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REDUCTION OF 1-FORMYL-1,2,3,4-TETRAHYDROQUINOLINE WITH ETHYLDIPHENYLSILANE

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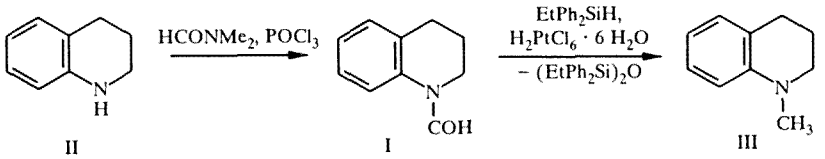
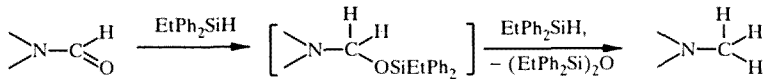
1-Formyl-1,2,3,4-tetrahydroquinoline (I) is a valuable intermediate in the synthesis of alkaloids and other therapeutic substances [1]. Literature methods for the preparation of compound I include reduction of quinoline with a mixture of formic acid and sodium formate [2], with formamide and formic acid [2], or with formic acid and lower alkyl ethers or acetone under vigorous conditions [1]. In other cases quinoline was treated with gaseous formic acid [3] or sequentially with formic acid and methyl formate [4]. Methylquinolinium iodide was also reduced to compound I with formic acid in the presence of sodium formate or triethylamine [5].

We have observed that compound I is readily obtained with a yield of 76% by Wilsmeier acylation of 1,2,3,4-tetrahydroquinoline (II) with dimethylformamide in the presence of phosphorus oxychloride at 60°C.



II I III

Reaction of the amide I with ethyldiphenylsilane in the presence of hexachloroplatinic acid gave 1-methyltetrahydroquinoline (III), the product of hydride reduction, rather than the expected addition product, the siloxymethylamine [6].



With a 1:2 mole/mole ratio of aldehyde:silane the yield of compound III was ~50% at 125°C.

^{1}H NMR spectra were recorded with a Bruker WH-90/DS spectrometer (TMS internal standard) and mass spectra were recorded with a Kratos MS-50 mass spectrometer or a Kratos MS-25 chromato-mass spectrometer (70 eV).

1-Formyl-1,2,3,4-tetrahydroquinoline (I). Phosphorus oxychloride (9.3 cm^3, 0.1 mol) was added over 40 min to a vigorously stirred and ice-cooled mixture of tetrahydroquinoline (13.3 g, 0.1 mol) and dimethylformamide (7.3 g, 0.1 mol) so that the temperature of the reaction mixture did not exceed 20°C. Stirring was continued for 3 h at 60°C. Ice (200 cm^3) was added to destroy the complex formed and the solution was adjusted to pH 6 with 0.5 M sodium hydroxide solution. The product was extracted with ether (3 x 50 cm^3). The ether extract was adjusted to pH 10 and dried over $MgSO_4$. After removal of ether, the residue was distilled in vacuum and the fraction with b.p. 148-150°C (9 kPa) was collected. Yield 12.2 g (76%). ^{1}H NMR spectrum ($CDCl_3$): 8.74 (1 H, s, COH), 7.71 (4 H, m, Ar), 3.78 (2 H, t, 2-CH_2), 2.80 (2 H, t, 4-CH_2), 1.98 ppm (2 H, m, 3-CH_2). Mass spectrum ,(*m/z*): 161 (M^+), 132 (M^+ — CHO).

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1-Methyl-1,2,3,4-tetrahydroquinoline (II). $H_2PtCl_6 \cdot 6H_2O$ (0.04 cm^3, 0.1 M in *iso*propanol) was added to a mixture of 1-formyl-1,2,3,4-tetrahydroquinoline (1.6 g, 10 mmol) and ethyldiphenylsilane (4.24 g, 20 mmol). The reaction mixture was heated at 125-150°C for 12 h. The reaction was monitored by gas–liquid chromatography and GC-MS. Yield ~50%.

Mass spectrum , *m/z (I, %)*: 147 (M^+, 72), 146 (M^+ — H, 100), 132 (M^+ — Me, 10), 130 (15), 117 (12), 91 (15), 77 (12).

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