# Cyclization of 2,6-Diones over H-ZSM-5: One-pot Synthesis of Dimethylphenols and Substituted $\alpha,\beta$-Unsaturated Cyclohexenones†

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2,6-Diones on treatment with zeolite H-ZSM-5 yield dimethylphenols (DMPs) or $\alpha,\beta$-unsaturated cyclohexenones.

There is an increasing demand for efficient and clean organic synthesis, and selectivity and recycling are the keys to achieve this. The last decade has witnessed a considerable resurgence of interest in the area of zeolite-induced organic transformations and excellent reviews on the uses of zeolites in organic synthesis have appeared.[1,2] Cyclizations of 2,5-diketones using ZSM-5 to obtain substituted furans have been reported.[3]

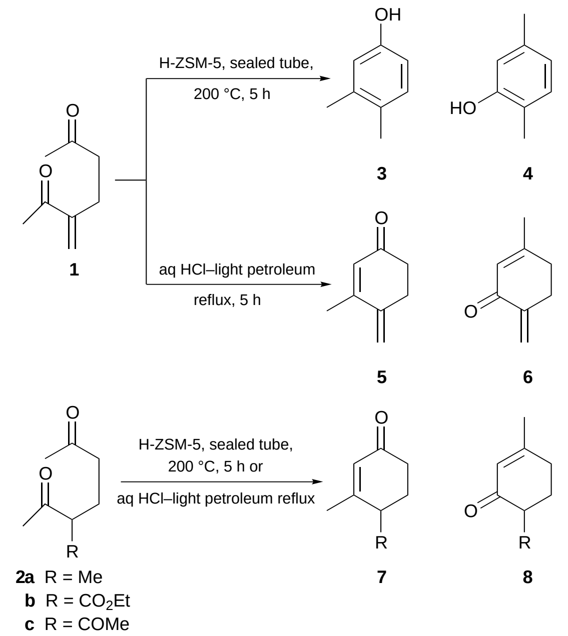
The synthetic utility of $\alpha,\beta$-unsaturated cyclohexenones in the elaboration of complex organic structures is well established.[4,5] Alkylphenols have found wide applications in the polymer industry. The carbamates of 3,4-DMP and 2,5-DMP show fungicidal and insecticidal activity.[6] The conventional procedure for the preparation of 3,4-DMP is through dienone–phenol rearrangement of 4,4-dimethylcyclohexa-2,5-dienone.[7,8] On the other hand, 2,5-DMP is obtained through acid-induced conversion of 2,5-dimethylcyclohexa-1,4-dione.[9] Recently, various authors[10,11] have studied the alkylation of phenol with methanol over zeolites to obtain mainly anisole and cresols along with minor amounts of xylenols. However, there is no report on the formation of 3,4- or 2,5-dimethylphenols or substituted cyclohexenones from zeolitic treatment of acyclic starting materials.

We report herein the cyclization of 2,6-diones over H-ZSM-5 and 4 M HCl to yield 3,4- and 2,5-dimethylphenols or the corresponding cyclohexenones.

Compound **1** was obtained by the dimerization of methyl vinyl ketone.[12] The hydrogenation of **1** over Pd–$H_2$ yielded **2a**. Compounds **2b** and **2c** were prepared from methyl vinyl ketone through Michael additions.[13]

The acid form of zeolites Na-ZSM-5 (Si/Al = 65) and Na-Y were obtained through successive ion exchange with 1 M $NH_4NO_3$ solution (3 times) and subsequent heating at 673 K for 6 h. The cyclization of **1** was carried out over H-ZSM-5 and H-Y in benzene in sealed tubes at 473 K for 5 h (Table 1). The usual work-up of the reaction mixture yielded the cyclized products, which were separated by column chromatography over silica gel.

As shown in Table 1, among the two catalysts, H-Y and H-ZSM-5, the latter was found to be highly active under pressure. The conversion was always $>90\%$ over H-ZSM-5. The 3,4-DMP and 2,5-DMP were found to be in the ratio 2:1 over both the zeolites. These catalysts, on the other hand, gave very little activity under reflux conditions ($<5\%$). The activity of the two zeolites may be correlated to the strength of the acid sites. H-Y (Si/Al = 2.4) has the highest number of acid sites, but the acid strength is weak as shown by temperature-programmed desorption of ammonia. The strength of the acid sites in H-ZSM-5 (Si/Al = 65) is much stronger, which may be necessary to obtain better yields. However, in these cyclizations the shape-selective behaviour of the zeolites could not be observed.



