It was reported by Tilak et al.\textsuperscript{1} that 1-(3'-methoxyphenyl)-2-phenylazetidine 1 appeared to be quite stable but it rearranged partially to 7-methoxy-2-phenyl-1,2,3,4-tetrahydroquinoline 2 when its solution in n-hexane was exposed to sunlight. 1-(3'-Methoxyphenyl)-2-phenylazetidine 1 also changes to 7-methoxy-2-phenyl-1,2,3,4-tetrahydroquinoline 2 on prolonged heating (Chart 1).

1-(3'-Methoxyphenyl)-2,4-dimethylazetidine 3 on irradiation with unfiltered ultraviolet light emitted by 125 watt mercury vapour lamp yielded 7-methoxy-2,4-dimethyl-1,2,3,4-tetrahydroquinoline 4. On pyrolysis at 290\textdegree under nitrogen and by treatment with 70\% sulphuric acid, 3 also gave 4 (This work was recently published\textsuperscript{2}) (Chart 2).

In Chapter IV we have described a stereoselective synthesis of cis-1-(3'-methoxyphenyl)-2-methyl-4-phenylazetidine 5 and trans-1-(3'-methoxyphenyl)-2-methyl-4-phenylazetidine 6. These compounds on exposure to ultraviolet light, or treatment with 70\% sulphuric acid or pyrolysis at 290\textdegree gave 2,4-disubstituted-1,2,3,4-tetrahydroquinolines.

cis-1-(3'-Methoxyphenyl)-2-methyl-4-phenylazetidine 5 on irradiation with unfiltered ultraviolet light emitted by 125 Watt mercury vapour lamp yielded a mixture of cis-7-methoxy-4-methyl-2-phenyl-1,2,3,4-tetrahydroquinoline 7 (36\%), cis-7-methoxy-2-methyl-4-phenyl-1,2,3,4-tetrahydro-
CHART 1

CHART 2
quinoline 2 (27%) and trans-7-methoxy-2-methyl-4-phenyl-1,2,3,4-tetrahydroquinoline 10 (36%) (Chart 3). trans-1-(3'-Methoxyphenyl)-2-methyl-4-phenylazetidine 6, on irradiation with unfiltered ultraviolet light yielded a mixture of 7 (46%), 2 (27%) and 10 (27%).

cis-Azetidine 5, on pyrolysis at 290°C, under nitrogen atmosphere, gave a mixture of 7 (37%), 2 (25%) and 10 (37%). trans-Azetidine 6, on pyrolysis as above gave a mixture of 7 (40%), 2 (40%) and 10 (20%).

cis-Azetidine 5, on treatment with 70% sulphuric acid, gave only 7 (70% yield). trans-Azetidine 6, on treatment with 70% sulphuric acid, gave trans-7-methoxy-4-methyl-2-phenyl-1,2,3,4-tetrahydroquinoline 8 as the exclusive product (60% yield) (Chart 3 and 4).

The structure assignments for compounds 7, 8, 2 and 10 was based on a study of their PMR spectra and comparison with authentic samples [synthesis of these compounds is discussed in Chapter II-B].

Discussion of (a) Mechanism of Rearrangement of the Azetidines 5 and 6, (b) Mechanism of Sulphuric Acid Cyclodehydration of o-Arylaminocarbinols discussed in Chapter II-A.

In photolysis and pyrolysis, no preferential formation of products was observed. However, the products 2 and 10 in which N-C(phenyl) bond in azetidines 5 and 6 is broken, are formed
\[ \text{CHART-4} \]
in greater proportion. One would have expected a greater 
sterespecificity in the photolysis of 5 and 6, but this 
was not observed. Both the photolysis and pyrolysis reactions 
therefore do not appear to be concerted as the end products 
do not confirm to Woodward-Hoffmann rule. Thus according to 
Woodward-Hoffmann rule one would have expected the cis-
azetidine 5 to yield trans-tetrahydroquinolines on pyrolysis 
and conversely 5 should have led to cis-tetrahydroquinolines 
on photolysis [see discussion on page 122 of Chapter IV].

