Ga SYSTEM

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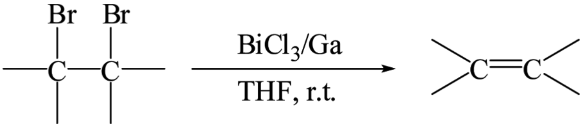
GRAPHICAL ABSTRACT



Abstract *BiCl$_3$/Ga was found to be a mild, efficient, and chemoselective system for the debromination of a series of functionally and structurally various* vic*-dibromides. A broad range of functional groups (ester, carboxy, aldehyde, methoxy, chloro, and ketone) was tolerated under the reaction conditions and only* trans *olefins were obtained in good yields.*

Keywords Alkene; bismuth; debromination; gallium

INTRODUCTION

The combination of bromination and reductive debromination has been used to temporarily protect double bonds, to purify olefins, and to introduce a new double bond in organic synthesis.[1] Although reductive debromination of *vic*-dibromides with various agents has been the subject of many reports, some of these methods are associated with limitations regarding poor yields, prolonged reaction times, and harsh reaction conditions.[2] Consequently, an efficient and mild procedure for debromination of *vic*-dibromides continues to be developed. The chemical reactivity of the BiCl$_3$/M system (M=Zn, Fe, Al, Mg, Sm) has been the subject of considerable interest, and the reducing ability of these systems has been extensively studied.[3] Because of the close resemblance of gallium to zinc in several respects, including first ionization, we reasoned that a BiCl$_3$/Ga system could serve as a protocol for the debromination of *vic*-dibromides. In recent years, gallium metal has drawn increasing attention for its unique properties such as low toxicity and high stability in water and air compared with other metals.[4] Bismuth(III) chloride is inexpensive, relatively

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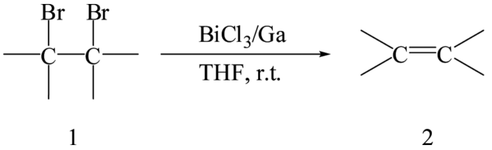
nontoxic, fairly water insensitive, and environmentally benign and has been used as a mild Lewis acid catalyst for synthetic transformations.

RESULTS AND DISCUSSION

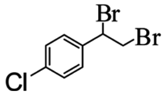
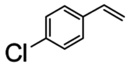
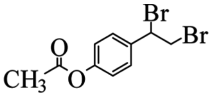
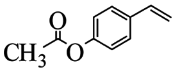
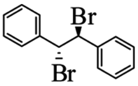
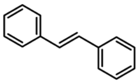
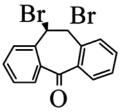
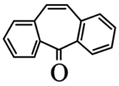
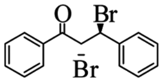
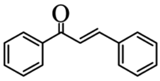
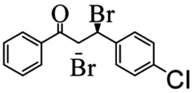
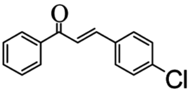
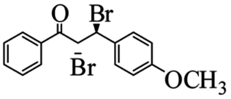
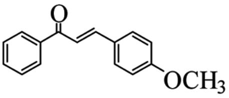
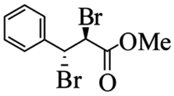
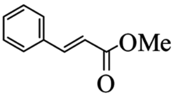
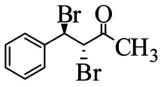
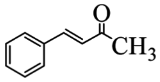
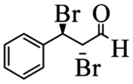
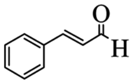
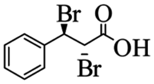
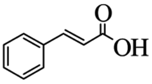
In continuation of our interest in exploring the utility of metal–metal salt system in organic synthesis,[5] we report here an efficient and mild method for debromination of *vic*-dibromides **1** to alkenes **2** with $BiCl_3/Ga$ system in tetrahydrofuran (THF) at room temperature. The reaction can be generalized as in Eq. (1).



