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ONE BILLIONHERTZ MICROWAVE ATHERMAL ACTION ON THE SYNTHESIS OF AROMATIC ESTERS AT NORMAL PRESSURE

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ABSTRACT

Benzoic acid or p-hydroxybenzoic acid undergoes rapid reaction with alcohol using H_2SO_4 as catalyst at normal pressure, under irradiating continuously of the 1 GHz and 50 mW microwave for 22–60 minutes to afford aromatic esters in 76–90% yields.

The application of microwave (MW) energy in organic chemistry is increasing rapidly¹⁻² since Gedye³ and Giguere⁴ reported it. There exist heating action⁵ and athermal action in chemical reaction under microwave irradiation.⁶⁻⁷ In our laboratory, a new method for synthesizing aromatic esters has been developed using a special microwave condition. This microwave

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condition has three features. First, the microwave frequency is $1.0 \times 10E9$ Hz other than $2.45 \times 10E9$ Hz. Second, the microwave power (50 mW) is far lower than microwave oven's, and there isn't microwave heating action but microwave athermal action. Finally, this microwave condition can act on classical synthetic systems in the state of reflux at normal pressure.

Richard Gedye had reported esterification systems⁸ of benzoic acid with alcohol in a sealed Teflon pressure-vessel in a microwave oven (2450 MHz, about 700 W) previously. However, these systems were less attractive because of abnormal pressure.³ The systems we reported here for synthesizing aromatic ester were accomplished in reflux state at normal pressure under athermal action of microwave⁹ (1 GHz and 50 mW).

$$p \cdot R^{1}C_{6}H_{4}CO_{2}H + R^{2}OH \xrightarrow{1.MW, -H_{2}O}{2.H_{2}SO_{4}} p \cdot R^{1}C_{6}H_{4}CO_{2}R^{2}$$

$$1 \qquad 2 \qquad 3a-h$$

Scheme 1. Esterification of aromatic acid with alcohol.

3a-h R¹R²: a. H-, Me-; b. H-, Et-; c. H-, Pr-; d. H-, Bue. HO-, Me-; f. HO-, Et-; g. HO-, Pr-; h. HO- Bu-

Quantities and concentrations of reactants were kept same in all sets of reactions. Under traditional reflux conditions, when benzoic acid or *p*-hydroxybenzoic acid was mixed with alcohol and some sulfuric and subjected to microwave (1 GHz and 50 mW) Irradiation for $22 \sim 60$ minutes, the aromatic esters were obtained in $76 \sim 90\%$ yield as shown in Scheme 1 and Table 1. Aromatic esters were identified by boiling point or melting point, IR or Elemental analysis data.

In conclusion, the present method of esterification had advantages over known methods. High yield, short time, safe condition and easy control of reaction made the method more attractive. The microwave athermal action is especially important to promoting those synthetic reactions in which temperature is strictly demanded at normal pressure.

EXPERIMENTAL

All reagents were commercially available and used without further purification. Continuous microwave irradiation was carried out with a microwave & laser therapeutic instrument (1 GHz, 50 mW)⁹ at atmospheric pressure. IR spectra were obtained on a Nicolet 740 FT-IR spectrometer. Elemental analyses were done on Perkin-Elmer 240C elemental analyzer.

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Tir Product (mi			Average Yield (%) ^a	Classical method		
	Time (min)	temp. (°C)		Time (min)	Temp. (°C)	Yield (%)
3 a	60	65	84	480	65	74 ¹⁰
3b	60	79	90	720	79	9711
3c	45	97	85	240	97	78 ¹²
3d	22	118	87	60	117	8212
3e	60	65	81	480	65	83 ¹³
3f	30	79	86	600	79	$87^{11,13}$
3g	30	97	78	240	97	8113
3h	30	118	76	60	118	79 ¹³

Table 1. Esters 3a-h Prepared Under Microwave Athermal Action

^aYield of pure isolated product; at least two experiments.

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3a: Benzoic acid, methyl ester; yield 84%, b.p. $197 \sim 200^{\circ}$ C (lit¹². b.p. $198 \sim 200^{\circ}$ C) IR v (cm⁻¹): 2960, 2880, 1720, 1600, 1452, 1315, 1276, 1176, 1111, 1070, 1027, 711. Anal. Calcd. for C₈H₈O₂: C, 70.58; H, 5.87. Found: C, 70.10; H, 5.71.

