2.1. Synthesis of 2-aryl-trans-decahydroquinolin-4-ones & -4-ols

In the preparation of titled compounds (both ketones and alcohols), hexane, toluene, and ethylacetate were used for recrystallization in most cases. Anhydrous sodium sulphate was used for drying ethereal solutions. In chromatography techniques silica gel (100-200 mesh) supplied by MERCK, petroleum ether, and sodium sulphate by Sd’s fine-chem Limited were used. All the melting points were uncorrected.

2.1.1. Preparation of substituted 2-aryl-trans-decahydroquinolin-4-ones

The preparation of the compounds was carried out by taking cyclohexene as starting material. The cyclohexene is first acetylated and then treated with corresponding aldehydes and ammonium acetate.

1-Acetylcyclohexene: To polyphosphoric acid (PPA) prepared from 70 g of $\text{P}_2\text{O}_5$ and 30 mL phosphoric acid held at 55-60 °C (bath temperature) cyclohexene (8.2 g 0.1 mole) and acetic acid (6.6 g, 0.11 mole) was added all at once. The reaction mixture was efficiently stirred and heated at this temperature for about 45 minutes. The dark-brown red product was worked up by pouring the material on ice-water (yield 400 mL). After decomposition of the complex, the mixture was further diluted to a total volume of about 500 mL and ammonium sulphate (200g) added and dissolved. The mixture was extracted with hexane (40 mL×5), washed with brine (40 mL×2) and dried over anhydrous sodium sulphate. The solvent was removed and the residue fractionated to furnish 4.45g (yield 50%) of acetyl cyclohexene, b.p. 80-83°/12 mm. The compound was characterized by its spectral data.

2-Phenyl-trans-decahydroquinolin-4-one: This was prepared by modification of the general method of preparation of aryl-piperidin-4-ones developed by Baliah et al1-5. 1-Acetyl-cyclohexene (12.4 g; 0.12 mole), benzaldehyde (10.6 g; 0.1 mole), dry ammonium acetate (9.5 g; 0.12 mole) and ethanol (20 mL) were mixed together and catalytic amount of piperidine was added, and the mixture was refluxed for about 2h, cooled and ether (200 mL) was added followed by addition of concentrated hydrochloric acid (20 mL). The mixture was stirred well and allowed to stand for
some time. The precipitated hydrochloride was filtered off and washed with a mixture of ethanol and ether (1:5) to remove colored impurities. The base was liberated by suspending the hydrochloride in acetone and adding strong ammonia till the hydrochloride was dissolved. Further dilution with water afforded the free base. The yield was 6.0 g (20%). The product was recrystallized with mixture of toluene and hexane. The recrystallized sample was melted\(^6\) at 98-99°C and further confirmed by its spectral data.

**2-p-Tolyl-trans-decahydroquinolin-4-one**: This was prepared by refluxing a mixture of 1-acetylcyclohexene (12.4 g; 0.1 mole), \(p\)-tolualdehyde (12.0 g; 0.1 mole), ammonium acetate (9.5 g, 0.12 mole) and alcohol (20 mL) in presence of a few drops of piperidine for about 2.0 hrs. The mixture was then worked up as described above when the corresponding decahydroquinolin-4-one was obtained in 25% yield. After recrystallization from mixture of toluene and hexane; the compound was melted\(^6\) at 96-97 °C and was also confirmed by its spectral data.

**2-p-Methoxyphenyl-trans-decahydroquinolin-4-one**: This was prepared by refluxing a mixture of 1-acetylcyclohexene (12.4 g; 0.1 mole) anisaldehyde (13.6 g; 0.1 mole) ammonium acetate (9.5 g; 0.12 mole) and alcohol (20 mL) in presence of a few drops of piperidine for about 30 min. The product was worked up as usual, when 12% yield of the crude ketone was obtained. This when recrystallized from mixture of toluene and hexane melted at 99-100°C. Baliah and Natarajan reported\(^6\) the 98-99 °C and further confirmed by its spectral data.

**2-o-Chlorophenyl-trans-decahydroquinolin-4-one**: The mixture of 1-acetylcyclohexene (12.4 g); 0.1 mole), \(o\)-chlorobenzaldehyde (12.0 g; 0.1 mole) ammonium acetate (9.5 g; 0.12 mole) alcohol (25 mL) and a few drops of piperidine was refluxed for about 3 hrs and worked out as usual. The yield of the crude ketone was 15%. Recrystallization from mixture of toluene and hexane afforded the pure compound melting at 85-86°C. Baliah and Natarajan\(^6\) reported m.p. of 84-85°C and further confirmed by its spectral data.
1-Propanoylcyclohexene: This was prepared by a method analogous to that used for the preparation of 1-acetylcyclohexene. To PPA (from 70.0 g of P₂O₅ and 30.0 mL of phosphoric acid) held at 55-60 °C (bath temperature) cyclohexene (8.2 g; 0.1 mole) and propanoic acid (8.2 g; 0.11 mole) were introduced all at once. The reaction mixture was efficiently stirred and heated at this temperature for about 45 min. The dark reddish brown product was poured into ice-water. After decomposition of the complex, the mixture was further diluted and ammonium sulphate was added and dissolved. The mixture was extracted with petroleum ether for several times. The combined extract was washed with a solution of sodium carbonate and then with water. After drying with anhydrous sodium sulphate, the solvent was removed and the residue was fractionated under reduced pressure to furnish 6.8 g of (about 50%) 1-propanoylcyclohexene, b.p. 85-88 °C/10 mm. The ketone was further characterized by its spectral data.

3-Methyl-2-phenyl-trans-decahydroquinolin-4-one: A mixture of 1-propanoylcyclohexene (13.6 g; 0.1 mole), benzaldehyde (10.6 g; 0.1 mole), ammonium acetate (9.5 g; 0.12 mole) alcohol (25 mL) and a few drops of piperidine was refluxed for about 3 hrs. The mixture was cooled and ether (200 mL) was added followed by concentrated hydrochloric acid (20 mL). The mixture was stirred well and kept aside for few hours. The precipitated hydrochloride was filtered off and washed with a mixture of ethanol-ether (1:5). The base was regenerated by adding ammonia solution to the suspension of hydrochloride in acetone, until it completely dissolved. On dilution with water, the base got separated. The yield was 20%. Recrystallization from mixture of toluene-hexane gave the pure compound melting at 131-132 °C and further confirmed by its ¹H NMR & Mass spectral data.

3-Methyl-2-p-tolyl-trans-decahydroquinolin-4-one: 1-Propanoylcyclohexene (13.6 g; 0.1 moles), p-tolualdehyde (12.0 g; 0.1 mole), ammonium acetate (9.5 g; 0.12 mole), alcohol (25 mL) and a few drops of piperidine were refluxed for 3 hrs. The mixture was then worked up as described above. The yield of the crude ketone was 25%. After recrystallization from mixture of toluene and hexane, it melted at 121-122 °C. Baliah and Natarajan reported the same m.p.
3-Methyl-2-\(p\)-chlorophenyl-trans-decahydroquinolin-4-one: A mixture of 1-propanoyl-cyclohexene (13.6 g; 0.1 mole), \(p\)-chlorobenzaldehyde (14.0 g; 0.12 mole), ammonium acetate (9.5 g; 0.12 mole) alcohol (25 mL) and a few drops of piperidine was refluxed for about 3-4 hours and the resulting mixture was worked up as usual. The crude ketone was obtained in 15% yield. When recrystallized from mixture of toluene and hexane, the compound melted at 105-106 °C and was similar to the value reported by Baliah and Natarajan\(^6\) (104-105°C) and further confirmed by its spectral data.

