Note

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Fischer cyclization over molecular sieves in presence of microwave irradiation

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Tetrahydrocarbazole has been synthesized from phenylhydrazine and cyclohexanone over various molecular sieve catalysts in presence of microwave irradiation. The yield of tetrahydrocarbazole is ~83% over HMCM-41 molecular sieve in a solvent-free system in presence of microwaves. The yield varies with respect to the microwave power. Various similar type of reactions have also been carried out.

Recently various organic reactions have been carried out in presence of microwave irradiation.[1-4] Caddick has reviewed[1] various organic reactions like aromatic substitution reactions, oxidation, cyclization, alkylation etc. carried out under microwave irradiation. The microwave heating is generally considered similar to fast thermal heating. But sometimes the rate of heating can be changed by varying the input microwave power and thereby selectivity may vary e.g. induced selectivity was reported in the sulphonation of naphthalene under microwave irradiation[5]. There are few references in the synthesis of tetrahydrocarbazole[6,7]. Bhattacharya *et al.*[8] reported the Fisher cyclization over montmorillonite clay in thermal conditions and Villemin *et al.*[6] reported under microwave irradiation. As the zeolites are shape selective, thermally stable uniform porous catalysts, in this paper, we report Fischer cyclization to tetrahydrocarbazole and related compounds under microwave irradiation in presence of molecular sieve catalysts.

Experimental Section

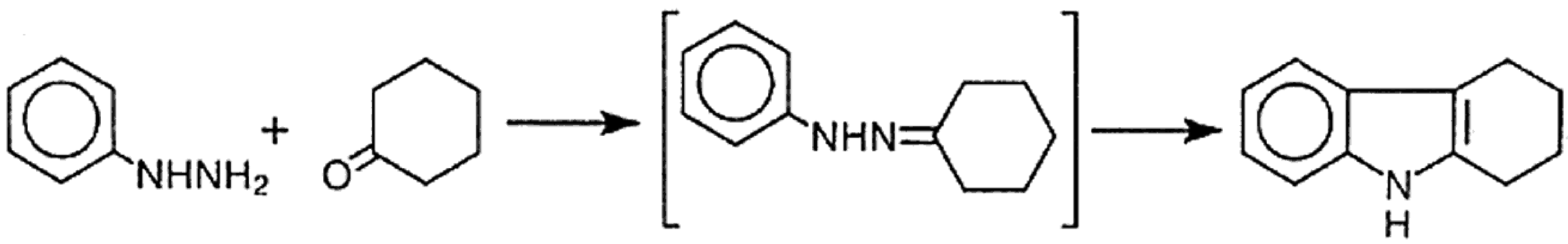
The pre-mixed phenylhydrazine (0.25mL) and cyclohexanone (0.26mL) were mixed with 0.5g solid catalyst in a pyrex bottle and closed with glasswool. The mixture was subjected to microwave irradiation for 3 min. (BPL Domestic microwave oven, with microwave frequency 2450 MHz, 1.2kW). After cooling the mixture was mixed with the solvent (ethyl acetate) and extracted the catalyst by filtration. The mixture was analyzed by Shimadzu GC-17A using SE-30 column, and the analysis was confirmed by NMR and GC- mass spectrometry.

Results and Discussion

In the reaction of phenylhydrazine and cyclohexanone over 0.5g HMCM-41 under microwave irradiation, 83.4% tetrahydrocarbazole was obtained within 3 min. By changing cyclohexanone using different ketones the reaction was carried out with phenylhydrazine and the results are given in **Table I**. The yields of the desired products were 94.2, 21.8 and 29.0% when cyclohexanone was replaced by 2-methylhexanone, cyclohexanol and methylethylketone respectively. But when cyclohexanone was replaced by cyclopentanol, acetone, acetophenone, tetralone, 2-pyrrolidone or caprolactum, the desired cyclic product was not observed (only in traces). The stoichiometric equation may be given as follows,

The results with different catalysts are given in **Table II**. The selectivities of tetrahydrocarbazole were 94.3, 99.7 and 92.6 at 97.5, 95.5 and 75.8 % conversions over HMCM-41, HY and HSAPO-5 catalysts respectively. Due to the smaller size of the intersection and pores in HZSM-5, the main product was not formed.

The effect of the variation of microwave power is depicted in **Table III**. Upto 30% input power, substantial major product was not obtained which is due to the lower heating rate and temperature. The selectivities of tetrahydrocarbazole were 93.9, 93.2 and 99.0 wt% at 40, 60 and 70% of microwave power respectively. At high power inputs, side product like aniline was obtained due to the higher heating rate and reaction temperature.



