

INORGANIC SOLIDS IN "DRY MEDIA"  
AN EFFICIENT WAY FOR DEVELOPING MICROWAVE IRRADIATION ACTIVATED ORGANIC REACTIONS

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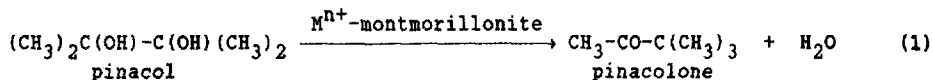
**Summary:** "Dry media" microwave irradiation accelerates pinacol rearrangement (on montmorillonite) or acetate alkylation (on alumina or silicagel) without the hazards due to high pressures in vessels when using solvents.

Microwave irradiation using commercial domestic ovens has been recently used to accelerate organic reactions, the high heating efficiency giving rise to remarkable rate enhancements and dramatic reductions of reaction times (1-4). The timeliness of this topic and the great impact caused by these procedures are evidenced by its recent inclusion in various mass audience journals (5). Nevertheless, these procedures are seriously limited because the use of solvents in microwave ovens gives rise to elevated temperatures and consequently high pressures, thus leading in some cases to dangerous situations.

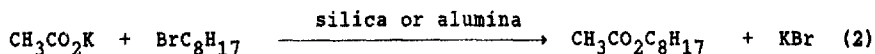
We have developed and describe here a novel way to induce organic reactions by microwave irradiation coupled to the use of reagents supported on solid inorganic materials in the absence of any solvent ("dry media" conditions) (6,7) in order to avoid the experimental difficulties arising from the utilization of homogeneous solutions.

Two model reactions have been selected:

i) a molecular rearrangement (conversion of pinacol to pinacolone), developed on a phyllosilicate ( $M^{n+}$ -montmorillonite) as solid support,



ii) an anionic alkylation (reaction of potassium acetate with 1-bromooctane) carried out either on silicagel or alumina.



Both of these reactions, which have different mechanisms, are well documented both in solution and on the indicated inorganic supports using conventional thermal treatment (8-11). Molecular rearrangement of substituted  $\alpha$ -glycols to carbonyl compounds takes place in the intracrystalline space of 2:1 charged phyllosilicates ( $M^{n+}$ -montmorillonites); the importance of the nature of the  $M^{n+}$  interlayer cation has been emphasized in this acid-catalyzed process (8,9). Silica, or better alumina, are suitable supports for anionic activation (10,11).

In the present experiments, reagents and supports were intimately mixed in the proportions already reported for the same reactions activated by thermal treatment in a conventional oven (8-11). The reactions were carried out in unsealed glass vessels (Pyrex<sup>R</sup>) though in some experiments polytetrafluoroethylene (Teflon<sup>R</sup>) ones were used, like in earlier work done with solutions (1,3). The microwave oven was a domestic (2450 MHz) Moulinex model FM 460. Conversion rates have been determined by a GC technique using a Perkin-Elmer gas chromatograph model 8410 and the characterization of the reaction products by IR and <sup>13</sup>C-NMR/MAS-CP spectroscopies. Wyoming montmorillonites from Upton (USA) with a particle size <2 $\mu$  have been used.

Table 1 shows the results of conversion of pinacol to pinacolone carried out in individual experiments (only one reaction vessel introduced in the oven) with the starting reagent adsorbed on different homoionic montmorillonites. The percentage of pinacol transformed by microwave irradiation (450 W) is compared with that achieved by classical thermal activation (100°C). The durations used were chosen so as to achieve the optimal yields, at least with the most active montmorillonites. They were 15 hours for conventional heating and 15 minutes for microwave activation. The dramatic saving in time evidences the high enhancement of the reaction rate.

**Table 1.** Molecular rearrangement of pinacol on  $M^{n+}$ -montmorillonite (a)  
Conversion (%) of pinacol to pinacolone (GC yields with internal standard)

| $M^{n+}$         | Conventional heating<br>(100°C, 15 h) | Microwave activation<br>(450W, 15 min) |
|------------------|---------------------------------------|--|
| Na <sup>+</sup>  | 5                                     | 38                                     |
| Ca <sup>2+</sup> | 2                                     | 23                                     |
| Cu <sup>2+</sup> | 30                                    | 94                                     |
| La <sup>3+</sup> | 80                                    | 94                                     |
| Cr <sup>3+</sup> | 99                                    | 98                                     |
| Al <sup>3+</sup> | 98                                    | 99                                     |

(a) Pinacol: 20 mg;  $M^{n+}$ -montmorillonite: 100 mg; Pyrex flask: 20 ml.