3-Methyl-2-\(p\)-methoxyphenyl-trans-decahydroquinolin-4-one: This compound got separated in the form of crystals when a mixture of 1-propanoylcyclohexene (13.6 g; 0.1 mole), anisaldehyde (13.6g; 0.1 mole) ammonium acetate (9.5 g; 0.12 mole) and alcohol (25 mL) was refluxed for about 2 hours in presence of few drops of piperidine and then allowed to cool. Ether (200 mL) was added and the mixture was kept at room temperature for a few hours until the separation of crystals was complete. The solid was then filtered off and washed with ether. The yield of the ketone was 20%. After recrystallization from benzene, it was melted at 156-157°C and was similar to the value reported by Baliah and Natarajan\(^6\) (155-156°C).

1-Methyl-2-phenyl-trans-decahydroquinolin-4-one:
This was prepared by the N-methylation of 2-phenyl-trans-decahydroquinolin-4-one. A mixture of 2-phenyl-trans-decahydroquinolin-4-one (5 g; 0.02 mole) formic acid (5 mL) and formaldehyde solution (40%, 6 mL) was allowed to stand at room temperature for about 15 days. The mixture was then poured into ice-water and made distinctly ammonical. The N-methyl derivative separated as a semi-solid mass. It was extracted with ether. The ether extract was dried and the hydrochloride of the base was liberated by adding concentrated hydrochloric acid (2 mL). The hydrochloride was filtered off, washed and recrystallized from a mixture of ethanol- ether (1:1) and gave a yield of 50%. It melted at 192-193°C (decamp). The pure hydrochloride was suspended in acetone, and liquor ammonia was added until the hydrochloride completely went into solution. On dilution with ice-water, a semi-solid was obtained which solidified on standing for a few days. Attempts for complete purification of this
N-methyl derivative by recrystallization were not successful. However the product was directly used for reduction and further confirmed by its spectral data.

**1,3-Dimethyl-2-phenyl-trans-decahydroquinolin-4-one:** A mixture of 3-methyl-2-phenyl-trans-decahydroquinolin-4-one (5 g; 0.02 moles), formic acid (5 mL) and formaldehyde solution (40%, 6 mL) was heated on a water bath for about 8 hrs. The mixture was poured into ice-water, and made distinctly ammonical with liquor ammonia. The N-methyl derivative separated as a solid. It was filtered off, washed and dried. The yield was 90%. It was recrystallized from few drops of toluene in hexane. The melting point of pure sample was obtained at 98-99°C and was similar to the value reported by Baliah and Natarajan⁷.

**2.2. Stereochemistry of reduction of 2-aryl-trans-decahydroquinolin-4-ones.**

Generally the reduction of cyclohexanone system can take place by the attack of the reducing agent on the carbonyl-carbon giving rise to two possible epimeric products namely axial and equatorial basing the attacking mode. When the equatorial alcohol is the predominant product, product development control is said to be operating. If it is assumed that the attacking reagent is attacking on the carbonyl group of decalin ring as shown in Fig. 1, i.e. by mode a and b, two products are obtained. The former mode leads to the more stable equatorial alcohol (α-form). On the other hand, in the present quinolin-4-one compounds the attack from the less hindered mode i.e. on face ‘b’ produces the less stable axial alcohol (β-form). When the axial alcohol is the predominant product in a reduction, steric approach control is said to be the predominant factor in deciding the stereochemistry of the product.

![Fig. 1](image-url)
In the present investigation the above synthesized 2-aryl-*trans*-decahydroquinoxolin-4-ones were reduced to their corresponding epimeric alcohols by the following chemical methods.

1. Reduction with sodium n-butanol
2. Meerwien-Ponndorf-Verley (M.P.V.) method
3. Reduction with sodium borohydride
4. Water mediated reduction with sodium borohydride

The stereochemical course of all these methods of reduction have been well established, from the studies on steroids\(^8\), cyclohexanones\(^{10,11-14}\), and piperidin-4-ones\(^{15-17}\). Further the studies on the reduction of cyclohexanones\(^{10}\) and decalones\(^{18}\) with an alkali metal and a proton donor, it was observed that the equatorial alcohols were more predominant products. Similar results were also reported by Balasubramanian and Padma\(^{16}\) in the reduction of 2,6-diarylpiperidin-4-ones, where equatorial alcohol was the predominant product. Such reduction proceeds *via* a carbanion intermediate (Scheme 1).

\[
\begin{align*}
\text{C} = \text{O} &+ 2 \text{e}^- &\rightarrow &\text{C} &\text{O} &\rightarrow &\text{C} &\text{OH} \\
\text{(Scheme 1)}
\end{align*}
\]

The central carbon of the carbanion intermediate is tetrahedrally hybridized and the barrier to inversion of this asymmetric carbon is small. The preferred configuration of this carbanion is that which gives rise to the more stable alcohol, when protonated. Thus, the predominant formation of the more stable equatorial alcohol in this type of reduction can be explained.

### 2.2.1. Reduction with Na/n-butanol.

Some of the 2-aryl-*trans*-decahydroquinoxolin-4-ones were reduced by sodium and n-butanol and were chromatographed. Relevant data were given in Table 1. In all the cases, only one epimer could be isolated in pure form. Small amounts of lower melting mixtures were also designated as the \(\alpha\)-form. Since, high yields of this form
could be isolated, the $\alpha$-form may be considered to have the hydroxyl group in the equatorial position of the twin-chair form of the decahydroquinolin-4-ols. Sodium alcohol reduction of ketoquinolizidines\textsuperscript{19} and piperidin-4-ones\textsuperscript{17} also give predominant amounts of the more stable equatorial alcohol.

Table 1: Reduction of 2-aryl\text-\textit{trans}-decahydroquinolin-4-ones with sodium and $n$-butanol.

<table>
<thead>
<tr>
<th>No</th>
<th>Compound</th>
<th>Yield of the crude alcohol (%)</th>
<th>Recovery of the $\alpha$-form (%)</th>
<th>M.P. of the pure epimer ($\alpha$-form) (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>2-Phenyl-\textit{trans}-decahydroquinolin-4-one</td>
<td>78-80</td>
<td>75</td>
<td>99-100</td>
</tr>
<tr>
<td>2</td>
<td>2-\textit{p}-Tolyl-\textit{trans}-decahydroquinolin-4-one</td>
<td>75</td>
<td>70</td>
<td>136-137</td>
</tr>
<tr>
<td>3</td>
<td>2-\textit{o}-chlorophenyl-\textit{trans}-decahydroquinolin-4-one</td>
<td>64-66</td>
<td>65</td>
<td>138-139(a)</td>
</tr>
<tr>
<td>4</td>
<td>2-\textit{p}-Methoxyphenyl-\textit{trans}-decahydroquinolin-4-one</td>
<td>75</td>
<td>80</td>
<td>118-120</td>
</tr>
<tr>
<td>5</td>
<td>1-methyl-2-phenyl-\textit{trans}-decahydroquinolin-4-one</td>
<td>25</td>
<td>&lt;20</td>
<td>125-126</td>
</tr>
<tr>
<td>6</td>
<td>3-methyl-2-phenyl-\textit{trans}-decahydroquinolin-4-one</td>
<td>80</td>
<td>70</td>
<td>131-132\textsuperscript{(a)}</td>
</tr>
<tr>
<td>7</td>
<td>3-methyl-2-\textit{p}-tolyl-\textit{trans}-decahydroquinolin-4-one</td>
<td>75</td>
<td>75</td>
<td>123</td>
</tr>
<tr>
<td>8</td>
<td>3-methyl-2-\textit{p}-chlorophenyl-\textit{trans}-decahydroquinolin-4-one</td>
<td>73-75</td>
<td>65</td>
<td>125-27</td>
</tr>
<tr>
<td>9</td>
<td>3-Methyl-2-\textit{p}-methoxyphenyl-\textit{trans}-decahydroquinolin-4-one</td>
<td>80</td>
<td>80</td>
<td>124-125</td>
</tr>
<tr>
<td>10</td>
<td>1,3-Dimethyl-2-phenyl-\textit{trans}-decahydroquinolin-4-one</td>
<td>70</td>
<td>75</td>
<td>112-113\textsuperscript{(a)}</td>
</tr>
</tbody>
</table>

General method for the reduction of decahydroquinolin-4-ones with sodium n-butanol:

A solution of the decahydroquinolin-4-one (1 g) in n-butanol (80 mL) was just heated to boil. Heating was stopped and sodium (25-30 equivalents) was added in small pieces at such rate that the solution was kept refluxing. After the addition of sodium, heating was continued until sodium butoxide began to separate. Methanol was added cautiously to destroy any unreacted sodium and to dissolve the precipitate formed. After the addition of water, the organic layer was separated, washed with water and the major portion of butanol distilled off. The residue was taken up in ether and dried. The decahydroquinolin-4-ol was obtained as the hydrochloride from the ethereal solution by the addition of dry ether (5 mL), saturated with hydrogen chloride. The precipitated hydrochloride was collected and washed with ether. The free base was obtained by suspending the hydrochloride in acetone and adding strong ammonia till the solution became clear. From the acetone solution, the decahydroquinolin-4-ol was precipitated by dilution with a large amount of water. It was filtered off, washed with water, dried and purified by chromatography on silica gel (100-200 mesh).

