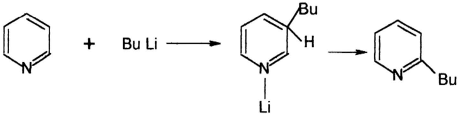
CHAPTER 5

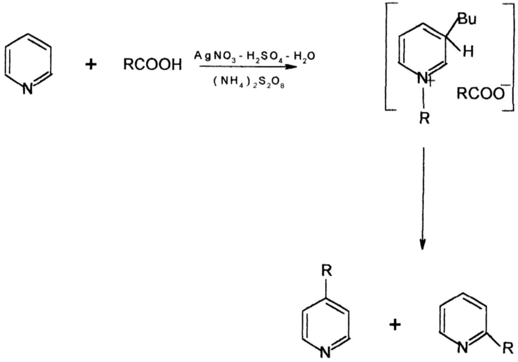
ALKYLATION OF HETEROCYCLES OVER H-Y ZEOLITE

5.1 Introduction

Alkylation play an important role as intermediates in the synthesis of various drugs, dyes and biological molecules (1). Direct alkylation of a heterocycle such as pyridine by the conventional Friedel-Crafts method is seldom successful as a preparative route (2). This is because (i) the pyridine ring is somewhat deficient in π-electron density and therefore is less susceptible to electrophilic aromatic substitution than benzene, and (ii) in the presence of the Friedel-Crafts catalysts like $AlCl_3$ which are Lewis acids, a pyridinium complex is formed which is even less reactive than free pyridine. Because of this difficulty alkylpyridines are synthesised by ring building rather than by direct alkylation. The reports on direct alkylation of pyridine are thus relatively less. On the other hand, the electron deficient nature of the pyridine ring makes nucleophilic reactions relatively more facile than with benzene. An example is Zeiger alkylation, where pyridine is alkylated using a reagent such as alkyllithium. Such alkylations give predominantly the 2-alkyl pyridines (3,4).



Another source of 2- and 4- alkylpyridines is the Ladenberg rearrangement of N-alkyl pyridinium ion on heating to 200- 300^{0}C (5). Both 2- and 4- products are obtained with equal selectivity.



Attempts to alkylate pyridine in the gas phase at high temperatures using zeolites have been reported (6-9). Direct vapour phase methylation of pyridine was studied over various supported Ni-oxide catalysts (6). Ni-substituted Y-type zeolite (Ni-Y) showed the highest catalytic activity. The vapour phase alkylation of pyridine with methanol over a fixed bed of alkali cation (such as Na^+, K^+, Rb^+, Cs^+)-exchanged X- and Y-type zeolites in an atmosphere of nitrogen has been reported (7,8). The products included the side chain alkylated products 2- and 4-ethylpyridines, and 2- and 4- vinylpyridines as well as the ring alkylated products, 2- and 4- methylpyridines and lutidines. However, with H^+ and Li^+-exchanged zeolites, the ring alkylated products,α, β, γ-picolines were formed in preference to β-picoline (9). The catalytic activity was most marked at higher reaction temperature and lower flow rates. The yield of vinylpyridines was highest with the Cs-Y catalyst at 450^0C, while the yield of vinylpyridines was highest with the Cs-X catalyst. Kameswari *et al* (10) have also reported on the vapour phase methylation of pyridine over H-Y, Na-Y, HZSM-5, mordenite, ZSM-22, SAPO-5 and β-zeolite catalysts. The major products formed were 2- 3- and 4-picolines, along with other alkylated products. Of the various zeolites studied for the methylation of pyridine, the Y-type zeolites proved to be most active.

A facile route to 3-alkylpyridines involving the reaction of piperidine with aldehydes over alumina has been described by Jayamani *et al* (11). A mixture of an aldehyde and piperidine dissolved in benzene or a benzene solution of the corresponding alkalidene bis-1-piperidine, when passed over alumina at 420°C gave, among other products, 3-alkylpyridine in 20-40% yield.

The vapour phase methylation of thiophene with methanol over HZSM-5 at 450°C has also been reported by several workers (12-14). The product contains 10% of 2-methylthiophene, 10% of 3-methylthiophene and 65% of 2,5-dimethylthiophene.

5.2 Experimental

H-Y zeolite was prepared according to the procedure described in Chapter 2. Pyridine, pyrrole, thiophene and isopropanol having a purity of over 99%, were commercial products, whose purity was tested by gas chromatograph. All experiments were carried out in a fixed bed reactor, as described in Chapter 2. The catalyst was placed in the reactor and heated to 500°C for 4 hours before use. The yields of the products were analysed by gas-chromatography and GC-MS. Gas chromatographic analyses were performed with a Shimadzu GC-17AAF chromatograph equipped with a flame ionisation detector and 5m x 0.22 mm i.d. methyl silicone column. The oven temperature was programmed from 30-220°C at the rate of 10°/min using nitrogen as carrier gas, and GC-MS using 30m x 0.22 mm i.d. 5% phenylmethyl siloxane column programming siloxane column programming: 60-260°C at the rate of 10°/min using helium as carrier gas.

5.2.1 *Characterisation of products*

Table 5.1 GC-Mass spectral data[a] of products obtained in the reaction between pyridine and isopropanol over over H-Y zeolite

products	[b]RT	[c]m/z
2-methylpyridine	3.2	$M^{+\cdot}$ 93(100), 78(23), 66(53), 51(28)
3-methylpyridine	4.0	$M^{+\cdot}$ 93(100), 78(7), 66(40), 51(17)
4-methylpyridine	6.1	$M^{+\cdot}$ 93(100), 78(4), 66(40), 51(8)
2-ethylpyridine	4.7	$M^{+\cdot}$107(47), 106(100), 92(4), 79(33), 65(9), 51(27)
2-isopropylpyridine	5.6	$M^{+\cdot}$ 121(13), 120(27), 106(100), 93(23), 78(27), 51(21)
3-isopropylpyridine	6.4	$M^{+\cdot}$ 121(4), 120(27), 106(29), 93(100), 78(13) 51(15)
4-isopropylpyridine	7.0	$M^{+\cdot}$ 121(57), 106(100), 93(7), 78(20), 51(29)
2,2'-dipyridine	13.3	$M^{+\cdot}$ 156(100), 128(50), 78(66), 52(91)
2,4'-dipyridine	14.5	$M^{+\cdot}$ 156(100), 128(40), 78(16), 52(40)

[a] Column : 5% Phenylmethylsiloxane, 30m;

Detector : Mass Selective Detector;

Carrier gas : He; Temp.programming at 10^0/min over the range $60-260^0$C

[b] Retention time in minutes, [c] Relative intensity is given in parenthesis.

