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Synthesis of Phloroglucinol Using Microwave-Assisted Reaction from TNT

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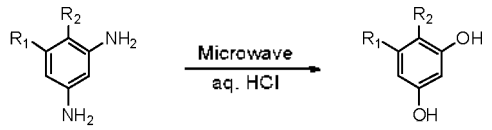
Millions of pounds of surplus energetic materials such as TNT, DNT and ammonium picrate have been disposed by open burning/detonation.[1] The use of open burning/detonation is becoming unacceptable due to public concern and environmental regulations. Therefore, the chemical conversion study of surplus energetic materials to higher value products would be highly desirable. The commercial conversion methods to Phloroglucinol (**4**) which is used in the pharmaceutical, cosmetics, textile-dying and photographic industries from TNT were developed.[2] However, this conventional synthesis was no longer used because of mainly environmental problems associated with waste disposal (Scheme 1).[3]

Recently, microwave assisted reaction has become a powerful tool in organic synthesis, which is being increasingly used to accelerate the organic reactions. Microwave assisted organic reactions have a remarkable merits of increased yields, reduced reaction time, suppressed side products and decreased environmental pollution.[4-6] Thus, use of microwave irradiation in organic synthesis has become a powerful method for the rapid synthesis of a variety of organic molecules with improved yield.

Here, we wish to report more eco-friendly synthetic procedure focusing on microwave-assisted reaction for the synthesis of Phloroglucinol (**4**) from TNT. First, TNT (**1**) is oxidized to 2,4,6-trinitrobenzoic acid and thermally decarboxylated to 1, 3,5-trinitrobenzene (**2**) in two steps 85% yield.[3] Subsequent reduction of **2** with hydrazine and Fe/C[7] delivered 1,3,5-triaminobenzene (**3**) in 95% yield. Hydrolysis of **3** in large excess of HCl solution at 110 °C for 24 hours produced Phloroglucinol (**4**) in only 50% yield along with unidentified side products. This results are consistent with the fact that aromatic substitution reaction with poor leaving groups by nucleophile proceeds very slowly with low yield.[8] On the other hands, when this reaction was run under microwave irradiation, the reaction proceeded rapidly. Different experimental conditions have been tested on **3** and **5** to find the best results. The best condition to occur reaction under microwave heating is that the observed temperature was 180 °C after 30 sec heating at 400 W and irradiation was continued for 15 min at the same power. The reaction rate and yields were significantly enhanced by microwave irradiation (Table 1). The rate enhancement under microwave irradiation may be attributed to the absorption of more microwave energy, which generates sufficient heat energy to promote the reaction. Phloroglucinol (**4**) and resorcinol (**6**) from TNT and DNT were rapidly obtained compared with the reaction under conventional heating (entries 1 and 2). Moreover, it was found that only 1.5 equivalent of HCl solution was sufficient to induce nucleophilic substitution reaction.

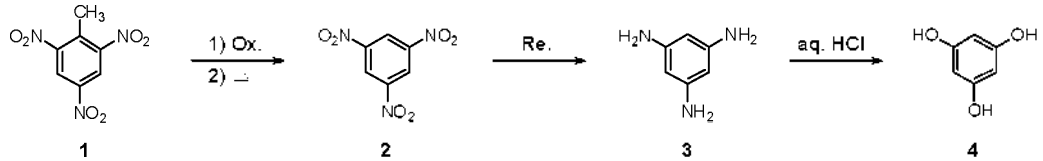
We have extended our study to the reactions of **7** and **9** with same conditions as shown in Scheme 2 to investigate substitution effect by changing from hydrogen to methyl group. Thus, TNT and DNT was directly reduced and reacted with HCl solution under microwave irradiation to afford the products **8** and **10** (entries 3 and 4). These results show that increased inductive effect by methyl group on the benzene ring has no significant difference under microwave assisted organic reaction.

In summary, we have prepared some hydroxy aromatic compounds in good yields using microwave irradiation. Main advantages of this article is that nucleophilic substitution reaction of aromatic compound with poor leaving group proceeded much more quickly and with higher yields under microwave irradiation than conventional heating. The future work including application of microwave irradiation to biologically active compound is under investigation in our laboratory.



