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FERMI RESONANCE IN THE INFRARED SPECTRA OF 3-PHENYL-2-CYCLOPENTENONES

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Some years ago Yates and Williams (1) investigated the infrared spectra of certain 3-phenyl-2-cyclopentenones that were anomalous in that two bands occurred in the carbonyl-stretching region. They established that association and rotational isomerism could be eliminated as the source of the bifurcation, as could the adventitious presence of the tautomeric 3-cyclopentenones. They concluded that the phenomenon was due to Fermi resonance (2) between the carbonyl-stretching vibration and a close-lying overtone that was tentatively identified as the first overtone of the out-of-plane bending vibration of the ethylenic C.2-H bond at 11.6-11.7 μ. This conclusion was corroborated by the fact that those compounds examined in which the C.2 hydrogen atom was replaced by a methyl group or a deuterium atom showed a single band in the carbonyl-stretching region and very weak or no absorption in the 11.6-11.7-μ region.

Further investigation has revealed that the structural requirements for the occurrence of Fermi resonance splitting of the carbonyl bands of 3-phenyl-2-cyclopentenones are more stringent than was originally thought. The relevant data are listed in Table I for thirteen such cyclopentenones, whose preparation and characterization will be discussed elsewhere. The seven compounds (1-7) that show two bands in the carbonyl-stretching region (3) have both a hydrogen atom at C.2 and two hydrogen atoms at C.5, whereas the six compounds (8-13) that show a single carbonyl-stretching band have one or

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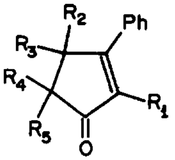
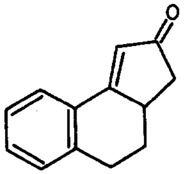
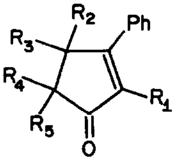
Table I. Infrared Spectra of 3-Phenyl-2-cyclopentenones

						$\lambda_{max}^{CCl_4}$ Carbonyl-stretching region	11.5-11.8-µ region
	R_1	R_2	R_3	R_4	R_5		
1	H	H	H	H	H	5.85, 5.97(sh)	11.62(mw)
2	H	Me	H	H	H	5.80, 5.90	11.75(mw)
3	H	Me	Me	H	H	5.81, 5.89	11.75(w,br)
4	H	Ph	H	H	H	5.83, 5.90	11.67(mw)
5	H	Ph	MeO	H	H	5.80, 5.87	11.65(w)
6	H	Ph	Ph	H	H	5.80(sh), 5.87	11.51(mw)
8	Me	H	H	H	H	5.86	-
9	H	H	H	Me	H	5.86	11.57(mw)
10[a]	Me	Ph	H	H	H	5.86	11.78(w)
11	Me	Ph	H	Me	H	5.86	-
12	H	Ph	H	Me	Me	5.86	11.47(mw)
13	H	Ph	H	Et	Et	5.86	11.50(mw)
7[b]						5.86, 5.98(mw)	11.75(w)

[a] Spectrum in CS_2. [b] We thank Professor A. L. Wilds for a sample of this compound; cf. A. L. Wilds and J. A. Johnson, Jr., *J. Amer. Chem. Soc.*, **68**, 86 (1946).

more alkyl groups at either or both of these positions. Corroboration for the view that Fermi resonance splitting requires the presence of three hydrogen atoms at the C.1 and C.5 positions was forthcoming from examination of the spectra of the ten deuterated derivatives of compounds 1-6 listed in Table II. With one exception, all of these spectra show the collapse of the split carbonyl-stretching bands in the spectra of the corresponding undeuterated compounds to single bands as a result of substitution of deuterium for hydrogen at either C.1 or C.5 or at both positions. The case of 3a is anomalous in that the carbonyl band shows a shoulder on the low wavelength side in spite of the absence of a hydrogen atom at C.2; the source of this anomaly has not been established, but it may be noted that the relative intensities of the two peaks are much less solvent dependent than in the case of compounds 1-7, which may indicate that the splitting has a different origin in this case.

Table II. Infrared Spectra of Deuterated 3-Phenyl-2-cyclopentenones

						$\lambda_{max}^{CCl_4}$ Carbonyl-stretching region	11.5-11.8-μ region
	R_1	R_2	R_3	R_4	R_5		
1a	D	D	D	D	D	5.86	11.70(vw)
2a	D	Me	D	D	D	5.86	-
3a	D	Me	Me	H	H	5.81(sh), 5.87	11.6-11.7(vw,br)
3b	H	Me	Me	D	D	5.82	-
3c	D	Me	Me	D	D	5.82	-
4a	D	Ph	D	D	D	5.87	-
5a	H	Ph	MeO	D	D	5.83	11.77(w)
6a	D	Ph	Ph	H	H	5.85	-
6b	H	Ph	Ph	D	D	5.84	-
6c	D	Ph	Ph	D	D	5.84	-

All of the compounds 1-7 show in their spectra medium to weak bands in the 11.50-11.75-μ region, which are absent or shifted in the spectra of their deuterated analogs. However, certain of the compounds 8-13 show absorption in this region also, and the occurrence of splitting cannot definitively be associated with the presence of such bands. If it is the overtones of vibrations giving rise to absorption in this region that are responsible for the Fermi resonance coupling with the carbonyl-stretching fundamentals, it is clear from the present results that the long-wavelength bands cannot be due to simple C.2-H bending vibrations. The alternative possibility exists that a combination vibration rather than an overtone is responsible for the coupling; again it can be concluded that C.2-H bending vibrations are not involved alone.

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(1) P. Yates and L. L. Williams, J. Amer. Chem. Soc., **80**, 5896 (1958).

(2) G. Herzberg, "Molecular Spectra and Molecular Structure. II. Infrared and Raman Spectra of Polyatomic Molecules," D. Van Nostrand Co., Princeton, N. J., 1945, p. 215.

(3) In all cases the effect on the relative intensities of the two peaks brought about by change in the polarity of the solvent was analogous to that reported earlier in the case of **4** (4).

(4) P. Yates, N. Yoda, W. Brown, and B. Mann, J. Amer. Chem. Soc., **80**, 202 (1958).