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THE INFRARED ABSORPTION OF CARBONYL GROUPS IN BRIDGED COMPOUNDS

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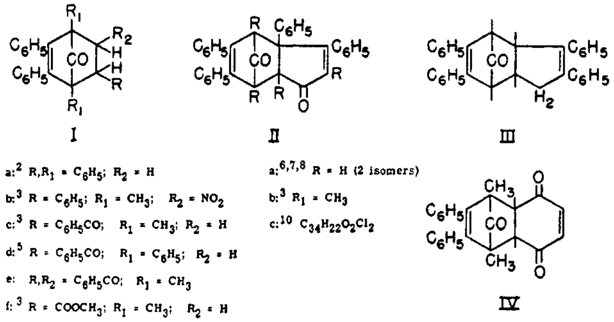
Since small-membered cyclic ketones have a carbonyl infrared absorption that is characteristic for the ring size (1), it seemed worth while to examine available carbonyl bridged compounds to see if they exhibited an analogous property. The substances of particular interest contain a six-membered ring with a *para*-bridge, the latter obviously being subject to considerable strain. Two types were studied (Fig. 1); in one (I) (seven representatives), there was only the ring and the bridge just mentioned, while others were bridged indenes [II, III (9)] and the naphthoquinone [IV (2–8, 10)]. In three of these (Ia, Ib, III), there was only one carbonyl group, the one that formed the bridge. The infrared absorption for carbonyl was found to be at 5.64 μ; the same band was also found in all the others. In the compounds containing additional ketonic carbonyl groups (Ic, Id, Ie, II) conjugated with a double bond, the characteristic absorption at 5.99 μ was also found; bands corresponding to ester (If) and acid (Ig) were likewise present at 5.79 μ and 5.88 μ, respectively. It may, therefore, be concluded that this band (5.64 μ) is characteristic for a *para*-carbonyl bridge in a six-membered ring.

All the substances mentioned also have one double bond, β,γ- to the bridge; it is conceivable that this relationship could be connected with the location of the band at 5.64 μ. That this is not true is evident from an examination of the saturated carbonyl bridge indenone, V (Fig. 2) which shows this same absorption (5.64 μ) (11).

There are two references (12, 13) in the old literature in which saturated and bridged six-membered bicyclic ketones, VI and VII (Fig. 2), are said to be formed. In each instance, a semicarbazone was isolated from the liquid mixture, resulting from pyrolysis of salts of hexahydroterephthalic and hexahydroisophthalic acids. A re-examination of the terephthalic acid product was carried out. The small liquid distillate was fractionated and each portion was submitted for possible identification, using both the mass spectrometer and infrared absorption. There was no indication that any components had the characteristic absorption at 5.64 μ. Attention has already been called (14) to the improbability of structure VII; the properties of the ketone and its semicarbazone are those of 1-methyl-3-cyclohexen-2-one. Both these structures (VI, VII), therefore, should be stricken from the literature.

The chemical properties of *para*-carbonyl bridge compounds of a six-membered ring are characteristic, and differ from those having larger rings (15). The infrared absorption is likewise different; three available ketones [VIII (16, 17), IX, X (19); Fig. 3] were examined. The carbonyl absorption of the solid (VIII) in a potassium bromide pressing was found to lie at 5.86 μ, whereas in chloroform solution (18) it appeared at 5.75 μ; the saturated ketone (IX) had a band at



I

a:[2] $R,R_1 = C_6H_5$; $R_2 = H$

b:[3] $R = C_6H_5$; $R_1 = CH_3$; $R_2 = NO_2$

c:[3] $R = C_6H_5CO$; $R_1 = CH_3$; $R_2 = H$

d:[5] $R = C_6H_5CO$; $R_1 = C_6H_5$; $R_2 = H$

e: $R,R_2 = C_6H_5CO$; $R_1 = CH_3$

f:[3] $R = COOCH_3$; $R_1 = CH_3$; $R_2 = H$

g:[4] $R,R_2 = COOH$; $R_1 = H$

II

a;[6,7,8] R = H (2 isomers)

