Reactions of *N*-benzylethanolamine over zeolites

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The possibility of the cyclodehydration of *N*-benzylethanolamine over zeolites to obtain nitrogen heterocycles was investigated. Intramolecular alkylation (cyclodehydration) has not been reported on zeolites. In the present study the reactions of *N*-benzylethanolamine over Na, H and Ce forms of Y and ZSM-5 zeolites at temperatures between 350 and 450°C were performed in a flow reactor. The cyclized product was not obtained. Compounds like ethylbenzene, styrene, 1,1-diphenylmethane, 1,2-diphenylethane, secondary amines and imines were formed.

INTRAMOLECULAR cyclization of acyl or aroyl derivative of the type RCH-CH-NHCOR with P_2O_5, PCl_3, $POCl_3$, $AlCl_3$, $ZnCl_2$, $FeCl_3$ in boiling benzene or toluene giving isoquinoline has been reported[1–4]. Ethanolamine itself over HZSM-5 has been reported to yield piperazine and diazatricyclooctane[5]. Since intramolecular alkylation has not been reported on zeolites, a study on the reactions of *N*-benzylethanolamine over zeolites has been carried out. The dehydration of propanol over zeolites had been reported in our earlier studies[6].

ZSM-5 and Y-type zeolites were obtained from IPCL, Thane, India, and Union Carbide, USA, respectively. H and Ce forms were prepared by ion exchange using standard procedures.

The reactions were carried out in a flow reactor made of a pyrex tube of 2.5 cm diameter and 40 cm length kept in a cylindrical ceramic furnace mounted with a downward slope. The catalyst (3 g) was kept in the middle isothermal region of the reactor. The space above the catalyst was packed with pyrex glass beads, which acted as a preheater zone. Provision was made to read the inside temperature of the catalyst zone by a thermocouple. Before each experiment, the catalyst was activated at 500°C for 4 h. Thereafter, the temperature was brought down to the reaction temperature in a stream of pure, dry nitrogen. The liquid mixture was introduced at the top of the reactor by means of an infusion pump. In a typical experiment a solution of 3 ml of *N*-benzylethanolamine in 27 ml of benzene was introduced at the rate of 10 ml/h into the catalytic reactor packed with 3 g of zeolite. The products were passed through a water-cooled condenser and collected in an ice-cooled receiver. The liquid products were analysed by GC-MS and identified by mass spectral fragmentation and by comparison with authentic samples. Gaseous products were not analysed.

The results of the reactions of *N*-benzylethanolamine over the zeolites at 350, 400 and 450°C are summarized in Tables 1 and 2. The conversion was 100% in all the reactions. The weight per cent recovery in the form of liquid condensate was 75–80%. Losses were due to gas formation (which was not analysed) and due to coke formation (analysed in some cases).

Capillary gas chromatography revealed up to 13 peaks, of which the more prominent 9 peaks could be identified by their mass spectra as discussed earlier. All these were monosubstituted benzene derivatives. Cyclized products which would be disubstituted benzenes were not formed under any of the reaction conditions. Ethanolamine itself over HZSM-5 zeolite has been reported to yield piperazine and diazatricyclooctane[5]. In the present study, no piperazine derivative could be identified.

Some of the products, especially diphenylmethane (**6**) and probably also ethylbenzene and styrene (**1** and **2**) seem to have arisen by the reaction of the fragments from *N*-benzylethanolamine with solvent benzene. Compound (**8**) may also arise via such a route (reaction of styrene with benzene). The other products can be classified into two categories. One arising from the dehydration of *N*-benzylethanolamine. These include the imines (**3** and **4**) and their hydrogenation product (**5**). Selectivity

Table 1. Reactions of *N*-benzylethanolamine over zeolite catalysts

Catalyst	Temp. (°C)	Wt. % composition of the products									
		1	2	3	4	5	6	7	8	9	Unidentified
Na–ZSM-5	350	13 19	2 0	13.18	5.5	15 2	13 07	26.06	5 0	4.3	2.0
Na–ZSM-5	400	3 10	5.27	6 82	4 47	10.90	13.94	33.11	15.74	3.60	3.0
Na–ZSM-5	450	2.2	7.04	4 17	1 93	7 13	17.43	38 06	15.38	1.91	4.75
H–ZSM-5	350	13 0	1.2	18 0	7.9	5 4	3.4	16.5	16.7	1.5	16 4
H–ZSM-5	400	5 0	6.3	6 6	6 6	7.3	4 4	20 8	16.8	1.5	25.3
H–ZSM-5	450	3 44	7 58	2 06	4.12	17.24	11.72	24.82	18.78	1.7	8.14

N-benzylethanolamine = 3 ml; benzene = 27 ml; weight of catalyst = 3 g; flow rate = 10 ml/h; conversion: 100% in all cases.