Chromatographic separation of the mixture of isomeric decahydroquinolin-4-ols:

For 1 g of the crude mixture was dissolved in 2 g of Silica Gel and 50 g of Silica gel (100-200 mesh) was used as column bed. Elutions were carried out with hexane, hexane-toluene (4:6), toluene and toluene-ethyl acetate (8:2) in the order given. About five fractions were collected with each eluent. The solvent was removed on hot plate and the last traces were removed under reduced pressure. The melting point and the yield of each fraction were determined. The fractions melting at the same temperature were collected and further purified by crystallization from suitable solvent.

2-Phenyl-trans-decahydroquinolin-4-ol (α-form): Reduction of 2-phenyl-trans-decahydroquinolin-4-one (1 g) by the above method afforded a crude product of about 0.80 g melting at 95-98°C. This was chromatographed and elution with toluene-ethyl acetate (8:2) gave 0.57 g of the corresponding alcohol (α-form). This after recrystallization from mixture of toluene and hexane the compound melted at 99-100°C and was confirmed by its spectral data (Fig. 2).
2-p-Tolyl-trans-decahydroquinolin-4-ol (α-form): Reduction of 2-p-tolyl-trans-decahydro-quinolin-4-one (1 g) by the above method gave 0.75 g of a mixture of epimeric alcohols melting in the range of 135-138°C. Chromatography of this product gave on elution with toluene-ethyl acetate (8:2), 0.54 g of the corresponding decahydroquinolin-4-ol (α-form). Recrystallization of the product from mixture of toluene and hexane gave pure crystals melting at 136-137°C. Baliah and Natarajan\textsuperscript{20} reported the same m.p. and further confirmed by its spectral data.

2-o-Chlorophenyl-trans-decahydroquinolin-4-ol (α-form): Reduction of 2-o-Chlorophenyl-trans-decahydroquinolin-4-one (1 g) by the above method gave about 0.65 g of the crude product melting in the range of 121-130°C. This was chromatographed and elution with benzene-ether (1:1) gave 0.42 g of the OH equatorially oriented alcohol (α-form). This on recrystallization from mixture of toluene and hexane gave pure crystals melting 137-138°C. Satyanarayana\textsuperscript{21,22} reported almost the same m.p. and further confirmed by its spectral data.

2-p-Methoxyphenyl-trans-decahydroquinolin-4-ol (α-form): Reduction of the corresponding ketones (1 g) by the above method afforded 0.75 g of the crude product melting in the range of 112-118°C. Chromatography of the product on elution with toluene-ethyl acetate (8:2) gave about 0.61 g of the corresponding alcohol (α-form). Recrystallization from mixture of toluene and hexane gave pure compound melting at 119-120°C. Satyanarayana\textsuperscript{21,22} was reported the same m.p. and further confirmed by its spectral data.

3-Methyl-2-phenyl-trans-decahydroquinolin-4-ol (α-form): Reduction of the corresponding ketone (1 g) by the above method gave a yield of about 0.81 g melting in the range of 127-130°C. This was chromatographed and on elution with benzene-ether (1:1) gave 0.57 g of OH-equatorially oriented alcohol (α-form). Recrystallization of the product from mixture of toluene and hexane gave needles melting at 130-131°C. Baliah and Natarajan reported\textsuperscript{20} the same m.p. and further confirmed by its spectral data\textsuperscript{22}. (Fig. 3)
3-Methyl-2-p-tolyl-trans-decahydroquinolin-4-ol (α-form): Reduction of the corresponding ketone (1g) by the above method gave about 0.75g of the crude melting in the range of 118-122°C. Chromatography of the product on elution with benzene-ether (1:1) gave about 0.55g of the OH-equatorially oriented alcohol (α-form). This on recrystallization with few drops of toluene in hexane gave pure crystals melting at 123-124°C. Satyanarayana\textsuperscript{21,22} was reported the same m.p. and further confirmed by its spectral data.

3-Methyl-2-p-chlorophenyl-trans-decahydroquinolin-4-ol (α-form): Reduction of the corresponding ketone (1.0 g) by the above method gave about 0.77g of the crude alcohol and it melted in the range of 100-105 °C. This was chromatographed on silica gel (100-200 mesh) and on elution with toluene-ethylacetate (8:2) gave about 0.49 g of the corresponding decahydroquinolin-4-ol (α-form). This on recrystallization from few drops of toluene in hexane gave pure crystals melting at 126-127 °C. Satyanarayana\textsuperscript{21,22} was reported the same m.p. and further confirmed by its spectral data.

3-Methyl-2-p-methoxyphenyl-trans-decahydroquinolin-4-ol (α-form): Reduction of the corresponding ketone (1 g) by the above method gave about 0.8 g of the crude product melting in the range of 116-120 °C. It is chromatographed and on elution with toluene-ethylacetate (8:2) gave 0.65 g OH-equatorially oriented alcohol (α-form). This on recrystallization from few drops of toluene in hexane gave pure compound melting at 123-124°C. Satyanarayana\textsuperscript{21,22} was reported the same m.p. and further confirmed by its spectral data.

1,3-Dimethyl-2-phenyl-trans-decahydroquinolin-4-ol (α-form): Reduction of 1,3-Dimethyl-2-phenyl-trans-decahydroquinolin-4-one (1.0 g) by the above method gave 0.71 g of the crude alcohol melting in the range of 105-110°C. This was chromatographed on silica gel (100-200 mesh) column and on elution with benzene-ether (1:1) gave 0.53 g of the corresponding decahydroquinolin-4-ol(α-form). Recrystallization of the product from few drops of toluene in hexane gave pure crystals melting at 112-113°C. Balaiah and Natarajan\textsuperscript{20} report the same m.p. and further confirmed by its spectral data\textsuperscript{22}. (Fig. 4).
2.2.2. Reduction by Meerwien-Ponndorf-Verley (M.P.V.) method.

The M.P.V. method of reduction leads to the predominant formation of the less stable axial alcohol\cite{23,24}. For highly hindered ketones the axial alcohol may be the only product formed. Two different mechanisms have been suggested for the M.P.V. reduction\cite{25}. According to one mechanism, the reaction proceeds via cyclic transition state\cite{23,25,26}, made up one molecule of the ketone and one molecule of the reducing agent, with one of the carbinol-hydrogen migrating as a hydride to the carbonyl carbon of the ketone\cite{27,28} as shown in (Scheme 2).

\[
\begin{align*}
\text{R}_1\text{C} & \equiv \text{O} \\
+ & \text{Al(OP_i}r\text{)_3} \\
\text{H}_3\text{C} & \equiv \text{O} \\
+ & \text{H}_3\text{C} \equiv \text{O}
\end{align*}
\]

(Scheme 2)

In an alternate mechanism, one molecule of aluminium isopropoxide gets coordinated to carbinol-oxygen, while from another molecule of the reagent, carbinol-hydrogen migrates as hydride to carbinol-carbon (Fig. 5)\cite{25,27}.

\[
\begin{align*}
\text{R}_1\text{C} & \equiv \text{O} \\
\text{H}_3\text{C} & \equiv \text{O}
\end{align*}
\]

Fig. 5

Both the mechanisms are in agreement with the finding that the hydrogen transferred to the carbonyl-carbon comes from the carbinol-carbon on the basis of deuterium tracer studies\cite{27,29}. The predominant formation of the less stable axial...
alcohol can be explained as follows: the attack of the hydride from the axial side of the carbonyl group is more hindered, compared to attack from the equatorial side. The latter mode will thus be preferred on steric grounds and this leads to the predominant formation of the less stable axial alcohol.

