REACTION OF 3-AMINO-2-CYCLOHEXEN-1-ONES WITH DIBENZOYLETHYLENE: REGIOSELECTIVE SYNTHESIS OF 4-OXOTETRAHYDROINDOLES AND 5-OXOTETRAHYDROQUINOLINES

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Reaction of 3-amino-2-cyclohexen-1-ones (Ia-c) with dibenzoylethylene gave either 4-oxotetrahydroindoles (IIa-c) or 5-oxotetrahydroquinolines (IVa-c) by the selection of reaction conditions.

The reaction of enaminoketone with 1,4-benzoquinone has been extensively investigated as the Nenitzescu indole synthesis. However, there is no report on the reaction of enaminoketone with acyclic 1,2-diacylethylene, which is expected to cyclize into both hydroindole and hydroquinoline rings. We are interested in the regioselective synthesis of hydroindole or hydroquinoline from the reaction of 3-amino-2-cyclohexen-1-one (I) with 1,2-diacylethylene. We now report that the reaction of (I) with dibenzoylethylene (DBE) gives an indole derivative (II) in acidic medium and gives a quinoline derivative (IV) under dehydrogenation condition. These reactions appear to offer a potentially useful synthetic method for the 2,3-disubstituted 4-oxotetrahydroindoles and 2,4-disubstituted 5-oxotetrahydroquinoline.
derivatives.

Treatment of the enaminoketone (Ia; R1=R2=Me) in acetic acid with DBE under reflux for 3 h gave a 47% yield of 3-benzoyl-

methyl-4,5,6,7-tetrahydro-6,6-dimethyl-4-oxo-2-phenylindole (IIa) [M+ 357; \( \nu_{\text{max}} \) 3440, 1680 and 1640 cm\(^{-1}\); \( \delta \) (CDCl\(_3\)) 0.95 (1H, bs), 1.8-2.1 (2H, m), 2.4-2.8 (8H, m), 5.47 (2H, s), 7.48 (2H, s), 7.83 (2H, s) and 8.94 (6H, s)], which is also obtained by prolonged heating in ethanolic solution.

The enaminoketone (Ia) was treated with DBE in ethanol under reflux in less than 4 h to give a 65% yield of 4-benzoyl-

1,4,5,6,7,8-hexahydro-7,7-dimethyl-5-oxo-2-phenylquinoline (IIIa) [M+ 357, \( \nu_{\text{max}} \) 3450, 1680 and 1610 cm\(^{-1}\); \( \delta \) (CDCl\(_3\)) 1.8-2.1 (2H, m), 2.4-2.8 (8H, m), 3.52 (1H, bs), 4.69 (1H, d, \( J \) 5 Hz), 4.91 (1H, dd, \( J \) 5 and 1.5 Hz), 7.70 (2H, s), 7.84 (2H, s), 8.82 (3H, s) and 8.91 (3H, s)], which is readily dehydrogenated in the presence of 5% Pd-C in xylene to give an 84% yield of 4-benzoyl-

5,6,7,8-tetrahydro-7,7-dimethyl-5-oxo-2-phenylquinoline (IVA) [M+ 355; \( \nu_{\text{max}} \) 1680 cm\(^{-1}\); \( \delta \) (CDCl\(_3\)) 1.8-2.7 (11H, m), 6.80 (2H, s), 7.50 (2H, bs) and 8.82 (6H, s)]. The quinoline (IVA) was also obtained in one-step in a 36% yield by directly refluxing in a solution of (Ia), DBE and 5% Pd-C in xylene. Thus, selection of reaction conditions was found to change the course (Ia)\( \rightarrow \) (IIa) into (Ia)\( \rightarrow \)(IVA).

Similar reactions to that employed for (Ia) converted (Ib; R1=Me, R2=N) and (Ic; R1=R2=H) to the corresponding 4-oxotetra-

hydrindoles (IIb,c) and 5-oxotetrahydroquinolines (IVb,c), res-
pectively. The results are summarized in the Table.

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\begin{array}{cccc}
\text{R}_1 & \text{R}_2 & \text{Conditions} & \text{Product Yield(%) mp(°C)} \\
\hline
\text{Ia} & \text{Me} & \text{Me} & \text{AcOH reflux 3 h} \\
& & & \text{IIa} \text{ 47} \text{ 200-203} \\
& & \text{EtOH reflux 2 days} \\
& & \text{EtOH reflux 4 h} \\
& \text{(CH}_3)_2\text{C}_6\text{H}_4,\text{Pd-C reflux 4 h} \\
\text{Ib} & \text{Me} & \text{H} & \text{AcOH reflux 5 h} \\
& & & \text{IIb} \text{ 50} \text{ 189-191} \\
& & \text{(CH}_3)_2\text{C}_6\text{H}_4,\text{Pd-C reflux 4 h} \\
\text{Ic} & \text{H} & \text{H} & \text{AcOH reflux 4 h} \\
& & & \text{IIc} \text{ 24} \text{ 188-190} \\
& & \text{(CH}_3)_2\text{C}_6\text{H}_4,\text{Pd-C reflux 5 h} \\
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REFERENCES


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