REACTIONS OF THE 3-BENZOYLPYRIDINE DIANION

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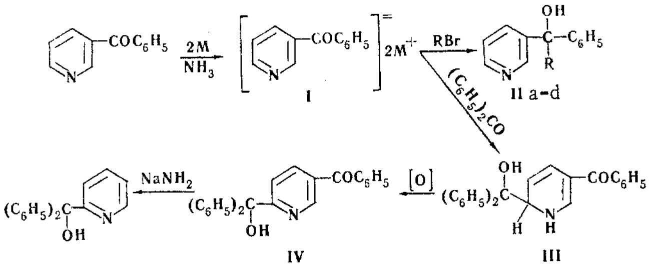
The dianions of aromatic ketones react with alkyl halides and carbonyl compounds to form tertiary-carbon-substituted carbinols [1]. We have found that the 3-benzoylpyridine dianion (I) [2] is alkylated by various alkyl halides to give quantitative yields of substituted (3-pyridyl)phenylcarbinols (II) and reacts with benzophenone to give the product of addition at the 6 position – 3-benzoyl-6-(diphenylhydroxymethyl)-1,6-dihydropyridine (III).



II a $R=C_2H_5$, b $R=i\text{-}C_3H_7$, c $R=t\text{-}C_4H_9$, d $R=CH_2C_6H_5$; $M=Na, Li$

There are absorption bands at 1650 ($C=O$), 3435 (NH), and 3555 and 3620 cm^{-1} (bonded and free OH groups) in the IR spectrum of III. The UV spectrum contains two maxima at 304 (log ε 3.84) and 360 nm (log ε 3.95), which are characteristic for 3-substituted 1,6-dihydropyridines [3]. The oxidation of III with benzoquinone gives 3-benzoyl-6-(diphenylhydroxymethyl)pyridine (IV), the cleavage of which by sodium amide in toluene gives the known (2-pyridyl)diphenylcarbinol.

The formation of dihydropyridine III might have been due to steric factors, but the sterically hindered isopropyl and tert-butyl bromides react with I to form carbinols IIb, c. It is possible that the alkylation of I and its reaction with carbonyl compounds proceed via different mechanisms: alkylation is an ionic reaction, while addition at the carbonyl group includes electron transfer and the formation of two anion radicals – benzophenone and 3-benzoylpyridine – as well as their interaction. The reactivities of an anion radical and the corresponding dianion of heterocyclic compounds may differ substantially [4]. In fact, the reaction of the benzophenone and 3-benzoylpyridine anion radicals led to the formation of III. The latter was also obtained in the reaction of the benzophenone dianion with 3-benzoylpyridine.

EXPERIMENTAL

3-Benzoyl-6-(diphenylhydroxymethyl)-1,6-dihydropyridine (III). An ether solution of 0.01 mole of benzophenone was added to a solution of 0.01 mole of I, obtained by the reaction of 3-benzoylpyridine with sodium in liquid ammonia. The mixture was neutralized by the addition of ammonium chloride, and the ammonia was removed by distillation. The residue was washed with water and ether and crystallized from aqueous alcohol and then from benzene to give 80% of a product with mp 103-104°. Found: C 82.3; H 6.4%. $C_{25}H_{21}NO_2$. Calculated: C 81.7; H 5.8%.

3-Benzoyl-6-(diphenylhydroxymethyl)pyridine (IV). A solution of 0.37 g of II and 0.11 g of benzoquinone in 20 ml of benzene was refluxed for 4 h, cooled, and washed with 10% sodium hydroxide solution,

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5% hydrochloric acid, and water. The benzene was removed by distillation to give 0.28 g (75%) of IV with mp 123-124° (from heptane). Found: C 82.6, H 5.7%. $C_{25}H_{19}NO_2$. Calculated: C 82.2; H 5.2%.

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