The 2012 World Congress on
Advances in Civil, Environmental, and Materials Research (ACEM' 12)
Seoul, Korea, August 26-30, 2012

Synthesis of Silica Nanoparticles from Silica Gel Waste and Their Catalytic Role

*Ali Ramazani [1)]

[1)] *Department of Chemistry, University of Zanjan, P O Box 45195-313, Zanjan, Iran*
[1)] e-mail: aliramazani@gmail.com

ABSTRACT

Silica NPs were prepared from silica gel HF254 residues. The morphology and grain size of the silica NPs was investigated by SEM (Fig. 1). Silica NPs were found to catalyze the synthesis of 2-(*N*,*N*-dialkylamino)-2,4,6-cycloheptatrien-1-one derivatives from an isocyanide, a primary amine, propionaldehyde and tropolone *via* Ugi-Smiles coupling reaction.

1. INTRODUCTION

In recent years, nanoparticles (NP) have attracted tremendous attention in catalysis because of their improved efficiency under mild and environmentally benign conditions in the context of ecological (Green) synthesis (Astruc 2005). Due to their enormously large and highly reactive surface area, nanoparticles have potential to exhibit superior catalytic activity in comparison to bulk counterparts (Lewis 1993). In the past, we have established a one-pot method for the preparation of organic compounds. As part of our ongoing program to develop efficient and robust methods for the synthesis of heteroatom-containing compounds (Ramazani 2012), we wish to report the preparation of a new class of 2-(*N*,*N*-dialkylamino)-2,4,6-cycloheptatrien-1-one derivatives **5a-h** by a novel four-component condensation reaction of propionaldehyde **1**, primary amines **2**, isocyanides **3** and tropolone **4** in the presence of silica (NP) in excellent yields (Scheme 1).

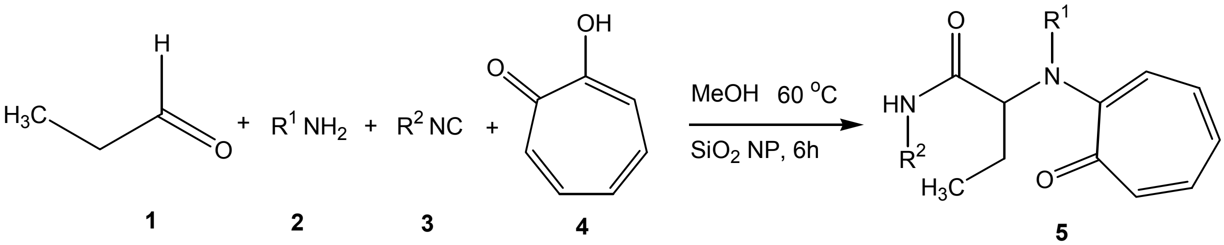
2. RESULTS AND DISCUSSION

Silica NPs were prepared from silica gel HF254 residues. The morphology and grain size of the silica NPs was investigated by SEM (Fig. 1). Silica NPs were found to catalyze the synthesis of 2-(*N*,*N*-dialkylamino)-2,4,6-cycloheptatrien-1-one derivatives from an isocyanide, a primary amine, propionaldehyde and tropolone *via* Ugi-Smiles coupling reaction. We have also used silica gel powder instead of silica NPs in this reaction, but increasing reaction times and decreasing yields of products were observed (Scheme 1 and Table 1). The use of just 0.2 g of silica NPs (per mmol of reactants) is sufficient

---

[1)] Professor

to push the reaction forward. Higher amounts of silica NPs (0.3 g) did not considerably improve the yields (Scheme 1 and Table 2).



5a:R^1= Benzyl, R^2= Cyclohexyl; **5b**:R^1= Benzyl, R^2= *tert*-Butyl; **5c**:R^1= *n*-Propyl, R^2= *tert*-Butyl; **5d**:R^1= *n*-Propyl, R^2= Cyclohexyl; **5e**:R^1= Benzyl, R^2= 1,1,3,3-tetramethylbutyl; **5f**:R^1= Cyclohexyl, R^2= *tert*-Butyl; **5g**:R^1= Cyclohexyl, R^2= 1,1,3,3-tetramethylbutyl; **5h**:R^1= Cyclohexyl, R^2= Cyclohexyl.