Table 5.2 GC-Mass spectral data[a] of products obtained in the reaction between pyrrole and isopropanol

products	[b]RT	[c]m/z
2-methylpyrrole	3.5	$M^{+\cdot}$ 81(67), 80(100), 53(23)
3-methylpyrrole	3.7	$M^{+\cdot}$ 81(63), 80(100), 53(23)
2-ethylpyrrole	5.1	$M^{+\cdot}$ 95(45), 80(100), 67(13), 66(4),53(19)
3-ethylpyrrole	5.5	$M^{+\cdot}$ 95(47), 80(100), 67(16), 66(5),53(19)
2-isopropylpyrrole	6.0	$M^{+\cdot}$ 109(47),94(100), 67(12), 77(5),53(4)
3-isopropylpyrrole	6.7	$M^{+\cdot}$ 109(33), 94(100), 67(12),77(4),53(3)

[a] Column : 5% Phenylmethylsiloxane, 30m; Detector : Mass Selective Detector; Carrier gas: He, Temp.programming at 10^{0}/min over the range 60-260^{0}C

[b] Retention time in minutes; [c] Relative intensity is given in parenthesis.

Table 5.3 GC-Mass spectral data[a] on products obtained in the reaction between thiophene and isopropanol

products	[b]RT	[c]m/z
2-methylthiophehe	3.1	$M^{+\cdot}$ 98(100), 69(13), 65(7), 58(8), 53(15)
2-ethylthiophehe	4.0	$M^{+\cdot}$ 112(39), 97(100), 69(8), 53(10)
2-isopropylthiophehe	5.1	$M^{+\cdot}$ 126(40), 111(100), 77(13)
3-isopropylthiophehe	5.4	$M^{+\cdot}$ 126(35), 111(100), 77(13)

[a]Column : 5% Phenylmethylsiloxane, 30m; Detector : Mass Selective Detector; Carrier gas: He, Temp.programming at 10^0/min over the range 60-260^{0}C

[b]Retention time in minutes; [c]Relative intensity is given in parenthesis.

Table 5.4 GC-Mass spectral data[a] of products obtained upon the passage of pyridine over heated H-Y zeolite at 350°C

products	[b]RT	[c]m/z
2-methylpyridine	3.2	$M^{+\cdot}$ 93(100), 78(23), 66(53), 51(28)
3-methylpyridine	4.0	$M^{+\cdot}$ 93(100), 78(7), 66(40), 51(17)
2-ethylpyridine	4.7	$M^{+\cdot}$ 107(47), 106(100), 92(4), 79(33), 65(9), 51(27)
3-ethylpyridine	5.7	$M^{+\cdot}$ 107(83), 106(51), 92(100), 79(20), 65(37) 51(25)
2,2'-dipyridine	13.3	$M^{+\cdot}$ 156(100), 128(50), 78(66), 52(91)
2,4'-dipyridine	14.5	$M^{+\cdot}$ 156(100), 128(40), 78(16), 52(40)

[a] Column : 5% Phenylmethylsiloxane, 30m; Detector : Mass Selective Detector; Carrier gas: He, Temp.programming at 10°/min over the range 60-260°C

[b] Retention time in minutes; [c] Relative intensity is given in parenthesis.

Table 5.4 GC-Mass spectral data[a] of products obtained upon the passage of pyrrole over heated H-Y zeolite at 350^{0}C

products	[b]RT	[c]m/z
2-ethynylpyrrole	3.5	$M^{+\cdot}$ 93(100), 80(39), 66(53), 51(25)
2-methylpyrrole	3.9	$M^{+\cdot}$ 81(67), 80(100), 53(23), 27(15)
3-methylpyrrole	4.1	$M^{+\cdot}$ 81(62), 80(100), 53(23), 27(15)
2-ethylpyrrole	5.0	$M^{+\cdot}$ 95(43), 80(100), 67(7), 66(7),53(19)
3-ethylpyrrole	5.1	$M^{+\cdot}$ 95(44), 80(100), 67(8), 66(9),53(20)
Indole	11.7	$M^{+\cdot}$ 117(100), 90(38), 63(18)
2-methylindole	13.1	$M^{+\cdot}$ 131(71), 130(100), 103(9), 77(19), 65(9), 51(13)
2,3,4,5-tetraethynylpyrrole	14.3	$M^{+\cdot}$ 171(32), 144(100), 128(53), 115(13) 91(8), 63(20)
carbazole	18.3	$M^{+\cdot}$ 167(100), 139(15), 83(13), 75(4), 69(5)
2-methylcarbazole	19.1	$M^{+\cdot}$ 181(100), 166(25), 152(16), 90(12), 77(13)

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[a] Column : 5% Phenylmethylsiloxane, 30m; Detector : Mass Selective Detector; Carrier gas: He, Temp.programming at 10^0/min over the range 60-260^{0}C

[b] Retention time in minutes; [c] Relative intensity is given in parenthesis.