**Scheme 1**

**Table 1** Cyclization of 2,6-diones over H-ZSM-5[a,b]

| Entry | Compound | Yield (%) | Products (ratio) |
|---|---|---|---|
| 1 | **1** | 90 | **3**+**4** (2:1) |
| 2 | **2a** | 85 | **7a**+**8a** (2:1) (R = Me) |
| 3 | **2b** | 90 | **7** (R = H) |
| 4 | **2c** | 90 | **7c**+**8c** (3:2) (R-COMe)[c] |

[a]All compounds showed satisfactory microanalysis and spectral properties. [b]Cyclization of **1** was carried out over H-Y zeolite (Si/Al = 2.4) and conversion was only 40%, therefore H-ZSM-5 was selected for the present studies. [c]Could not be separated by column chromatography, characterized through GC–MS and the spectral properties of mixture.

These reactions were repeated using 4 M HCl–light petroleum.[14] The comparative yields of the products obtained are shown in Table 2. Cyclization of **1** with aq. HCl–light petroleum under reflux conditions gave cyclohexenones (**5** and **6**). However, treatment of **1** with aq. HCl–light petroleum at 200 °C in a sealed tube yielded minor amounts (8%) of dimethylphenols (**3** and **4** in the ratio of 1:2) and mainly polymeric material.

The possible mechanism is the acid-catalysed mono-enolization of the diketone followed by cyclization and subsequent dehydration which leads to the cyclohexenones. In compound **1** further isomerization of the exocyclic double bond gives phenols. Interestingly, it was found that the cyclization of compound **2b** is accompanied by de-ethoxycarbonylation leading to 3-methylcyclohexenone.

In conclusion, the present procedure for acid-catalysed cyclization of 2,6-diones over zeolite H-ZSM-5 offers a

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**Table 2** Cyclization of 2,6-diones with aq. HCl

| Entry | Compound | Time ($t$/h) | Yield (%) | Products (ratio) |
|---|---|---|---|---|
| 1 | **1** | 5 | 8[a,b] | **3**+**4** (1:2) |
| 2 | **1** | 5 | 50 | **5**+**6** (1:1.2)[c] |
| 3 | **2a** | 4 | 91 | **7a**+**8a** (3:2) (R = Me) |
| 4 | **2b** | 9 | 87 | **7** (R = H) |
| 5 | **2c** | 3 | 87 | **7c**+**8c** (3:2) (R = COMe)[c] |

[a] No starting material was recovered; compound **1** polymerizes. [b] Cyclization was carried out in sealed tube at 200 °C in 4 M HCl (1.5 ml) and light petroleum (0.75 ml). [c] Could not be separated by column chromatography; characterized through GC–MS and spectral properties of the mixture.

unique method for the synthesis of dimethylphenols and $\alpha,\beta$-unsaturated cyclohexenones.

## Experimental

$^1$H NMR spectra were recorded at 60 MHz on Hitachi R-600 and Bruker WM-500 FT-NMR spectrometers. IR spectra were recorded on a Perkin Elmer 681 spectrometer. Mass spectra were recorded with Hewlett Packard (GC-5890, MS-5972) spectrometer at 70 eV. Column chromatography was done on silica gel (100–200 mesh), slurry packed, employing increasing amounts of ethyl acetate in light petroleum (bp 60–80 °C) as eluting solvent.

(a) *General Procedure for Cyclization of* 2,6-*Diones over H-ZSM-5.*—A mixture of the 2,6-dione (4 mmol), the zeolite (200 mg) and dry benzene (2 ml) was heated in a sealed glass tube at 473 K for 5 h. The catalyst was filtered off and washed with ethyl acetate (5 × 5 ml) and the combined filtrates were concentrated under reduced pressure. The residue was subjected to column chromatography over silica gel to yield the products (Table 1).

(b) *Cyclization using Aq. HCl–Light Petroleum.*—A mixture of 4 M HCl (20 ml) and the 2,6-dione (6 mmol) in light petroleum (30 ml) was refluxed with stirring for the period mentioned in Table 2. After cooling, the two layers were separated and the organic layer was washed with saturated $NaHCO_3$ solution, and then dried over $Na_2SO_4$. The residue obtained after evaporation of solvent under reduced pressure was chromatographed over silica gel to yield the products (Table 2).

*Synthesis of* **2a**.—A stirred solution of the enone **1** (560 mg, 4 mmol) in dry methanol (30 ml) was hydrogenated over Pd–C (10%; 100 mg) under hydrogen atmosphere at room temperature for 3 h. The reaction mixture was filtered and the catalyst was washed with the same solvent. The combined filtrates were concentrated *in vacuo* to yield compound **2a** (540 mg), $\nu_{max}$/cm$^{-1}$ (neat) 1711; $\delta_H$ (60 MHz, $CDCl_3$) 3.2 (1 H, m), 2.1 (6 H, s, 2-$COCH_3$), 1.15 (3 H, d, $J$ 6 Hz), 2.3–1.5 (4 H, m).

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