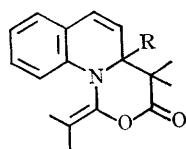


## The Addition of Dimethylketen to some Heterocyclic Bases

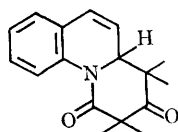
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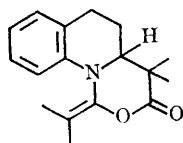
FOLLOWING the investigation of the structure of the adduct of acridine and dimethylketen,<sup>1</sup> it was suggested that the adduct of dimethylketen and quinoline might have the structure (Ia) rather than the  $\beta$ -keto-amide structure (II) originally proposed by Staudinger.<sup>2-4</sup> A recent communication<sup>5</sup> supporting this suggestion prompts us to report the results of our investigation.



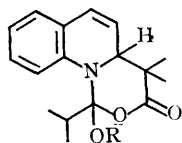
(I) a; R=H  
b; R=Me



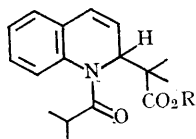
(II)



(III)



(IV) a; R=H  
b; R=Me



(V) a; R=H  
b; R=Me

The reaction of dimethylketen with quinoline in ether at 0° gave Staudinger's adduct C<sub>17</sub>H<sub>19</sub>NO<sub>2</sub>, [m.p. 82°;  $\lambda_{\max}$  (EtOH) 237, 285, 342 m $\mu$  (log  $\epsilon$  4.35, 3.44, 3.60);  $\nu_{\max}$  1746, 1703 cm.<sup>-1</sup>] whose n.m.r. spectrum shows signals consistent with the structure (Ia). Three singlets at  $\tau$  8.13 (3 protons), 8.48 (3 protons) and 8.78 (6 protons) are assigned to the two methyl groups of the isopropylidene moiety and the *gem*-dimethyl group respectively; an ABX system accounts for signals at  $\tau$  5.71, 4.43, and 3.45 ( $J = 5.5$  and 9.5 c./sec.), and absorption between  $\tau$  2.7—3.7 accounts for four aromatic protons. Ozonolysis of the adduct gave acetone, identified as its dinitrophenylhydrazone and hydrogenation gave a dihydro-derivative (III) [m.p. 96—97°;  $\lambda_{\max}$  (EtOH) 266 m $\mu$ , (log  $\epsilon$  4.09);  $\nu_{\max}$  1760, 1695 cm.<sup>-1</sup>]. The infrared spectra of the adduct and its dihydro-derivative are consistent with the presence of the unsaturated ester group, and the ultraviolet spectra confirm that ring closure occurs on to the 2-position of the quinoline skeleton, rather than on to the 4-position, which might be expected by analogy with the addition of dimethylketen to 9-methyl-acridine.<sup>6</sup> Further support for this position of ring closure comes from a study of the adduct of dimethylketen with quinaldine<sup>3</sup> (Ib) C<sub>18</sub>H<sub>21</sub>NO<sub>2</sub> [m.p. 120—121°;  $\lambda_{\max}$  (EtOH) 239, 284, 342 m $\mu$ , log  $\epsilon$  4.44, 3.51, 3.74);  $\nu_{\max}$  1743, 1703 cm.<sup>-1</sup>]. The n.m.r. spectrum of this compound shows no sign of long-range coupling of the methyl group of the quinaldine moiety with the proton on the adjacent position of the heterocyclic ring, which

<sup>1</sup> S. A. Procter and G. A. Taylor, *J. Chem. Soc.*, in the press.

<sup>2</sup> H. Staudinger and H. W. Klever, *Ber.*, 1906, **39**, 968.

<sup>3</sup> H. Staudinger and H. W. Klever, *Ber.*, 1907, **40**, 1149.

<sup>4</sup> H. Staudinger, H. W. Klever, and P. Kober, *Annalen*, 1910, **374**, 1.

<sup>5</sup> J. C. Martin, V. A. Hoyle, and K. C. Brannock, *Tetrahedron Letters*, 1965, 3589.

<sup>6</sup> S. A. Procter and G. A. Taylor, unpublished results.

would be expected if the adduct had a 1,4-dihydroquinoline structure.

Acid hydrolysis of the quinoline adduct gave the acid  $C_{17}H_{21}NO_3$  [m.p.  $153^\circ$ ;  $\lambda_{\max}$  (EtOH) 238, 274  $m\mu$ , ( $\log \epsilon$  4.50, 3.67);  $\nu_{\max}$  1705, 1665  $cm^{-1}$ ], previously described by Staudinger.<sup>3,4</sup> The n.m.r. spectrum of this compound strongly supports the assignment of the cyclic structure (IVa), since the signals in the spectrum of the adduct, due to the isopropylidene group, are replaced by doublets at  $\tau$  8.73, 9.12 (3 protons each) and a septet at  $\tau$  6.73 (1 proton,  $J = 6.5$  c./sec.) indicating an isopropyl group with a marked difference in the magnetic environment of the methyl groups. This large difference could be attributed either to asymmetric substitution of the adjacent carbon atom, or restricted rotation about the C-CHMe<sub>2</sub> bond,

neither of which would be expected for the alternative amido-acid structure (Va). Similar evidence indicates that the methyl ester of this acid  $C_{18}H_{23}NO_3$  [m.p.  $58^\circ$ ;  $\lambda_{\max}$  (EtOH) 239, 274  $m\mu$ , ( $\log \epsilon$  4.44, 3.66),  $\nu_{\max}$  1750, 1665  $cm^{-1}$ ], obtained either from the reaction of the adduct with methanolic sulphuric acid<sup>3,4</sup> or from the reaction of the acid with diazomethane must be the pseudo-ester (IVb).

The adducts of dimethylketen with 2,6-dimethylquinoline<sup>3</sup> and isoquinoline<sup>4</sup> have been prepared, and an adduct with phenanthridine  $C_{21}H_{21}NO_2$  [m.p. 161—162°;  $\lambda_{\max}$  (EtOH) 232, 278, 340  $m\mu$ ; ( $\log \epsilon$  4.23, 3.83, 3.76),  $\nu_{\max}$  1748, 1708  $cm^{-1}$ ] has also been obtained. In all cases the spectroscopic data are consistent with the assignment of structures similar to (I).

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