3, $R_1 = NH_2$, $R_2 = H$ **4**, $R_1 = OH$, $R_2 = H$
5, $R_1 = H$, $R_2 = H$ **6**, $R_1 = H$, $R_2 = H$
7, $R_1 = NH_2$, $R_2 = CH_3$ **8**, $R_1 = OH$, $R_2 = CH_3$
9, $R_1 = H$, $R_2 = CH_3$ **10**, $R_1 = H$, $R_2 = CH_3$

Scheme 2



1 2 3 4

Scheme 1. Commercial Product of Phloroglucinol (**4**) from TNT (1)

Table 1. Conversion of **3**, **5**, **7** and **9** to **4**, **6**, **8** and **10** promoted by microwave.

Entry	Starting Material	Product[a]	Time (min)[b]	Temp (°C)	Yield (%)[c]
1	3	4	10	150	61
				180	70
				210	82
			15	150	65
				180	85
				210	85
			30	150	79
				180	84
				210	85
2	5	6	10	150	59
				180	68
				210	78
			15	150	62
				180	82
				210	82
			30	150	73
				180	81
				210	82
3	7	8	10	150	72
				180	78
				210	84
			15	150	81
				180	90
				210	89
			30	150	85
				180	89
				210	90
4	9	10	10	150	68
				180	75
				210	82
			15	150	78
				180	86
				210	86
			30	150	81
				180	85
				210	86

[a]All products were characterized by ^{1}H NMR and FT-IR. [b]Microwave irradiation was carried out at 400 Watts using Initiator microwave oven. [c]Yield refers to pure products after chromatography or recrystallization.

Experimental Section

General. All proton nuclear magnetic resonance (NMR) spectra were recorded on a Varian Unity Inova spectrometer at 300 MHz and are reported in parts per million (ppm) on the δ scale relative to chloroform-d_1 or DMSO-d_6. IR spectra were recorded on a Varian FT-IR spectrometer using KBr optics. Analytical thin layer chromatography (TLC) was performed with E. Merck pre-coated TLC plates, silica gel 60F-254, layer thickness 0.25 mm. Column chromatography was done with silica gel 60 (70 - 230 mesh ASTM) from E. Merck mostly by gravity. Initiator 400 W microwave oven was used to perform the reaction.

Phloroglucinol (4): The solution of 1,3,5-triaminobenzene (**3**, 1.0 g, 8.85 mmol), 36% HCl (4.0 g, 40.0 mmol, 1.5 eq.) and H_2O (10.0 mL) was placed into microwave oven at 180 °C and irradiated for the period listed in Table 1. The reaction mixture was extracted with ethyl acetate (3 × 5 mL). The combined organic layers were dried over anhydrous $MgSO_4$ and solvent was removed under reduced pressure to obtain the crude product. Pure product was obtained by recrystallization with ether and methanol as white solid (0.93 g, 95%). m.p. 217 ~ 220 °C; ^{1}H NMR (300 MHz, DMDO-d_6) δ 9.0 (s, 3H), 5.64 (s, 3H); IR (KBr) υ_{max} 3430, 1620, 1490 cm^{-1}.

Resorcinol (6): m.p. 109 ~ 111 °C; ^{1}H NMR (300 MHz, DMDO-d_6) δ 9.15 (s, 2H), 6.93 (dd, J = 8.2, 8.1 Hz, 1H), 6.21 (m, 3H); IR (KBr) υ_{max} 3240, 1610, 1490 cm^{-1}.

2,4,6-Trihydroxytoluene (8): m.p. 213 ~ 219 °C; ^{1}H NMR (300 MHz, DMDO-d_6) δ 8.81 (s, 2H), 8.68 (s, 1H), 5.84 (s, 2H), 1.92 (s, 3H); IR (KBr) υ_{max} 3230, 1630, 1470 cm^{-1}.

2,4-Dihydroxytoluene (10): m.p. 105 ~ 106 °C; ^{1}H NMR (300 MHz, DMDO-d_6) δ 8.89 (br, 2H), 6.84 (d, J = 8.8 Hz, 1H), 6.28 (d, J = 2.0 Hz, 1H), 6.20 (dd, J = 8.8, 2.0 Hz, 1H), 2.05 (s, 3H); IR (KBr) υ_{max} 3330, 1620, 1480 cm^{-1}.

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