(1)

The new reagent system was generated by the addition of gallium metal to a stirred solution of bismuth(III) chloride in THF under sonication. Sonication were carried out in a BRANSONIC ultrasonic cleaner bath, which delivered a 47 kHz wave, with a fixed electrical power of 125 Watts. To gauge the scope and limitations of this methodology, various substituted *vic*-dibromides were subjected to this protocal at room temperature. We found that *vic*-dibromides on treatment with $BiCl_3/Ga$ system in THF solution are smoothly converted into the corresponding alkenes in good yields. The good yields of the debromination products demonstrate the efficiency of this new method. To ensure the role of gallium, a controlled experiment was carried out using *vic*-dibromides with $BiCl_3$ without gallium metal, which failed to yield any desired product. A 2:1 ratio of gallium and $BiCl_3$ was the best ratio in terms of yield and reaction time. THF has been found to be the most suitable solvent for the reaction. The results of the reaction are summarized in Table 1, which shows a series of functionally and structurally various *vic*-dibromides. Clearly, a broad range of functional groups (ester, carboxy, aldehyde, methoxy, chloro, and ketone) were tolerated under the reaction conditions and only *trans* olefins were obtained. The sensitive carbonyl group remains intact without any further reduction under the reaction condition (entries 4–10). In comparison with other procedures, the present procedure reduced *vic*-dibromides in better yields and showed a good chemoselectivity under mild conditions. The notable advantages of this methodology are mild reaction conditions, simple manipulation, good yields, and tolerance of various functional groups. No overreduction of the produced alkene was observed with any substrate.[6] Some of the *vic*-dibromides in the table are commercially available or could be prepared conveniently from the corresponding precursors through known olefin halogenation reactions.[7] Although the reaction mechanism is still not clearly understood at this time, the reaction can be envisaged to proceed in two stages. In the first, bismuth(III) chloride is probably reduced by gallium to form a low-valent bismuth species, which in the subsequent step would debrominate *vic*-dibromides **1** to give the corresponding alkenes **2** through a SET (single-electron transfer) process. The reducing property exhibited by metal–metal salt combinations proceeds through transfer of one electron from the metal surface to the substrate. In such

Table 1. Reductive debromination of *vic*-dibromides with $BiCl_3$/Ga system

Entry	Substrate	Product	Time (h)	Yield (%)[a]
1			0.5	93
2			0.5	96
3			0.5	94
4			1.5	88
5			1.5	91
6			1.0	87
7			0.5	86
8			0.5	94
9			0.5	91
10			1.0	85
11			0.5	92

[a] Isolated yields. The products are commercially available and were characterized by comparision of their spectral data with authentic samples.

combinations, the elementary metal part needs to be more electropositive than the metal part of the salt. The involvement of zero-valent bismuth resulting from the transmetallation of bismuth chloride with gallium metal may be presumed.[8] We have been able to demonstrate the utility of the $BiCl_3/Ga$ system for effecting chemoselective debromination of the *vic*-dibromides.

CONCLUSION

In summary, we have demonstrated that the $BiCl_3/Ga$ system mediates an efficient and mild conversion of *vic*-dibromides to the corresponding alkenes. Although the scope and limitations were not fully established, the present method could be a practical alternative to the conventional method. Further work on the application of the $BiCl_3/Ga$ system is in progress.

EXPERIMENTAL

All reagents were used as received. THF was distilled from sodium benzophenone immediately prior to use. The ^1H NMR spectra were recorded on a FT-Bruker AF-300 instrument (300 MHz for ^1H NMR; 75 MHz for ^{13}C NMR) using tetramethylsilane (TMS) as an internal standard. Infrared (IR) spectra were obtained on a Perkin-Elmer 16 F PC FT-IR Shimadzu. Thin-layer chromatrographic (TLC) analysis was performed on silica-gel plates (Merck, 60 F-254). All products were purified by flash column chromatography using silica gel 60 (79–230 mesh, Merck).

A typical procedure for the debromination of *vic*-dibromides is as follows: Gallium (140 mg, 2.0 mmol) and bismuth(III) chloride (315 mg, 1.0 mmol) were mixed in THF (4 mL). The resulting mixture was stirred at room temperature for 0.5 h under sonication[8] to produce a solution of the low-valent bismuth–gallium complex. 1,2-Dibromo-1,2-diphenylethane (170 mg, 0.5 mmol) was then added to this solution. The mixture was stirred for 0.5 h at room temperature, and the progress of the reaction was followed by TLC. After completion of the reaction, the solvent was removed under reduced pressure. The residue was extracted with ether and washed successively with brine. The organic layer was separated and dried over anhydrous Na_2SO_4. The crude product was purified by silica-gel column chromatography (hexane–ethyl acetate = 15:1) to afford *trans*-stilbene (85 mg, 94%).

ACKNOWLEDGMENT

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