Some of the 2-aryl-trans-decahydroquinolin-4-ones were reduced by the M.P.V. method and products were purified by chromatography on silica gel (100-200 mesh) and then by recrystallization from a suitable solvent. The relevant data are given in Table 2.

Table 2: Reduction of 2-aryl-trans-decahydroquinolin-4-ones by the M.P.V. Method.

<table>
<thead>
<tr>
<th>No</th>
<th>Compound Name</th>
<th>Yield of the crude alcohol (%)</th>
<th>Recovery of the β-form (%)</th>
<th>M.P. of the pure epimer (β-form) (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>2-Phenyl-trans-decahydroquinolin-4-one</td>
<td>75-80</td>
<td>75</td>
<td>178-179</td>
</tr>
<tr>
<td>2</td>
<td>2-p-Tolyl-trans-decahydroquinolin-4-one</td>
<td>80-85</td>
<td>75</td>
<td>208-09(1)</td>
</tr>
<tr>
<td>3</td>
<td>2-o-chlorophenyl -trans-decahydroquinolin-4-one</td>
<td>68-70</td>
<td>70</td>
<td>103-104</td>
</tr>
<tr>
<td>4</td>
<td>2-p-Methoxyphenyl-trans-decahydroquinolin-4-one</td>
<td>80</td>
<td>75</td>
<td>180-181</td>
</tr>
<tr>
<td>5</td>
<td>1-methyl-2-phenyl-trans-decahydroquinolin-4-one</td>
<td>70</td>
<td>60</td>
<td>162-163</td>
</tr>
<tr>
<td>6</td>
<td>3-methyl-2-phenyl-trans-decahydroquinolin-4-one</td>
<td>75</td>
<td>85</td>
<td>154-155(1)</td>
</tr>
<tr>
<td>7</td>
<td>3-methyl-2-p-tolyl-trans-decahydroquinolin-4-one</td>
<td>80</td>
<td>80</td>
<td>145-146</td>
</tr>
<tr>
<td>8</td>
<td>3-methyl-2-p-chlorophenyl-trans-decahydroquinolin-4-one</td>
<td>70</td>
<td>80</td>
<td>173-74</td>
</tr>
<tr>
<td>9</td>
<td>3-Methyl-2-p-methoxyphenyl-trans-decahydroquinolin-4-one</td>
<td>80-82</td>
<td>80</td>
<td>158-59</td>
</tr>
<tr>
<td>10</td>
<td>1,3-Dimethyl-2-phenyl-trans-decahydroquinolin-4-one</td>
<td>70-73</td>
<td>90</td>
<td>92-93(1)</td>
</tr>
</tbody>
</table>


In the M.P.V. reduction of the above ketones, only one epimer could be isolated. This was found to be different from the epimers obtained on reduction of the ketones with sodium n-butanol and was designated as the β-form. Small amounts of
low-melting mixture were also obtained. Since the M.P.V. reduction leads to the predominant formation of the less stable axial epimer, especially with hindered ketones of this type studied, the β-forms of the decahydroquinolin-4-ols obtained may be considered to have the hydroxyl group in the axial position. Balasubramanian and Padma\textsuperscript{17} from similar studies on piperidin-4-ones got predominant yields of the β-form (axial hydroxy) of piperidin-4-ols.

As seen from the Table 2, a methyl group at C-3 (that is α to the carbonyl carbon) increases the relative proportion of the β-form obtained on reduction, but still some amount of the α-form is also obtained.

<table>
<thead>
<tr>
<th>No</th>
<th>Compound reduced</th>
<th>Yield of the crude mixture of epimeric alcohols (%)</th>
<th>Recovery of α-form (%)</th>
<th>Recovery of β-form (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>2,6-Diphenylpiperidin-4-one</td>
<td>80</td>
<td>29</td>
<td>53</td>
</tr>
<tr>
<td>2</td>
<td>3-methyl-2,6-diphenyl-piperidi-4-one</td>
<td>83</td>
<td>22</td>
<td>57</td>
</tr>
<tr>
<td>3</td>
<td>3,5-dimethyl-2,6-diphenyl-piperidin-4-one</td>
<td>82</td>
<td>-</td>
<td>73</td>
</tr>
<tr>
<td>4</td>
<td>1,3,5-trimethyl-2,6-diphenyl-piperidin-4-one</td>
<td>87</td>
<td>16</td>
<td>74</td>
</tr>
</tbody>
</table>

The 2-phenyl and 2-aryl-\textit{trans}-decahydroquinolin-4-ones 1 and 2 (Table 2) which may be considered to be sterically analogous to 3-methyl-2,6-diphenylpiperidin-4-ones, gave exclusively the β-form. This may be due to the presence of additional \textit{syn}-axial hydrogen in the decahydroquinoline system, which further decreases the probability of an axial approach of the hydride to the carbonyl-carbon. In the case of 3,5-dimethyl-2,6-diphenylpiperidin-4-one and its N-methyl derivative (entries 3 and 4 Table 3), the reduction leads to the formation of the β-form almost exclusively, just as in the analogous 3-methyl-2-phenyl-\textit{trans}-decahydroquinolin-4-ones and its N-methyl derivative (entries 6 to 10, Table 2).
General procedure for the reduction decahydroquinolin-4-ones with the Meerwien-Ponndorf-Verley (M.P.V) method: Clean, dry aluminum wire (2.2 g; 0.08 mole) cut into small pieces was added to anhydrous isopropyl alcohol (80 mL) contained in a 500 mL flask fitted with a reflux condenser. A calcium chloride guard tube was fitted at the top of the condenser. Mercuric chloride (0.2 g) was added and the mixture was heated on a steam bath. When the liquid was boiling, dry carbon tetrachloride (1 mL) was added down the condenser and heating was continued. In a few minutes, a vigorous hydrogen began and the evolution mixture turned black. It was necessary to discontinue heating to moderate the reaction. After the reaction had slackened, refluxing was resumed and continued until all the aluminium had dissolved (about 8 hrs). The resulting solution of aluminium isopropoxide in isopropyl alcohol was used directly for the reduction.

The decahydroquinolin-4-one (0.02 mole) in isopropyl alcohol (40 mL) was added to the solution of aluminium isopropoxide in isopropyl alcohol-water was drained off the condenser. The guard-tube was removed and splash-head was fitted and a second condenser was fitted to the splash-head for downward distillation. The uncooled upright condenser served as a partial fractionating column. A boiling chip was added and the solution was refluxed on a stream-bath (30-40 minutes) at such a rate that 5-10 drops of the distillate were collected per minute. Water was then circulated through the upright condenser and the total reflux was maintained for ten minutes. The water was again drained off the reflux condenser and the first five drops of the distillate were collected and tested for acetone. Sufficient amount of dry isopropyl alcohol was added to the flask to maintain the volume. If the test for acetone was positive, the refluxing, distilling and testing operations were repeated till the test was negative. After a negative test (1 to 1.5 hrs), most of the excess isopropyl alcohol was removed by distillation under slight reduced pressure. The cooled residue was hydrolyzed with ice-cold water containing sodium hydroxide (50 g). After allowing to stand for an hour, the mixture was extracted with benzene several times; the benzene extract was washed with water and dried. On removal of the solvent, the crude product of reduction was obtained as solid. The crude product was subjected to chromatography.
2-Phenyl-trans-decahydroquinolin-4-ol (β-form): This was prepared by the reduction of 2-Phenyl-trans-decahydroquinolin-4-one (5 g) by the above method. The yield of the crude product melting in the range 172-176 °C was about 3.8 g. It was chromatographed on silica gel (100-200 mesh) column and on elution with toluene-hexane (8:2) mixture, afforded about 2.9 g of the corresponding decahydroquinolin-4-ol (β-form). Recrystallization from benzene gave pure crystals of the compound melting at 177-178 °C. Baliah and Natarajan report the same m.p. and further confirmed by its spectral data (Fig. 6).

