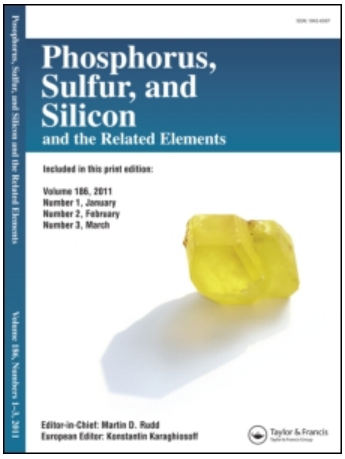

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DIELS-ALDER REACTION OF MYRCENE WITH CARBONYL CONTAINING DIENOPHILES SUPPORTED ON SILICA GEL UNDER MICROWAVE IRRADIATION

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DIELS-ALDER REACTION OF MYRCENE WITH CARBONYL CONTAINING DIENOPHILES SUPPORTED ON SILICA GEL UNDER MICROWAVE IRRADIATION

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Diels-Alder reactions of myrcene (7-methyl-3-methene-1,6-octadiene) with carbonyl containing dienophiles supported on silica gel under microwave irradiation have been studied.

Keywords: Cycloaddition reaction; Diels-Alder reaction; microwave; mycerene; regioselectivity

The Diels-Alder reaction is a concerted $(4\pi + 2\pi)$ cycloaddition reaction of a conjugated diene on a dienophile. This reaction is one of the most useful C—C bond forming reactions and provides several pathways toward the simultaneous construction of substituted cyclohexenes with a high degree of regioselectivity, diastereoselectivity, and enantioselectivity.[1]

Reagents and substrates impregnated on mineral solid supports have popularity in organic synthesis because of their selectivity and ease of manipulation.[2] Recently, there has been growing interest in the application of microwave irradiation in chemical reactions.[3] Microwave assisted reactions under dry conditions are especially appealing as they provide an opportunity to work with open vessels thus avoiding the risk of high pressure and with a possibility of upscaling the reaction on the preparative scale.[4]

Several examples of solid supported Diels-Alder reactions mostly on polymeric support including classical intermolecular, inverse electron demand, hetero and intramolecular Diels-Alder reaction have

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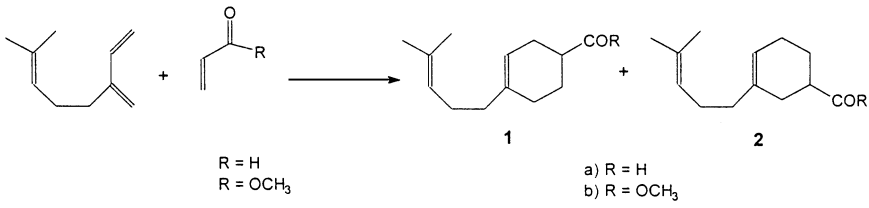
been reported and can be found in an excellent review article by Yli-Kauhaluoma.[5]

Myrcene (7-methyl-3-methene-1,6-octadiene) prepared by craking β-pinene which was obtained from turpentine oil, and can react with different dienophile giving rise to a variety of fragrant compounds or their intermediate.[6] The reaction of myrcene with carbonyl containing dienophiles can give para/meta regioselectivity. For example, reaction of myrcene with acrolein or methyl acrylate can give para/meta isomers (Scheme 1).[6]



SCHEME 1

In this article I report that the reaction of myrcene with acrolein and with methyl acrylate supported on silica gel under microwave irradiation give a high para/meta regioselectivity and the reaction rates are also enhanced dramatically.

The result of the reaction between myrcene with acrolein and myrcene with methyl acrylate at different temperature without any catalyst recently has been reported.[7] In the thermal reaction, the yield of the "para" adduct is greater than that of the "meta" adduc.[8] The selectivity of the cycloadduct is decreased with increasing the reaction temperature. Therefore we can not obtain the "para" adduct in high yield by increasing the temperature.

D. Yin et al.[7] have reported a regioselective Diels-Alder reaction of myrcene with carbonyl containing dienophiles catalyzed by Lewis acids. We obtained almost the same regioselectivity by using silica gel as solid support and microwave irradiation. The regioselectivity of p/m for 1a/2a was 10:5 and for 1b/2b was 4:9. In the thermal reaction the p/m regioselectivity has been reported to be 2.6 and 2 respectively.[7]

In conclusion, silica gel can be used as an excellent support for regioselective Diels-Alder reactions of myrcene under microwave irradiation. These conditions have the advantages of offering a practical and environmentally benign protocol that decrease the time, gives a cleaner reaction and leads to easier work up.

EXPERIMENTAL SECTION

The products are known and their physical data were identified by comparison with those reported in the literature.[7]

Reaction of Myrcene with Acrolein and Methyl Acrylate (General Procedure)

Myrcene (200 mg, 1.47 mmol) was put onto silica gel (0.5 g) which was moistened with water (2 drops) in a small beaker. The appropriate dienophile (1.47 mmol) was added to the beaker and mixed with the supported myrcene thoroughly. The beaker was placed in a microwave oven for 10 min. The progress of the reaction was monitored by TLC. To the product mixture $CHCl_3$ (10 mL) was added. The mixture was filtered and the solvent was evaporated. The crude residue was passed through a small coloumn packed with silica gel using petroleum ether/chloroform (5:5, v:v) as eluent to obtain the Diels-Alder product. Conversion of myrcene in the reaction with acrolein was 85% and its regioselectivity was 10:5. The Conversion of myrcene for the reaction with methyl acrylate was 98.5 and its p/m regioselectivity was 4:9.

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