Causes of the Multiple Carbonyl Bands of Furan- and Thiophen-2-carbaldehydes, Alkyl Furan-2-carboxylates, and 2-Furoyl Chloride

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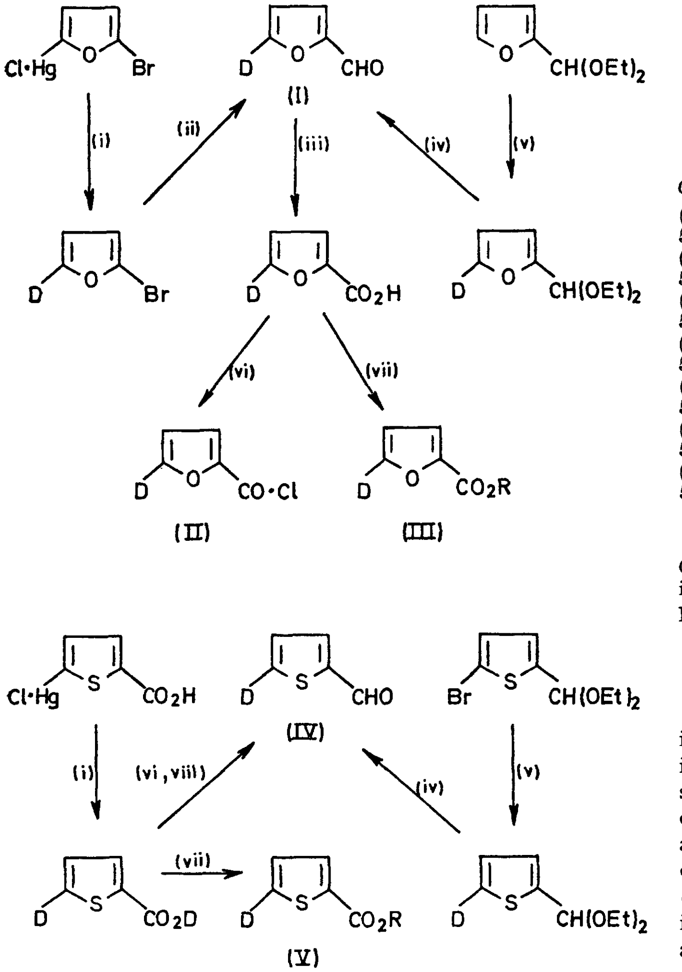
Summary Study of the 5-deuterio-analogues shows that the multiple i.r. carbonyl absorptions of furan- and thiophen-2-carbaldehydes, alkyl furan-2-carboxylates, and 2-furoyl chloride are caused by Fermi resonance and/or rotational isomerism.

WORK by different groups[1] and by us[2] led to the conclusion that the i.r. carbonyl doublet of furan-2-aldehyde (1700 and 1681 cm^{-1}, in CCl_4) arises from rotational isomerism, and it seemed reasonable that this explanation applied also to the main absorptions of thiophen-2-aldehyde (1688 and 1677 cm^{-1}). Three features, none by itself apparently very important, were difficult to accommodate on this basis: (i) while the data from detailed studies of heterocyclic 2-esters could be processed satisfactorily to give reasonable values for the energy differences between rotamers,[3] the same procedures produced surprising results with the aldehydes, (ii) it was not possible to rationalise completely the i.r. results[4] with the n.m.r. data for furan-2-aldehyde,[5] and (iii) the synthesis of a range of furan-2- and thiophen-2-aldehydes[6] showed that carbonyl doublets occur only rarely with these compounds. More seriously, the recent study[7] of the –CH^{18}O and –CDO analogues of thiophen-2-aldehyde suggests that Fermi resonance may be a contributing, or even the main, factor in causing the doublet absorption. Finally, the observation (see Table) that 2-furoyl chloride has four appreciable bands in the carbonyl region establishes that rotational isomerism alone cannot be the general explanation of multiple absorptions in heterocyclic compounds having C=O groups at position 2.



SCHEME.

Reagents: (i), $DCl–D_2O$; (ii) Bu^nLi, then $Me_2N{\cdot}CHO$; (iii), $AgNO_3–NH_3–H_2O$; (iv), $HCl–H_2O$; (v), Bu^nLi, then D_2O; (vi), $SOCl_2$; (vii), H_2SO_4–MeOH (R = Me) or $Me_2C{=}CH_2$ R = Bu^t); (viii), $LiAlH(OBu^t)_3$.

TABLE

I.r. spectra of (I)—(V) *and the non-deuteriated analogues*

Compound		ν		
(I)		1693		
5-H analogue	1700(3)	1681(1)		
(II)		1767(1·6)	1756(1)	
5-H analogue	1797(1)	1780(3)	1756(6)	1744(3)
(III) R=Me	1740(1·1)	1725(1)		
5-H analogue	1740(1·1)	1725(1)		
(III) R = Bu^t	1729(1)	1711(1·2)		
5-H analogue	1729(1)	1711(1·2)		
(IV)	1688(7)	1672(1)		
5-H analogue	1688(15)	1677(7)	1659(1)	
(V) R = Me	1721·5			
5-H analogue	1721·5			
(V) R = Bu^t	1710			
5-H analogue	1710			

The positions (cm^{-1}) of distinct bands (1800—1600 cm^{-1}, CCl_4 solutions at 303 K, spectral slit-width 1·7 cm^{-1}) are followed, in parentheses, by the relative optical densities of the components of multiple absorptions.

In order to distinguish clearly between rotational isomerism and Fermi resonance as the cause of carbonyl doublets in particular cases, we prepared the 5-deuterio-analogues shown in the Scheme. Since the 2-aldehydes are the central compounds, each was prepared by two routes: n.m.r. and m.s. examinations confirmed their structures. The i.r. consequences (see Table) of the 5-H → 5-D change are: (i) with furan-2-aldehyde the doublet (1700 and 1681 cm^{-1}) is replaced by a singlet (1693 cm^{-1}), (ii) with thiophen-2-aldehyde the band at 1659 cm^{-1} disappears (this band is so weak that it is reasonable to refer to the other two as the "doublet"), and the intensity of the lower frequency component of the doublet is considerably reduced, (iii) the four component absorption of 2-furoyl chloride is replaced by a doublet, and (iv) the absorptions of the esters (either doublets or singlets) are unchanged. Thus, the observed multiple absorptions are caused completely or mainly by Fermi resonance with the aldehydes, by a combination of Fermi resonance and rotational isomerism with 2-furoyl chloride, and (very probably) by rotational isomerism alone with the esters.

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