2-p-Tolyl-trans-decahydroquinolin-4-ol (β-form): This was prepared by the reduction of 2-p-tolyl-trans-decahydroquinolin-4-one (5 g) by the above method. The yield of the crude product melting in the range 205-207 °C was about 4.2 g. Chromatography of the product gave on elution with toluene gave about 3.1 g the corresponding alcohol (β-form). Recrystallization in few drops of toluene in hexane gave pure crystals melting at 208-09°C. Baliah and Natarajan report the same m.p. 207-208 and further confirmed by its spectral data.

2-o-Chlorophenyl-trans-decahydroquinolin-4-ol (β-form): Reduction of 2-o-chloro-phenyl-trans-decahydroquinolin-4-one (5 g) by the above method gave about 3.4 g of the crude product melting in the range 96-100 °C. Chromatography of the product gave on elution with toluene 2.4g of the corresponding decahydroquinolin-4-ol (β-form). Recrystallization from toluene in hexane yielded 2.0g of the pure compound melting at 103-104°C and further confirmed by its spectral data.

2-p-Methoxy-phenyl-trans-decahydroquinolin-4-ol (β-form): Reduction of 2-p-methoxy-phenyl-trans-decahydroquinolin-4-one (5 g) by the above method yielded crude product (4.0g) melting in the range 165-175 °C. Chromatography of the product gave on elution with toluene 2.5g of the corresponding decahydroquinolin-4-ol (β-form). Recrystallization of the product from few drops of toluene in hexane gave pure crystals of the compound melting at 181-182 °C and further confirmed by its spectral data.
1-Methyl-2-phenyl-trans-decahydroquinolin-4-ol (β-form): 1-methyl-2-phenyl-trans-deca-hydroquinolin-4-one (5 g) by the above M.P.V. reduction method gave about 3.5 g of the crude product melting in the range 125-135 °C. Chromatography of the product on elution with toluene gave about 2.0 g of the 1-methyl-2-phenyl-trans-decahydroquinolin-4-ol, (β-form). Recrystallization of the same from toluene in hexane gave pure compound melting at 164-165°C and further confirmed by its spectral data.

3-Methyl-2-phenyl-trans-decahydroquinolin-4-ol (β-form): Reduction of the corresponding ketone (5.0 g) by the above method gave 3.5 g of the crude product melting in the range of 149-152 °C. Chromatography of the product on elution with toluene afforded about 3.0 g of the OH-axially oriented alcohol (β-form). Recrystallization from toluene-hexane gave pure crystals of the compound melting at 154-155 °C. Baliah and Natarajan report the same m.p. and further confirmed by its spectral data (Fig.7)

3-Methyl-2-p-tolyl-trans-decahydroquinolin-4-ol (β-form): This was prepared by the M.P.V. reduction of 3-methyl-2-phenyl-trans-decahydroquinolin-4-one (5.0 g). About 4.0g of crude product melting in the range 135-140°C was obtained. This was subjected to chromatography. On elution with hexane-toluene (6:4) mixture, about 3.2g of the corresponding decahydroquinolin-4-ol (β-form) was obtained. Recrystallization of this from in toluene containing hexane gave pure compound melting at 145-146°C and further confirmed by its spectral data.

3-Methyl-2-p-chlorophenyl-trans-decahydroquinolin-4-ol (β-form): Reduction of 3-methyl-2-p-chlorophenyl-trans-decahydroquinolin-4-one, (5.0 g) by the above method yielded a crude product (3.5 g) melting in the range 160-170°C. Chromatography of this product on elution with hexane-toluene mixture, about 2.8 g of the corresponding alcohol (β-form) was obtained. Recrystallization of this from few drops of toluene in hexane gave pure compound melting at 173-174 °C and further confirmed by its spectral data.
3-Methyl-2-p-methoxyphenyl-trans-decahydroquinolin-4-ol (β-form): 3-methyl-2-p-methoxyphenyl-trans-decahydroquinolin-4-one (5.0 g) was subjected to the reduction by the above method. About 4.1 g of the crude product melting in the range of 140-152°C was obtained. The product was chromatographed and on elution with toluene gave about 3.2 g of the corresponding OH-axially oriented alcohol (β-form). This product on recrystallization from few drops of toluene in hexane affords the pure compound melting at 158-159°C and further confirmed by its spectral data.

1,3-Dimethyl-2-phenyl-trans-decahydroquinolin-4-ol (β-form): Reduction of the corresponding ketone (5.0 g) by the above method afforded about 3.6 g of the crude alcohol melting in the range of 85-89°C. This was subjected to chromatography and on elution with hexane-toluene (6:4) about 2.6 g of the OH-axially oriented alcohol (β-form) was obtained. Recrystallization of the product from toluene-hexane gave pure compound melting at 92-93°C. Balaiah and Natarajan report the same m.p. and further confirmed by its spectral data. (Fig. 8)

2.2.3. Reduction with sodium borohydride
Stereochemistry of metal hydride reductions of cyclohexanones and steroidal ketones have been investigated. Stereochemical influence of a remote polar substituent on the Monson et al. The stereochemical course of metal hydride reductions is largely governed by product development control. Lithium aluminium hydride reductions of cyclic ketones which are unhindered give predominant yields of the more stable equatorial alcohols. But, if the ketones are hindered (example: if a methyl group is present the axial position at C-3) significant proportions of less stable axial isomer may also form. Reductions with sodium borohydride always yield larger proportions of the axial epimers (compared to reductions with lithium aluminium hydride). This can be explained by considering the modes of decomposition of the metal hydrides (Fig. 9).

\[ M_1^+ + M_2H_4^- \quad \text{I} \]
\[ M_1H + M_2H_3 \quad \text{II} \]

(Fig. 9)
The more ionic sodium borohydride decomposes more easily by route (I) than by route (II). With $M_2H_4^-$ ion, the attack on the carbonyl-carbon takes place more easily from the equatorial side as the attack from the axial side is sterically hindered. With $M_3H_3$, however, the preference for the equatorial attack is lesser. Thus sodium borohydride which dissociates preferentially by route (I) gives comparatively larger amounts of the axial alcohol.

The transition states for the two modes of attack of metal hydride ion on a cyclohexanone ring system can be represented as in (Fig. 10a and 10b).

Some of the 2-aryl-trans-decahydroquinolin-4-ones were reduced with sodium borohydride. The products were chromatographed on alumina and the epimers were separated and recrystallized from suitable solvent. The relevant data are given in Table 4.

The 2-aryl-trans-decahydroquinolin-4-ones, 1 to 4 (Table 4) gave high yields of one isomer on reduction. No other pure product could be isolated. Small amounts of lower-melting mixtures were also got in both the cases, in the initial fractions of chromatographic separations. The isomer which was obtained in high yields was identical with the $\alpha$-isomer obtained on sodium n-butanol reduction of the aryl-trans-decahydroquinolin-4-ones. Hence, it should have the hydroxy group in the stable equatorial position. When 1-methyl-2-phenyl-trans-decahydroquinolin4-one was subjected to sodium borohydride reduction, only one isomer was obtained on chromatographic separation and it was eluted in the earlier fraction and it was found to be identical with $\beta$-isomer obtained in the M.P.V. reduction of the corresponding
ketones. Small amounts of low melting mixture were also got from which no other pure product could be isolated. Hence, the isomer must have the hydroxy group in the axial position. However, the $\alpha$-form of the alcohol was not obtained either in sodium n-butanol reduction or sodium borohydride reduction. The exact reason could not be established.