1. C_6H_5–CH_2–CH_3
2. C_6H_5–CH=CH_2
3. C_6H_5–CH_2–N=CH–CH_3
4. C_6H_5–CH=N–CH_2–CH_3
5. C_6H_5–NH–CH_2–CH_3
6. C_6H_5–CH_2–C_6H_5
7. C_6H_5–CH_2–CH_2–C_6H_5
8. C_6H_5–CH(CH_3)C_6H_5
9. C_6H_5–CH_2–N=CH–C_6H_5

Table 2. Reaction of *N*-benzylethanolamine over zeolite catalysts

Catalyst	Temp. (°C)	Wt. % composition of the products									
		1	2	3	4	5	6	7	8	9	Unidentified
Na–Y	350	10 3	3 6	28 0	3 2	4 4	9.7	17 6	2.9	10 1	10.2
Na–Y	400	5 7	4 7	18 0	4 6	5.7	10 2	25.0	3 9	9 1	13.1
Na–Y	450	3 9	9 7	13 0	6 9	7 8	12.0	27 7	4 7	8 0	6.3
H–Y	350	8.9	3.5	9 2	6 4	8 0	14 9	19 4	1.7	5.4	22 0
H–Y	400	4 8	8 4	6 0	4 0	9.2	6.5	26.7	3 8	4.5	26 0
H–Y	450	1 8	10.7	5.2	2 1	11 4	6.0	30.7	9 6	4 7	17.8
Ce–Y	350	8 3	4 2	9 3	10 8	6.9	6 5	21.7	7.4	12.5	12 4
Ce–Y	400	7.3	5 1	5 3	9 1	5 3	9 8	29.1	8.0	11 0	10 0
Ce–Y	450	4 7	8 8	4 5	4 9	2 9	11.57	35 3	9 6	10 8	7.0

N-benzylethanolamine = 3 ml, benzene = 27 ml, weight of catalyst = 3 g; flow rate = 10 ml/h.

Table 3.