Table 5.4 GC-Mass spectral data[a] of products obtained upon the passage of thiophene over heated H-Y zeolite at 350^{0}C

products	[b]RT	[c]m/z
2-methylthiophehe	3.1	$M^{+\cdot}$ 98(100), 69(13), 65(7), 58(8), 53(15)
2-ethylthiophene	4.0	$M^{+\cdot}$ 112(39), 97(100), 69(8), 53(10)
3-ethylthiophene	4.6	$M^{+\cdot}$ 112(38), 97(100), 69(9), 53(21)
2-ethynylthiophene	4.7	$M^{+\cdot}$ 110(100), 84(27), 66(36), 58(19), 51(16)
3-ehynylthiophene	4.9	$M^{+\cdot}$ 110(100), 84(27), 66(36), 58(19), 51(16)
2,3-diethynylthiophene	8.3	$M^{+\cdot}$ 136(100), 121(40), 94(47), 73(31), 65(30)
Benzothiophene	8.8	$M^{+\cdot}$ 134(100), 108(7), 89(13), 63(16)
2-ethylbenzothiophene	9.9	$M^{+\cdot}$ 148(100), 104(80), 94(33), 76(87)
Bithiophene	10.7	$M^{+\cdot}$ 166(100), 140(33), 125(53), 69(31)

[a]Column : 5% Phenylmethylsiloxane, 30m; Detector : Mass Selective Detector; Carrier gas: He, Temp.programming at 10^{0}/min over the range 60-260^{0}C; [b]Retention time in minutes; [c]Relative intensity is given in parenthesis.

5.3 Results and Discussion

5.3.1 Alkylation of pyridine with isopropanol

The GC trace of the mixture of products obtained in the reaction between pyridine and isopropanol over H-Y zeolite is shown in Fig.5.1. The major products of the reaction are 2- and 3-isopropylpyridines. Scheme. 5.1 lists all the identified products, namely, 2,3, and 4- methylpyridines, 2-ethylpyridine, 2- and 3- isopropylpyridines, 2-2'dipyridine and 2-4'dipyridine.

Effect of temperature

A mixed vapour of pyridine and isopropanol, (1:3 ratio) was passed over the H-Y zeolite at different temperatures. As shown in Table 5.7, the percentage conversion of pyridine increased from 6% at 350^0C to 13% at 500^0C. Previous workers also report similar poor yields for the vapour phase methylation of pyridine. The reason resides in the deactivation of the aromatic ring relative to aniline towards electrophilic substitution. It was also observed that the selectivity for the major product, 2-isopropylpyridine, increased with temperature, but not that of 3-isopropylpyridine which showed a decrease. This may be due to the reactivity of 3-isopropylpyridine to form other alkylated products.

Table 5.7 Alkylation of pyridine with isopropanol[a] over H-Y zeolite: Effect of temperature

Temp (^0C)	Flow rate (mL/hr)	% Conv of pyridine	% Selectivity of products[b] (1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)	(9)
350	5	6.0	4.9	4.3	2.8	1.9	42.7	31.9	5.5	4.5	1.5
450	5	11.1	4.8	3.8	2.4	1.8	47.0	31.0	6.0	2.6	0.6
500	5	13.0	4.3	3.4	1.8	1.9	55.3	25.8	6.8	0.6	0.1

[a] mole ratio pyridine/isopropanol : 1/3

[b] selectivity = [mole% yield of product ÷ mole % conversion of pyridine] x 100

(1) = 2-methylpyridine (2) = 3-methylpyridine (3) = 4-methylpyridine

(4) = 2-ethylpyridine (5) = 2-isopropylpyridine (6) = 3-isopropylpyridine

(7) = 4-isopropylpyridine (8) = 2,2'-dipyridine (9) = 2,4'-dipyridine

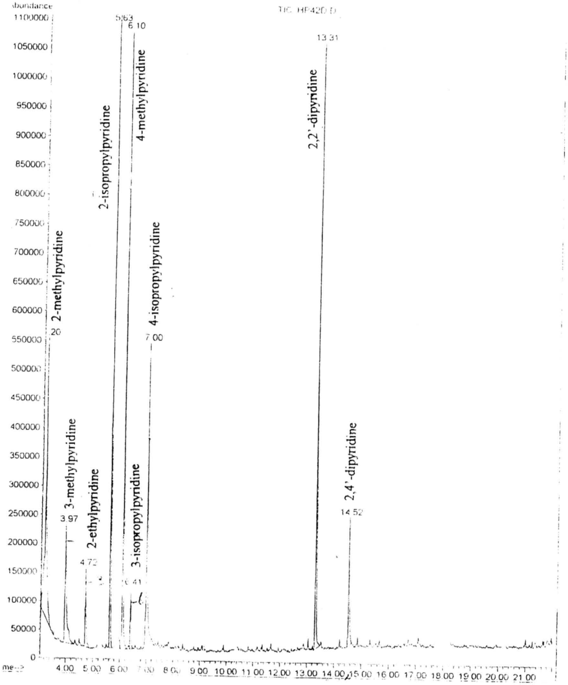
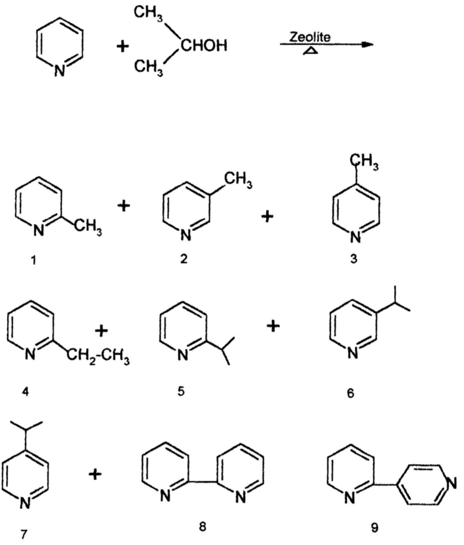


Fig. 5.1 *GC trace of the products obtained in the reaction of pyridine and isopropanol over H-Y zeolite at 350°C*



1. 2-methylpyridine　2. 3-methylpyridine　3. 4-methylpyridine

4. 2 -ethylpyridine　5. 2-isopropylpyridine　6. 3-isopropylpyridine

7. 4-isopropylpyridine　8. 2-2'-dipyridine　9. 2-4'-dipyridine

Scheme 5.1 *Products obtained in the reaction of pyridine with isopropanol over H-Y zeolite.*