Table 4: Reduction of 2-aryl-\textit{trans}-decahydroquinolin-4-ones with sodium borohydride.

<table>
<thead>
<tr>
<th>No.</th>
<th>Compound</th>
<th>Yield of the crude mixture of epimeric alcohols (%)</th>
<th>Epimers Recovered (%) Form</th>
<th>M.P. of the pure epimers (\°C) Forms</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>$\alpha$ $\beta$</td>
<td>$\alpha$ $\beta$</td>
</tr>
<tr>
<td>1</td>
<td>2-Phenyl-\textit{trans}-decahydroquinolin-4-one</td>
<td>75</td>
<td>65 10</td>
<td>97-98 178-179(a)</td>
</tr>
<tr>
<td>2</td>
<td>2-\textit{p}-Tolyl-\textit{trans}-decahydroquinolin-4-one</td>
<td>80</td>
<td>66 10</td>
<td>137-38 208-09(a)</td>
</tr>
<tr>
<td>3</td>
<td>2-\textit{o}-chlorophenyl-\textit{trans}-decahydroquinolin-4-one</td>
<td>65-70</td>
<td>60 05</td>
<td>138-39 104-05</td>
</tr>
<tr>
<td>4</td>
<td>2-\textit{p}-Methoxyphenyl-\textit{trans}-decahydroquinolin-4-one</td>
<td>75</td>
<td>70 10</td>
<td>118-19 181-182</td>
</tr>
<tr>
<td>5</td>
<td>1-Methyl-2-phenyl-\textit{trans}-decahydroquinolin-4-one</td>
<td>80</td>
<td>25 65</td>
<td>125-126 164-165</td>
</tr>
<tr>
<td>6</td>
<td>3-Methyl-2-phenyl-\textit{trans}-decahydroquinolin-4-one</td>
<td>75</td>
<td>40 40</td>
<td>130-31 153-154(a)</td>
</tr>
<tr>
<td>7</td>
<td>3-Methyl-2-\textit{p}-tolyl-\textit{trans}-decahydroquinolin-4-one</td>
<td>75</td>
<td>35 50</td>
<td>122-123 147-48</td>
</tr>
<tr>
<td>8</td>
<td>3-Methyl-2-\textit{p}-chlorophenyl-\textit{trans}-decahydroquinolin-4-one</td>
<td>68-70</td>
<td>35 45</td>
<td>126-27 173-74</td>
</tr>
<tr>
<td>9</td>
<td>3-Methyl-2-\textit{p}-methoxyphenyl-\textit{trans}-decahydroquinolin-4-one</td>
<td>75</td>
<td>35 50</td>
<td>123-24 158-59</td>
</tr>
<tr>
<td>10</td>
<td>1,3-Dimethyl-2-phenyl-\textit{trans}-decahydroquinolin-4-one</td>
<td>65</td>
<td>40 55</td>
<td>111-12 91-93(a)</td>
</tr>
</tbody>
</table>

The ketones 6 to 10 (Table 4) on reduction gave two isomers in approximately the same yields. The isomers which were eluted first were identical with the β-forms of the alcohols obtained on reduction of the corresponding ketones by M.P.V. method. Hence, these alcohols must have their hydroxy group in the axial position. The isomers which were eluted as second fraction identical with α-form of the alcohols obtained when the corresponding ketones were subjected to sodium n-butanol reduction. Hence, these isomers must have their hydroxyl group in the equatorial position. The order of elution also supports the conformations assigned to these alcohols. It has also been observed\(^\text{16,34}\) that the more hindered axial alcohol will be less strongly adsorbed and hence will be eluted first. The less hindered equatorial epimers which is strongly absorbed on alumina will be eluted as the second fraction.

The reason for the higher yields of the β-form in the sodium borohydride reduction of ketones from 5 to 10 can be explained if a distorted chair form is assumed for the heterocyclic ring. An equatorial methyl on the carbon adjacent to the carbonyl-carbon exerts more or less the same steric hindrance to axial or equatorial approach of the reducing agent in a perfect chair conformation. If the heterocyclic ring is slightly flattened at the carbonyl end, the axial approach of the reagent becomes more hindered when compared to equatorial approach, because of greater steric hindrance from the methyl group for the former mode. This leads to a comparatively larger proportion of the β-form. In 1, 3-dimethyl-2-phenyl-trans-decahydroquinolin-4-one, this type of flattening of the heterocyclic ring will be more pronounced, so that a significantly higher proportion of the β-form is obtained in the reduction.

Radhakrishnan et al\(^\text{15}\) observed similar increase in the proportion of the β-form in the lithium aluminium hydride reduction of 2, 6-diphenyl-4-piperidones when methyl groups are introduced in both 3 and 5 positions and also when the resulting piperidone was N-methylated.

**General procedure for the reduction of decahydroquinolin-4-ones with sodium borohydride:** To a solution of the ketone (2.0 g) in isopropyl alcohol (100 mL), powdered sodium borohydride (1-1.5 g) was added and the mixture was refluxed on a
steam bath for about 6-8 hours. After removing most of the solvent, the residue was treated with water. The mixture was acidified with acetic acid. After the evolution of hydrogen ceased, ammonia was added. The solid that separated was filtered off, dried and dissolved in benzene and then filtered, the solvent was removed and the residue was subjected to chromatography. The same chromatographic procedure as discussed earlier was adopted. The compounds eluted in earlier fraction were equivalent to those obtained in M.P.V. method (β-form). Later fractions contain β-forms which are equivalent to those obtained in the sodium n-butanol reduction.

2-Phenyl-trans-decahydroquinolin-4-ol (α- and β-form): Reduction of the corresponding ketone (2.0 g) by the above method yielded about 1.5 g of the mixture of epimeric alcohols. Chromatography of the product, on elution with toluene afforded about 0.2 g of the OH-axially oriented alcohol (β-form). Recrystallisation of the same from toluene gave pure crystals of the compound melting at 178-179°C. On further elution with ether gave about 1.0 g of the OH-equatorially oriented alcohol (α-form). This on recrystallization from few drops of toluene in hexane gave pure crystals melting at 97-98°C.

2-p-Tolyl-trans-decahydroquinolin-4-ol (α- and β-form): Reduction of the corresponding ketone (2.0 g) by the above method yielded about 1.6 g of the mixture of epimeric alcohols. Chromatography of the product on elution with toluene gave about 0.2 g of the OH-axially oriented alcohol (β-form). Recrystallization of the product from toluene in hexane afforded pure compound melting at 208-209 °C. On further elution with ether gave about 1.0 g of the OH-equatorially oriented epimer (α-form). This on recrystallization from few drops of toluene in hexane gave pure compound melting at 137-138 °C.

2-o-Chlorophenyl-trans-decahydroquinolin-4-ol (α- and β-form): Reduction of the corresponding ketone (2.0 g) by the above method yielded about 1.3 g of the mixture of epimeric alcohols. Chromatography of the product on elution with toluene gave about 0.1 g of the OH-axially oriented alcohol (β-form). Recrystallization of the product from toluene-hexane mixture afforded pure crystals of the compound melting at 104-105°C. On further elution with toluene-ethylacetate (8:2) gave about 0.9 g of
the OH-equatorially oriented alcohol (α-form) is obtained. This on recrystallization from toluene in hexane gave pure compound melting at 138-139 °C.

