

Synthesis of Tricyclo[6.3.0.0^{2,6}]undec-2(6)-en-7-one from the corresponding Spirolactone Using Zeolite. Use of the Zeolite as a Microreaction Vessel

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Spirolactone **1** is converted into the tricyclic enone **2** by adsorbing the reactant onto a zeolite and carrying out the reaction inside the zeolite pores; the product is recovered by extraction with methanol.

Enones are important intermediates in organic synthesis. A convenient method for the synthesis of polycyclic enones of the type **2** is the acid-catalysed reaction of a spirolactone such as **1**.^{1,2} The best reagent for this purpose has been shown to be a mixture of P₂O₅ in methanesulfonic acid used in large excess.¹

The method suffers from the need to use a large excess of the methanesulfonic acid-P₂O₅ reagent and the rather difficult working up procedure. In recent years there have been several reports on the use of zeolites for selective organic transformations leading to the synthesis of fine chemicals.³ The reaction under discussion, being an acid-catalysed intramolecular acylation appeared to be ideally suited for zeolite catalysis. Our initial attempts to bring about the conversion of **1** into **2** by heating a solution of **1** in hexane in an autoclave with a catalytic quantity of HY-zeolite (substrate:catalyst weight ratio, 10:1) did not result in any conversion and filtration of the catalyst followed by evaporation of the hexane gave back the unconverted starting material. However, the recovered catalyst, upon extraction with methanol, gave an organic material that corresponded to product **2** (UV and IR spectra).

It was suspected that the adsorbed substrate may have been undergoing reaction but that the products were not desorbing and coming out into the liquid phase, thus preventing further reaction. It was proposed to make use of this behaviour to our advantage by employing a large excess of the zeolite. In further studies, enough zeolite to completely adsorb the substrate from the solution was used. Under these conditions, while the zeolite undoubtedly catalyses the reaction, it is required in stoichiometric quantity.

The spirolactone **1** was synthesized as reported elsewhere.² Y-zeolite (LZ-Y 62 a gift from Union Carbide, USA) was used as the source of the HY-zeolite. HZSM-5 was prepared from Hisilite (Na form) obtained as a gift from IPCL, CATAD Division, Thane, India.

The reaction on HY-zeolite was optimized with respect to temperature, reaction time and catalyst:substrate ratio. A solution of 1 g of the lactone **1** in 150 ml dry hexane was taken in a Teflon-lined autoclave. To this were added, 10 g of HY-zeolite, previously heated at 300–400 °C for 12 h and cooled in a dry atmosphere.

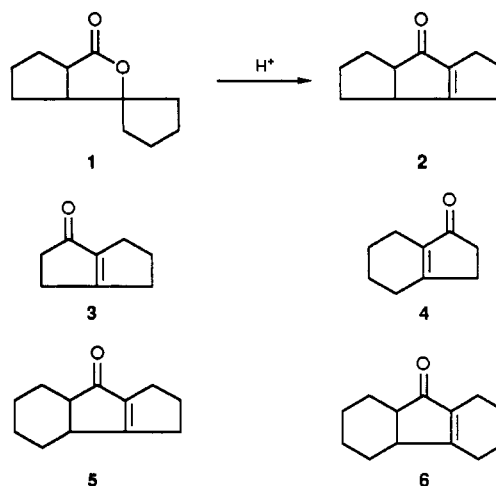


Table 1 Comparison of the yield of enone **2** over different zeolites and in different solvents. *T* 150 °C; *t* 6 h

| Catalyst | Amount of catalyst/g | Amount of substrate/g | Solvent | Product yield (mol%) |
|----------------|----------------------|-----------------------|-----------------------|----------------------|
| HY-Zeolite | 10 | 1.0 | Hexane | 90 |
| HEMT | 1 | 0.1 | Hexane | 64 |
| H-Zeolite Beta | 1 | 0.1 | Hexane | 52 |
| H-ZSM-5 | 1 | 0.1 | Hexane | 0 |
| HY-Zeolite | 10 | 1.0 | Methanol | 19 ^a |
| HY-Zeolite | 5 | 0.5 | Methanol:Hexane (1:1) | 31 ^a |
| HY-Zeolite | 5 | 0.5 | Methanol:Hexane (1:4) | 58 ^a |
| HY-Zeolite | 0.2 | 1.0 | Methanol:Hexane (1:4) | 8 ^a |

^a Enone content estimated by UV analysis of the product mixture.

In one experiment the mixture was filtered after stirring. The hexane phase contained no detectable amount of the substance.

The mixture was heated with stirring at 150 °C for 6 h, after which it was filtered. The hexane filtrate did not contain any dissolved matter. The zeolite was extracted by refluxing with methanol (3 × 50 ml). The recovered zeolite could be activated and reused. Evaporation of the methanol furnished the enone **2** in 90% yield in essentially pure state (single peak in HPLC and TLC). It was further purified by chromatography over silica gel. The UV [λ_{max} (methanol): 244 nm, $\epsilon = 7600$], IR (1686 and 1628 cm^{-1}), PMR, CMR and mass spectra were in agreement with the reported data.² The results with HY and other zeolites are listed in Table 1.

EMT and zeolite beta are large pore zeolites like HY-zeolite. In these cases also the substrate was completely adsorbed by the zeolite from hexane solution. On the other hand, ZSM-5, a medium pore zeolite, did not adsorb the spirolactone from solution. After heating, the unconverted lactone remained in the solution and could be recovered. Extraction of the catalyst by methanol did not yield any product.

This technique has been applied successfully for the synthesis of enones **3–6** from the respective spirolactones.

The present reaction is an example in which the zeolite, in addition to being a catalyst, also functions as a reaction vessel in which the product is held under the conditions of the reaction. There are several reported⁴ studies of the photochemistry of ketones entrapped in zeolites cavities where interesting selectivities are observed. Use of bromine adsorbed on zeolite for selective bromination has recently been reported.⁵ In such examples the zeolite pores also function as reaction vessels of molecular dimensions. The present example demonstrates that even when strong adsorption of the product at the active site and lack of diffusion out of the pores limits the 'catalysis' role of the zeolite, the system can still be adapted to perform reactions on a synthetically useful scale.

Since it was found that methanol could be used to extract the product from the catalyst, some experiments were done to find out if, by the use of a solvent of appropriate polarity, the reaction could be performed in a catalytic manner. Methanol and methanol-hexane mixtures were used as solvent. These results are listed in Table 1. In these cases, depending upon the solvent polarity, part of the organic material was present in the solvent and the rest inside the catalyst from which it was recovered by methanol extraction. The presence of the unconverted lactone and the product enone was easily observed in the IR spectrum of the mixture, in which the lactone had a strong band at 1760 and the enone at 1686 cm^{-1} . The enone content in the combined mixture was quantitatively

estimated by UV spectroscopy. When methanol alone was used as solvent the conversion was low. It was not ascertained whether this was due to a competitive adsorption by methanol or due to the deactivation of the catalyst by methanol in any other way. The conversion improved somewhat when mixtures containing less methanol were used. With the 1:4 methanol-hexane mixture 58% conversion was obtained. However, the product was mostly present on the catalyst rather than in the solution. In this solvent, when the substrate:catalyst weight ratio was changed to 5:1, the conversion dropped to 8%. Thus, our attempts, so far, to bring about the reaction with a catalytic quantity of zeolite have failed. However, further attempts with other solvent systems and reaction conditions are being continued. The enones are important organic intermediates and the present technique, which enables them to be prepared in useful quantities by a simple procedure, promises to be of use as an organic laboratory reaction.

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