Scheme 1 Four-component synthesis of 2-(*N*,*N*-dialkylamino)-2,4,6-cycloheptatrien-1-one derivatives **5** in the presence of silica (NP) (Table 1).

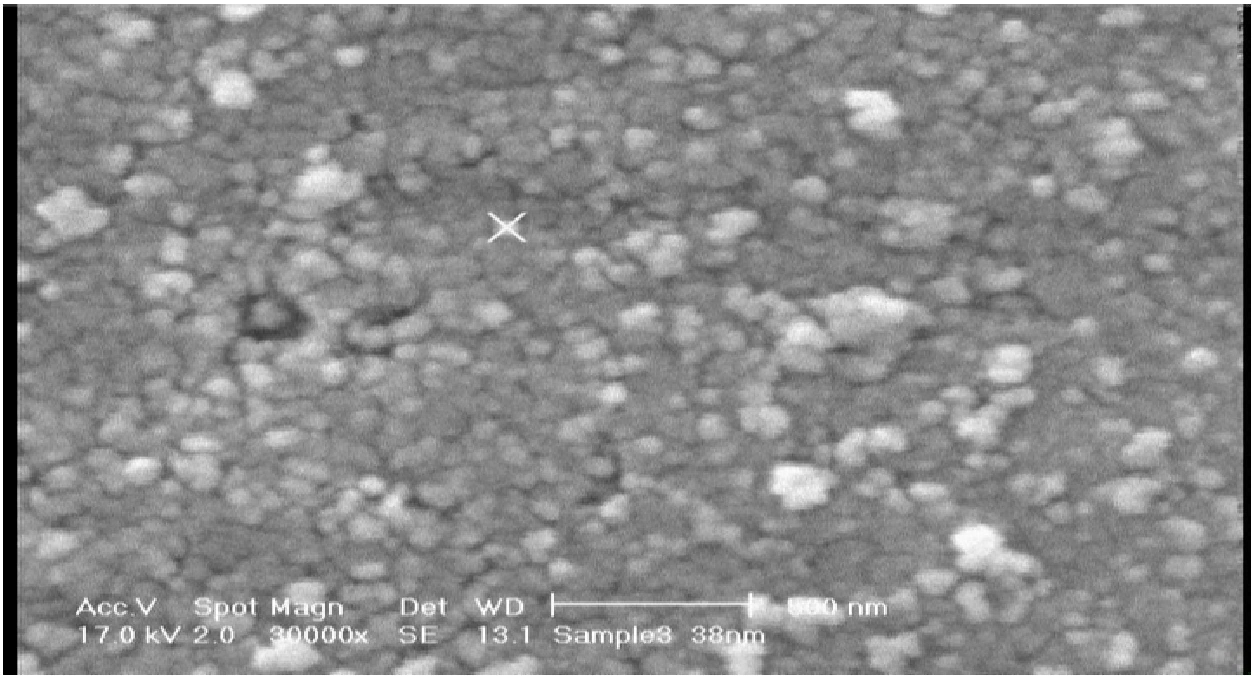


Fig. 1 SEM of the synthesized silica nanoparticles.

Table 1 SiO_2 NP-promoted synthesis of 2-(*N*,*N*-dialkylamino)-2,4,6-cycloheptatrien-1-one derivatives **5**.

5	R^1	R^2	Yield (%)[b])
a	Benzyl	Cyclohexyl	92
b	Benzyl	*tert*-Butyl	90
c	*n*-Propyl	*tert*-butyl	83
d	*n*-Propyl	Cyclohexyl	80
e	Benzyl	1,1,3,3-tetramethylbutyl	85
f	Cyclohexyl	*tert*-butyl	75
g	Cyclohexyl	1,1,3,3-tetramethylbutyl	70
h	Cyclohexyl	Cyclohexyl	79

[a])See Scheme 1; 0.2 g SiO_2 NP/mmol reactants were applied. [b]) Yield of isolated **5.**

Table 2 Synthesis of 2-(*N*,*N*-dialkylamino)-2,4,6-cycloheptatrien-1-one derivatives **5a** from the reaction of propionaldehyde, benzylamine , cyclohexyl isocyanide and tropolone under various conditions.

