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NOTE

Perkin Reactions under Microwave Irradiation

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The fast synthesis of cinnamic acid and its derivatives by Perkin reaction (**3a-c**) has been achieved under few minutes by microwave irradiation instead of 4-8 h taken by conventional heating under reflux. The yield of the products under microwave irradiation synthesis have been found better.

Key Words: Perkin reaction, Cinnamic acid, Microwave irradiation.

The condensation of aromatic aldehydes with acid anhydrides is called the Perkin reaction. When the anhydride has two α -hydrogens, dehydration always occurs¹. However, synthesis of cinnamic acid by the reaction of benzaldehyde with acetic anhydride in the presence of base requires 4-8 h of heating under reflux².

Microwave irradiation is an efficient and environmentally-benign method to activate various organic transformations to afford products in higher yields in shorter reaction periods and involving a very small amount of solvent³⁻¹⁰.

Melting points were taken in open capillaries and are uncorrected. Purity of the compound was checked by TLC. IR spectra were recorded on Perkin-Elmer 157 spectrometer on KBr. ¹H NMR spectra were recorded in CDCl₃ on a Bruker WM 400 MHz spectrometer, using TMS as an internal reference. Mass spectra were measured on Jeol JMS-300 spectrometer at 70 eV.

General procedure: A mixture of benzaldehyde or its derivative (**1a-c**) (0.05 mol), acetic anhydride (**2**) (7.5 g, 7 mL, 0.073 mol) and freshly fused and finely powdered sodium acetate (2.5 g, 0.03 mol) was irradiated with microwaves at 40 % (320 W) level in a Kenstar OM-20 ESP (800 W) unmodified domestic oven operating at 2450 MHz for 5 min. The mixture while still hot was poured into about 25 mL of water contained in 250 mL round-bottomed flask which had been fitted for steam distillation. A saturated aqueous solution of sodium carbonate was added with vigorous

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shaking until the mixture became alkaline. The solution was steam distilled until all the unchanged benzaldehyde or its derivative was removed. The residual solution was cooled and filtered at the pump from resinous by-products. The filtrate was acidified by adding conc. HCl slowly and with vigorous stirring. When cold, the crude cinnamic acid or its derivative was filtered at the pump, washed with cold water and drained well. The crude product was recrystallized from an appropriate solvent to obtain cinnamic acid or its derivative (**3a-c**).

Cinnamic acid (3a): Colourless crystals from a mixture of 3 volumes of water and 1 volume of rectified spirit, yield 70 %, m.p. 132-133° (lit.² 133°) (Found : C, 72.87; H, 5.40. $C_9H_8O_2$ requires : C, 72.92; H, 5.42 %); IR(KBr, v_{max} , cm⁻¹) 3000-2500 (O-H), 1686 (C=O), 1636 (C=C); ¹H NMR (δ_H) (CDCl₃, TMS) 6.41 (1H, d, = CH.CO₂), 7.73 (1H, d, Ph·CH), 7.17-7.69 (5H, m, Ar-H), 11.90 (1H, s, CO₂H); MS(m/z) 148 (M⁺, 100), 147(M⁺-H), 131(M⁺-OH), 130(M⁺-H₂O), 103 (M⁺-COOH), 102(130-CO), 77(103-C₂H₂), 51(77-C₂H₂).

4-Methyl cinnamic acid (3b): Colourless needles from ethanol, yield 72 %, m.p. 198-199° (lit.¹¹ 198-199°) (Found : C, 74.07; H, 6.17. $C_{10}H_{10}O_2$ requires: C, 74.15; H, 6.13 %); IR (KBr, v_{max} , cm⁻¹) 3000-2500 (O-H), 1680 (C=O), 1632 (C=C); ¹H NMR (δ_{H}) (CDCl₃, TMS) 2.32 (3H, s, Ar-CH₃), 6.4 (1H, d, = CH·CO₂), 7.72 (1H, d, Ar.CH), 7.15-7.65 (4H, m, Ar-H), 11.85 (1H, s, CO₂H); MS(m/z) 162 (M⁺, 100), 161(M⁺- H), 145(M⁺-OH), 144(M⁺- H₂O), 117(M⁺- COOH), 116(144-CO), 91(117- C₂H₂), 65(91-C₂H₂).

4-Methoxy cinnamic acid (3c): Colourless needles from EtOH, yield 73 %, m.p. 169-170° (lit.¹² 170°) (Found: C, 67.41; H, 5.52. $C_{10}H_{10}O_3$ requires: C, 67.45; H, 5.54 %); IR (KBr, v_{max} , cm⁻¹) 3000-2500 (O-H), 1678 (C=O), 1630 (C=C), 1245 (C-O-C); ¹H NMR (δ_H) (CDCl₃, TMS) 3.72 (3H, s, Ar-OCH₃), 6.38 (1H, d, = CH·CO₂), 7.70 (1H, d, Ar.CH), 7.15-7.62 (4H, m, Ar-H), 11.80(1H, s, CO₂H); MS(m/z) 178 (M⁺, 100), 177(M⁺-H), 163(M⁺-CH₃), 171(M⁺-OH), 160(M⁺- H₂O), 135(163 -CO), 133(M⁺-COOH), 132(160 - CO), 107(133 -C₂H₂), 81(107-C₂H₂) (**Scheme-I**).



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Conclusion

The reaction time for Perkin reaction is reduced to only 5 min by using microwave irradiation from 4-8 h of heating under reflux. The yield of the product is also improved.

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