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Chemical Papers 67 (1) 40–50 (2013)
DOI: 10.2478/s11696-012-0238-z

ORIGINAL PAPER

Substituted homoallenyl aldehydes and their derivatives. Part 2: Azines

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Received 21 March 2012; Revised 7 June 2012; Accepted 11 June 2012

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

This paper deals with the preparation of a variously substituted non-symmetrical azine set. The starting molecule for their preparation was a protected hydrazone. The protection was performed applying Zwierzak's method. This procedure is based on the transfer of hydrazine to diethylhydrazidophosphate, which reacts with aldehydes to produce protected hydrazones. In the second step of the procedure, under the action of sodium hydride, the addition of another aldehyde affords non-symmetrical azines in the reaction with the protected hydrazine. The procedure was shown to be a useful and effective method. In this, the second part of our study, we present results devoted to the preparation and full identification of non-symmetrical azines.

Keywords: allenyl, azine, aldehyde, hydrazone, deprotonation, non-symmetrical

Introduction

The preparation of protected hydrazones is the first part of azine synthesis by Zwierzak's method (Zwierzak & Sulewska, 1976; Koziara et al., 1986). We used this method with some changes to the synthetic pathway (Galeta et al., 2013) and we report here on the success of the second step, in which protected hydrazones under the treatment of sodium hydride react with the submitted aldehyde to produce non-symmetrical azines. Our targets were azines containing an allenyl skeleton (Schweizer & Lee, 1984; Schweizer et al., 1987). Syntheses of numerous organic compounds with biological activity have been based on the allenyl synthon (Zimmer, 1993; Brandsma, 2001; Brandsma & Nedolya, 2004; Krause & Hashmi, 2004; Brandsma, 2004; Brasholz et al., 2009). In the past, symmetrical azines were used in the preparation of fused cyclic compounds in intra-molecular criss-cross cycloaddition reactions (Zachová et al., 2005) leading to four fused five-membered rings and for research into their interesting transformations when treated with electrophiles (Galeta & Potáček, 2012; Zachová et al., 2006, 2009). Non-symmetrical azines serve as educts for the preparation of fused tricyclic heterocyclic systems by combined intra-intermolecular criss-cross cycloaddition (Galeta et al., 2009, 2011; Man et al., 2002, 2004, 2005).

Experimental

Unless stated otherwise, all reagents were purchased from commercial (Sigma–Aldrich, USA) supplier and used as received. Diethyl ether and toluene were distilled from sodium/benzophenone prior to use. All reactions were carried out under a dry argon atmosphere and monitored by TLC (Merck F_{254} silica gel; Merck, Germany). Products were separated by liquid chromatography with a Horizon HPFC System (Biotage, Sweden) fitted with Biotage Si 12+M and Si 25+M columns. FTIR spectra were recorded with a GENESIS ATI (Unicam, UK) spectrometer. ^{1}H NMR and ^{13}C NMR spectra were recorded with a Bruker Avance 300 spectrometer (Bruker, USA) op-

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