Effect of flow rate

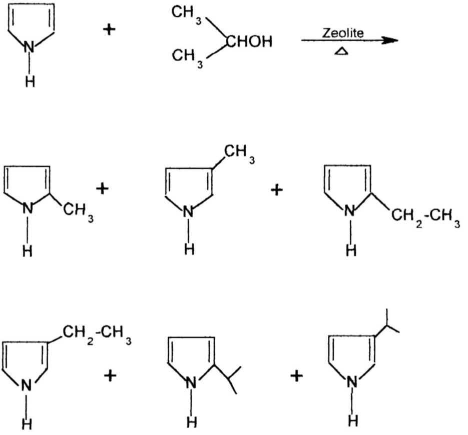
The liquid feed, which is a 1:3 molar mixture was passed over the catalyst (H-Y) at 350^{0}C at different flow rates as recorded in Table 5.8. it was observed that the conversion of pyridine dropped from 6% to 2.6% when the flow rate was increased from 5 to 15mL/hr. However, a higher selectivity for 3-isopropylpyridine was noted upon increasing the flow rate, which was the major product relative to 2-isopropylpyridine. An increase in the flow rate results in a decrease in contact time of the reactants with the catalyst, which in turn results in a decreased level of alkylation. The higher preference for the 3-isopropylpyridine over 2-isopropylpyridine may be the result of thermodynamic influence on the reaction.

5.3.2 Alkylation of pyrrole with isopropanol

The products of the alkylation of pyrrole with isopropanol over H-Y zeolite are 2- and 3-methylpyrrole, 2- and 3-ethylpyrrole, 2- and 3-isopropylpyrrole, 3-ethynylpyrrole and N-isopropylpyrrole as listed in scheme 5.2.

Effect of temperature

The influence of temperature on activity and product distribution are shown in Table 5.9. The alkylation of pyrrole over H-Y zeolite yielded mainly 2- and 3-isopropylpyrrole, along with small quantity of other alkylated products.



1. 2-methylpyrrole
2. 3-methylpyrrole
3. 2-ethylpyrrole
4. 3-ethylpyrrole
5. 2-isopropylpyrrole
6. 3-isopropylpyrrole

Scheme 5.2 *Products obtained in the reaction of pyrrole with isopropanol over H-Y zeolite*

Temperature has a marked effect on the conversion of pyrrole and the product distribution. As, expected, the pyrrole conversion increases with temperature. With increased reaction temperature, that is up to 350^0C, the selectivity towards 2-isopropylpyrrole increases; with a increase of temperature, the selectivity towards 2-isopropylpyrrole decreases. This may be due to the disproportionation of 2-isopropylpyrrole to other products at higher temperature.

Effect of flow rate

Table 5.10 shows the influence of flow rate on product distribution and conversion. The reactions were carried out at 350^0C with pyrrole/isopropanol ratio 1:3 over H-Y zeolite. The conversion of pyrrole decreased with increase in rate of flow of the reagents over the catalyst. But the selectivity towards 2- and 3-isopropylpyrrole increased with increase of flow rate. At a flow rate of 15mL/hr, the conversion of pyrrole was only 7.1%; but the selectivity of 2-isopropylpyrrole was 31.0% and that of 3-isopropylpyrrole was 62.1%. This is probably because at higher flow rates, the formation of secondary reactions is lessened.

Table 5.8 Alkylation of pyridine with isopropanol[a] over H-Y zeolite: Effect of flow rate

Temp	Flow rate	% Conv. of	% Selectivity of products[b]								
(^{0}C)	(mL/hr)	pyridine	(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)	(9)
350	5	6.0	4.9	4.3	2.8	1.9	42.7	31.9	5.5	4.5	1.5
350	10	5.1	4.2	3.8	2.4	0.8	41.6	40.2	6.2	0.8	--
350	15	2.6	4.0	2.4	2.6	0.4	34.3	51.4	4.9	--	--

[a] mole ratio pyridine/isopropanol : 1/3

[b] selectivity = [mole% yield of product ÷ mole % conv. of pyridine] x 100

(1) = 2-methylpyridine (2) = 3-methylpyridine (3) = 4-methylpyridine

(4) = 2-ethylpyridine (5) = 2-isopropylpyridine (6) = 3-isopropylpyridine

(7) = 4-isopropylpyridine (8) = 2,2'-dipyridine (9) = 2,4'-dipyridine

Table 5.9 Alkylation of pyrrole with isopropanol[a] : Effect of temperature

Temp	Flow rate	[b]Catalyst	% Conv.	% Selectivity of products[c]								
(^{0}C)	(mL/hr)		pyrrole	(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)	up
150	5	H-Y	1.4	4.2	12.5	8.6	4.8	31.9	33.2	4.8	--	--
200	5	H-Y	1.6	1.5	8.0	7.5	3.8	37.2	29.2	2.8	--	0.6
250	5	H-Y	4.9	6.8	14.8	5.3	5.0	44	23.1	2.1	–	1.0
300	5	H-Y	10.0	8.5	6.7	4.9	4.1	46.3	24.0	3.8	–	1.7
350	5	H-Y	13.8	7.6	2.5	3.2	1.5	52.0	26.0	2.0	4.2	1.0
400	5	H-Y	16.1	12.5	4.9	6.3	2.4	45.1	23.3	1.8	2.2	1.5
450	5	H-Y	26.1	14.0	7.3	8.1	3.6	36.3	18.9	1.4	2.0	8.4
500	5	H-Y	46.1	15.2	8.3	8.0	3.5	33.6	16.4	0.3	1.9	12.8

[a]pyrrole/isopropanol : 1/3 mole; [b]wt of catalyst:4g

selectivity = [mole% yield of product/ mole% conversion of pyrrole] x100

(1) = 2-methylpyrrole (2) = 3-methylpyrrole (3) = 2-ethylpyrrole

(4) = 3-ethylpyrrole (5) = 2-isopropylpyrrole (6) = 3-isopropylpyrrole

(7) = 3-ethynylpyrrole (8) = N-isopropylpyrrole up = unidentified products

Table 5.10 Alkylation of pyrrole with isopropanol[a] over H-Y zeolite[b]: Effect of flow rate

Temp (^{0}C)	Flow rate (mL/hr)	% Conv. of pyrrole	% Selectivity of products[c] (1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)	up
350	5	13.8	7.6	2.5	3.2	1.5	52.0	26.0	2.0	4.2	1.0
350	10	10.4	4.1	4.2	2.1	2.2	58.0	28.4	0.2	0.8	---
350	15	7.1	2.4	1.2	1.4	1.9	62.1	31.0	--	---	---