2-p-Methoxy-phenyl-trans-decahydroquinolin-4-ol (α- and β-form): Reduction of the corresponding ketone (2.0 g) by the above method yielded about 1.5 g of the crude product containing the epimeric alcohols. Chromatography of the product on elution with toluene gave about 0.2 g of the OH-axially oriented alcohol (β-form). Recrystallization of the product from toluene-hexane mixture afforded pure crystals of the compound melting at 181-182°C. On further elution with toluene-ethylacetate (8:2) gave about 1.0 g of the OH-equatorially oriented alcohol (α-form). This on recrystallization from toluene-hexane mixture ether gave pure compound melting at 118-119 °C.

1-Methyl-2-phenyl-trans-decahydroquinolin-4-ol (α- and β-form): reduction of 1-methyl-2-phenyl-trans-decahydroquinolin-4-one (2.0 g) by the above method gave about 1.6 g of the mixture of epimeric alcohols. Chromatography of the product on elution with toluene gave about 1.0 g of the OH-axially oriented alcohol (β-form) and remaining contains about 25% α-form. Recrystallization of the product from few drops of toluene in hexane gave pure compound melting at 164-165°C. On further elution with ether gave greasy like product, which could not be purified.

3-Methyl-2-phenyl-trans-decahydroquinolin-4-ol (α- and β-form): Reduction of the corresponding ketone (2.0 g) by the above method yielded about 1.5 g of the mixture of epimeric alcohols. Chromatography of the product, on elution with toluene afforded about 1.3 g of the OH-axially oriented alcohol (β-form). This on recrystallization from toluene-hexane mixture gave pure crystals of the compound melting at 153-154°C. On further elution with toluene-ethylacetate (8:2) afforded about 0.6 g of the OH-equatorially oriented alcohol (α-form). Recrystallization of the product from toluene-hexane mixture gave needle shaped compound melting at 130-131 °C.

3-Methyl-2-p-tolyl-trans-decahydroquinolin-4-ol (α- and β-form): Reduction of the corresponding ketone (2.0 g) by the above method yielded about 1.5 g of the crude
mixture of epimeric alcohols. Chromatography of the product on elution with toluene-ethylacetate (9:1) gave about 0.75 g of the OH-axially oriented alcohol (β-form). This on recrystallization from toluene in hexane afforded pure compound melting at 147-48°C. On further elution with toluene-ethylacetate (9:1) gave about 0.5 g of the OH-equatorially oriented alcohol (α-form). This on recrystallization from toluene in hexane gave pure compound melting at 122-123 °C.

3-Methyl-2-\textit{p}-chlorophenyl-\textit{trans}-decahydroquinolin-4-ol (α- and β-form): Reduction of the corresponding ketone (2.0 g) by the above method produced about 1.3 g of the mixture of epimeric alcohols. Chromatography of the product on elution with mixture of hexane-toluene gave about 0.6 g of the OH-axially oriented alcohol (β-form). This on recrystallization from toluene in hexane afforded pure compound melting at 173-174°C. On further elution with toluene-ethylacetate (9:1) gave about 0.5 g of the OH-equatorially oriented alcohol (α-form). Recrystallization of the product from few drops of toluene in hexane gave pure crystalline compound melting at 126-127 °C.

3-Methyl-2-\textit{p}-methoxyphenyl-\textit{trans}-decahydroquinolin-4-ol (α- and β-form): Reduction of the corresponding ketone (2.0 g) by the above method yielded about 1.5 g of the crude mixture of epimeric alcohols. Chromatography of the product on elution with toluene gave about 0.7 g of the OH-axially oriented epimer (β-form). On recrystallization from toluene in hexane afforded pure alcohol melting at 158-159°C. On further elution with toluene-ethylacetate (9:1) gave about 0.5 g of the OH-equatorially oriented alcohol (α-form). This on recrystallization from few drops of toluene in hexane gave pure compound melting at 123-124 °C.

1,3-Dimethyl-2-phenyl-\textit{trans}-decahydroquinolin-4-ol (α- and β-form): Reduction of the corresponding ketone (2.0 g) by the above method produced about 1.4 g of the mixture of epimeric alcohols. Chromatography of the crude product on elution with petroleum ether-benzene (1:1) gave about 0.66 g of the OH-axially oriented alcohol (β-form). This on recrystallization from mixture of toluene in hexane afforded pure compound melting at 92-93°C. On further elution with toluene-ethylacetate (9:1) gave
about 0.5 g of the OH-equatorially oriented alcohol (α-form). Recrystallization of the product from toluene-hexane gave pure compound melting at 110-112 °C.

2.2.4. Water mediated reduction of carbonyl compounds with NaBH₄

**General procedure for the Reduction of carbonyl compounds with sodium borohydride in water as green medium:** In reduction with sodium borohydride (NaBH₄) 0.5 gm of ketone was dissolved in 5ml of water in 50ml flask and stirred for about 5 min using magnetic stirrer. To this solution/emulsion was added equivalent molar ratio of sodium borohydride in small portions for about 15 min and reaction mixture was stirred continuously at room temperature. Progress of the reaction was monitored by silica gel TLC plates with the solvent system n-hexane (9.5mL) and ethyl acetate (0.5mL), as mobile phase. After completion of the reaction 1mL of 0.5N H₂SO₄ aqueous solution were added slowly for complete decomposition of borohydride and the product was separated by extraction with 2×5 mL of diethyl ether. The alcohol products ratio obtained from column chromatography from the reduction of ketones (entries 1 to 6) were given below (Table 5). The products i.e. alcohols were confirmed by their spectral data (Fig. 11 & 12).

The products of epimeric alcohols obtained by this method were similar to the method of NaBH₄ in alcohol. But the ratio of the products obtained was of slight variation. Particularly in respect of entry ‘3’ of Table 5 i.e., for 1-methyl-2-phenyl-*trans*-decahydroquinolin-4-one, the product obtained (α-form) was of reasonable yields compared to other methods produced low yields. This method tested for compounds of the entries 1 to 6.
Table 5: Reduction of 2-aryl-trans-decahydroquinolin-4-ones in water as green medium with sodium borohydride.

<table>
<thead>
<tr>
<th>No</th>
<th>Compound</th>
<th>Yield of the crude mixture of epimeric alcohols (%)</th>
<th>Epimers Recovered (%)</th>
<th>M.P. of the pure epimers (°C)</th>
<th>Forms (α)</th>
<th>Forms (β)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>2-phenyl-trans-decahydroquinolin-4-one</td>
<td>75</td>
<td>70</td>
<td>10</td>
<td>97-98</td>
<td>178-179&lt;sup&gt;a&lt;/sup&gt;</td>
</tr>
<tr>
<td>2</td>
<td>2-&lt;i&gt;p&lt;/i&gt;-tolyl-trans-decahydroquinolin-4-one</td>
<td>80</td>
<td>70</td>
<td>10</td>
<td>137-38</td>
<td>208-09&lt;sup&gt;a&lt;/sup&gt;</td>
</tr>
<tr>
<td>3</td>
<td>1-methyl-2-phenyl-trans-decahydroquinolin-4-one</td>
<td>80</td>
<td>45</td>
<td>40</td>
<td>125-126</td>
<td>164-165</td>
</tr>
<tr>
<td>4</td>
<td>3-methyl-2-phenyl-trans-decahydroquinolin-4-one</td>
<td>75</td>
<td>40</td>
<td>10</td>
<td>130-31</td>
<td>153-154&lt;sup&gt;a&lt;/sup&gt;</td>
</tr>
<tr>
<td>5</td>
<td>3-methyl-2-&lt;i&gt;p&lt;/i&gt;-chlorophenyl-trans-decahydroquinolin-4-one</td>
<td>70</td>
<td>45</td>
<td>40</td>
<td>126-27</td>
<td>173-74</td>
</tr>
<tr>
<td>6</td>
<td>1,3-dimethyl-2-phenyl-trans-decahydroquinolin-4-one</td>
<td>60</td>
<td>55</td>
<td>40</td>
<td>111-12</td>
<td>91-93&lt;sup&gt;a&lt;/sup&gt;</td>
</tr>
</tbody>
</table>


2.3. KINETIC MEASUREMENTS

2.3.1. MATERIALS & METHODS

Purification of materials: The required alcohols and ketones were purified by recrystallization from suitable solvents to constant melting points. The samples were dried in vacuum before use.
**Acetic Acid**

Acetic acid glacial (Excelar), supplied by ‘Qualigens Fine Chemicals’, was refluxed with chromium trioxide for 6 h and fractionally distilled. The faction boiling at 390-391K was collected and was used.

