

The Addition of Dimethylketen to some Heterocyclic Bases; a Correction

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IN a previous Communication¹ we suggested that the products of hydrolysis and methanolysis of the adduct of dimethylketen with quinoline (I) had the structures (II), as opposed to the structures (III) originally proposed by Staudinger.² The assignment of the pseudo-ester structures was based upon the very large difference (*ca.* 0.4 τ) between the n.m.r. absorptions of the methyl groups in the isopropyl group. The possibility that this might be due to the asymmetric centre at position 2 of the quinoline skeleton was discounted in view of the

size of this splitting which was thought to indicate that the isopropyl group was immediately adjacent to an asymmetric centre.³ However, further study leads us to withdraw our earlier suggestion in favour of Staudinger's original structures (III).

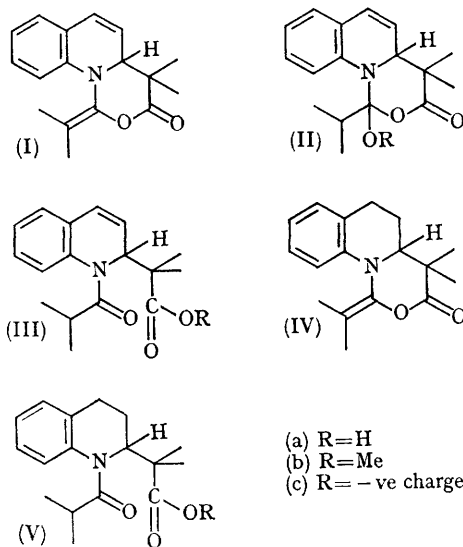
The dihydro-derivative (IV) of the adduct (I) on hydrolysis or methanolysis gives products whose n.m.r. spectra show that, here too, the isopropyl group gives rise to two methyl doublets, split by about 0.4 τ . However, there are strong absorptions at 1665 cm.^{-1} in the infrared spectra of these

compounds, which can only be due to the presence of an amide carbonyl group, excluding the possibility of structures akin to (II), and confirming (V) as correct. Previously the infrared absorption at approximately 1665 cm^{-1} observed in the spectra of the hydrolysis and methanolysis products of (I) had been ascribed to the double bond at position 3 of the quinoline system in (IIa) and (IIb), the corresponding absorption in the spectrum of (I) being at 1652 cm^{-1} . Now that the n.m.r. spectra can no longer be adduced as conclusive evidence for the existence of compounds of structure (II), this infrared absorption, which probably obscures the absorption due to the C=C group, can be assigned to the amide carbonyl group in (III).

Further evidence against structure (IIa) for the hydrolysis product of (I) comes from a study of the n.m.r. spectrum in acid and alkaline solution. In both cases, the isopropyl group shows the same large splitting of the methyl doublets. It is most unlikely that the anion would adopt the cyclic structure (IIc) rather than the open structure (IIIc), in which the negative charge would be delocalised, and the splitting of the methyl doublets must therefore be due to the asymmetry at position 2 of the quinoline skeleton.

To confirm this conclusion, an authentic sample of 1-isobutyryl-2-methyl-1,2,3,4-tetrahydroquinoline was prepared, and its n.m.r. spectrum was

examined. Three methyl doublets were observed, those attributed to the isopropyl group being separated by 0.22τ .



(Received, March 21st, 1966; Com. 178.)

¹ R. N. Pratt, S. A. Procter and G. A. Taylor, *Chem. Comm.*, 1965, 574.

² H. Staudinger and H. W. Klever, *Ber*, 1907, **40**, 1149; H. Staudinger, H. W. Klever, and P. Kober, *Annalen*, 1910, **374**, 1.

³ G. M. Whitesides, D. Holtz, and J. D. Roberts, *J. Amer. Chem. Soc.*, 1964, **86**, 2628.