

ORIGINAL PAPER

Synthesis of cinnamic acid-derived 4,5-dihydrooxazoles

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

A range of cinnamic units containing 4,5-dihydrooxazoles was prepared using two different synthetic routes. The first method was based on the transformation of substituted cinnamic or benzoic acids to 2-styryl-4,5-dihydrooxazoles. Several derivatives containing phenolic groups were prepared in this manner. The second approach consisted of a reaction between the 4,5-dihydrooxazole moiety and double bond-containing compounds. These compounds contain two or more reactive centres capable of providing polymerisations and also organic reactions. (© 2013 Institute of Chemistry, Slovak Academy of Sciences

Keywords: cinnamic acid derivatives, 4,5-dihydrooxazole, conjugated unsaturated bond, 2oxazolines

Introduction

Polymers which contain unsaturated bonds play an important role in polymer chemistry where they can be involved in radical or photochemical processes. Radical reactions include radical polymerisation, grafting, or crosslinking. Photoreactions proceeding subsequent to irradiation can be divided into a reversible *trans/cis* photoisomerisation, a photocyclisation, (2 + 2) photodimensition, or a photoreduction (Rabek, 1987). E/Z isomerisations of azo compounds (Suginome, 1995) and alkenes, especially 1,2diphenylethenes (stilbene)s and derivatives of cinnamic acids (Saltiel et al., 1995), are well known. The mechanism of the photoisomerisation of stilbenes has been the subject of extensive study over the last few decades. Stilbene undergoes isomerisation from the stable trans-form to the Z-form upon irradiation at 280-320 nm. This photoreaction proceeds via the lowest triplet state (¹t^{*}) of stilbene (Saltiel & Sun, 1989; Papper & Likhtenshtein, 2001). Stilbenes and derivatives of cinnamic acids can also provide photoinitiated (2+2) cycloaddition, both in solution (Kaupp, 1995), and in solid state (Cohen et al., 1964; Bertmer et al.,

2006; Nagarathinam et al., 2008). The cyclodimerisation of unsaturated compounds was used in syntheses of organic compounds (König et al., 1996) or for photocrosslinking of unsaturated polymers (Rabek, 1987; Nagarathinam & Vittal, 2006). Irradiation of polymeric unsaturated anhydrides derived from cinnamic acids leads to the formation of an insoluble polymer (Pinther et al., 1992) which indicates the course of a photocrosslinking process. Micelle crosslinking can be achieved by (2 + 2) cycloaddition reaction of co-polymer-containing amphiphilic comonomers and comonomers bearing a cinnamic chromophore with light ($\lambda > 270$ nm) (Szczubialka et al., 1999). The crosslinking was rapid and was concluded in several minutes. In this case, irradiation of the micelle solution resulted in a decrease in the polymer absorption band around 280 nm.

4,5-Dihydrooxazoles, also known as 2-oxazolines, are members of a large family of cyclic imino ethers. 4,5-Dihydrooxazoles react with different functional groups in ring-saving reactions as well as in ringopening reactions (Kronek et al., 1998a). Formation of the 4,5-dihydrooxazole ring can occur in several ways (Kronek et al., 1998b). The most common way

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