[a] pyrrole:isopropanol: 1/3 mole; [b] wt of catalyst: 4g

[c] selectivity = [mole% yield of product/mole% conversion of pyrrole] x100

(1) = 2-methylpyrrole (2) = 3-methylpyrrole (3) = 2-ethylpyrrole

(4) = 3-ethylpyrrole (5) = 3-isopropylpyrrole (6) = 2-isopropylpyrrole

(7) = 3-ethynylpyrrole (8) = N-isopropylpyrrole up = unidentified products

5.3.3 Alkylation of thiophene with isopropanol

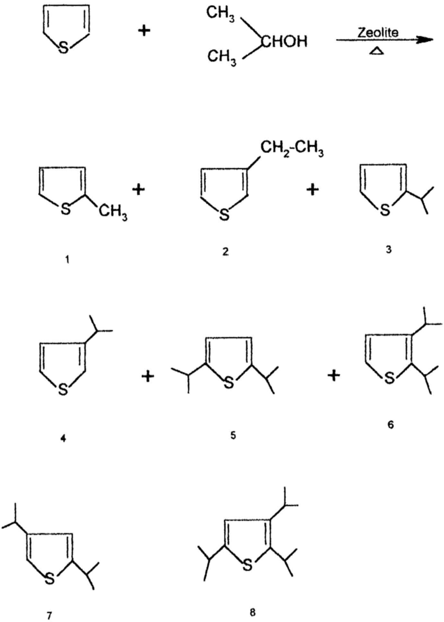
The products of the alkylation of thiophene with isopropanol over H-Y zeolite are 2-methylthiophene, 2-ethylthiophehe, 2- and 3- isopropylthiophene and trace amount of dialkylated products (Scheme 5.3).

Effect of temperature

A mixed vapour of thiophene and isopropanol, (1:3 mole ratio) was passed over H-Y zeolite at different temperatures. The general trend for the alkylation-reaction is that the conversion usually increases with increase in temperature and reaching a steady state at high temperatures (15-17). Here also the thiophene conversion increases with temperature. As shown in Table 5.11, the percentage conversion of thiophene increased from 2.4% at 150^{0}C to 39.4% at 500^{0}C.

Effect of flow rate

Table 5.12 summarises the results of alkylation of thiophene with isopropanol, over H-Y zeolite at different flow rates. Conversion of thiophene decreased with increased in rate of flow of the reagents over the catalyst. The conversion of thiophene was 37.0 at 5mL/hr; and decreased to 28.0% at 15mL/hr. But the selectivity of 3-isopropylthiophene increased with decrease of contact time; under the flow rate of 15mL/hr, the selectivity for 3-isopropylthiophene was 47.1%. The major product of the reaction was 2-isopropylthiophene. As the flow rate increases the selectivity towards 2-isopropylthiophene decreases from 30.8 to 18.2%.



1. 2-methylthiophene
2. 2-ethylthiophene
3. 2-isopropylthiophene
4. 3-isopropylthiophene
5. 1-5-diisopropylthiophene
6. 2-3-diisopropylthiophene
7. 2-4-diisopropylthiophehe
8. 2-3-5-triisopropylthiophene

Scheme 5.3 *Products obtained in the reaction of thiophene with isopropanol*

Table 5.11 Alkylation of thiophene with isopropanol[a] over H-Y zeolite[b]: Effect of temperature

Temp (^{0}C)	Flow rate (mL/hr)	% Conv. of thiophene	% Selectivity of products (1)	(2)	(3)	(4)	(5)	(6)	up
150	5	2.4	10.5	6.2	47.5	34.4	---	---	0.2
200	5	3.7	4.8	6.6	50.9	30.6	---	---	7.1
250	5	5.2	1.9	10.2	55	28.8	---	---	4.1
350	5	37	16.8	6.7	33.8	30.8	4.3	5.8	1.8
400	5	37.4	5.4	4.0	47.3	31.2	4.2	5.9	2.0
450	5	38.8	5.1	3.4	48.4	32.1	4.0	5.0	2.0
500	5	39.4	2.0	2.2	50.2	34.0	3.5	5.3	2.8

[a] thiophene:isopropanol: 1/3 mole; [b] wt of catalyst : 4g

(1) = 2-methylthiophene (2) = 2-ethylthiophene (3) = 2-isopropylthiophene

(4) = 3-isopropylthiophene (5),(6) = dialkylated products

up = unidentified products

Table 5.12 Alkylation of thiophene with isopropanol[a] over H-Y zeolite[b]: Effect of flow rate

Temp	Flow rate	% Con. of	% Selectivity of products						
(^{0}C)	*(mL/hr)*	*thiophene*	*(1)*	*(2)*	*(3)*	*(4)*	*(5)*	*(6)*	*up*
350	5	37.0	16.8	6.7	33.8	30.8	4.3	5.8	---
350	10	34.1	24.3	9.2	42.2	21.0	1.8	---	---
350	15	28.0	26.2	7.4	47.1	18.2	1.1	---	---

[a]thiophene:isopropanol : 1/3 mole; [b]wt of catalyst : 4g

(1) = 2-methylthiophene (2) = 2-ethylthiophene

(3) = 3-isopropylthiophene (4) = 2-isopropylthiophene

(5), (6) = dialkylated products up = unidentified products

5.3.4 Molecular transformation of pyridine, pyrrole and thiophene over H-Y zeolite

The fate of pyridine, pyrrole and thiophene vapours when passed over a fixed bed of H-Y zeolite in the neat was examined at different temperatures. The products collected were examined by GC-MS and results are shown in Tables 5.13 through 5.15. It was evident that all the three heterocycles suffered molecular transformations which were more pronounced at higher temperatures. In the case of pyridine, the products obtained were 2 and 3-methylpyridines, 2- and 3- ethylpyridines, 2-2'-dipyridines and 2-4'- dipyridines (scheme 5.4). The GC trace of the products obtained in the reaction of pyridine over H-Y zeolite is shown in Fig.5.2. Of these, the bipyridine products are clearly the result of molecular transformations occuring on the zeolite surface, while the alkylated pyridines owe their origin to electron- impact fragmentation of the pyridine molecule when analysed by the GC-MS technique. Indeed the ring cleavage pattern of pyridine as reported in the literature (15) yields fragment ion peaks at m/e 39, 40, 51, 52, 65, 66, 67, 77, 78, 79. The most prominent peaks found in our mass spectral trace at m/e 51, 66, 77, 78 &79 are in accord with this. Confirmation that the presence of zeolite is necessary for the molecular transformation of pyridine to the bipyridines was shown by passage of pyridine vapour at a flow rate of 5mL/hr through the reactor in the absence of zeolite. The GC-MS analysis of the sample collected in the cold trap following passage through the reactor showed no trace of bipyridines (Fig. 5.3).

