

REASSIGNMENTS OF THE C=C AND C=O STRETCHING VIBRATIONS  
IN SIX-MEMBERED  $\alpha,\beta$ -UNSATURATED LACTAMS

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A new method for differentiating the lactam C=O infrared (IR) absorption from the C=C absorption in the six-membered,  $\alpha,\beta$ -unsaturated lactam system has been developed by utilizing association of dichloroacetic acid or a similar carboxylic acid with the lactam C=O, which decreases the frequency of the lactam C=O absorption by 20-40  $\text{cm}^{-1}$ . On the basis of such an association shift as well as the results obtained from solvent shift experiments with the lactams 1, 2, 4, and 6-8, the lactam C=O and the conjugated C=C absorptions observed for each of the  $\alpha,\beta$ -unsaturated lactams 3-8 in the 1590-1670  $\text{cm}^{-1}$  region were differentiated from each other. As a result, it has now become clear that in six-membered lactams the carbonyl frequency is slightly (10-20  $\text{cm}^{-1}$ ) lowered by conjugation with a double bond, in line with the usual lowering. This is the opposite of what has been proposed in the literature. In addition, the deuterated  $\alpha,\beta$ -unsaturated lactam 10 was prepared from the exocyclic methylene lactam 9 by treatment with NaOD in a mixture of  $\text{D}_2\text{O}$  and EtOD. This deuterium labeling was found to decrease the frequency of the 1666  $\text{cm}^{-1}$  absorption, assigned to the C=C stretching vibration, by 17  $\text{cm}^{-1}$ , supporting the correctness of the above differentiation.

