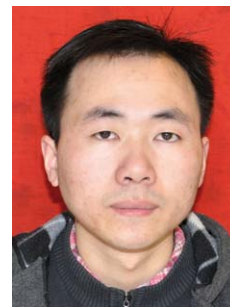


SYNLETT Spotlight 429

Carbon Tetrabromide

Compiled by Zhong-Yan Cao



This feature focuses on a reagent chosen by a postgraduate, highlighting the uses and preparation of the reagent in current research

Zhong-Yan Cao was born in Bozhou, P. R. of China, and received his B.Sc. from East China Normal University in 2010. Currently he is pursuing his Ph.D. under the supervision of Professor Jian Zhou at the same university. His research interests focus on the development of new catalysts and new methodologies for constructing tetrasubstituted carbon centers.

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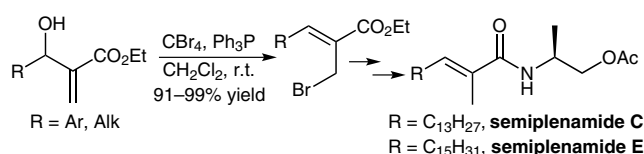
Introduction

Carbon tetrabromide, also known as tetrabromomethane, is a commercially available white solid which is stable at room temperature and can be easily handled. It is prepared either by the complete bromination of methane or by the reaction of tetrachloromethane with aluminum bromide. In combination with a tertiary phosphine, it has been used for the bromination of various functional groups, such as alcohols (Appel reaction),¹ N-heterocycles,² ethers,³ and for converting aldehydes/ketones into 1,1-dibromo-

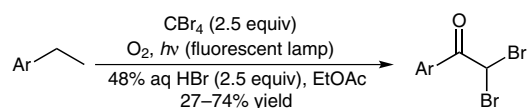
alkenes⁴ or alkynes⁵ (Corey–Fuchs reaction). In addition, carbon tetrabromide is a highly efficient catalyst for versatile reactions, including acylation of phenols, alcohols and thiols,⁶ acetalization and tetrahydropyranlation⁷ and oxidation of aromatic methyl ketones⁸ or alkenes⁹ to carboxylic acids under very mild conditions. Carbon tetrabromide can further promote the synthesis of thioureas and thiuram disulfides.¹⁰ Apart from these applications, carbon tetrabromide is also used as a crystal growth¹¹ and chain transfer agent¹² in polymer chemistry.

Abstracts

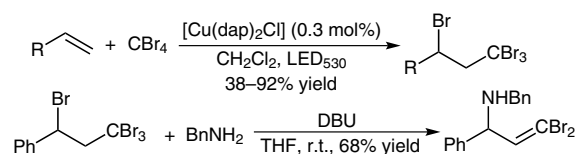
(A) A highly stereoselective synthesis of Z-allyl bromides from Baylis–Hillman adducts has been realized using CBr₄ and Ph₃P. The product can be further elaborated into the natural bioactive fatty acid amides semiplenamides C and E.¹³



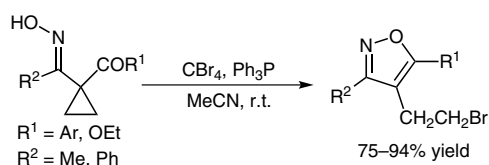
(B) Selective aerobic photooxidative dibromination of ethyl aromatics to dibromoacetophenones has been achieved using CBr₄, visible light and molecular oxygen.¹⁴



(C) CBr₄ can participate in atom transfer radical additions to olefins using a visible-light photocatalyst. The 1,1-dibromoalkenes are obtained after further manipulation.¹⁵



(D) Dong et al. reported the preparation of fully substituted isoxazoles from cyclopropyl oximes using a combination of CBr₄ and Ph₃P as the bromination reagent.¹⁶



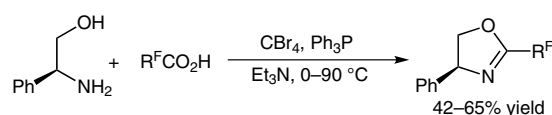
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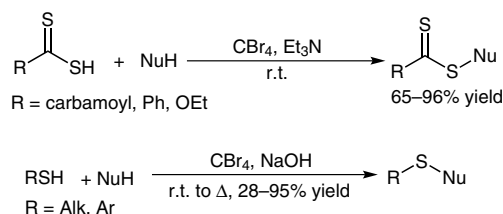
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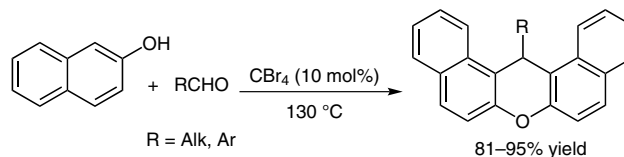
(E) Chiral 1,3-oxazoline heterocycles bearing fluorinated aliphatic chains (R^F) were obtained from a tandem one-pot reaction promoted by a combination of CBr_4 and Ph_3P . The product skeleton is present in many bioactive molecules, natural products, organomaterials and ligands for asymmetric catalysis.¹⁷



(F) In the presence of CBr_4 , dithiocarbamates and thioethers were prepared by reaction of dithioic acids, generated in situ, or thiols with nucleophiles such as active methylene compounds or *N*-methyl indole at room temperature.¹⁸



(G) Benzoxanthenes owning spectroscopic properties for leuco dyes, laser technology and fluorescent materials can be prepared using CBr_4 as the catalyst under solvent-free conditions.¹⁹



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