

S Y N O P S I S

Part I, Barrier to Rotation in Methyl 2-(8-Quinolyl)-6-oxocyclohex-1-enylacetate : Comparative Study of the Effective Bulk of a Nitrogen Lone pair in Quinoline and of a Naphthalene Hydrogen.

In previous papers from our laboratory<sup>1</sup>, the free energy of activation of restricted rotation about the aryl-cyclohexenone bond in a number of substituted arylcyclohexenones (e.g., 1) was determined by dynamic N.M.R. utilising the coalescence temperature of the AB-quartet of the side-chain methylene protons. The highest barrier (95.4 kJ or 22.8 kcal mol<sup>-1</sup>) was encountered in the 1-naphthyl derivative (1) originating from a peri-interaction between 8-H of naphthalene and 3-H<sub>2</sub> of the cyclohexenone moiety. The study has now been extended to a 8-quinolyl derivative (2) in which 8-H is replaced by a nitrogen lone pair with the idea that it will permit a direct correlation of their effective bulks.

Methyl 2-(8-quinolyl)-6-oxocyclohex-1-enylacetate (2) was synthesised from 8-acetylquinoline (3) (Chart I) employing a general method<sup>2</sup> which consisted of the condensation of its Mannich base methiodide (4) with ethyl  $\beta$ -oxo-adipate (5) and subsequent hydrolysis and esterification of the product (6). This is perhaps the first example of formation of a Mannich base from an aminoketone and the conventional procedure did not work the product being a tar, perhaps due to an intramolecular  $\alpha$ -proton abstraction by quinoline nitrogen and subsequent polymerisation of the resultant vinyl ketone. The desired Mannich base was finally obtained in 30%.

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1. D. Nasipuri, P.K. Bhattacharya, and G.T. Furst, J.C.S. Perk II, 1977, 356.

2. D. Nasipuri and A. Bhattacharya, Indian J.Chem., 1972, 10, 799.