

The catalytic olefination reaction of aldehydes and ketones with CBr_3CF_3

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Abstract

The new approach of catalytic olefination reaction (COR) has been used to convert aromatic and aliphatic aldehydes and ketones to 2-bromo-3,3,3-trifluoroprop-1-enes by the treatment of corresponding hydrazones with CBr_3CF_3 under copper(I) catalysis conditions. The reaction proceeds stereoselectively, the target alkenes were obtained in good yields.

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1. Introduction

The trifluoromethyl group and its fluorinated homologues are one of the most important substituents in modern organic and medicinal chemistry due to their unique stereoelectronic and biological properties. An unprecedented set of properties of CF_3 or R_f groups is electronegativity, lipophilicity, high chemical and biological stability and steric volumes similar to methyl or alkyl groups sterical volume.

Commercially available 2-bromo-3,3,3-trifluoropropene is widely used for the synthesis of many trifluoromethyl containing compounds. This reagent can be used as the starting material for trifluoromethylated acetylenes [1], trifluoromethylated polyfunctionalized cyclopropanes [2], trifluoromethyl-substituted enamines [3], trifluoromethyl propargyl alcohols [4], fluorine-containing optically active allylic alcohols [5], alpha-(trifluoromethyl)styrenes [6], esters and amides of 2-(trifluoromethyl)acrylic acid [7]. These examples indicate that the combination of trifluoromethyl group and bromine in adjacent position of double

bond is very synthetically useful and opens up synthetic possibilities.

At the same time there is very little information about synthesis and reactions of the substituted analogs of 2-bromo-3,3,3-trifluoropropene. CBr_3CF_3 has never been used for its preparation. Syntheses of 1-bromo-1-trifluoromethylalkenes containing only aliphatic fragments have been reported. They have been synthesized by base-promoted elimination of corresponding 1-trifluoromethyl-1,2-dibromoalkanes [8] or by palladium-catalyzed trifluoromethylation of 1,1-dibromoalkenes [9]. It is known that pharmaceutical and agricultural chemicals that contain di- and trifluoromethyl groups have been the subject of increased research activity in recent years [10,11].

Recently, we reported a novel catalytic olefination reaction (COR) of aldehydes and ketones [12–20]. It was found that *N*-unsubstituted hydrazones of carbonyl compounds could be smoothly transformed into the various substituted alkenes by treatment with polyhaloalkanes in the presence of catalytic amounts of CuCl . Based on COR we elaborated a novel approach to synthesis of dichloroalkenes [12], dibromoalkenes [13] vinylbromides [14] and vinyliodides [15] from aromatic and heteroaromatic carbonyl precursors as well as aliphatic

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compounds [16]. We found also COR applicable for the preparation of fluorocontaining alkenes using such chlorofluorocarbons as CCl_3F [17], CCl_3CF_3 , $\text{CCl}_2\text{FCClF}_2$ [18] and also CBr_2F_2 [19] and $\text{CF}_2\text{BrCF}_2\text{Br}$ [20] as C_1 - and C_2 -building blocks.

According to the proposed mechanism, the reaction of copper(II) salt with hydrazone should involve formation of copper-carbene complex which reacts with polyhalogenalkane to form the desired alkene and copper(II) salt regeneration. *Sym*-azine formation is the result of copper-carbene complex and diazoalkane reaction (Scheme 1) [18].

The olefination with CBr_3CF_3 should result in the interesting substituted analogs of 2-bromo-3,3,3-trifluoropropene (*vide supra*). In accordance with our model of “catalytic olefination activity” [21], CBr_3CF_3 should be a very active reagent for catalytic olefination (the most reactive of all fluorinated compounds which we have used earlier) and should to provide high yields of desired products with aldehydes and ketones. The high difference in steric volumes of CF_3 group and bromine atom permit us to hope for high stereoselectivity of reaction.

