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THE CARBONYL FREQUENCY OF DIPHENYLCYCLOPROPENONE.

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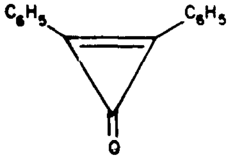
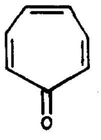
In the infrared spectra of disubstituted cyclopropenones, e.g.diphenylcyclopropenone (I), there appear two intense frequencies, at about 1850 and 1630 cm^{-1}, respectively. In general, it has been assumed that the former band is the carbonyl frequency. In a recent review (2), Krebs has suggested to invert this assignment and to consider the 1630 cm^{-1} band as the stretching mode of the carbonyl group, whilst the 1850 cm^{-1} band is said to be characteristic of the disubstituted cyclopropene system. Breslow and co-workers (3) have tentatively adopted these assignments. The present paper supports Krebs' proposal and enlarges upon it: the intense band at 1850 cm^{-1} is ascribed to the disubstituted triafulvene system as a "molecular frequency".

The method we used for a decision was Bellamy's (4-6) solvent variation technique. It is based on the observation that the carbonyl frequency $\nu_{C=0}$ in solvents of different polarity shows a pattern: for a given substance, a band will represent the carbonyl frequency, if the relative change in frequency $\frac{\Delta\nu_{C=0}}{0}$ with the solvent shows the same pattern as for a known carbonyl compound. We have compared I with tropone (II) (which also shows two bands in the carbonyl region), in which the charge distribution is expected to be similar to that prevailing in the cyclopropenone system and for which the relevant data are known (7,8). As ν_0, the frequency in the vapor phase or in a paraffin hydrocarbon as solvent has been adopted. Table I shows our experimental data for I and compares the $\frac{\Delta\nu_{C=O}}{\nu_0}$ values for I and II. It follows that only the 1630 cm^{-1} band of I shows the same solvent dependence as that band of II which has been shown before to represent the stretching mode of the carbonyl. The slope of the graph ("solvent slope") is 1.60, practically identical with that of tropone (1.66) (7). Thus, the 1630 cm^{-1} band of (I) represents its carbonyl frequency.

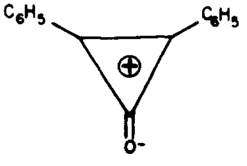
By inference, the intense 1850 cm^{-1} band of I must be assigned differently. We propose that it is a "molecular frequency" (9), not of the R.C=C.R system in I (2) (an intense frequency of 1850 cm^{-1} for this system seems unlikely), but of the disubstituted triafulvene system in its pseudoaromatic form (Ia). The 1850 cm^{-1} band of (I) would thus be parallel to "band I" of tropone (10).



I



II



Ia

It should be noted that also the band at 1850 cm^{-1} of I is dependent on the solvent. This tends to support the view recently expressed by Andreades (11) that the two intense infrared bands of I are coupled.

In some 1,2-disubstituted cycloprop-1-enes an infrared absorption appears in the neighbourhood of 1850 cm^{-1}: sterculic acid, 1,2,3,3-tetramethylcyclopropene and 1,2-dimethyl-3-(1-indenyl)-cyclopropene. In several other compounds of this type, there appear bands at about 1800 cm^{-1}. However, in all these cases, the intensity of the band is weak and cannot be compared with that of the 1850 cm^{-1} band discussed here.

Ketone I is thus best considered as 1-oxa-3,4-diphenyl-triafulvene.

The results obtained permit an alternative (and, in our opinion, preferable) explanation of the infrared frequency of the diamagnetic Ni^{0} complex $(C_{15}H_{10}O)_3$ Ni(CO) formed from I and nickel carbonyl. Bird and Hollins (12) have considered the medium strong band at 1720 cm^{-1} in this complex as the 1850 cm^{-1} band of I shifted by coordination, since the same kind of shift has been observed in analogous complexes of cyclopentadienone (13). In view of the diagonally opposite electronic character of the cyclopentadienyl and cyclopropenyl system, "coordination" of I should <u>raise</u> the carbonyl frequency (because it decreases the contribution of the pseudoaromatic form Ia), if coordination of a cyclopentadienone system <u>lowers</u> that frequency. Therefore, the band at 1720 cm^{-1} is the <u>upwards</u> shifted carbonyl frequency (1630 cm^{-1}) of I, whilst the band at 1642 cm^{-1} of the complex of tetraphenyl-cyclopentadienone $(C_{29}H_{20}O)Fe(CO)_3$ is the <u>downward</u> shifted C=O frequency (1715 cm^{-1}) of this ketone (14). Equally, the complex formed from 3,4-diphenylcyclopentadienone and iron carbonyl absorbs at 1647 and 1637 cm^{-1}(15), and that originating from 2,3-diphenylindone at 1631 cm^{-1} (16,17). This explanation is supported by the behaviour of tropones in metal carbonyl complexes; the carbonyl frequency of tropone (in carbon tetrachloride) lies at 1595 cm^{-1}, that of the complex $(C_7H_6O)Fe\ (CO)_3$ at 1637 cm^{-1} (18), and the analogous complex of 2,4,6-triphenyltropone has its carbonyl absorption at 1623 cm^{-1}.

T A B L E I

Comparison of the Infrared Spectrum of Diphenylcyclopropenone (I) and Tropone (II) in Various Solvents.

Solvent	Diphenylcyclopropenone				Tropone[b)]			
	Band I $\nu(cm^{-1})$	Band II $\nu(cm^{-1})$	Band I $\frac{\Delta\nu}{\nu_0}x10^3$	Band II $\frac{\Delta\nu}{\nu_0}x10^3$	Band I $\frac{\Delta\nu}{\nu_0}x10^3$	Band II $\frac{\Delta\nu}{\nu_0}x10^3$	Band I $\frac{\Delta\nu \text{vapor}}{\nu_0}\times10^3$	Band II $\frac{\Delta\nu \text{vapor}}{\nu_0}\times10^3$
n-Heptane (ν_0)	1865	1646	-	-	-	-	3.6	6.8
Diethyl ether[a)]	1851	1678	7.5	4.9	-	1.2	3.6	8.1
Carbon tetra-chloride	1857	1637	4.3	5.5	-	4.4	3.6	11.2
Carbon disulfide	1853	1634	6.4	7.3	0.6	5.6	4.2	12.9
Dioxane	1854	1633	5.9	7.9	1.8	7.5	5.4	14.3
Chloroform	1846	1624	10.2	13.4	6.1	12.5	9.7	19.2
Acetonitrile	1846	1600	10.2	27.9	6.7	10.6	10.3	17.4

[Notes: (a) The solvent in the case of tropone was diisopropyl ether, not diethyl ether.
(b) Data from ref.8.]

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well into the homologous series of cycloalkanones (cyclobutanone 1784, cyclopentanone 1750, cyclohexanone 1725, cycloheptanone 1700 cm^{-1}).

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