# COMPARATIVE STUDY OF ε-CAPROLACTAM SYNTHESIS USING DIFFERENT ENERGY SOURCES AND A NATURAL CLAY AS CATALYST.

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**Abstract:** We report a new method for the production of ε-caprolactam from cyclohexanone and $NH_2OH.HCl$ using different sources of energy in presence of a Mexican clay in dry medium.

**Introduction.**

One of the classical reactions in organic chemistry is the Beckmann rearrangement (1). An important industrial application of this process is in the synthesis of ε-caprolactam, which is the raw material for obtaining Nylon 6. Recently, this lactam has been prepared by the Beckmann reaction of cyclohexanone oxime and using a zeolite as catalyst (2), or by refluxing a suspension of 6-aminocaproic acid previously supported in zeolite, silica gel or alumina (3). We have reported previously the use of a natural clay as acid catalyst in several organic reactions, such as the regeneration of carbonyl compounds from their oxime derivatives (4,5). In the case of *p*-hydroxy and *p*-methoxy acetophenone oximes; the carbonyl compound was not regenerated, but the corresponding amides were obtained through the Beckmann rearrangement. This observation and the fact that oximes can be prepared in dry medium (6), led us to consider the transformation reaction of aromatic aldehydes into the corresponding nitriles in a one step reaction. Also in this case the Beckmann rearrangement was observed. We present here, the results of a comparative study for the synthesis of ε- caprolactam when cyclohexanone and $NH_2OH◊HCl$ are irradiated with infrared, ultrasound, microwave or heat as energy sources using a natural clay (Table 1).

**Results and Discussion.**

Table 1 shows that when weak bases, such as $Na_2CO_3$ or $NaHCO_3$ are used, the yield of ε-caprolactam increases in all but one case (ultrasound). The best conversion (92%) was obtained with infrared radiation. Although the acid character of the natural clay satisfy the conditions required for the Beckmann rearrangement, in earlier experiments using more acidic conditions, we found that the caprolactam yield was near zero with microwave energy. Therefore, we decided to add weak basic compounds to the reaction mixture and found surprisingly that the yields increased dramatically when infrared or microwave radiation was used. We suggest, in accord with Sato and coworkers (2), that the active site in the catalyst is a neutral moiety; hence, the role of base is thought to be to neutralize the hydroxyl amine hydrochloride so the free hydroxyl amine could undergo nucleophillic attack on the cyclohexanone. We propose that the oxime is formed as an intermediate and it can give the Beckmann rearrangement or carbonyl compound regeneration. This behavior is clearly observed when infrared, microwave and thermal energy were used. However, when ultrasound energy was used, the oxime was one of the main reaction products.

**Table 1 Synthesis of ε-Caprolactam**

| Method | Base | Yield (%) | | |
|---|---|---|---|---|
| | | cyclohexanone | oxime | ε-caprolactam |
| Infrared | none | 24 | 0 | 76 |
| (A) | $Na_2CO_3$ | 62 | 0 | 38 |
| | $NaHCO_3$ | 8 | 0 | 92 |
| Microwave | none | 94 | 1 | 5 |
| (B) | $Na_2CO_3$ | 55 | 0 | 45 |
| | $NaHCO_3$ | 89 | 1 | 10 |
| Thermal | none | 59 | 0 | 41 |
| (C) | $Na_2CO_3$ | 48 | 2 | 50 |
| | $NaHCO_3$ | 49 | 0 | 51 |
| Ultrasound | none | 96 | 3 | 0 |
| (D) | $Na_2CO_3$ | 55 | 42 | 3 |
| | $NaHCO_3$ | 43 | 53 | 3 |

**Experimental**

General Procedure. A mixture of the natural bentonite (5g), cyclohexanone (0.2g, 2mmol) hydroxylamine hydrochloride (0.1g, 3mmol) and with (8) or without basic compound, was magnetically stirred and irradiated for 30 minutes (no solvent.). After cooling to room temperature, the reaction mixture was poured into a Buchner funnel containing celite, washed with acetone and concentrated under vacuum. The yields were determined by GC (H-P model 5890/1). Method A (Infrared). The source was a 250W commercial infrared lamp . Method B (Microwave). A commercial microwave oven, Kenmore Model DMR 604 at 2450 MHz, was used. Method C (Thermal). The sample was heated up to 175 $^{o}$C using a commercial heating mantle. Method D (Ultrasound). The source was a Ultrasound apparatus model 234A, at 24505 MHz.

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**References and Notes**

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(8) The molar concentration of $Na_2CO_3$ and $NaHCO_3$ are 8 and 12 mmol, respectively.

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