

Communications

Conventional, Microwave Induced and Photochemical Fries Rearrangement of Resorcinol Diacetate

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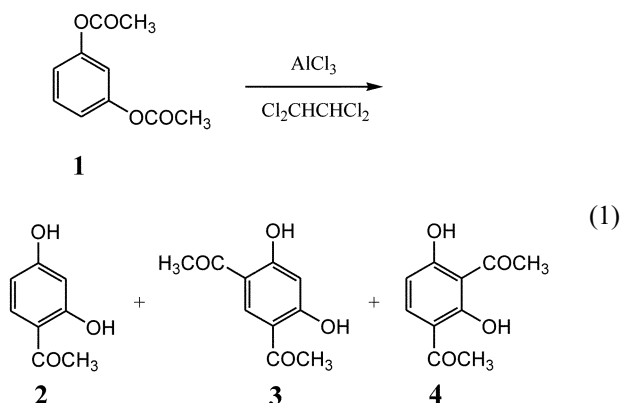
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The substituted resorcinol unit is a basic building block of a large number of naturally occurring valuable polyketide metabolite.¹ However, syntheses of 2-substituted resorcinols were long and unproductive procedures. Acylation of resorcinol is known to occur at 4-position (ortho to one hydroxyl) rather than 2-position (ortho to both hydroxyls).²

Since research in our laboratory required a substantial quantity of acetylated resorcinol, we wish to report a convenient synthetic ways of diacetylated resorcinols through the Fries rearrangement.

A conventional Fries reaction of resorcinol diacetate (**1**) in AlCl_3 -1,1,2,2-tetrachloroethane complex results 2',4'-dihydroxyacetophenone (**2**), 4,6-diacetylresorcinol (**3**) and 2,4-diacetylresorcinol (**4**) (Eq. (1)).



Microwave³ irradiation (MWI) of resorcinol diacetate (**1**) in 1,1,2,2-tetrachloroethane with AlCl_3 also produced the

substituted resorcinols **2**, **3** and **4**. The product yields are shown in Table 1.

Earlier studies⁴ have shown that the Fries rearrangement of resorcinol diacetate with AlCl_3 results rearrangement products **2** and **3**, however, 2-substituted resorcinol **4** was not obtained.

Microwave irradiation did not show any non-thermal effect on the reaction, however, the reaction time was decreased to 15 min. to obtain maximum yields of products. This short reaction time might be ascribed to fast heating upon microwave irradiation as compared to conventional heating (Table 1).

Irradiation⁵ of diacetate **1** in diethylether solution at 254 nm produced **2** and **4**, but the product **3** was not obtained, and the product yields are very low (Table 1) due to the electrophilic nature of substituent which comes from the initial photo-Fries product of **1**. In general, the presence of certain electron-withdrawing substituent (for instance acetyl group) in the phenolic ring was found to inhibit the photo-Fries rearrangement.⁶

In conclusion, a conventional and MWI Fries reaction of resorcinol diacetate are good synthetic way of 2-substituted

Table 1. The product distribution for the Fries rearrangement

| Reaction condition | Duration | Product distribution (%) | | |
|--------------------|----------|--------------------------|----|----|
| | | 2 | 3 | 4 |
| Conventional | 150 min | 26 | 8 | 42 |
| MWI | 15 min | 14 | 13 | 48 |
| UV-irradiation | 600 min | 9 | | 3 |

resorcinol derivatives and MWI method did not show any non-thermal effect on the reaction.

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References

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 2. Stealey, M. A.; Shone, R. L.; Miyano, M. *Synthetic Communications* **1990**, *20*(12), 1869.
 3. A modified domestic microwave oven which produces 2450 MHz radiation (700W) was used for irradiation.
 4. Blatt, A. H. *Org. Reaction*; Wiley: New York, U.S.A., 1940; Vol. 1, p 342.
 5. A solution of 129 mg of 1 in 20 mL of diethylether was transferred to a quartz cell and degassed with purified nitrogen. The sample was irradiated with 16-RPR-254 nm lamps for 10 hours.
 6. Miranda, M. A. *Organic Photochemistry and Photobiology*; Horspool, W. M.; Song, P. S., Eds.; CRC Press: New York, U.S.A., 1995; p 570.
 7. Product **4**: ^1H NMR (CDCl_3 , 300 MHz) δ 2.57 (s, 3H), 2.77 (s, 3H), 6.47 (d, $J = 9.0$ Hz, 1H), 7.79 (d, $J = 9.0$ Hz, 1H), 14.23 (s, 1H), 14.79 (s, 1H); ^{13}C -NMR (CDCl_3 , 300 MHz) δ 26.38, 33.76, 109.76, 110.14, 112.23, 137.99, 168.42, 171.09, 203.15, 205.81; IR (neat) 3380, 1640 cm^{-1} ; HRMS Calcd. for $\text{C}_{10}\text{H}_{10}\text{O}_4$: 194.0579 Found 194.0577.
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