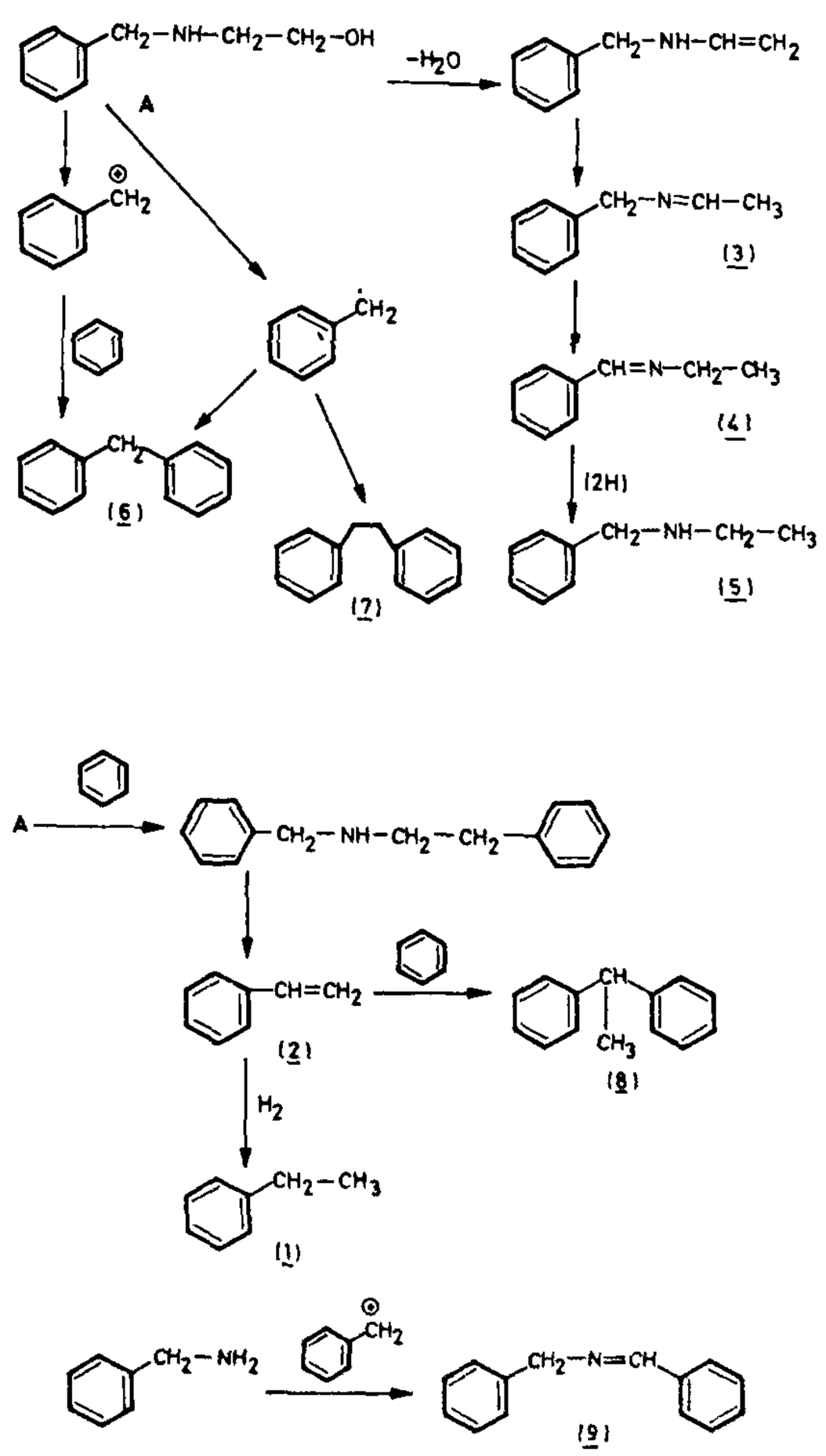
Catalyst	Oxidation temp. of coke (°C)	Wt. of carbon (g)	Percentage loss of NBEA
Na–ZSM-5	500	0 1623	11.18
H–Y	500	0 1745	12.21
Ce–Y	500	0.2019	14 11

Weight of catalyst = 3 g (after 3 h of use); reaction conditions: 10% *N*-benzylethanolamine (NBEA) in benzene (30 ml), rate of flow = 10 ml/h; temp. = 400°C.

for these products is highest on the Na–Y catalyst at 350°C. One of the major products, 1,2-diphenylethane (7), is formed in most of the high-temperature reactions of benzyl derivatives, probably via benzyl radical. The probable routes for the formation of the products in Scheme 1 are only suggestive. The product composition under different conditions does not give evidence for any shape selectivity. The expected cyclized heterocyclic compound was not formed, may be due to the high temperatures under which the reactions were carried out. The investigation will be continued at lower temperatures in batch type to see the possibility of cyclodehydration of *N*-benzylethanolamine.

Essentially all catalysts deactivate over a long period of use. Some types of deactivations are only temporary in the sense that the catalyst can be regenerated to restore all or part of the activity lost. Reversible deactivation is caused most frequently by carbonaceous deposit on the catalyst due to side-reactions. The deposits reduce the activity by blocking of pores in the matrix or binder and by covering active sites. Coking, ageing and regeneration of a large number of zeolites have been reported[7–11]. Derouane[12] has classified various ways in which coke may cause pore blockage. Acidic catalysts may deactivate because of the chemisorption by basic compounds containing nitrogen, as well as by compounds containing oxygen or sulphur. In some cases, simple heating of the catalyst in an inert atmosphere to desorb these poisons will restore the activity. Otherwise, regeneration can be achieved by heating at elevated temperatures in a stream of air.

FORMATION OF PRODUCTS FROM N-BENZYLETHANOLAMINE



Scheme 1.