Entry	Catalyst[a]) or solvent	Temp (ºC)	Time (h)	Yield (%)[b])
1	MeOH	60	24	65
2	H_2O	90	24	57
3	neat	90	24	35
4	MeOH / Silica gel powder(Merck) (0.2 g)	60	24	77
5	MeOH /SiO_2 NP (0.1 g)	60	6	83
6	MeOH /SiO_2 NP (0.2 g)	60	6	92
7	MeOH /SiO_2 NP (0.3 g)	60	6	92

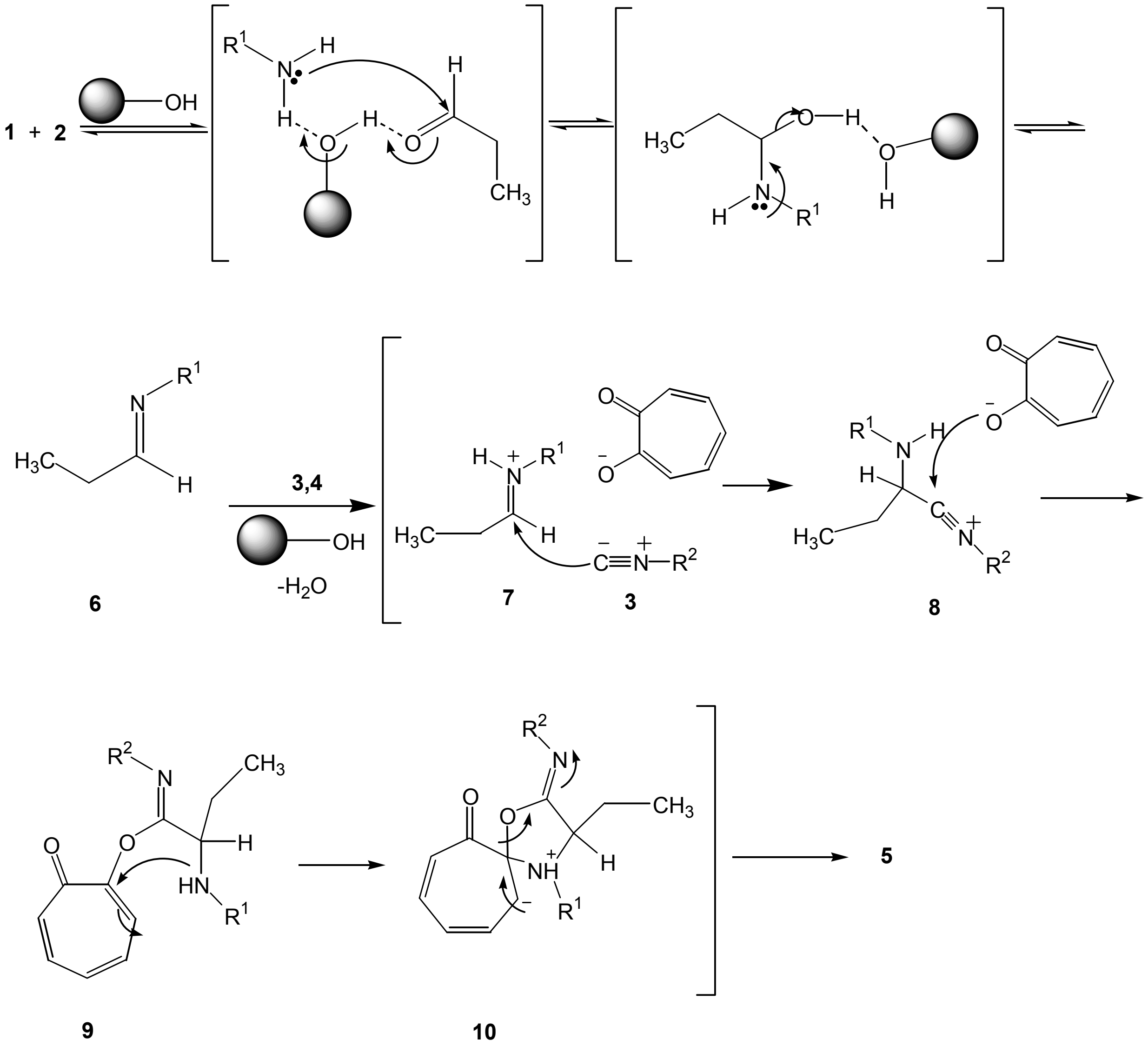
[a])Amount of SiO_2 catalyst per mmol of reactants. [b])Yields of isolated **5a**.

