Application of Microwave Heating Techniques for Dry Organic Reactions

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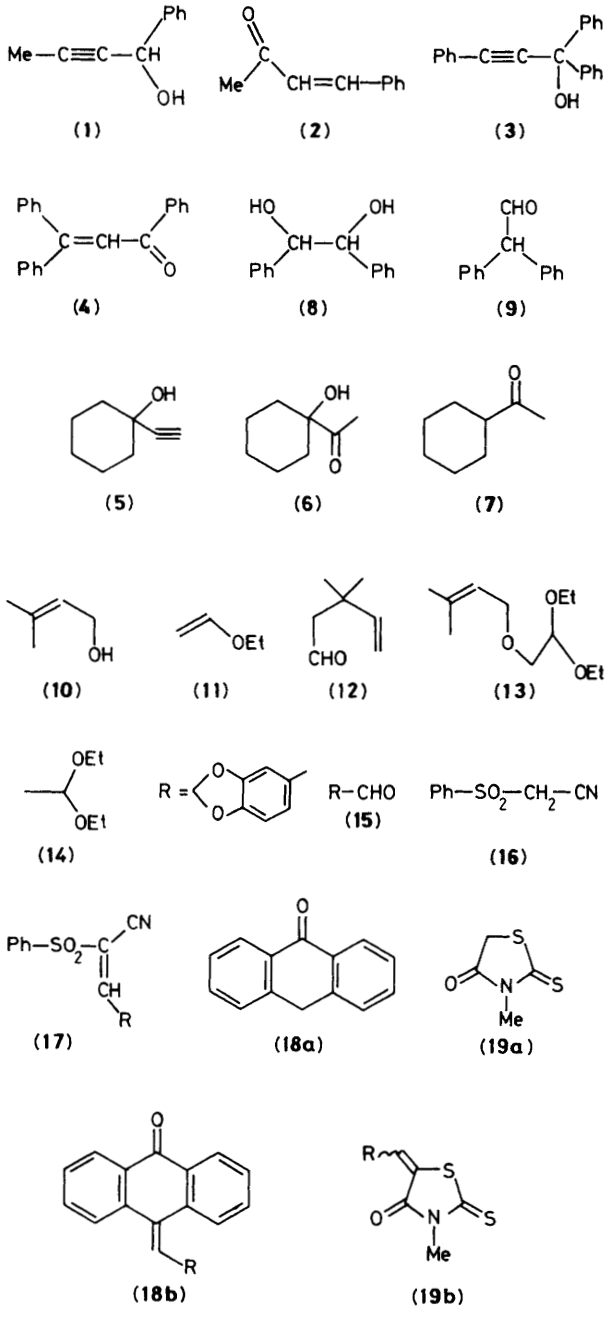
A commercially available microwave oven operating at 2450 MHz has been used for activation of organic compounds adsorbed on inorganic solids.

Recently several publications have described the use of commercially available microwave ovens for accelerating the rate of chemical processes. Applications concern reactions in solution, as the acceleration of nucleophilic substitution reactions[1] or the preparation of short lived radiopharmaceuticals;[2] solid–liquid reaction in the dissolution of geological samples,[3] or reaction of solids in the synthesis of inorganic compounds[4] and in the reticulations of polymers.[5] We describe here new results in the activation of organic compounds adsorbed onto inorganic solids (dry organic



reactions). Generally dry reactions were performed at room temperature,[6] the poor thermal diffusion of the inorganic solids (silica, alumina, clay) was an obstacle for homogeneous thermal activation of these types of reactions. Inorganic oxides (alumina, silica) do not absorb microwaves at 2450 MHz and so are not an obstacle for the transmission of microwaves. In dry reaction, hydroxyl groups, water and organic compounds present on the surface of these inorganic oxides strongly absorb microwaves and these species are activated by microwaves.

We report that acetylenic alcohol (**1**) adsorbed onto K10 or KSF clay, acidic montmorillonite type phyllosilicate, at room temperature does not react. Microwave irradiation gave the rearranged product (**2**) (92%). In a typical experiment, the alcohol (**1**) (3 mmol) in solution in CH_2Cl_2 was absorbed onto KSF clay (1 g), solvent was evaporated *in vacuo*. The dry solid extracted after 2 days gave the pure alcohol (**1**).

The solid was irradiated by microwaves (270 W, 5 mn) in a sealed Teflon vessel and after cooling at room temperature, was extracted by elution with MeCN. The product was recrystallised from ethanol after evaporation of the solvent (95%).†

For comparison, the alcohol (**1**) (3 mmol) was absorbed onto KSF clay (1 g), and the mixture was heated (170 °C, 5 mn) at the temperature attained by the solid just after microwave irradiation (170 °C). Under these conditions we obtained a trace of rearranged product (**2**) (<2%).

Under microwave irradiation (270 W, 5 mn), (**3**) gave (**4**) (98%), and (**5**) gave a mixture of (**6**) (51%) and (**7**) (41%). Pinacol rearrangement of (**8**) to (**9**) (98%) was also easy. A mixture of the alcohol (**10**) and ether (2 equiv.) (**11**) was adsorbed onto KSF, after microwave irradiation (160 W, 5 mn), a mixture of aldehyde (**12**) (75%), and acetals (**13**) (20%), and (**14**) was obtained. In this experiment acid catalysis of clay,[7] surface activation of the solid in a (3,3) sigmatropic reaction,[8] and microwave activation were used. Under similar conditions the thermal activation (135 °C, 5 mn) gave no trace of the aldehyde.

Microwave activation was possible with basic solid, dry reaction of piperonal (**15**) (5 mmol) and the sulphone (**16**) (5 mmol) adsorbed onto potassium fluoride on alumina (3 g), at room temperature to give a poor yield of the condensation product (**17**) (2%). The mixture irradiated by microwaves (55 W, 20 mn) yielded (**17**) (95%). Rhodanine (**19a**) or anthrone (**18a**) with piperonal (**15**) condensed to (**19b**) (90%) and (**18b**) (62%) under similar conditions (55 W, 20 mn).

By comparison, under similar conditions with thermal activation (60 °C, 5 mn) the reactions yielded (**17**) (3%), (**18b**) (20%), and (**19b**) (12%).

We believe that our results show a potentially valuable microwave activation of organic compounds adsorbed onto inorganic solids.

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† Figures in parantheses give yields of crystallised products. All products were characterised by elemental analysis and their i.r. and ^{1}H n.m.r. spectra.