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ORIGINAL PAPER

Substituted homoallenyl aldehydes and their derivatives. Part 1: Homoallenyl aldehydes and protected hydrazones

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Dedicated to Professor Štefan Toma on the occasion of his 75th birthday

The paper presents a simple synthesis of substituted propargyl vinyl ethers and their subsequent thermally-initiated Claisen rearrangement leading to various 3-substituted homoallenyl aldehydes. Several methods, including Sonogashira coupling, base-promoted substitution on the triple bond by sodium amide or butyllithium, and the preparation of substituted propargyl alcohols, were used in the initial step. Phosphate-protected homoallenyl aldehyde hydrazone derivatives were synthesised and fully characterised. The stereochemistry of 9-anthracene carbaldehyde hydrazone, which, surprisingly, afforded both *cis* and *trans* isomers, was established using X-ray analysis.

Keywords: homoallenyl aldehyde, hydrazone, Claisen rearrangement, isomerisation

Introduction

In the past, the chemistry of allenyl synthon was neglected. In the early 1990s, we began experiments which involved the preparation and exploitation of allenyl compounds (Potáček et al., 1993). Homoallenyl aldehyde and its various substituted derivatives became the key starting molecule and substrate for subsequent work. Finally, we found that Claisen rearrangement of propargyl vinyl ethers provided a general method for their preparation (Black & Landor, 1965). We have published a number of papers dealing with the chemistry of allenyl compounds (Marek et al., 1994, 1995a, 1995b, 1997; Man et al., 2002, 2004, 2005, 2006a, 2006b; Buchlovič et al., 2008, 2010a; Galeta et al., 2009, 2011) and also one which provides the methodology for substituting the triple bond of propargyl vinyl ether (Zachová et al., 2005). These selected publications clearly indicate that allenyl synthon serves as an intra-molecular dipolarophile or centre, where the final products of reactions are always cyclic derivatives with one ring, or bicyclic, tricyclic, and tetracyclic skeletons. We have also published papers describing further transformations of these products (Zachová et al., 2006, 2009; Buchlovič et al., 2010b, 2012; Galeta & Potáček, 2012). However, despite this accumulated work, the possibility of performing experiments on the triple bond continues to play a key role and we have encountered failure many times. For this reason, we also comment briefly on some of our less successful reactions.

The preparation of protected hydrazones is the first part of azine synthesis following Zwierzak's method (Koziara et al., 1986). We utilise this method but with some improvements to the procedure which have enabled us to contribute here with some new derivatives.

Experimental

Unless stated otherwise, all reagents were purchased from commercial suppliers and used as received. THF and benzene were distilled from sodium/benzophenone before use. Dichloromethane (DCM) was dried with calcium chloride, distilled from P_2O_5 and stored over dry 3 Å molecular sieves. All reactions

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