

Use of tribromoisocyanuric acid to conversion of alkynes into α,α -dibromo ketones

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INTRODUCTION

Tribromoisocyanuric acid (Figure 1) have been recently shown to be an efficient brominating agent, due to its ability of bromonium (Br^+) ion transfer to unsaturated substrates. This reagent has been used in the bromination of 1,3-dicarbonyl compounds, aromatic rings, dibromination and cobromination¹ of alkenes, and also in diverse oxidation reactions². TBCA is a stable solid that can be easily synthesized from isocyanuric acid, NaOH and KBr in the presence of oxone¹. It has the advantage of high atom economy in comparison to similar systems such as N-bromosuccinimide (NBS) and N-bromosaccharin (NBSac). Furthermore, in the reactions involving TBCA, isocyanuric acid left at the end of the reaction as a by-product and can be recovered by filtration and reused to produce more TBCA.

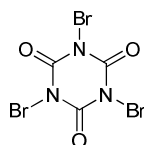


Figure 1: Tribromoisocyanuric acid

The trichloroisocyanuric acid (TCCA), analogues of TBCA also have been used in the chlorination of unsaturated substrates. Hiegel and co-workers demonstrated of TCCA is able to convert alkynes into α,α -dichloro ketones³. However, the bromination of alkynes using TBCA has not been reported yet.

RESULTS AND DISCUSSION

In the present work, we here examined the conversion of 1-phenyl-1-butyne, phenylacetylene, 1-octyne and 3-hexyne into the corresponding α,α -dibromo ketones.

The alkynes reacted with 1 equivalent of TBCA in the presence of acetic acid. The reactions were followed for GC-MS and the products were characterized by ¹H and ¹³C NMR. The products formed were Markovnikov type exclusively (Table 1).

Table 1. Conversion alkynes into α,α -dibromo ketones.

$$\text{R}-\text{C}\equiv\text{C}-\text{R}' \xrightarrow[\text{r.t., 4,5h}]{\text{TBCA, AcOH}} \text{R}-\text{C}(=\text{O})-\text{C}(\text{Br})_2-\text{R}'$$

substrate	products	Crude Yield (%)
		60
		88
		92
		92

CONCLUSION

The present work describes the utilization of tribromoisocyanuric acids as an efficient bromination reagent for conversion of alkynes into α,α -dibromo ketones.

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REFERENCES

- De Almeida, L. S.; Esteves, P. M.; de Mattos, M. C. S. *Tetrahedron Lett.* 2009, 50, 3001.
- Zolfigol, M. A.; Niknam, K.; Bagherzadeh, M.; Ghorbani-Choghmarani, A.; Koukabi, N.; Hajjani, M.; Kolvari, E. J. *Chin. Chem. Soc.* 2007, 54, 1117.
- Hiegel, G.A.; Bayne, C.D.; Ridley, B. *Synthetic Comm.* 2003, 33, 1997.