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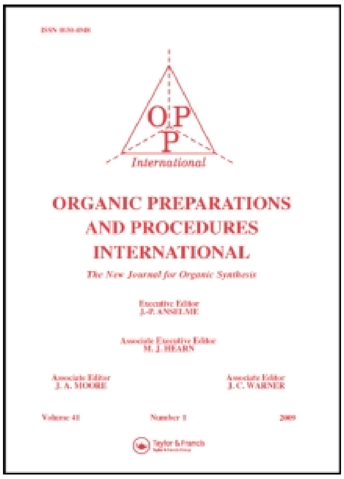

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2,4-DIETHYLQUINOLINE - AN EXTENSION OF THE COMBES SYNTHESIS

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2,4-DIETHYLQUINOLINE - AN EXTENSION OF THE COMBES SYNTHESIS

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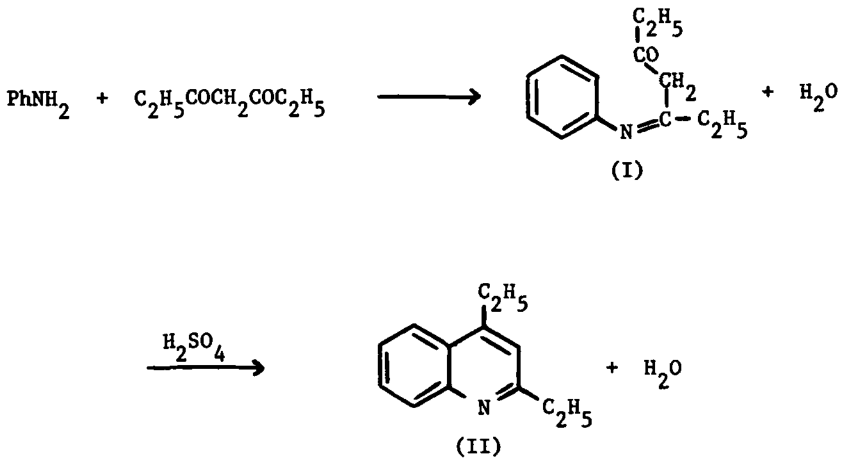

(I)

(II)

A sample of 2,4-diethylquinoline (II) was needed for use as a gas-liquid chromatographic reference compound. The most convenient synthesis of this compound appeared to be from 3,5-heptanedione by the Combes reaction. Although this reaction[1] has been applied many times with acetylacetone to produce 2,4-dimethylquinoline derivatives[2], a synthesis commencing with a higher β-diketone has not been reported.

Although 2,4-diethylquinoline has not been previously synthesised, several workers have identified it as a reaction product. Zobian and coworkers[3] have identified it (by nmr) as a product of aromatisation of 2,4-diethyl-2-methyl-1,2-dihydroquinoline. Nozaki and his group[4] reported that 2,4-diethylquinoline was formed in 6% yield by photochemical alkylation of quinoline in the presence of propionic acid; 2-ethyl- and 1,2,3,4-tetrahydro-4-ethyl- quinoline were also identified as reaction products.

From the properties of our synthesised material, it would appear that the "diethylquinoline" isolated by Reher[5] from the thermal rearrangement of N-ethylquinolinium iodide was 2,4-diethylquinoline. This is to be expected since 2-ethyl and 4-ethylquinoline were also identified and the formation of a 2,4-disubstituted derivative would be in accordance with the products obtained from the thermal rearrangement of N-ethylpyridinium iodide.[6]

EXPERIMENTAL

3,5-Heptanedione monoanil(I). - A mixture of 3,5-heptanedione[7] (14.1 g., 0.11 mole) and freshly distilled aniline (9.31 g., 0.10 mole) was boiled under gentle reflux for 1.5 hrs. and allowed to cool. Distilled water (50 ml.) was added and the product extracted with benzene and dried over anhydrous magnesium sulphate. Removal of the solvent left the anil (16.4 g., 81%) as a yellow oil which was used directly in the next stage without further purification.

2,4-Diethylquinoline(II). - Conc. sulphuric acid (90 ml.) was cooled to below 5° and the anil (I) prepared above (16.4 g.) was added in 1 ml. portions over a period of 15 min. The solution was then heated on the water bath for an additional 30 min. After cooling, the reaction mixture was made alkaline with solid sodium hydroxide and the product was extracted with ether and dried over anhydrous magnesium sulphate. Removal of the solvent left 2,4-diethylquinoline (8.7 g., 47% [8]) as a pale yellow liquid, bp. 286-287°/760 mm., (lit.[5] bp. 282.8-284.8°).

Anal. Calcd. for $C_{13}H_{15}N$: C, 84.3; H, 8.2; N, 7.6. M: 185.3.

Found: C, 84.1; H, 8.3; N, 7.8. M(non-aqueous titration): 186.1.

The chloroplatinate was obtained as microcrystalline orange-yellow prisms, mp. 224° (decomp.), (lit.[5] mp. 217°).

Anal. Calcd. for $C_{26}H_{32}Cl_6N_2Pt$: Pt, 25.0. Found: Pt, 24.8.

The picrate crystallised from methanol as long yellow needles, mp. 177-178° (decomp.), (lit.[4] mp. 173-174°).

Anal. Calcd. for $C_{19}H_{18}N_4O_7$: C, 55.1; H, 4.4; N, 13.5.

Found: C, 55.4; H, 4.5; N, 13.6.

NMR(100 MHz, CCl_4) : two overlapping quartets at 6.97-7.23τ (CH_2), two overlapping triplets which gave a four-line pattern at 8.57-8.79τ (CH_3), multiplet at 1.95-2.76τ (carbocyclic ring protons), singlet at 3.04τ (proton at C-3). Zobian *et al.*[3] reported two 2-proton quartets at 7.13 and 7.02τ (CH_2) and a 6-proton triplet at 8.63τ (CH_3).

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8. Yield based on aniline originally used.

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