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Spotlight 326

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

Bromotrichloromethane

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Introduction

Readily synthesized by Meunier et al. in 1938, bromotrichloromethane (BrCCl₃) is a reagent of choice in organic synthesis. In recent years, many applications of this reagent have been reported. It can be used to synthesize esters, oxidize heterocycles, allow alkoxy ring-closure reactions, perform α-bromination of sulfones, achieve radical addition on alkenes and radical cyclization of 1,6-dienes or synthesize dichloroalkenes. Some of these reactions were used at a final stage of complex total syntheses. Moreover, bromotrichloromethane is cheap, commercially available and stable at room temperature without any observed decomposition.

Abstracts

(A) Esterification is one of the most important reaction in organic synthesis. Numerous methods have been reported, but few of them proceed under photolytic conditions. Hwu et al. developed a new atom-economy condensation between carboxylic acids and alcohols using BrCCl₃ to furnish esters in high yields.

(B) The most common oxidizing method of thiazolines implies MnO₂ under classical conditions or microwaves activation. The use of BrCCl₃/DBU combination constitutes an efficient alternative way for this purpose. Recently, these conditions were applied in the final step of the total synthesis of largazole analogues. In some cases, due to lower yields with DBU, another base was required (NaOMe, t-BuOK, NaH or LDA).

(C) The homolysis of the N–O bond of N-alkoxy thiazolethiones delivered an alkoxyl radical. This intermediate cyclized stereospecifically to give a carbon-centred tetrahydrofurylmethyl radical which was further trapped by BrCCl₃ as a source of bromine atom.

(D) Radical-anion radical pair reactions (RARP) allowed α-bromination of alkylphenyl sulfones in the presence of a KOH/t-BuOH mixture. The products are formed in high yields and are stable under these reaction conditions.

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(E) Nedelec and co-workers\textsuperscript{10} reported the addition of the trichloromethyl radical to alkenes with moderate selectivities. More recently, the group of Mirzabekova developed a new method for generating this radical and the method was directly applied to the total synthesis of permethrinic acid.\textsuperscript{11}

(F) Homolytic cleavage of the metal–metal bond of $[\text{Mn}_2(\text{CO})_{10}]$ generates two manganese pentacarbonyl radicals which can perform hydrogen or halogen atom abstraction reactions.\textsuperscript{12a} In the presence of bromotrichloromethane, bromine atom transfer reactions can also be carried out on 1,6-dienes.\textsuperscript{12b}

(G) gem-Dichloroolefins are valuable products in organic synthesis. Nenajdenko et al.\textsuperscript{13} developed a convenient olefination method for the synthesis of dichloroalkenes from hydrazones using BrCCl$_3$ and in the presence of CuCl as catalyst.

References