

A Novel One Pot Synthesis of Several 1(2,4 Dinitro Phenyl) – 3 Phenyl – 4 Methoxy Carbonyl Pyrazolidines Via 1,3 – Dipolar Cycloaddition Approach.



Chemistry

KEYWORDS : Pyrazolidine, Green synthesis, aldehydes, hydrazine.

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ABSTRACT

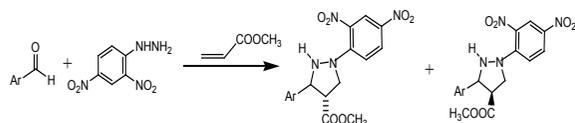
Several pyrazolidine derivatives have been synthesized in excellent yields when aromatic aldehyde, vinyl acetate and 2,4 dinitro phenyl hydrazine were refluxed in toluene for one hour.

Introduction

Pyrazolidine is a five membered ring containing three carbon and two nitrogen atoms. One pot synthesis of nitrogen containing heterocycles from alkyl dihalides, primary amines and hydrazines under microwave irradiation in aqueous medium is reported [1]. Aryl hydrazines react with 3-butynol in presence of zinc triflate to form pyrazolidines [2]. Various 1 acyl – 5 hydroxy – 4,5- dihydro – 1 H – pyrazoles have been prepared in good yields from the corresponding 2 alkyn-1-ones [3]. The pyrazolidine derivatives are biologically active compounds and are known to possess anti-inflammatory [4], antibacterial [5], anticonversant [6], antidepressant [7] and analgesic activity [8]. These facts have encouraged us to design the pyrazolidine synthesis and to study their biological activities. In this connection we have already reported the synthesis of pyrazolidine derivatives [9]. In continuation to our earlier work, we have prepared several derivatives of pyrazolidine derivatives using easily available raw materials.

Result and discussion

Dipolar cycloaddition of azomethine imines form in situ from aromatic or aliphatic aldehydes and 2,4 dinitro phenyl hydrazine with electron deficient dipolarophiles produced pyrazolidines. The addition of 1,3 dipole to an alkene for the synthesis of five membered rings is a classical reaction in organic chemistry. In present method we would like to report 1,3 dipolar cycloaddition reaction of aromatic aldehydes, 2,4 dinitro phenyl hydrazine and vinyl acetate to form pyrazolidine derivatives in high yield. The reaction was carried out with Dean-Stark apparatus using toluene as a solvent. The removal of solvent furnished pyrazolidines as crude products, which were purified by column chromatography and were characterize by IR and PMR spectroscopy.



Experimental Section

General Procedure – Benzaldehyde (1.5 g, 14.15 mmol), 2,4 DNP reagent (2g, 10.1 mmol) and vinyl acetate (1g, 11.6 mmol) were placed in a round bottom flask equipped with Dean-Stark ap-

paratus. The reaction was carried out under reflux condition for 1 hour using toluene as a solvent. The solvent was removed by distillation to form crude pyrazolidine derivative. The column chromatographic purification furnishes syn diastereomer as a major product. The trans diastereomer was obtained in trace quantity. The results are summarized in the following table.

Sr. No.	Aldehyde	Solvent	Percent yield	M.P. °C
1	p-chloro benzaldehyde	Toluene	85	275
2	Benzaldehyde	Toluene	90	232
3	Cinnamaldehyde	Toluene	87	240
4	Anisaldehyde	Toluene	80	330
5	p-hydroxy benzaldehyde	Toluene	82	358
6	p-nitro benzaldehyde	Toluene	89	248
7	Salicylaldehyde	Toluene	78	196
8	Acetaldehyde	Toluene	78	322

Spectral data for tetrahydropyrazole derivative

1 (product of p-chlorobenzaldehyde)

IR (KBr cm) 1758, 1618, 1512, 1305, 742

PMR (DMSO d6 ppm) 7.3 -7.8 (m, 7H), 5.8 (br:s 1H) 5.2 (d, J=6Hz, 1H) 4.0 (m, 2H) 3.3 (broad signal 4H)

Conclusion

In the present article, we are reporting a green method for synthesis of pyrazolidine derivatives. The reaction proceeds through 1,3 dipolar addition to furnish syn diastereomer as a major product.

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