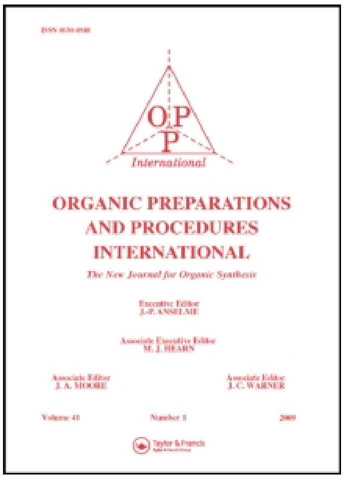

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2, 4, 5, 8-TETRAMETHYLOUINOLINE. A CLARIFICATION

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2,4,5,8-TETRAMETHYLQUINOLINE. A CLARIFICATION

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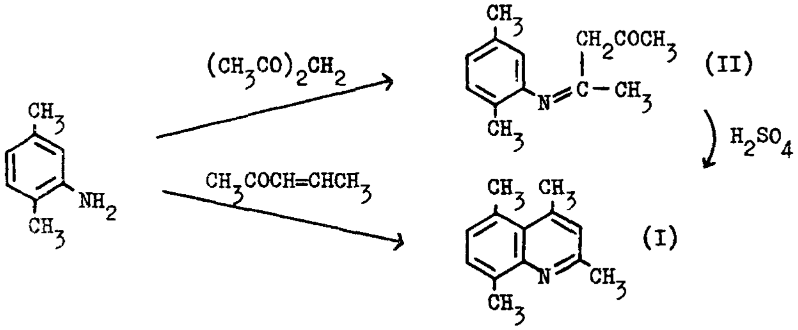

A sample of 2,4,5,8-tetramethylquinoline (I) was needed for use as a gas-liquid chromatographic reference compound. Reference to the literature on the synthesis of this compound[1-3] presented a confused and contradictory situation.

The compound was first prepared in 1920 by Mikeska[1] via the Beyer synthesis. A mixture of acetone and paraldehyde was allowed to age to produce 3-pentene-2-one which was then treated with 2,5-dimethylaniline to produce the quinoline (mp. reported as 131°), but no analytical data were given. The compound was later prepared[2] by the Combes reaction by cyclisation of the anil derivative (II) obtained from 2,5-dimethylaniline and acetylacetone which gave the quinoline, mp. 48°. Although an elemental analysis was reported, no reference was made to the previous preparation.[1] During the course of a study of the infrared spectra of alkylquinolines, Karr and coworkers[3] also attempted to prepare 2,4,5,8-tetramethylquinoline by the Combes reaction, but reported that cyclisation of the intermediate anil (II) to the quinoline was not possible, although a small yield of an impure product was obtained by another technique.

In view of these contradictory reports, we have repeated the synthesis of this compound by each of the previous techniques[1,2] in order to clarify the situation and to ascertain the correct nature and properties of the synthesised products. We have found that the Combes synthesis does produce the desired quinoline with properties similar to those previously reported,[2] the identity of the product being confirmed by nmr spectroscopy. The Beyer synthesis[1] also produced the same quinoline with similar properties, and hence the previously reported mp. 131° must be in error.

It would appear that the sample isolated by Karr and coworkers[3] was very impure, and hence their IR spectral data should be disregarded. The peak which they reported at 788 cm^{-1} could have been due to the presence of residual 2,5-dimethylaniline which has a strong absorption at 792 cm^{-1}. The picrate crystallised from ethanol as yellow needles, mp. 163-4°, (lit.[2] mp. 161°).

NMR (100 MHz, CCl_4) : 2.81τ(1H, d, J=7.0 Hz, H_6), 3.06τ(1H, d, J=7.0 Hz, H_7), 3.14τ(1H, s, H_3), 7.26τ(6H, s, $C\underline{H}_3$), 7.37τ(3H, s, $C\underline{H}_3$), 7.42τ(3H, s, $C\underline{H}_3$). (lit.[4] $J_{67}=7.2 \pm 0.3$ Hz).

IR (CS_2 soln.) : 881 (w), 858 (m), 820 (s), 802 (w), 745 (w), 695 (m) cm^{-1}. (lit.[3] : 857 (m), 818 (s), 788 (m), 783 (m), 702 (m) cm^{-1}).

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