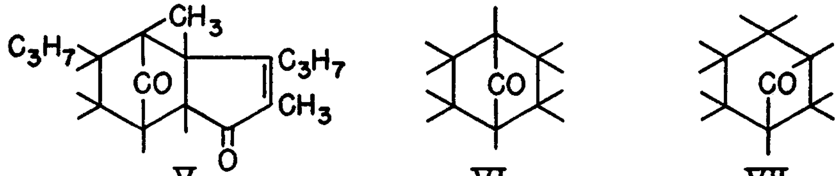
b:[3] $R_1 = CH_3$

c:[10] $C_{34}H_{22}O_2Cl_2$

III

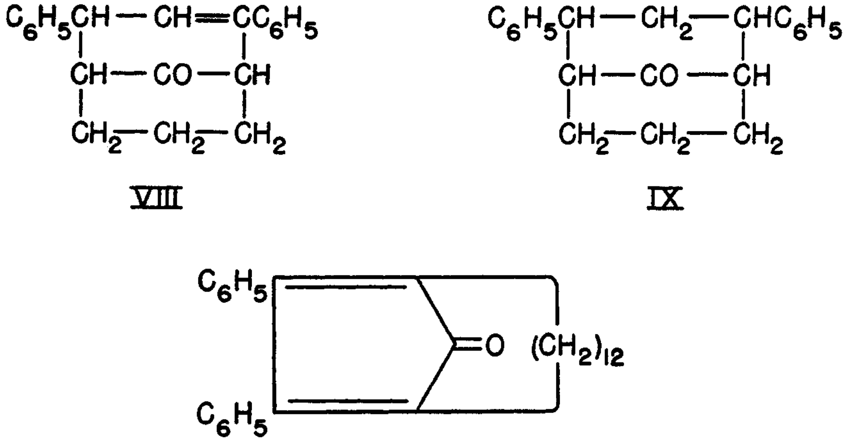
IV

FIG. 1



V VI VII

FIG. 2



VIII IX

X

FIG. 3

5.84 μ in the same solvent, while that of the macrocyclic ketone (X) was at 5.88 μ.

Discovery of this characteristic infrared absorption band (5.64 μ) makes it possible to distinguish between structures of isomers in cases where the chemical evidence alone does not permit one to assign a structure unequivocally; it also necessitates corrections in a few instances. The largest group are the products of Grignard reactions; they will form the subject of the following paper.

Infrared absorptions in the 5–7 μ region only are shown in Fig. 4, although

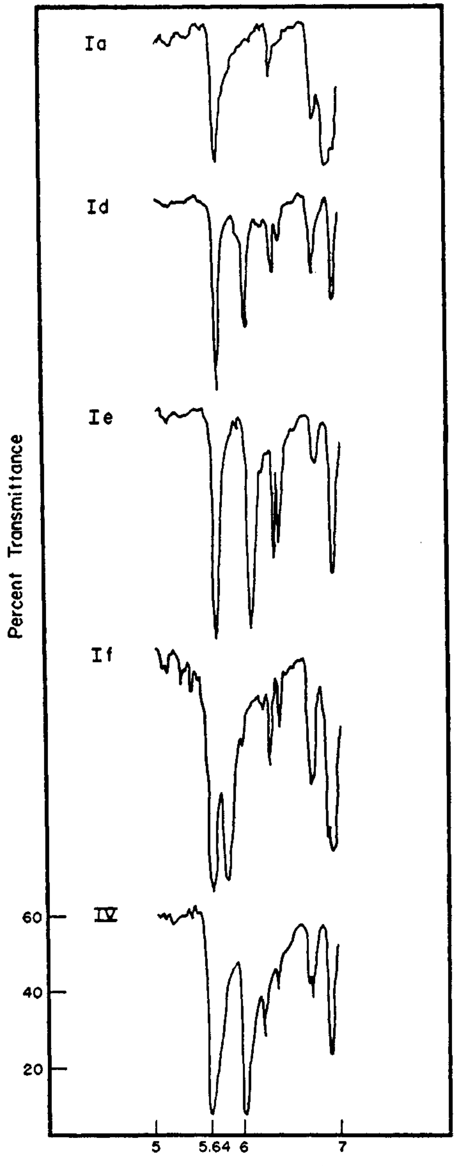


FIG. 4: INFRARED ABSORPTION OF CARBONYL BRIDGE COMPOUNDS IN THE REGION 5–7 μ.

measurements were made over the entire range from 2 to 15 μ. These spectra were obtained on a Baird double-beam recording spectrophotometer (20), using rock-salt optics. Samples were prepared either as Nujol mulls or as pressed plates in potassium bromide (21, 22).

EXPERIMENTAL

All the substances examined, except IV, had been previously prepared. In the absence of specific information, several procedures were employed in heating the barium salt of *trans*-hexahydroterephthalic acid.[1] The largest amount of distillate was formed when copper helices were thoroughly mixed in to increase the heat transfer. Infrared spectra were run on different fractions of the distillate; in no case was there any absorption at 5.64 μ.

5,8-Dimethyl-6,7-diphenyl-1,4,9-trioxo-4a,5,8,8a-tetrahydro-5,8-methanonaphthalene (IV). A mixture of 13 g. of the bimolecular product (IIa), 12.8 g. of *trans*-dibenzoylethylene, and 40 ml. of benzene was refluxed for 4 hours, the solvent was removed, and the residue was triturated with methanol. It was recrystallized from an ethyl acetate-methanol mixture; the yield was 23 g.; m.p. 146° (from *n*-propyl alcohol).

Anal. Calc'd for $C_{35}H_{28}O_3$: C, 84.6; H, 5.7.
Found: C, 84.7; H, 5.6.

SUMMARY

The infrared absorptions of numerous carbonyl bridge compounds have been determined. Those substances which have a 1,4-(*para*)bridge across a six-membered ring have a characteristic band at 5.64 μ. This property can be useful in giving proof of structure. In larger rings, this carbonyl absorption band appears at 5.84–5.88 μ.

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