ACTION OF GRIGNARD REAGENTS ON N-ACYLQUINOLINIUM SALTS IN SITU

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We were able to show that N-acylquinolinium salts in situ react with organomagnesium compounds just like other quaternary quinolinium salts that do not have an exocyclic electrophilic center, rather than at the carbonyl group, to form 2-substituted 1-acyl-1,2-dihydroquinolines:

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Careful addition of a Grignard reagent to a mixture of quinoline and acyl halide results in the formation primarily of compound I. When the order of mixing the reagents is reversed, under which conditions the reaction proceeds in excess organomagnesium compound, I undergoes further transformation under the influence of the Grignard reagent to form σ -substituted quinolines (II) through the loss of a proton and an acyl residue. The acyl residue is converted to the corresponding tertiary alcohol (III) in the process. Thus by the reaction of quinoline, benzoyl chloride, and methylmagnesium iodide in one case we obtained 1benzoyl-2-methyl-1,2-dihydroquinoline (I, $R = C_6H_5$, $R' = CH_3$) with mp 119-120°C (from acetone) and R_f 0.5 [on aluminum oxide with benzene—hexane—chloroform (6:1:30)]. IR spectrum: 1650 cm⁻¹ (C=O). PMR spectrum: (in trifluoroacetic acid with the chemical shifts given with respect to a hexamethyldisiloxane internal standard): a doublet from the CH₃ group (δ 1.14 ppm, J 6.0 Hz), a quartet from the proton in the 2 position (δ 4.62 ppm, J 6.0 Hz), and a multiplet from the olefin and aromatic protons at 6.4-8.8 ppm. Found: C 82.2; H 6.2; N 5.8%. C₁₇H₁₅NO. Calculated: C 81.9; H 6.1; N 5.6%. The compound was converted to quinaldine as a result of alkaline hydrolysis.

Quinoline, quinaldine, and dimethylphenylcarbinol were present in the reaction mixture, according to gas-liquid chromatography, when the order of mixing the reagents was reversed.

Similarly, we obtained 1-benzoyl-2-phenyl-1,2-dihydroquinoline (I, $R = R' = C_6H_5$) with mp 114-115° (from petroleum ether) by the reaction of N-benzoylquinolinium chloride in situ with phenylmagnesium bromide. Found: C 85.2; H 5.7; N 4.6%. $C_{22}H_{17}NO$. Calculated: C 84.9; H 5.5; N 4.5%. The alkaline hydrolysis of this compound gave 2-phenylquinoline with mp 86-87°. The picrate of this compound melts at 191-192° [1].

The previously [2] described 1-benzoyl-2-(p-dimethylaminophenyl)-1,2-dihydroquinoline was obtained by the reaction of an N-benzoylquinolinium salt with p-dimethylaminophenylmagnesium bromide.

After we had already formulated our letter to the editor, there appeared a brief communication [3] regarding the one-step synthesis of N-carbethoxy-1,2-dihydropyridines by the reaction of pyridine with Grignard reagents in the presence of ethyl chloroformate.

LITERATURE CITED

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