The structures of the products were deduced from their IR, ^{1}H NMR, ^{13}C NMR spectra and Mass spectrometery. For example the ^{1}H NMR spectrum of **5a** consisted of a triplet for the CH_3 of *n*-proyl (δ = 0.79 ppm, J = 7.4 Hz), several multiplets for the cyclohexyl and *n*-propyl (δ =0.86-2.10 ppm) moieties, a multiplet for the NCH (δ = 3.80 - 4.02 ppm) of cyclohexyl moiety, an AB-quartet for CH_2 of $PhCH_2$ (δ = 4.50 ppm, J = 16.8 Hz), a triplet for the NCH (δ = 4.55 ppm, J = 7.0 Hz) of acyclic part, a douplet for the tropolone hydrogen (δ = 6.53 ppm, J = 10.4 Hz), a triplet for the tropolone hydrogen (δ = 6.63 ppm, J = 9.0 Hz), a triplet for the tropolone hydrogen (δ = 6.84 ppm, J = 10.2 Hz), a multiplet for a tropolone hydrogen and phenyl group (δ = 7.07-7.35 ppm) and a douplet for the NH which was exchangeable with D_2O (δ = 8.69 ppm, J = 8.0 Hz). The ^{13}C NMR spectrum of **5a** showed 20 distinct signals. Partial assignment of these signals is given in the experimental section. The ^{1}H and ^{13}C NMR spectra of compounds **5b–h** were similar to those of **5a**, except for the aromatic or aliphatic moieties, which exhibited characteristic signals with appropriate chemical shifts.

A possible mechanism for the present reaction is shown in Scheme 2, which envisages a tandem sequence. On the basis of the chemistry of isocyanides, it is reasonable to assume that the first step may involve the formation of imine **6** by the condensation reaction of primary amine **2** with propionaldehyde **1**, the next step may involve nucleophilic addition of the isocyanide **3** to the imine intermediate **7,** leads to nitrilium intermediate **8.** This intermediate may be attacked by the conjugate base of the tropolone **4** to form 1:1:1 adduct **9**. The intermediate **9** may undergo a Smiles rearrangements to afford the isolated 2-(*N*,*N*-dialkylamino)-2,4,6-cycloheptatrien-1-one derivatives **5** *via* intermediate **10**. It may be speculated that the polar amphoteric surface (hydroxyl groups of the silica (NP)) facilitates the interaction of adsorbed weak acidic and basic components due to stabilization of the corresponding transition states and intermediates by H-bonding. This interaction with the neighboring silanol groups is shown in Scheme 2 for the first reaction step. Participation of two proximate silanol groups (one as a H-bond donor and the other as an H-bond acceptor) in the reaction mechanism also seems to be plausible.

3. CONCLUSION

In summary, We believe that the reported method offers a mild, simple, and efficient route for the preparation of 2-(*N*,*N*-dialkylamino)-2,4,6-cycloheptatrien-1-one derivatives **5** from propionaldehyde **1**, primary amine **2**, isocyanide **3** and tropolone **4** in the presence of silica (NP). Its ease of work-up, high yields and fairly mild reaction conditions make it a useful addition to modern synthetic methodologies.



Scheme 2 Proposed mechanism for the formation of 2-(*N*,*N*-dialkylamino)-2,4,6-cycloheptatrien-1-one derivatives **5** in the presence of silica (NP).

REFERENCES

Astruc, D., Lu, F. and Aranzaes, J. R. (2005), “Nanoparticle catalysis” *Angew. Chem. Int. Ed.* **44** (48), 7852-7872.

Lewis, L. N. (1993), “Chemical catalysis by colloids and clusters” *Chem. Rev.* **93** (8), 2693-2730.

Ramazani, A., Shajari, N., Mahyari, A., Ahmadi, Y. (2011), “A novel four-component reaction for the synthesis of disubstituted 1,3,4-oxadiazole derivatives” Mol. Divers. **15** (2), 521-527.