In the acid-catalysed ring expansion of 5 and 6 the 
\( \text{N} - \text{C} - \text{CH}_3 \) bond in 5 and 6 is preferentially broken and the 
relative stereochemistry of the phenyl and methyl groups in 
the azetidines is retained in the tetrahydroquinolines 7 and 8. 
This result appears surprising in view of the fact that 
carbonium ion formed on the scission of \( \text{N} - \text{C} - \text{CH}_3 \) bond (in a 
non-concerted sequence of reactions) is prone to attack from 
both the surfaces and one would have expected an equimolecular 
mixture of 7 and 8. It is also surprising that acid (\( \text{H}_2\text{SO}_4 \)) 
induced ring expansion of the azetidines 5 and 6 should not 
have yielded any of the tetrahydroquinolines 9 and 10 since 
a benzylic carbonium ion (A), may have been expected to be 
formed to a larger extent than the carbonium ion on a secondary 
carbon atom (B) (Chart 5). The exclusive formation of 7 from 5 
and 8 from 6 on sulphuric acid treatment is however interesting 
in view of the fact that it has been observed earlier in 
Chapter II-A that cyclodehydration of the carbinols 12 and 14
on treatment with sulphuric acid, also yielded only \( g \) (numbers for carbinols \( 12 \) and \( 14 \) and their precursors \( 11 \) and \( 13 \) from which they are derived by \( \text{NaBH}_4 \) reduction shown in the following Chart correspond to compounds \( 15 \) and \( 22 \) and to \( 11 \) and \( 21 \) respectively in Chapter II-A, Chart 2, page 35) (Chart 6).

From the above results it appears that cyclodehydration of \( 12 \) and \( 14 \) to \( g \) by treatment with 70% \( \text{H}_2\text{SO}_4 \) may be occurring through the intermediate formation of the trans azetidine \( 6 \). It is also interesting to note that the normally expected tetrahydroquinoline \( 9 \) and \( 10 \) are not formed when \( 12 \) and \( 14 \) are treated with sulphuric acid.

It is also conceivable that sulphuric acid induced conversion of the cis-azetidine \( 5 \) to \( 7 \) may be also taking place by intermediate formation of the carbinol \( 15 \) which then cyclizes to \( 7 \) (see Chapter II-A, page 35, Chart 2), (carbinol \( 15 \) is derived from the ketone \( 18 \) by \( \text{NaBH}_4 \) reduction. Compounds \( 15 \) and \( 16 \) shown below are same as compounds \( 13 \) and \( 18 \) shown in Chart 2, Chapter II-A) (Chart 7).

Conversely \( 15 \) may be getting converted to \( 7 \) through the intermediate involvement of the cis-azetidine \( 5 \).

The absence of the formation of \( g \) (compound \( 16 \) in Chapter III) in the sulphuric acid cyclodehydration of the carbinol \( 17 \) (derived from the ketone \( 18 \) by \( \text{NaBH}_4 \) reduction), (compounds \( 17 \) and \( 18 \) correspond to compounds \( 10 \) and \( 9 \) in
CHART 7

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CHART 8
Chart 2, Chapter II-A) and the carbinol $15$ appears somewhat surprising. Similarly the formation of rearranged tetrahydroquinolines $9$ and $10$ in the sulphuric acid cyclodehydration of $17$ is also difficult to explain since intermediate formation of azetidines $5$ and/or $6$ from $17$ cannot be invoked to explain these results. It has already been shown earlier that both the azetidines $5$ and $6$ on sulphuric acid treatment do not yield either $9$ or $10$ but give $7$ and $8$ respectively (Chart 8).

As of now, therefore, the formation of the rearranged tetrahydroquinolines $9$ and $10$ by sulphuric acid cyclodehydration of the carbinol $17$ is not explicable.
EXPERIMENTAL

Photolysis of 1-(3'-methoxyphenyl)-2,4-dimethylazetidine 3:

Azetidine 3 (0.5 g) was dissolved in cyclohexane (500 ml) and irradiated with unfiltered ultraviolet light emitted by 125 watt mercury vapour lamp for 3 hr. Solvent was evaporated and reaction product was distilled under vacuum to give 7-methoxy-2,4-dimethyl-1,2,3,4-tetrahydroquinoline 4 as yellow oil, b.p. 150°/2.13 x 10⁻² mm (0.31 g, yield 62%). (Found: C, 75.5; H, 8.9; N, 7.4. C₁₂H₁₇NO requires: C, 75.3; H, 8.9; N, 7.2%).

The compound 4 was characterised by its spectral analysis and identification with authentic sample.

Pyrolysis of 1-(3'-methoxyphenyl)-2,4-dimethylazetidine 3:

Azetidine 3 (0.5 g) was dissolved in decalin (500 ml) and pyrolysis was carried out at 290° under nitrogen atmosphere for 3 hr. Solvent was evaporated and reaction product was distilled under vacuum to give 7-methoxy-2,4-dimethyl-1,2,3,4-tetrahydroquinoline 4 as yellow oil, b.p. 150°/2.13 x 10⁻² mm, (0.25 g, yield 50%), (Found: C, 75.5; H, 8.7; N, 7.5. C₁₂H₁₇NO requires: C, 75.3; H, 8.9; N, 7.3%).

Compound 4 was characterised by its spectral analysis and identification with authentic sample.