3b: Benzoic acid, ethyl ester; yield 90%, b.p. $211 \sim 213^{\circ}$ C (lit¹². b.p. $211 \sim 213^{\circ}$ C) IR v (cm⁻¹): 2960, 2934, 2880, 1720, 1600, 1452, 1315, 1280, 1182, 1111, 1070, 1027, 950, 711. Anal. Calcd. for C₉H₁₀O₂: C, 71.98; H, 6.66. Found: C, 71.59; H, 6.58.

3c: Benzoic acid, propyl ester; yield 85%, b.p. $226 \sim 228^{\circ}$ C (lit¹². b.p. $227 \sim 228^{\circ}$ C) IR v (cm⁻¹): 2960, 2880, 1720, 1600, 1452, 1390, 1317, 1276, 1176, 1111, 1070, 1030, 940, 711. Anal. Calcd. for C₁₀H₁₂O₂: C, 73.76; H, 7.33. Found: C, 73.20; H, 7.19.

3d: Benzoic acid, butyl ester; yield 87%, b.p. $242 \sim 249^{\circ}$ C (lit¹². b.p. $243.5 \sim 249.5^{\circ}$ C) IR v (cm⁻¹): 2960, 2920, 2880, 1740, 1600, 1450, 1315, 1260, 1176, 1105, 1070, 1027, 711. Anal. Calcd. for C₁₁H₁₄O₂: C, 74.15; H, 7.81. Found: C, 73.69; H, 7.63.

3e: *p*-Hydroxybenzoic acid, methyl ester; yield 81%, m.p. $125 \sim 128^{\circ}$ C (lit¹². m.p. $125 \sim 128^{\circ}$ C) IR v (cm⁻¹): 3300, 2960, 1680, 1600, 1580, 1512, 1440, 1315, 1276, 1230, 1152, 1120, 952, 711. Anal. Calcd. for C₈H₈O₃: C, 63.15; H, 5.26. Found: C, 62.87; H, 5.21.

3f: *p*-Hydroxybenzoic acid, ethyl ester; yield 86%, m.p. $115 \sim 119^{\circ}$ C (lit¹². m.p. $116 \sim 119^{\circ}$ C) IR v (cm⁻¹): 3210, 2960, 1680, 1600, 1580, 1440, 1360, 1310, 1276, 1230, 1172, 1170, 852, 761. Anal. Calcd. for C₉H₁₀O₃: C, 65.04; H, 6.17. Found: C, 65.27; H, 6.03.



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3g: *p*-Hydroxybenzoic acid, propyl ester; yield 78%, m.p. 96°C (lit.¹² m.p. 96.2°C) IR v (cm⁻¹): 3280, 2970, 1680, 1600, 1580, 1512, 1450, 1371, 1276, 1230, 1162, 1111, 952, 781. Anal. Calcd. for $C_{10}H_{12}O_3$: C, 66.64; H, 6.66. Found: C 66.19; H, 6.41.

3h: *p*-Hydroxybenzoic acid, butyl ester; yield 76%, m.p. $67 \sim 69^{\circ}$ C (lit.¹² m.p. $67 \sim 69^{\circ}$ C) IR v (cm⁻¹): 3370, 2950, 1680, 1600, 1580, 1508, 1450, 1315, 1276, 1210, 1162, 1120, 952, 850, 771, 699. Anal. Calcd. for C₁₁H₁₄O₃: C, 68.02; H, 7.20. Found: C, 67.81; H, 7.03.

General Procedure for 3a-h

A mixture of aromatic acid 1(0.50 mol), alcohol 2(1.00 mol) and oil of vitriol (0.02 mol) was placed in a 250 mL four-necked and round-bottomed flask connected with refluxing equipment. Under reflux condition, the reaction system was subjected to microwave (1 GHz and 50 mW) irradiation for 22~60 minutes. The evolved water was collected in Dean-Start apparatus. After irradiation, the excessive alcohol was evaporated, and the reaction mixture was cooled to room temperature. Then, the mixture was transferred to a 500 mL beaker containing 200 mL cool water. Water phase (or liquid phase) was removed while organic phase (or solid phase) was washed with saturated aqueous sodium bisulfite solution and water, dried with magnesium sulfate, and evaporated to give crude product. Products **3a–d** were purified by distillation and products **3e–h** were purified by recrystallization from CH₃CH₂OH.

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