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Molecular Iodine: An Efficient Catalyst for the Synthesis of Tetrahydrobenzo[b]pyrans

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Abstract: An iodine/DMSO system is introduced as an excellent catalyst in three-component coupling reactions of tetrahydrobenzo[b]pyran synthesis. The reaction proceeds quickly under very mild reaction conditions.

Keywords: aldehydes, malononitrile, molecular iodine, tetrahydrobenzo[b]pyran

INTRODUCTION

Tetrahydrobenzo[b]pyrans are an important class of organic compounds that attracts considerable attention because of their wide range of biological activities. These compounds show anticoagulant, anticancer, spasmolytic, diuretic, and anti-ancaphylactia activity[1] Polysubstituted tetrahydrobenzo[b]pyrans constitute a structural unit of a series of natural products.[2]

The conventional methods used for the synthesis of 4*H*-benzo[b]pyrans were reported in acetic acid or dimethyl formamide.[3,4] Some improved methods are also reported for the synthesis of tetrahydrobenzo[b]pyran derivatives using hexadecyltrimethyl ammonium bromide and sodium bromide catalysts[5,6] and synthesis by utilizing the reactants in solid or molten states.[7]

In recent years, the use of molecular iodine in organic synthesis has received considerable attention. Because of numerous advantages associated with this ecofriendly element, iodine has been explored as a powerful

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Address correspondence to Rajendra P. Pawar, Organic Chemistry Synthesis Laboratory, Dnyanopasak College, Parbhani 431401, India. E-mail: rppawar@yahoo.com

catalyst for various organic transformations.[8] The acidity of iodine makes it capable of binding with the aldehyde carbonyl oxygen, increasing the reactivity of the parent carbonyl compounds.[9]

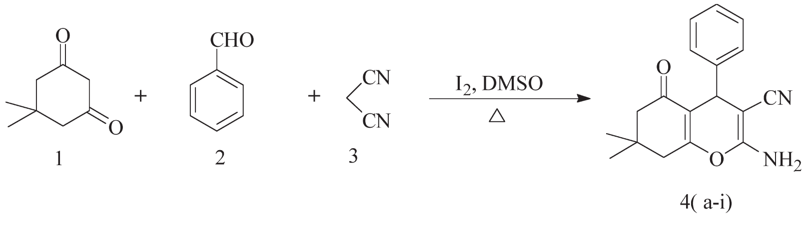
RESULTS AND DISCUSSION

To examine the catalytic activity of iodine in solvent dimethylsulphoxide, the reaction conditions of benzaldehyde and dimedone with malononitrile were optimized (Scheme 1). In the present communication, the products were synthesized by adding iodine (10 mmol%) to a solution of dimedone, aromatic aldehydes, and malononitrile in the solvent dimethylsulphoxide. The mixture was stirred at 120°C. The results suggest that the optimized system of 10 mmol% of catalyst is active enough to complete the reaction in 3–4 h. However, the same reaction does not proceed in the absence of iodine and dimethylsulphoxide even after stirring the reaction mixture at 120°C for 10 h.

The excellent result led us to expand this catalytic system of iodine/dimethylsulphoxide (DMSO). Almost all reactions were completed in 3–4 h at 120°C, although the yields of the products were highly dependent on the substrate used. The generality of the system was also confirmed by using other aromatic aldehydes for the reactions (Table 1). Both electron-rich and electron-deficient substituted aromatic aldehydes produced an excellent yield of products. The iodine/DMSO system has good activity for a variety of substrates. This procedure is significant from the viewpoint of avoiding pollution and practical industrial process.

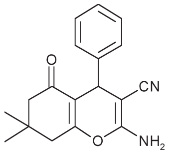
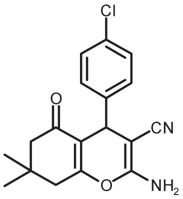
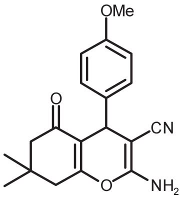
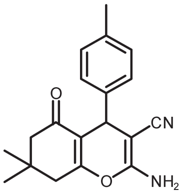
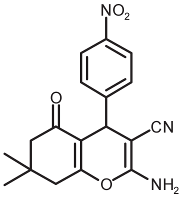
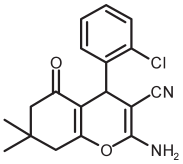
General Procedure for the Synthesis of 2-Amino-3-cyano-7,7-dimethyl-5-oxo-4-phenyl-5,6,7,8-tetrahydro-4*H*-benzo[b]pyran (4a)

A mixture of 1,3-cyclic dimedones **1a** (10 mmol), benzaldehyde **2a** (10 mmol), malononitrile **3a** (10 mmol), and molecular iodine (10 mmol%) in DMSO (10 ml) was stirred at 120°C for 3–4 h. The progress of reaction was monitored by thin-layer chromatography (TLC). After completion of the reaction, the reaction mixture was cooled and poured onto crushed ice



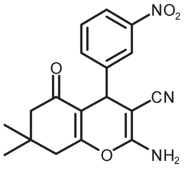
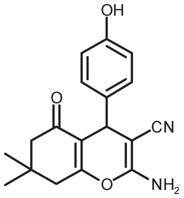
Scheme 1.

Table 1. Iodine catalyzed synthesis of tetrahydrobenzo[b]pyran derivatives

Entry	Products	Time (h)	Yield (%)^a	Mp (°C)
4a		3.2	92	231 (233[10])
4b		3.5	88	208 (207–209[10])
4c		3.5	90	199 (198–200[10])
4d		3.6	90	211 (208–210[10])
4e		4.0	85	133 (130–132[10])
4f		3.8	85	130 (130–132[10])

(*continued*)

Table 1. Continued

Entry	Products	Time (h)	Yield (%)[a]	Mp (°C)
4g		4.0	86	215 (210–212[10])
4h		3.8	80	209 (206–208[11])

[a] Refers to isolated yield.

and further stirred for 10–15 min. The solid separated was filtered and washed with aqueous sodium thiosulphate solution (to remove excess iodine) and water. The crude product was crystallized in ethanol to afford pure tetrahydrobenzo[b]pyran **4a** (92% yield).

Entry **4a**

IR (KBr) ν_{max} 3395, 3287, 2932, 2202, 1685, 1600 cm^{-1}. ^{1}H NMR (300 MHz): δ 1.05 (s, 3H, CH_3), 1.15 (s, 3H, CH_3), 2.16–2.31 (m, 2H, CH_2), 2.47 (s, 2H, CH_2), 4.38 (s, 1H, CH), 4.59 (s, 2H, NH_2), 7.12–7.34 (m, 5H, Ar-H).

Entry **4c**

IR (KBr) ν_{max} 3376, 3316, 2199, 1683, 1140, 1035 cm^{-1}. ^{1}H NMR (300 MHz): δ 1.05 (s, 3H, CH_3), 1.11 (s, 3H, CH_3), 2.16–2.27 (m, 2H, CH_2), 2.45 (s, 2H, CH_2), 3.78 (s, 3H, OCH_3), 4.38 (s, 1H, CH), 4.59 (s, 2H, NH_2), 6.82 (d, $J = 9.6$ Hz, 2H, Ar-H), 7.17 (d, $J = 8.0$ Hz, 2H, Ar-H).

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