The Reaction of Ethylenediamine with β-Oxo-esters. Evidence for Ketimine–Enamine Tautomerism

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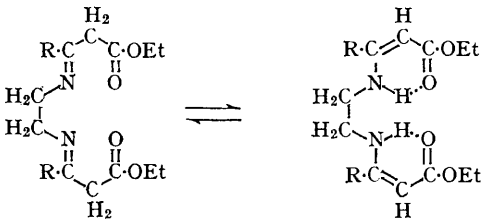
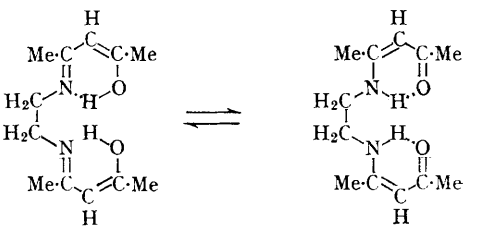
OLZEWSKI and MARTIN[1] have suggested that failure of ethyl acetoacetate to condense normally with tetrakisethylenediamine-μ-dichloro-dinickel(II) may be due to the formation of a β-oxo-amide rather than a β-oxo-imine or a β-ethoxycarbonyl-imine. We have investigated the reaction of ethylenediamine with a variety of β-oxo-esters. Condensation takes place smoothly in ethanol at 60° to give the products (I and II; R = Me, CO_2Et, $CH_2{\cdot}CO_2Et$).



(I) (II)

The infrared spectrum of the condensate (R = $CH_2{\cdot}CO_2Et$) shows no C=N absorption but an intense, very sharp singlet N–H stretch at 3344 cm.$^{-1}$. The additional hydrogen-bond stabilisation in the enamine (II) obviously favours the formation of this tautomer rather than the ketimine (I). For (R = $CH_2{\cdot}CO_2Et$) the following assignments can be made: ν (free CO_2Et) 1722 cm.$^{-1}$; ν (H-bonded CO_2Et) 1688 cm.$^{-1}$; ν (C–N), 1335 cm.$^{-1}$; ν (C=C, conjugated to CO, cisoid enhanced) 1602 cm.$^{-1}$.

The n.m.r. spectrum of (II; R = $CH_2{\cdot}CO_2Et$) at 60 Mc./sec. and 22° has a signal at very low fields (δ = 8·64 p.p.m. in $CDCl_3$) with reference to tetramethylsilane, a characteristic feature of intramolecularly hydrogen-bonded protons.[2] A vinyl proton also occurs at δ = 4·57 p.p.m. Integration of the spectrum indicates essentially complete conversion into the enamine tautomer (II). The ultraviolet spectra of the enamine in 95% ethanol has an intense band ($\epsilon = 4{\cdot}4 \times 10^4$) at 282 mμ due to the presence of the αβ-unsaturated-carbonyl chromophore.



(III) (IV)

The compound described appears to be the first example of pure ketimine–enamine tautomerism in which the enamine tautomer is favoured.[3] The examples quoted by Dudek and Holm[4] for compounds prepared by the reaction of diamines and β-diketones are complicated by the additional tautomerism (III) ⇌ (IV).

Satisfactory analytical data have been obtained on all compounds.

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[2] R. W. Hay and P. P. Williams, *J.*, 1964, 2270.
[3] P. L. Pickard and G. W. Polly, *J. Amer. Chem. Soc.*, 1954, **76**, 5169.
[4] G. O. Dudek and R. H. Holm, *J. Amer. Chem. Soc.*, 1961, **83**, 2099.