

ASSIGNMENT OF INFRARED BANDS OF DIPHENYLCYCLOPROPENONE

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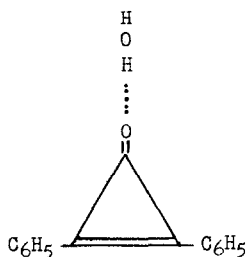
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Assignment of two characteristic strong bands, ca. 1850 and 1630  $\text{cm}^{-1}$  of diphenylcyclopropenone (I) has been discussing. Recently, Yoshida and coworkers assigned the band at 1630  $\text{cm}^{-1}$  to carbonyl stretching on the basis of solvent shift. We wish to report isolations of crystalline complexes of I with water and with acetylene alcohols, and infrared spectral studies on those in relating to the assignment.

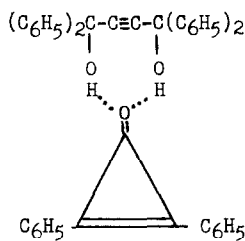
Recrystallization of I from water-saturated methylene chloride gave monohydrate (II), colorless needles, mp 87.5°. The hydrate was also obtained by allowing to stand a suspension of I in water at room temperature for a few days, or by heating the suspension for a few minutes. Anal. Calcd. for  $\text{C}_{15}\text{H}_{12}\text{O}_2$ : C, 80.36; H, 5.36. Found: C, 80.16; H, 5.16. IR: 3440 with shoulders at 3470 and 3400 ( $\nu\text{OH}$ ), 620 and 600  $\text{cm}^{-1}$  ( $\delta\text{OH}$  out-of-plane). By replacing the water of II with deuterium oxide,  $\nu\text{OH}$  shifted to 2593 and 2510, and  $\delta\text{OH}$  to ca. 450  $\text{cm}^{-1}$  region. An 8.0% weight loss observed after heating of II at 80° (1 mm) for 2 hr was well agreed with the theoretical amounts of water 8.0%. The remained crystals were identified as I, mp 119-120° (lit. mp 119-120°).

The characteristic bands of I appeared at 1858, 1848, 1626 and 1619  $\text{cm}^{-1}$ . On the hydrate II, the former two bands coalesced to one peak, 1842, and the latter ones shifted to 1605  $\text{cm}^{-1}$ . The bands in 1630  $\text{cm}^{-1}$  region which shifted more than 14  $\text{cm}^{-1}$  toward lower frequency, would be assign-

\* Infrared spectra were recorded on a grating photometer, in crystalline state unless noted otherwise.



II



IV

ed to the carbonyl stretching. The value of the shift was greater than that recorded for I in carbon tetrachloride containing methanol, about  $10\text{ cm}^{-1}$  (5)

The cyclopropenone I showed the band at  $1341\text{ cm}^{-1}$  which is probably due to C-CO-C skeleton vibration. On the other hand, II had two peaks,  $1349$  and  $1363\text{ cm}^{-1}$ , and both peaks were caused no change by replacing the water with deuterium oxide. Although it is not clear which is C-CO-C vibrational band, it is reasonable to consider that the band was shifted toward higher frequency by hydrogen-bonding.

The most striking spectral difference between I and II was observed in the region due to out-of-plane deformation of aromatic hydrogens. Four bands in I,  $785$ ,  $760$ ,  $700$  and  $680\text{ cm}^{-1}$ , turned into two ones,  $715$  and  $685\text{ cm}^{-1}$  in II. The phenomena would be interpreted as follows: Out-of-plane deformation of ortho-hydrogen atoms of the phenyl rings in I is restricting by each other repulsion, and distinguished from that of other hydrogens. The hydrogen-bonding would give some effect which decrease the restriction, forcing all hydrogens spectrally equivalent. A similar interpretation has been reported by Luttke for the spectral difference between cis- and trans-stilbenes.

A mixture of 1,1,4,4-tetraphenylbut-1-yne-1,4-diol (III) and I was dissolved in benzene by warming to afford the 1:1 complex (IV), colorless needles, mp  $138-139^\circ$ . Anal. Calcd. for  $\text{C}_{43}\text{H}_{32}\text{O}_3$ : C, 86.58; H, 5.37. Found: C, 86.96; H, 5.34. IR:  $3337(\text{OH})$ . The molar ratio was determined by alkaline hydrolysis of IV. Treatment of 1 mole of IV in alkaline medium under the condition (1) that I was hydrolyzed to cis-1,2-diphenylacrylic acid, afforded each 1 mole of the acid and III. By the same method, the 1:2 complex (VI) of 1,1,6,6-tetraphenylhexa-2,4-diyne-1,6-diol (V) and I was prepared, colorless prisms, mp  $149^\circ$ . Anal. Calcd. for  $\text{C}_{60}\text{H}_{42}\text{O}_4$ :

C, 87.17; H, 5.08. Found: C, 87.42; H, 5.33. IR:  $3230\text{ cm}^{-1}$  ( $\nu_{\text{OH}}$ ). The molar ratio was determined by the same method employed for IV.

The hydroxy stretching of IV and VI shifted toward lower frequency,  $273$  and  $380\text{ cm}^{-1}$ , respectively, from those of corresponding acetylene alcohols, III and V. By infrared studies on the complexes prepared from III- $d_2$  and from V- $d_2$ , those bands were assigned to hydrogen-bonded hydroxy stretching.

Infrared bands of IV and VI in the regions of  $1850$  and  $1630\text{ cm}^{-1}$  were more complicated than those of II. The complex IV showed peaks at  $1850$ ,  $1828$ ,  $1815$ ,  $1595$ ,  $1580$  and  $1570\text{ cm}^{-1}$ . Similar peaks,  $1850$ ,  $1825$ ,  $1815$ ,  $1595$ ,  $1580$  and  $1570\text{ cm}^{-1}$  were observed for VI. All bands in  $1630\text{ cm}^{-1}$  region shifted toward lower frequency than  $1600\text{ cm}^{-1}$ . The band at  $1850\text{ cm}^{-1}$ , however, remained unshifted even though two bands appeared newly in the region of  $1815$ - $1828\text{ cm}^{-1}$ . The data would support again the assignment of the band at  $1630\text{ cm}^{-1}$  to carbonyl stretching.

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