Coke formation during the reaction was determined by heating the catalyst at 500°C for 6 h in a current of air. The carbon dioxide evolved was absorbed in a known volume of the standard barium hydroxide solution. The barium carbonate formed was separated quantitatively. After drying it was weighed. The weight of carbon was determined gravimetrically. The unreacted barium hydroxide solution was titrated against hydrochloric acid. From this the weight of coke on catalyst was determined volumetrically also. Coke formation was maximum on Ce–Y catalyst. The acidity of the cerium form of zeolite is higher than that of H and Na forms. It is observed that the formation of coke from the amines is more on more acidic forms of zeolite.

N-benzylethanolamine reacts over Y and ZSM-5 zeolites at 350–450°C to yield a variety of products, including imines formed by dehydration, products formed by reaction with the solvent benzene and 1,2-diphenylethane. However, the expected cyclodehydration could not be achieved.

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Production of singlet oxygen by sanguinarine and berberine

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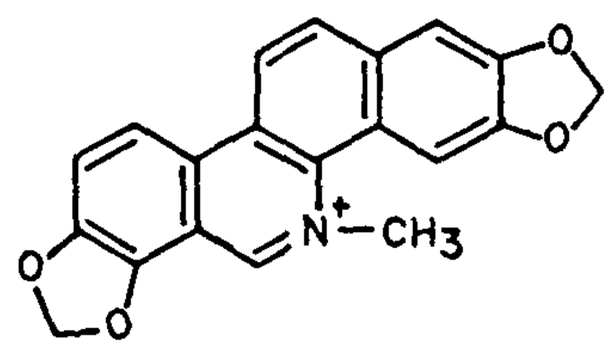
Production of singlet oxygen by sanguinarine and berberine has been studied from absorption spectroscopy measurements using dimethylfuran as the singlet oxygen acceptor. Comparative spectroscopic studies show that the rate of singlet oxygen generation of sanguinarine is higher than that of berberine.

ALKALOIDS occupy an important position in applied chemistry and play an indispensable role in medicinal chemistry. Alkaloids with fused aromatic rings have the potential to form a molecular complex with DNA and are of particular interest because they exhibit a broad range of biological activities[1–6]. Sanguinarine (Structure I, Figure 1) is a benzophenanthridine alkaloid while berberine (Structure II, Figure 1) is a benzodioxolobenzoquinolizine alkaloid. Both compounds have been reported to possess antitumour, antimicrobial and various other biological properties[5,6]. It has been shown that both compounds bind to DNA by a mechanism of intercalation[7–13]. Recently, a large number of biologically active compounds, some of them accepted to be potent drugs, have been found to produce singlet oxygen – an excited form of molecular oxygen that is involved in many photosensitized biological activities[14–22]. In this communication we describe our attempts to demonstrate the production of singlet oxygen by sanguinarine and berberine from absorption spectroscopy measurements.

Sanguinarine chloride and berberine chloride were purchased from Aldrich Chemical Co., St. Louis, MO, USA, and Sigma Chemical Co., St. Louis, MO, USA, respectively, and were used after checking their purity



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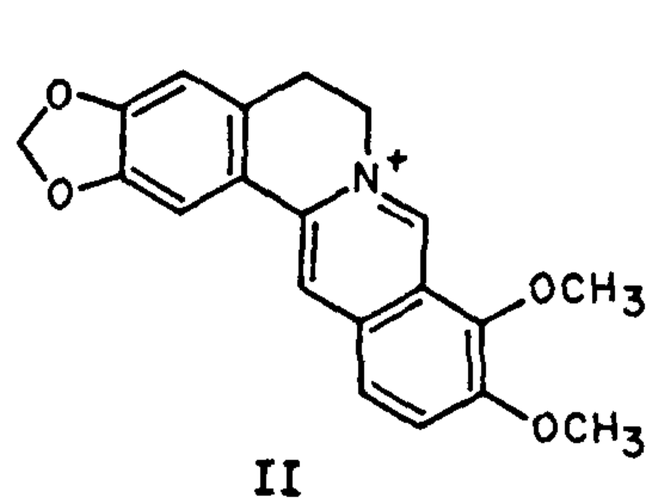

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Figure 1. *Chemical structures of sanguinarine (structure I) and berberine (structure II).*

*For correspondence.