In this paper, we have investigated the olefination of aromatic and aliphatic aldehydes and ketones **1** with CBr_3CF_3 . This approach would open a new straightforward way to the synthesis of alkenes having CF_3 group and bromine atom in adjacent positions. The presence of bromine atom also opens the possibility of functionalization via organometallic compounds using metallation (lithium-bromine exchange, for example) or by direct bromine substitution with different nucleophiles. The functionalized alkenes prepared bearing trifluoromethyl group should be very interesting building blocks for many purposes, for example, Diels–Alder reaction with electron-rich dienes should be suitable for the synthesis of six-membered cyclic compounds bearing CF_3 group; another possibility is the construction of CF_3 -substituted heterocycles.

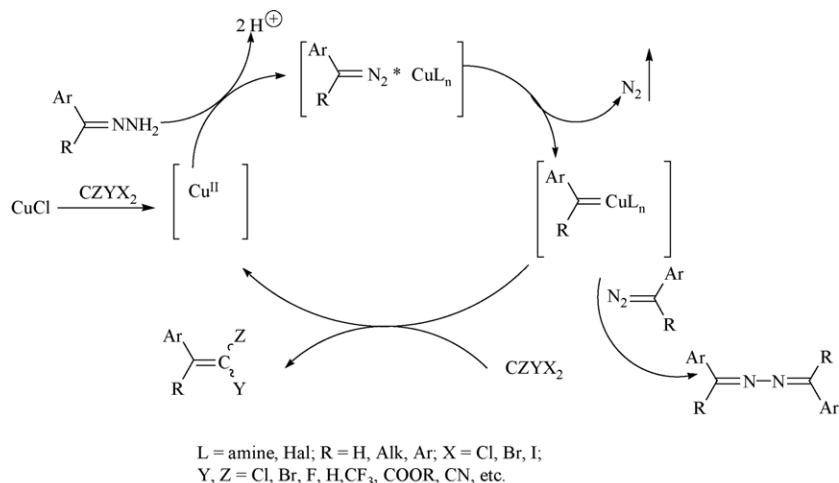
2. Results and discussion

Previously CBr_3CF_3 was used as the C_2 -fluorocontaining block in the synthesis of 2,2-dibromo-3,3,3-trifluoro-1-phenylpropan-1-ol by condensation with benzaldehyde [22]. Also it was applied in the synthesis of trifluoromethylpyrazoles [23] and in the telomerisation reaction with some fluorinated alkenes [24]. CBr_3CF_3 was prepared by AlBr_3 promoted isomerisation of the commercially available $\text{CF}_2\text{BrCF}_2\text{Br}$ [24]. We found that Halon™ CBr_3CF_3 under catalysis of CuCl reacts with hydrazones of aldehydes and ketones **2** to form 2-bromo-3,3,3-trifluoroprop-1-enes **3** (Scheme 2). These alkenes contain trifluoromethyl group and bromine atom adjacent at the double bond that can be useful for synthesis of new trifluoromethyl compounds. Synthesis of similar 1-bromo-1-trifluoromethylalkenes containing only aliphatic fragments has been reported by the base-promoted elimination of corresponding 1-trifluoromethyl-1,2-dibromoalkanes [8] or by palladium-catalyzed trifluoromethylation of 1,1-dibromoalkenes [9]. The necessity of using harsh conditions (high temperature and pressure), dry solvents, expensive and toxic reagents and also low stereoselectivity are significant disadvantages of these approaches.

2.1. Optimization of the reaction conditions

Previously we elaborated two types of solvent and base systems for the catalytic olefination reaction with various polyhalogenalkanes [12–19]. DMSO as solvent and aqueous ammonia as base were found optimal for synthesis of chloro-, bromo-, and iodo-substituted alkenes [12–16]. However, the 1,2-ethylenediamine-ethanol system is required for activation of fluorinated compounds in the COR process [17–20].

These two types of solvent and base systems were tested in the reaction between prepared in situ 4-chlorobenzaldehyde hydrazone **2a** and CBr_3CF_3 . Using DMSO and aqueous



Scheme 1.

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