**Other Reagents**

Cetyltrimethylammonium bromide, Potassium dichromate, Potassium iodide, Sulphuric acid used was all A.R grade. Doubly distilled water was used for all purposes.

In order to reach the aim of the author a spectrophotometric method was followed for the CTADC oxidation of synthesized alcohols and ketones.

**2.3.2. Kinetic procedure for the oxidation of alcohols and ketones with CTADC:**

The oxidation kinetics of 2-aryl-trans-decahydroquinolin-4-ones and 2-aryl-trans-decahydroquinolin-4-ols by CTADC in the presence of aqueous acetic acid was investigated using a UV-Visible spectrophotometric method and all the kinetic measurements were carried out at 350nm. The measurements were performed at 30°C, 40°C and 50°C. The temperature was controlled by using thermostat of accuracy ±0.1°C. The required amount of CTADC solution was prepared by dissolving the necessary amount of CTADC in the solvent medium. The medium used was 50:50(v/v) acetic acid: water mixture containing 6N H₂SO₄. The solutions of the substrate compounds (ketones and alcohols) were prepared by dissolving the appropriate quantity of the compounds in the same solvent, so that the concentration of the substrates were maintained always higher than the concentration of CTADC. The substrate solution and the CTADC solutions were thermally equilibrated. The reaction was initiated by mixing equal volumes of CTADC to substrates and the progress of the reaction was followed spectrophotometrically by monitoring the decrease in absorbance at 350nm (Fig.13). The second order conditions were followed for determining the rates of the reactions.
2.3.3. Product Analysis

**Product Analysis of Alcohols:** A mixture of alcohol and CTADC was allowed to react in aqueous acetic acid (50%, v/v) in presence of sulphuric acid (6.0 N). The concentration of CTADC was maintained higher than the concentration of alcohols. The resulting mixture was kept aside at 30 °C temperature for about two days. The mixture turned reddish green, indicating the formation of reduced Cr (III). The mixture was then treated with 10% NaOH solution in order to make the solution becomes slightly basic nature, extracted with chloroform. A crude product was obtained after distillation of the chloroform layer. Later it was subjected to column chromatography for further purification with Hexane: Ethyl acetate in 6:4 (R_f=0.5). Finally the product was confirmed by IR & $^1$HNMR of corresponding ketones. A similar observation was also reported$^{35}$ in the oxidation of alicyclic alcohols to ketones.

**Product Analysis of Ketones:** A mixture of ketones and CTADC was allowed to react in aqueous acetic acid (50%, v/v) in presence of sulphuric acid (6.0 N). The concentration of CTADC was maintained slightly excess than the concentration of ketones. The resulting mixture was kept aside at 30°C temperature for 2-3 days. The mixture turned reddish green, indicating the formation of reduced Cr(III). After that the reaction mixture was neutralized with saturated solution of sodium carbonate,
extracted with ether and the combined ether extract separated and the product was obtained after distillation of the ether layer.

2.3.4. Instrumental Data

**Spectral**

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Specification</th>
</tr>
</thead>
<tbody>
<tr>
<td>Wavelength Range</td>
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</tr>
<tr>
<td>Spectral Band pass</td>
<td>1.0 nm</td>
</tr>
<tr>
<td>Wavelength Accuracy</td>
<td>± 0.3nm</td>
</tr>
<tr>
<td>Wavelength Repeatability</td>
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</tr>
<tr>
<td>Baseline Flatness</td>
<td>± 0.001A</td>
</tr>
<tr>
<td>Drive speed</td>
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</tr>
<tr>
<td>Light source</td>
<td>Deuterium / Tungsten Halogen Lamps</td>
</tr>
<tr>
<td>Photometric Range</td>
<td>0-200% T, -0.3- 3.0 A</td>
</tr>
<tr>
<td>Detector</td>
<td>Wide range Photo Diode</td>
</tr>
</tbody>
</table>

**Data Processing**

- Microprocessor mode: Spectrum, Discrete λ, Concentration & Time Scan
- PC Mode: Spectrum, Overlay, Time scan, discrete λ, Ratio metric, Concentration, ε–factor, Up to 4th order derivate, Peak Picking, spectra zooming and Data saving and Retrieving.

**Data Presentation**

- Dimensions (mm): 625 L × 430 L × 206 H
- Power Requirement: AC 110V/ 60 Hz Or 220 V/ 50 Hz
- Net Weight: 28 Kg

2.3.5. Stoichiometry

**Stoichiometry of alcohols**

The stoichiometry of the reaction was determined by performing the experiment at 30°C. A number of reaction mixtures containing excess of CTADC than alcohols were kept in a thermostat at 30°C for 12 hours at varying concentrations of CTADC. The disappearance of Cr(VI) was followed, until the absorbance values
become constant and was found that 1 mole of the reagent was used for 3 moles of alcohol. The stoichiometric equation can be written as,

\[ 3 \text{ R - OH} + \text{CTADC} \rightarrow \text{C=O} + \text{Cr(III)} \]

**Stoichiometry of Ketones**

The stoichiometry of the reaction was determined by allowing a known excess of the oxidant CTADC to react with the substrate in solvent medium at 30°C and the unreacted CTADC was estimated. The stoichiometry was found to be in the mole ratio of 1:1 for oxidant to substrate.

\[ \text{R}_2\text{C}=\text{O} + \text{CTADC} \rightarrow \text{Product} + \text{Cr(III)} \]

**2.3.6. Calculation of the rate constants**

The rate constants were calculated using the second order rate equation:

\[ k_2 = \frac{2.303 \log\left(\frac{b}{a-x}\right)}{t\left(\frac{a-b}{a(b-x)}\right)} \]

Where,

- \( a = \) Initial concentration of substrate in moles/lit
- \( b = \) Initial concentration of CTADC in moles/lit
- \( x = \) Amount of CTADC reacted in time \( t \) (seconds)
- \( t = \) Reaction time in seconds.
SPECTRA OF REPRESENTATIVE COMPOUNDS
(FIGURES: 2 TO 12)
Fig. 2: H NMR spectrum of 2-phenyl-4-(3-decaloylquinolin-1-yl) (α-form) (Solvent=CDCl3).
Fig. 3: $^1$H NMR spectrum of 3-methyl-2-phenyl-trans-decahydroquinolin-4-ol (α-form) (Solvent=CDCl₃).
Fig. 4: $^1$H NMR spectrum of 1,3-dimethyl-2-phenyl-trans-decahydroquinolin-4-ol (α-form) (Solv: CDCl$_3$).
Fig. 6: $^1$H NMR spectrum of 2-phenyl-trans-decahydroquinolin-4-ol (β-form) (Solvent=CDCl$_3$).
Fig. 7: $^1$H NMR spectrum of 3-methyl-2-phenyl-*trans*-decahydroquinolin-4-ol (β-form) (Solvent=CDCl$_3$).
Fig. 8: $^1$H NMR spectrum of 1,3-dimethyl-2-phenyl-trans-decahydroquinolin-4-ol (β-form) (Solvent=CDCl₃).

Fig. 11. $^1$H NMR spectrum of 2-p-tolyl-trans-decahydrquinolin-4-ol (α-form) (Solvent= d$_2$-DMSO).
Fig. 12: Mass spectrum of 2-p-tolyi-9H-decahydroquinolin-4-ol (α-form) (Solvent: d<sub>6</sub>-DMSO).
2.4. REFERENCES