In conclusion, tetrahydrocarbazole was prepared from phenylhydrazine and cyclohexanone via Fisher cyclization in high yield (> 83.3 %) and similar reactions were carried out over molecular sieve catalysts in presence of microwave irradiation.

Table I — Fischer cyclization : Reactant variation

Catalyst = MCM -41 (0. 5 g), Microwave power = H1, Time =3 min; Molar ratio of $R_1 : R_2 = 1:1$; (a) Bracketted number shows the selectivity of product. Yield and selectivities were based on phenyl hydrazine

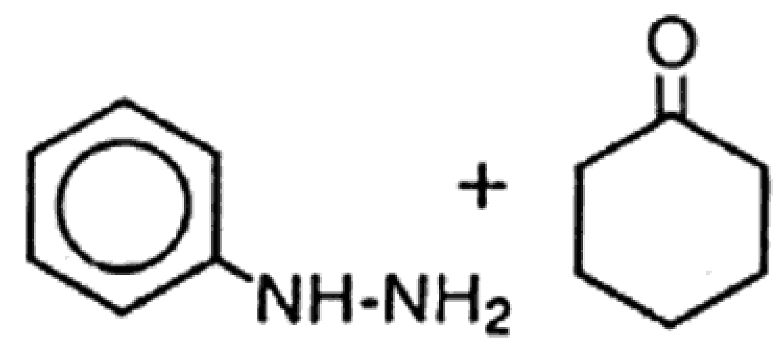
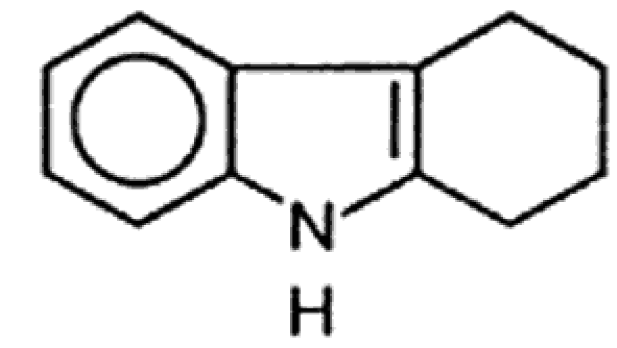
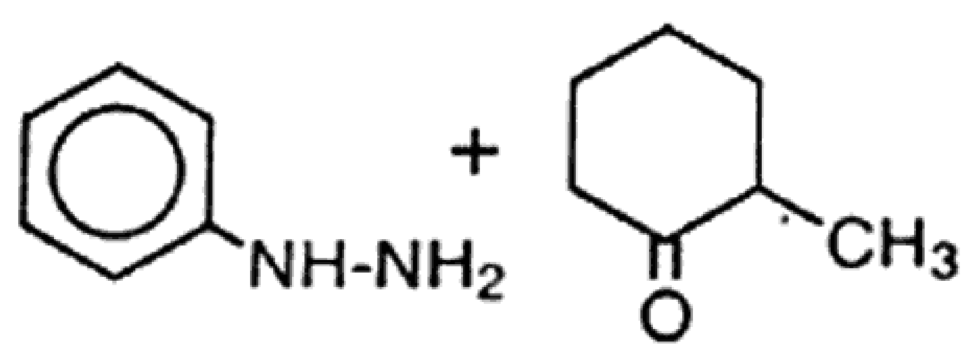
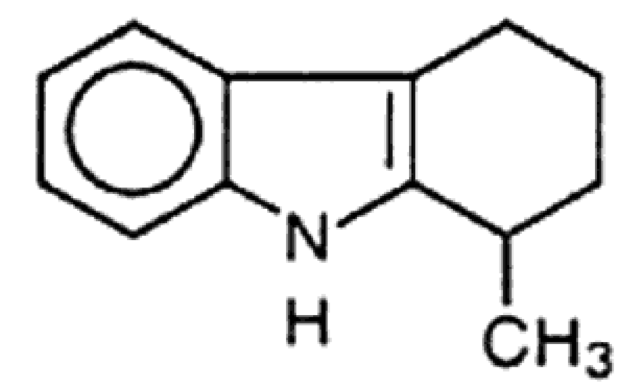
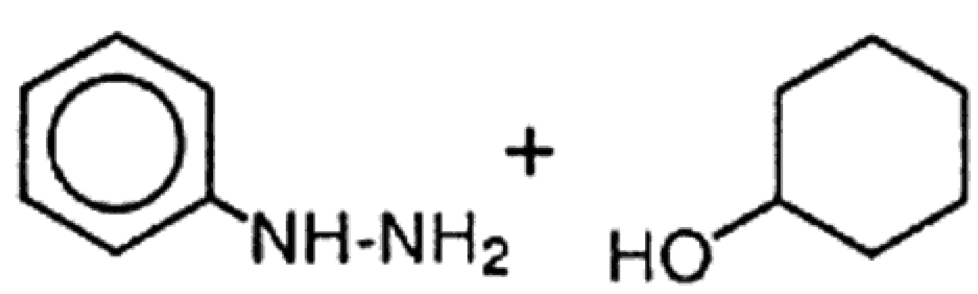
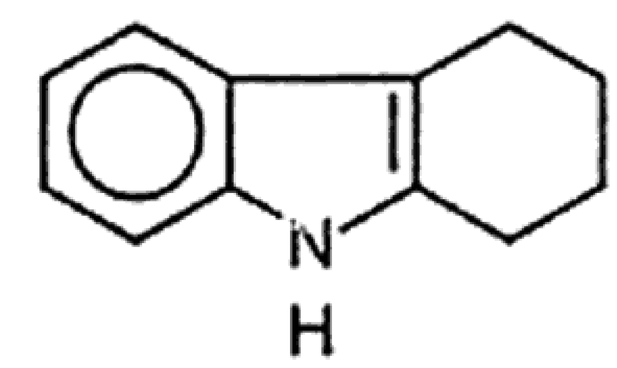
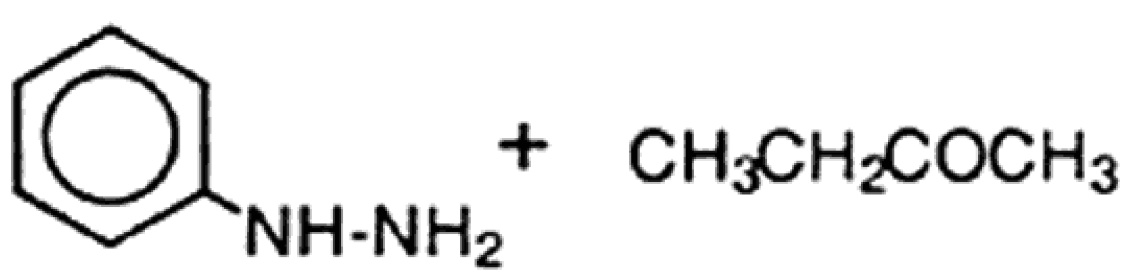
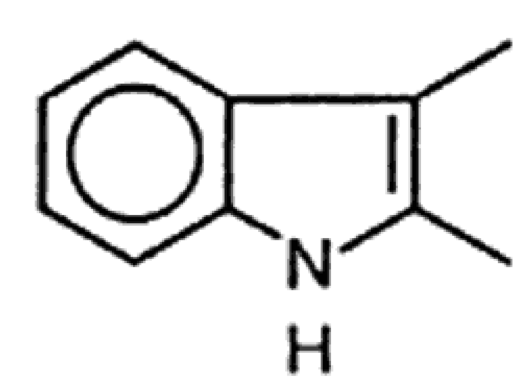
Sl No.	Reactants	Products	% Yield of the product
1			83.4(93.3)[a]
2			94.2(94.2)[a]
3			21.8(60.7)[a]
4			29.0(29.0)[a]