Table 5.13 Reaction of pyridine over H-Y zeolite: Effect of temperature

Temp (^{0}C)	% Conv. of pyridine	% Selectivity of products (1)	 (2)	 (3)	 (4)	 (5)	 (6)	 up
350	56.3	6.2	4.2	1.8	1.7	40.7	22.3	23.1
400	58.4	1.9	1.6	1.0	0.6	45.5	25.3	24.2
450	62.0	0.6	0.7	0.6	0.6	46.1	24.9	26.5

wt of catalyst = 6g; flow rate = 5mL/hr

(1) = 2-methylpyridine (2) = 3-methylpyridine (3) = 2-ethylpyridine

(4) = 3-ethylpyridine (5) = 2,2'-dipyridine (6) = 2,4'-dipyridine

up = unidentified products

Table 5.14 Reaction of pyrrole over H-Y zeolite : Effect of temperature

Temp (0C)	Flow rate (mL/hr)	% Conv. of pyrrole	% Selectivity of products (1)	 (2)	 (3)	 (4)	 (5)	 (6)	 (7)	 (8)	 (9)	 (10)	 up
300	5	37.5	12.1	54.3	1.5	1.5	0.4	13.2	0.8	1.4	4.7	1.6	8.3
350	5	49.8	13.5	54.7	1.6	1.0	0.5	13.0	0.5	2.8	4.7	0.5	7.2
400	5	58.7	12.4	55.0	1.5	0.5	0.5	13.4	0.7	1.4	4.8	0.6	9.2
450	5	71.0	12.2	55.2	1.6	0.5	0.5	13.8	0.5	1.3	4.9	0.8	8.6

(1) = 2-ethynylpyrrole (2) = 2-methylpyrrole (3) = 3-methylpyrrole

(4) = 2-ethylpyrrole (5) = 3-ehylpyrrole (6) = indole

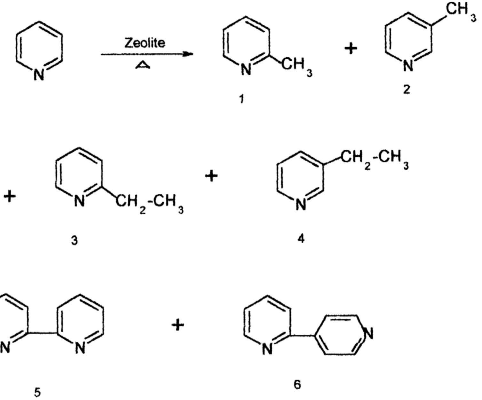
(7) = 2-methylindole (8) = 2,3,4,5-tetraethynylpyrrole

(9) = carbazole (10) = 2-methylcarbazole up = unidentified products

Table 5.15 Reaction of thiophene over H-Y zeolite: Effect of temperature

Temp	Flow rate	% Conv. of	% Selectivity of products										
(^{0}C)	(mL/hr)	thiophene	(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)	(9)	(10)	up
200	5	2.0	15.8	5.8	16.0	4.0	6.6	2.6	6.6	3.8	22.2	2.6	14.0
250	5	3.0	6.8	8.1	13.9	8.3	12.1	4.8	10.2	7.9	13.6	2.4	11.9
300	5	5.0	4.4	12.1	10.4	8.4	13.0	6.0	12.9	8.3	6.4	8.8	9.3
350	5	14	3.0	12.4	3.6	13.0	15.7	7.7	12.9	10.8	1.3	4.4	15.2
400	5	27	2.9	7.2	3.1	15.7	7.4	5.7	7.6	18.0	3.0	2.2	26.7
450	5	58	2.0	5.2	3.0	15.9	3.6	5.2	3.6	18.5	4.0	3.0	36.0

(1) = 2-methylthiophene
(2) = 2-ethylthiophene
(3) = 3-ethylthiophene
(4) = 2-ethynylthiophene
(5) = 3-ethynylthiophene
(6) = 3-methyl 2-ethylthiophene
(7) = 2,3-diethythiophene
(8) = benzothiophene
(9) = 2-methylbenzothiophene
(10) = bithiophene
up = unidentified products



1. 2-methylpyridine
2. 3-methylpyridine
3. 2-ethylpyridine
4. 3-ethylpyridine
5. 2-2'-dipyridine
6. 2-4'-dipyridine

Scheme 5.4 *Products obtained upon the passage of pyridine over heated H-Y zeolite*

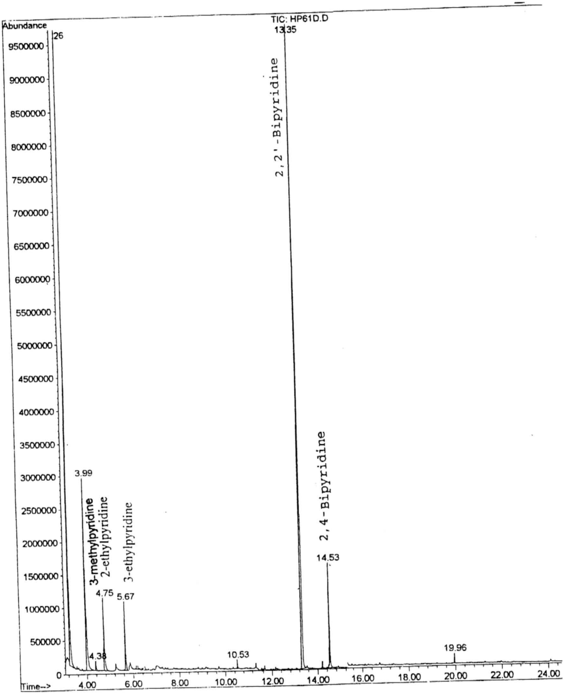


Fig. 5.2 *GC trace of the products obtained upon the passage of pyridine over H-Y zeolite at 350^{0}C*

