factor as 0.05, the figure which applies in acetolysis, leads to a K_e value of *ca.* 5×10^{-11}. The standard molar free energy of the [3.2.0] ester I exceeds that of the [2.2.1] isomer III by *ca.* 14,000 cal./mole.

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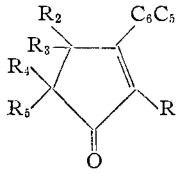
THE ANOMALOUS INFRARED SPECTRA OF SOME CYCLOPENTENONES

Sir:

It has been reported[1] recently that the infrared spectrum of 3,4-diphenyl-2-cyclopenten-1-one (I) in carbon tetrachloride solution is anomalous in that two bands of comparable intensity occur in the carbonyl-stretching region at 5.82 and 5.90 μ; this bifurcation was observed also with solutions in other solvents and with solid state spectra. The spectrum of 2,5-dimethyl-3,4-diphenyl-2-cyclopenten-1-one (II) showed a single band (5.86 μ, CCl_4), as did that of *cis*-3,4-diphenylcyclopentanone (III) (5.74 μ, $CHCl_3$). Since this region is of such extraordinary importance in the application of infrared spectroscopy to structural studies, it was of considerable interest to determine the origin and generality of this phenomenon.

Two possible sources—association or the presence of a mixture of Δ^2 and Δ^3 isomers—already have been eliminated.[1] Further, the perseverance of the double band in the solid state spectra and ultraviolet spectral studies made it most unlikely that the phenomenon is due to the presence of rotational isomers. There remained the possibility of Fermi resonance[2] between the carbonyl vibration and a close-lying overtone. There is in fact a band at 11.63 μ[3] in the spectrum of I which may be tentatively assigned to the out of plane bending vibration of the single ethylenic C-H bond of I.[4] The first overtone of this band should fall very close to the position anticipated for the simple carbonyl stretching frequency of I. That the splitting of the carbonyl band does indeed appear to depend upon the presence of a band at 11.6–11.7 μ has been determined by the examination of the spectra of a series of cyclopentenones. Compounds II, IV and V, all without ethylenic hydrogen, show only very weak or no absorption in this region and have single carbonyl-stretching bands, while compounds I, VI and VII, with single ethylenic hydrogen and bands at 11.6–11.7 μ, have split carbonyl bands. The case of VIII is instructive: the compound possesses a single ethylenic hydrogen but its bending band falls at 11.45 μ and a single carbonyl band is observed.[5]



I, $R_1 = H, R_2 = C_6H_5, R_3 = R_4 = R_5 = H$
II, $R_1 = CH_3, R_2 = C_6H_5, R_3 = R_4 = H, R_5 = CH_3$
IV, $R_1 = CH_3, R_2 = C_6H_5, R_3 = R_4 = R_5 = H$
V, $R_1 = CH_3, R_2 = R_3 = R_4 = R_5 = H$
VI, $R_1 = R_2 = R_3 = R_4 = R_5 = H$
VII, $R_1 = H, R_2 = CH_3, R_3 = R_4 = R_5 = H$
VIII, $R_1 = H, R_2 = C_6H_5, R_3 = H, R_4 = R_5 = CH_3$
IX, $R_1 = D, R_2 = C_6H_5, R_3 = R_4 = R_5 = D$

Confirmation for this view was obtained by the preparation of 3,4-diphenyl-2-cyclopenten-1-one-2,4,5,5-d_4 (IX) by heating I in dioxane with deuterium oxide and sodium carbonate; IX was obtained as colorless needles, m.p. 109.5–110° (*Anal.* Calcd. for $C_{17}H_{10}D_4O$: atom % excess D, 28.57. Found: D, 28.69). The spectrum of IX had no band at 11.63 μ and showed a single carbonyl band at 5.86 μ. Also the deuterated product obtained by similar treatment of VII lacked the band in the 11.6–11.7 μ region and had a single band at 5.86 μ in place of the two bands of VII at 5.81 and 5.89 μ.

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[1] P. Yates, N. Yoda, W. Brown and B. Mann, THIS JOURNAL, **80**, 202 (1958).

[2] G. Herzberg, "Infrared and Raman Spectra of Polyatomic Molecules," D. Van Nostrand Co., New York, N. Y., 1945, p. 215; E. B. Wilson, Jr., J. C. Decius and P. C. Cross, "Molecular Vibrations," McGraw-Hill Book Co., New York, N. Y., 1955, p. 198.

[3] This and subsequently quoted band positions are for solutions in carbon tetrachloride.

[4] *Cf.* P. Yates, M. I. Ardao and L. F. Fieser, THIS JOURNAL, **78**, 650 (1956); R. N. Jones, F. Herling and E. Katzenellenbogen, *ibid.*, **77**, 651 (1955).

[5] It may be noted that for all of these compounds the first overtones belong to the same symmetry species as the carbonyl-stretching fundamental and thus Fermi resonance is allowed; *cf.* ref. 2.

BOOK REVIEWS

Actualités Biochimiques. No. 20. Aspects Actuels de la Biochimie des Acides Aminés et des Protéines. By J. T. EDSALL, Professeur a l'Université Harvard. Publiées sous la direction de Marcel Florkin et Jean Roche. Masson et Cie., Éditeurs, 120, boulevard Saint-Germain, Paris 6e, France. 1958. 156 pp. 16 × 24 cm. 2.000 fr.

Unlike the review of a manuscript that of a book is something like reviewing a TV program—it's too late to do anything about it. In the present instance, however, this reviewer would not have done anything about it even if he had had the opportunity. In this comparatively short monograph the topics for consideration have been carefully selected, are lucidly presented and bring the reader right up to work in progress in the biophysical chemistry of the amino acids, peptides and proteins. In many respects it may be considered a supplement to the earlier ACS monograph on this subject by Cohn and Edsall.

The volume under review is the result of a series of lectures by Professor Edsall at the College of France and at the Sorbonne in late 1955 and early 1956. Translated into easily read French by Professor Jean Roche and associates the material has been published as number 20 in the "Actualites Biochimiques" paperback series. The almost simultaneous