Acid-catalysed rearrangement of 1-(3'-methoxyphenyl)-2,4-dimethylazetidine 3:

To a mixture of azetidine 3 (0.5 g) and crushed ice (5 g),
70% sulphuric acid (5 ml) was added gradually with shaking. This mixture was warmed on boiling water bath for thirty minutes. The mixture was kept at room temperature for 48 hr., neutralised with aqueous sodium hydroxide and then extracted with ether. The ether extract on work up gave an oil, which was distilled under vacuum to give 7-methoxy-2,4-dimethyl-1,2,3,4-tetrahydroquinoline 4 as yellow oil, b.p. 150°/2.13 x 10^{-2} mm (0.29 g, yield 58%), (Found: C, 75.0; H, 8.8; N, 7.4. C_{12}H_{17}NO requires: C, 75.3; H, 8.9; N, 7.3%).

Compound 4 was characterised by spectral analysis and identification with authentic sample.

**Photolysis of cis-1-(3'-methoxyphenyl)-2-methyl-4-phenylazetidine 5:**

Azetidine 5 (0.5 g) was dissolved in cyclohexane (500 ml) and irradiated with unfiltered ultraviolet light emitted by 125 Watt mercury vapour lamp for 3 hr. The work up as above gave pale yellow oil, b.p. 145°/9.56 x 10^{-3} mm (0.25 g, yield 50%), (Found: C, 81.3; H, 6.4; N, 5.6. C_{17}H_{17}NO requires: C, 81.2; H, 6.8; N, 5.6%), which was proved to be a mixture of 7, 9 and 10 in 36:27:36 ratio respectively as characterised by VPC analysis.

**Photolysis of trans-1-(3'-methoxyphenyl)-2-methyl-4-phenylazetidine 6:**

Azetidine 6 (0.5 g) was dissolved in cyclohexane (500 ml)
and irradiated with unfiltered ultraviolet light emitted by 125 Watt mercury vapour lamp for 3 hr. Solvent was evaporated and work up as above gave pale yellow oil, b.p. 140-45°/9.56 x 10^{-3} mm (0.21 g, yield 42%), (Found: C, 81.5; H, 6.5; N, 5.5. C_{17}H_{17}NO requires: C, 81.2; H, 6.8; N, 5.6%), which was proved to be a mixture of 7, 9 and 10 in 46:27:27 ratio respectively as characterised by VPC analysis.

Pyrolysis of cis-1(3'-methoxyphenyl)-2-methyl-4-phenylazetidine 5:

Azetidine 5 (0.5 g) was dissolved in decalin (500 ml) and pyrolysed at 290° under nitrogen atmosphere for 3 hr. Solvent was evaporated and work up as above gave pale yellow oil, b.p. 140°/9.56 x 10^{-3} mm (0.23 g, yield 46%), (Found: C, 81.5; H, 7.0; N, 5.8. C_{17}H_{17}NO requires: C, 81.2; H, 6.8; N, 5.6%), which was proved to be a mixture of 7, 9, 10 in 37:26:37 ratio respectively as characterised by VPC analysis.

Pyrolysis of trans-1-(3'-methoxyphenyl)-2-methyl-4-phenylazetidine 6:

Azetidine 6 (0.5 g) was dissolved in decalin (500 ml) and pyrolysis was carried out at 230° under nitrogen atmosphere for 3 hr. The solvent was evaporated and work up as above gave pale yellow oil, b.p. 145°/9.56 x 10^{-3} mm (0.25 g, yield 50%), (Found: C, 81.5; H, 6.7; N, 5.4. C_{17}H_{17}NO requires: C, 81.2; H, 6.8; N, 5.6%), which was proved to be a mixture of 7, 9, 10 in 40:40:20 ratio respectively as characterised by VPC analysis.
Acid-catalysed rearrangement of cis-1-(3'-methoxyphenyl)-2-methyl-4-phenylazetidine 5:

To a mixture of azetidine 5 (0.5 g) and crushed ice (5 g), 70% sulphuric acid (5 ml) was added gradually and on work up as above gave 7 as colourless needles crystallised from methanol, m.p. 92° (0.35 g, yield 70%), (Found: C, 81.5; H, 7.1; N, 5.5. C_{17}H_{17}NO requires: C, 81.2; H, 6.8; N, 5.6%) which was characterised by its spectral analysis and comparison with authentic sample.

Acid-catalysed rearrangement of trans-1-(3'-methoxyphenyl)-2-methyl-4-phenylazetidine 6:

To a mixture of azetidine 6 (0.5 g) and crushed ice (5 g), 70% sulphuric acid (5 ml) was added gradually and on work up as above gave 8 as colourless oil, b.p. 100°/9.56 x 10^{-2} mm (0.30 g), (yield 60%), (Found: C, 81.4; H, 7.1; N, 6.0. C_{17}H_{17}NO requires: C, 81.2; H, 6.8; N, 5.6%) which was characterised by its spectral analysis and comparison with authentic sample.
REFERENCES


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