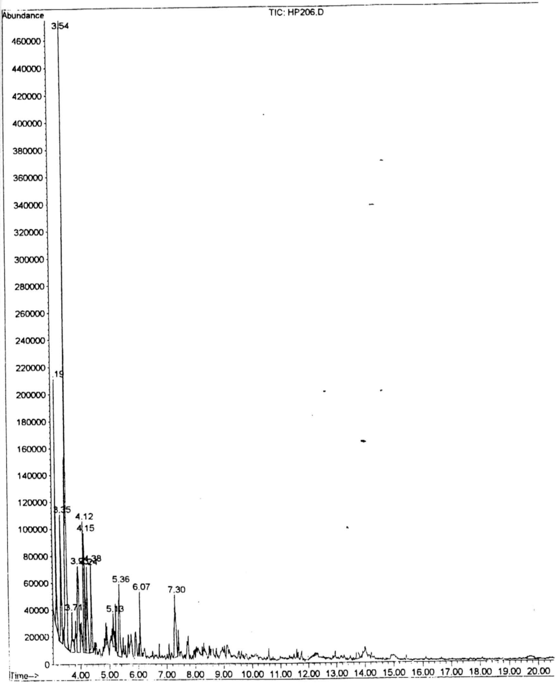
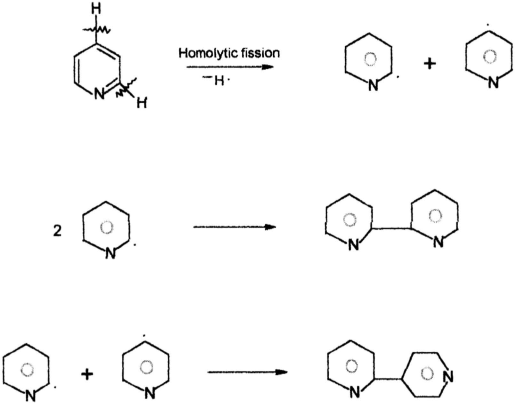


Fig. 5.3 *GC trace of the products obtained upon the passage of pyridine through the flow reactor at 350^{0}C in the absence of zeolite*

A possible pathway for the formation of pyridine to 2-2'- and 2-4'-dipyridines is shown below (Scheme 5.5).



Scheme 5.5 *Mechanism for the formation of bipyridines*

The results on the pyrrole and thiophene transformations are given in Tables 5.14 and 5.15, respectively. The GC trace of the products obtained upon the passage of pyrrole and thiophene over heated H-Y zeolite are given in Figures 5.4 and 5.5, respectively.

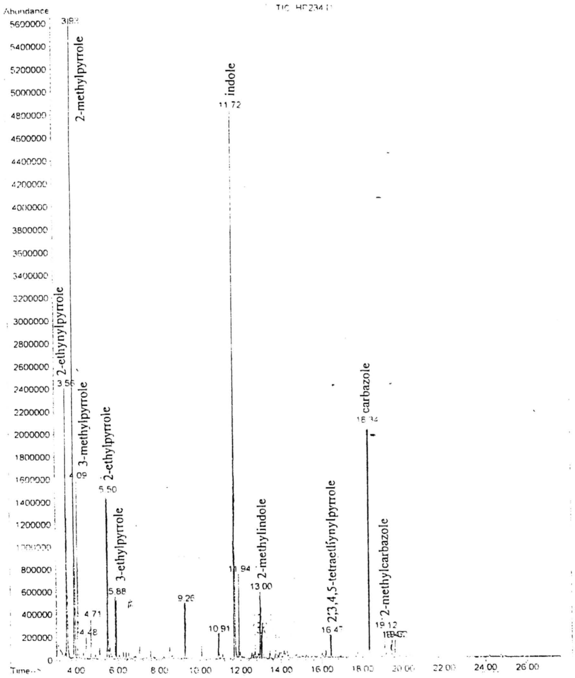


Fig. 5.4 *GC trace of the products obtained upon the passage of pyrrole over H-Y zeolite at 350°C*

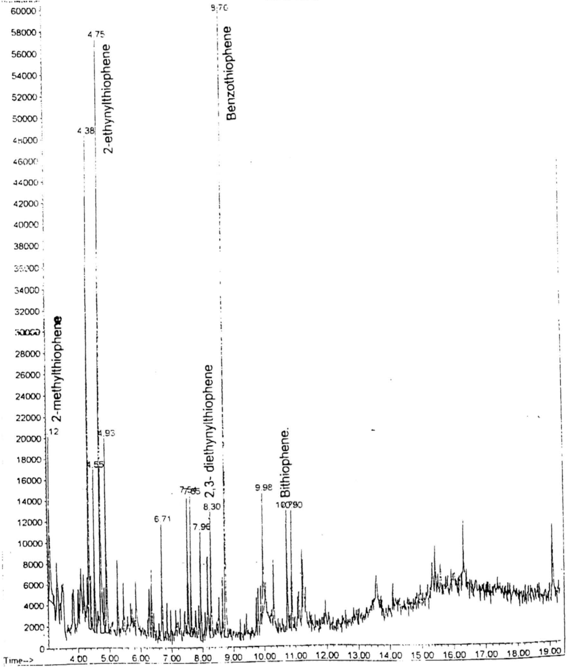
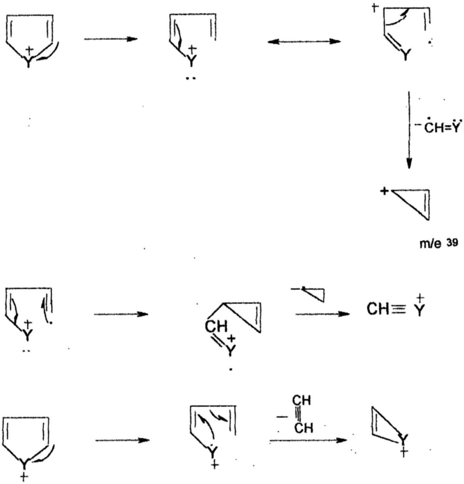