Table II — Fischer cyclization : Catalyst variation

Product = Tetrahydrocarbazole; R_1= Phenylhydrazine;R_2= cyclohexanone; I = Phenylhydrazone (intermediate); Molar ratio = 1:1 (Cyclohexanone: phenyl hydrazine); Catalyst weight = 0.5g; Microwave power = H_1; Time = 3min

Sl No.	Catalyst	% Conversion of phenylhydrazine	Liquid product selectivity(%)		
			Product	Intermediate	Others
1	MCM-41	97.5	94.3	3.3	2.4
2	HY	95.5	99.9	-	-
3	SAPO-5	71.8	92.6	-	7.4

Table III — Fischer cyclization: Microwave power variation

Product = Tetrahydrocarbazole; R_1: Phenylhydrazine;R_2; cyclohexanone; I = Phenylhydrazone (intermediate); Catalyst = MCM-41; Time=3min, Catalyst weight: 0.5g; Molar ratio = 1:1 (Cyclohexanone: phenyl hydrazine)

Sl No.	Microwave power	% Conversion of phenylhydrazine	Liquid product selectivity(%)		
			Product	Intermediate	Others
1	40	98.0	93.9	4.8	1.3
2	50	98.2	95.8	4.2	-
3	60	97.2	93.2	4.3	2.5
4	70	99.2	99.0	1.0	-
5	80	99.9	96.2	3.8	-
6	H1	97.5	94.3	3.3	2.4

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