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PREPARATION OF QUINOLINE DERIVATIVES FROM SCHIFF BASE AND VINYL ETHER CATALYZED BY DICOBALT OCTACARBONYL

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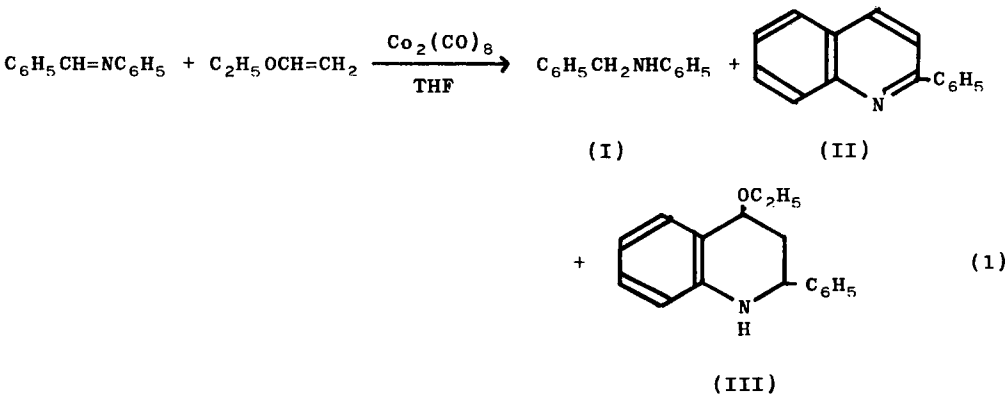
It has previously been shown that Schiff bases react with carbon monoxide in the presence of metal carbonyl catalysts to yield phthalimidine derivatives (1,2). It has also been reported that Schiff bases react with vinyl ethers in the presence of $BF_3 \cdot O(C_2H_5)_2$ to produce 2-substituted-4-alkoxy-1,2,3,4-tetrahydroquinoline (3,4). In this paper we wish to report the preparation of quinoline derivatives by the reaction between Schiff base and vinyl ether using dicobalt octacarbonyl as catalyst.

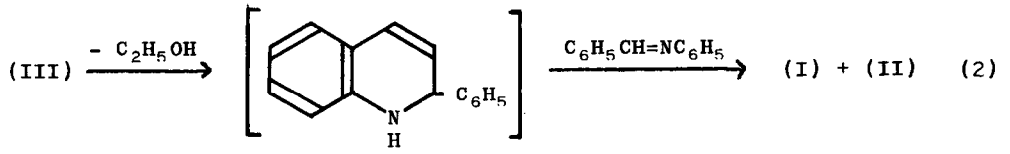
A catalytic amount of dicobalt octacarbonyl (1 g) was added to a solution of a mixture of 10 g of benzaldehyde anil and 4 g of ethyl vinyl ether in 50 ml of tetrahydrofuran under nitrogen atmosphere, and the solution was stirred at room temperature for 4 hr.. The reaction mixture was passed through the



(I) (II) (III) (1)

column of alumina in order to eliminate the catalyst. After removal of the solvent from the solution, the residue was fractionally distilled under reduced pressure to give 2.5 g of N-benzylaniline (I) (b.p. 118-119° (2 mm.); benzoyl derivatve, m.p. 107°), 5 g of 2-phenylquinoline (II) (b.p. 140-142° (2 mm.), m.p. 83-84°) and 1.5 g of 2-phenyl-4-ethoxy-1,2,3,4-tetrahydroquinoline (III) (b.p. 155-160° (2 mm.), m.p. 76-77°). These products were confirmed by direct comparison of their melting points and i.r. spectra with those of the authentic samples.

A possible reaction course for the formation of these products involves the first formation of (III) by the addition reaction of ethyl vinyl ether to benzaldehyde anil, and loss of ethanol from (III) to form an unstable dihydroquinoline derivative. Then this dihydroquinoline intermediate transfered two hydrogen atoms to benzaldehyde anil to produce (I) and (II).



In order to confirm this consideration, (III) was treated with dicobalt octacarbonyl in the reaction condition as described above. Then, 2-phenylquinoline was also obtained in addition to 2-phenyl-1,2,3,4-tetrahydroquinoline. On the basis of this evidence, it is considered that the reaction scheme (2) is reasonable.

We are continuing our investigation of catalytic mechanism and exploring the scope of the reaction.

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