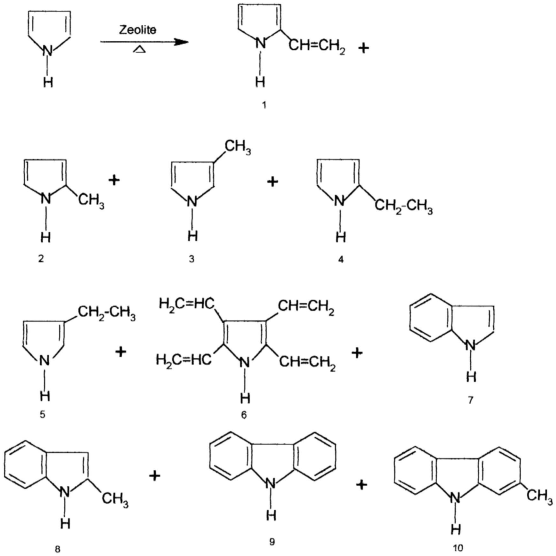
Fig. 5.5 *GC trace of the products obtained upon the passage of thiophene over H-Y zeolite at 350⁰C*

Both these five membered ring systems show very similar ring cleavage patterns in their mass spectra (15), as sketched below (Scheme 5.6).



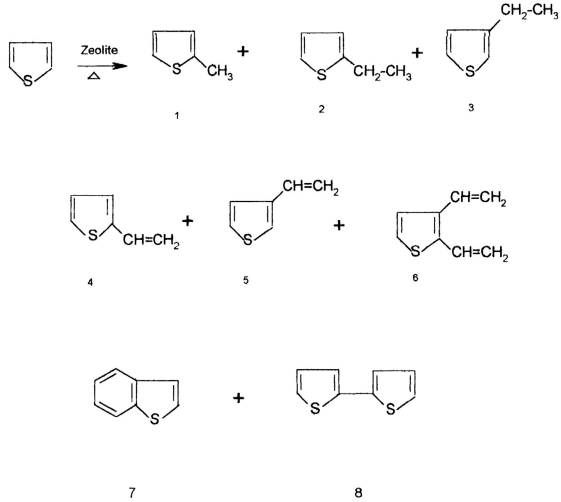
Scheme 5.6 *Mass fragmentation pathways for thiophene and pyrrole*

The electron-impact fragment ions in the case of pyrrole and thiophene can be accounted for the basis of the products 1-6 indicated in Schemes 5.7 and 5.8 respectively.



1. 2-ethynylpyrrole
2. 2-methylpyrrole
3. 3-methylpyrrole
4. 2-ethylpyrrole
5. 3-ethylpyrrole
6. 2,3,4,5-tetraethynylpyrrole
7. Indole
8. 2-methylindole
9. Carbazole
10. 2-methylcarbazole.

Scheme 5.7 *Products obtained upon contacting pyrrole over heated H-Y zeolite*



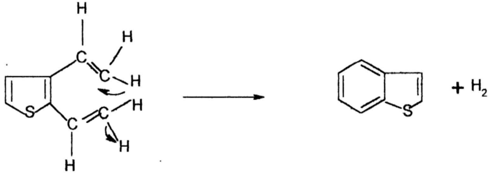
1. 2-methylthiophene 2. 2-ethylthiophene 3. 3-ethylthiophehe

4. 2-ethynylthiophene 5. 3-ethynylthiophene 6. 2,3-diethynylthiophene

7. Benzothiophene 8. Bithiophene.

Scheme 5.8 *Products obtained upon contacting thiophene over heated H-Y zeolite*

The molecular transformation products obtained over zeolite in the case of pyrrole are indole and carbazole, along with their 2-methyl derivatives; the latter are conceivably by-products arising during the course of mass spectral analysis. In the case of thiophene, the following molecular transformation products were identified; benzothiophene and bithiophene. Taking the case of thiophene first, it is noted from the comparison of peak concentrations, that products such as 1-6 are in greater concentrations in the zeolite-contacted sample than in the non-contacted sample. Product 6 is implicated strongly in the formation of benzothiophene, which could occur by the following pathway (Scheme 5.9).



Scheme 5.9 *Mechanism for the formation of benzothiophene*

Likewise, in the case of pyrrole, compound 6 (Scheme 5.7) which is found in much greater amount in the zeolite- contacted sample is the likely precursor for carbazole. Indole could conceivably occur by Diels- Alder reaction between product 1 (2-ethynylpyrrole) and ethylene. The 2-methyl derivatives of indole and carbazole which are low in content probably occur in the GC-MS as a result of electron-impact fragmentation on these parent molecules.

5.4 Conclusion

Isopropylation of pyridine, pyrrole and thiophene were carried out on H-Y zeolite. The major products of the alkylation of pyridine with isopropanol are 2- and 3-isopropylpyridines. The conversion of pyridine increases with temperature. The alkylation of pyrrole over H-Y zeolite yielded mainly 2- and 3-isopropylpyrroles, along with small quantity of other alkylated products. Here also the temperature has a marked effect on the conversion of pyrrole and the product distribution. The pyrrole conversion increases with temperature. The products of the alkylation of thiophene with isopropanol over H-Y zeolite are 2-methylthiophene, 2-ethylthiophene, 2- and 3-isopropylthiophenes and trace amount of dialkylated products. Molecular transformation of pyridine, pyrrole and thiophene were carried out over H-Y zeolite at different temperatures. Molecular transformation of pyridine over zeolite yielded mainly 2-2'- and 2-4'-bipyridines. In the case of pyrrole, the molecular transformation products are indole and carbazole. Molecular transformation products identified in the case of thiophene are benzothiophene and bithiophene.