A large rate enhancement was also achieved in the anionic alkylation of potassium acetate by 1-bromooctane using alumina or silicagel as support (Table 2).

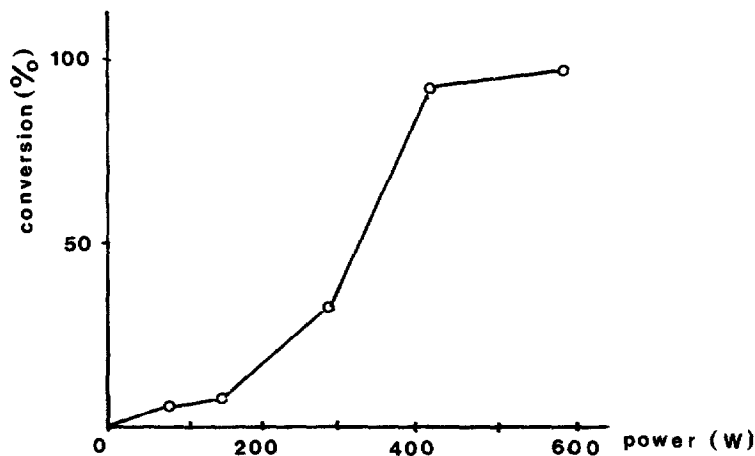
**Table 2.** Anionic alkylation of  $\text{CH}_3\text{CO}_2\text{K}$  by  $\text{BrC}_8\text{H}_{17}$  on alumina or silica (a)  
Conversion (%) of  $\text{BrC}_8\text{H}_{17}$  to  $\text{CH}_3\text{CO}_2\text{C}_8\text{H}_{17}$

| Substrate               | Conventional heating<br>(100°C, 5 h) | Microwave activation<br>(600 W, 10 min) |
|-------------------------|--------------------------------------|---|
| $\text{Al}_2\text{O}_3$ | 93±1                                 | 91±3                                    |
| $\text{SiO}_2$          | 69.5±0.5                             | 82±12                                   |

(a)  $\text{CH}_3\text{CO}_2\text{K}$  + support: 1.00 g;  $\text{CH}_3\text{CO}_2\text{K}$ : 0.2 g (1.7 mmol);  
 $\text{BrC}_8\text{H}_{17}$ : 0.17 g (0.88 mmol); Pyrex flask: 20 ml.

The effect of the microwave power on the yield of the ester is represented in Figure 1.

**Figure 1.** Conversion of  $\text{BrC}_8\text{H}_{17}$  on silica as support (reaction 2) as a function of the microwave power. Reaction time: 10 minutes



In the experimental conditions adopted, the conversion percentage is strongly increased by irradiation at powers higher than 450 W.

The upper part of the vessels used remains cool, so they can be easily handled and opened for work-up without delay, as no pressure develops during treatment.

On the other hand, we have observed that the presence of several reaction vessels in the oven (simultaneous experiments) decreases in general the efficiency of the processes. This effect, which is obviously related to the amount of material absorbing the power emitted, and is well known in the domestic uses of microwave ovens, has been found previously in drying (12). The use of Teflon vessels can affect the yield of the reactions, which can be related to the different microwave absorption and energy transmission abilities of the material. For instance, in the same conditions as those described in Table 2, the replacement of glass by Teflon causes a large decrease in the conversion of  $\text{BrC}_8\text{H}_{17}$  on alumina (conversion =  $8\pm 1.5\%$ ), whereas on silica as support only a slight decrease is observed (conversion =  $76\pm 12\%$ ).

Further investigations are clearly needed to understand the phenomena described. Nevertheless, our results show already that organic synthesis on mineral supports in "dry media conditions" can be successfully induced by microwave irradiation. This gives rise to easier, more efficient and more secure processes than when microwave irradiation of organic compounds in solution is applied, avoiding the hazards generated by the solvents.

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