REASSIGNMENTS OF THE C=C AND C=O STRETCHING VIBRATIONS IN SIX-MEMBERED α,β-UNSATURATED LACTAMS

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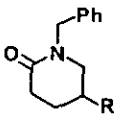
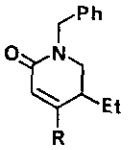
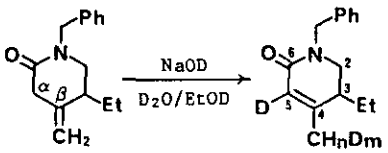
A new method for differentiating the lactam C=O infrared (IR) absorption from the C=C absorption in the six-membered, α,β-unsaturated lactam system has been developed by utilizing association of dichloroacetic acid or a similar carboxylic acid with the lactam C=O, which decreases the frequency of the lactam C=O absorption by 20-40 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 α,β-unsaturated lactams 3-8 in the 1590-1670 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 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 α,β-unsaturated lactam 10 was prepared from the exocyclic methylene lactam 9 by treatment with NaOD in a mixture of D_2O and EtOD. This deuterium labeling was found to decrease the frequency of the 1666 cm^{-1} absorption, assigned to the C=C stretching vibration, by 17 cm^{-1}, supporting the correctness of the above differentiation.



1: R = H
2: R = Et



3: R = H
4: R = Me
5: R = CH_2CO_2H
6: R = CH_2CO_2Me
7: R = CH_2CO_2Et
8: R = CH_2CONH_2



9 → 10