The Reaction of Diacetylacetone with Hydroxylamine

By LAWSON G. WIDEMAN

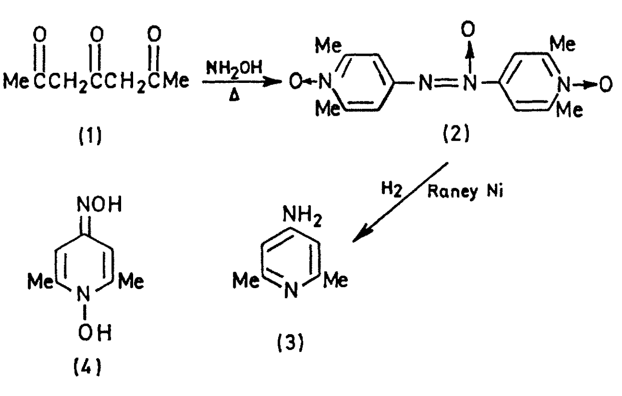
(*Research Division, The Goodyear Tire and Rubber Company, Akron, Ohio* 44316)

Summary When diacetylacetone is treated with hydroxylamine for 5 days at 65° an azoxy-dimer (**2**) is formed.

PAST investigations of the ammonia or amine reactions with diacetylacetone have shown that cyclization occurs and monomeric 2,6-lutidones are formed.[1,2]

In contrast to these results, when diacetylacetone (**1**) was treated with 3 molar equiv. of hydroxylamine in aqueous medium at 65° for 5 days, an azoxy-dimer (**2**) was isolated in 70% yield. This dimer gave an analysis correct for $C_{14}H_{16}N_4O_3$ and was readily hydrogenated in the presence of Raney nickel at room temperature to 4-amino-2,6-lutidine (**3**), which was compared with authentic material.[3] Dimer (**2**) was shown to be 4,4′-azoxydi-2,6-lutidine 1,1′-dioxide by the fact that it had spectral data identical with those of material synthesised from 2,6-dimethyl-4-pyrone and hydroxylamine in sunlight[4] and showed an undepressed mixed m.p. [233—235° (decomp.)] with this material.

If the reaction is arrested shortly after its initiation, small amounts of intermediate (**4**) can be isolated. A control experiment shows that (**4**) is not formed *via* a pyrone intermediate.



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[2] D. Cook, *Canad. J. Chem.*, 1963, **41**, 1435.
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