GREENER CHEMICAL SYNTHESES USING ALTERNATIVE REACTION CONDITIONS AND MEDIA

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A solvent-free approach that involves microwave (MW) exposure of neat reactants (undiluted) catalyzed by the surfaces of recyclable mineral supports such as alumina, silica, clay, or 'doped' surfaces is presented which is applicable to a wide range of cleavage, condensation, cyclization, rearrangement, oxidation and reduction reactions including rapid one-pot assembly of heterocyclic compounds from *in situ* generated reactive intermediates. MW-assisted solventless preparation of ionic liquids and their application in alkylation reaction and metal-catalyzed chemical transformations is described.

Aqueous *N*-alkylation of amines by alkyl halides to produce tertiary amines and synthesis of *N*-azacycloalkanes, an important class of building blocks in natural products and pharmaceuticals, can be achieved by a simple, efficient and eco-friendly MW protocol. This double *N*-alkylation of primary amines readily assembles two C-N bonds in a S_N2-like heterocyclization sequence which cannot be fully realized under conventional heating conditions. The MW-assisted reaction proceeds in aqueous potassium carbonate and leads to the formation of a variety of five-membered heterocycles, e.g. isoindole, pyrazole and pyrazolidine etc. by condensation of amines or hydrazines with alkyl 1,3-dihalides or -ditosylates. Similarly, classical nucleophilic substitution reactions can be revisited in aqueous medium by reacting alkyl halides or tosylates with alkali azides to provide azides and thiocyanides in the absence of a phase transfer catalyst. These MW-assisted 'greener' chemical transformations circumvent the need for multi-step processes that use expensive metal catalysts and accommodate reactive functional groups because of mild reaction conditions. Additional advantages include considerably reduced reaction times, and minimization or elimination of byproducts.

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