

## The Chelation of 3-(*p*-Hydroxybenzylidene)-2,4-pentanedione with the Thallous Ion

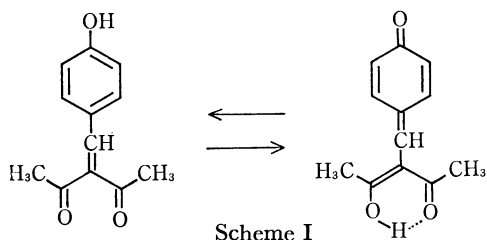
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A thallous compound of 3-(*p*-hydroxybenzylidene)-2,4-pentanedione was synthesized and its structure was determined by means of the infrared and proton magnetic resonance spectra. This compound was regarded as a thallous phenolate derivative; however, the effect of chelation by the 2,4-pentanedione moiety due to a long-range anionotropy was observed. The acetyl proton exchange of the Tl(I) compound in D<sub>2</sub>O was observed by a PMR investigation. It was found that the methyl-proton exchange was inhibited by chelation.

Metal chelates of 2,4-pentanedione (acetylacetone), which behaves as an enol, have been well-studied. When two protons at the 3-position of acetylacetone are substituted, no stable metal chelates can be formed, since no such enolization can occur. Although 3-(*p*-hydroxybenzylidene)-2,4-pentanedione (POBAA) has no proton at the 3-position since it is occupied by a benzylidene linkage, it can be drawn as a pair of tautomers, in one of which the 2,4-pentanedione moiety enolizes by a long-range conjugation through the *p*-hydroxyphenyl group, as is shown in Scheme I. It can, therefore, be assumed that the tautomer forms metal chelates as ordinary acetylacetonates.



3-(*o*-Hydroxybenzylidene)-2,4-pentanedione was also considered to enolize in the same sense. It had been synthesized by the condensation of salicylaldehyde with acetylacetone.<sup>1)</sup> It, however, turned out in our investigation that the product was not the diketo compound but a ketol, *i.e.*, 3-acetyl-2-hydroxy-2-methyl-2*H*-chromene. It is, therefore, omitted from the present investigation; the structure proof will be reported elsewhere.

Several attempts were made to isolate transition metal chelates of POBAA; however, they all resulted in failure. Only a thallous salt was isolated as crystals, and spectroscopic observations of it revealed that it was not a simple phenolate but was characteristic of a complex salt; the Tl(I) ion showed some interaction with the 2,4-pentanedione moiety, as had been expected. This paper will deal with the structure determination of the Tl(I) compound by means of electronic, infrared, and proton magnetic resonance spectroscopy. A thallous salt of 3-(*m*-hydroxybenzylidene)-2,4-pentanedione (MOBAA) was also investigated for the sake of comparison.

### Experimental

All the melting points are uncorrected. The IR spectra were determined in potassium bromide disks with a Hitachi

EPI-S2 spectrophotometer, while the electronic spectra were measured in ethanol with a Hitachi EPS-3T spectrophotometer. The PMR spectra were recorded at 60 MHz in CDCl<sub>3</sub>, methanol, dimethylsulfoxide, and a D<sub>2</sub>O solution with a Hitachi Model R-24 NMR spectrometer. The chemical shifts are quoted as  $\tau$  values relative to tetramethylsilane in CDCl<sub>3</sub> or DSS (sodium 2,2-dimethyl-2-silapentane-5-sulfonate) in D<sub>2</sub>O.

**3-(*p*-Hydroxybenzylidene)-2,4-pentanedione (POBAA).** A solution of 12.2 g (0.1 mol) of *p*-hydroxybenzaldehyde and 10.2 g (0.1 mol) of acetylacetone in 30 ml of ethanol was cooled to  $-15^{\circ}\text{C}$ ; 30 drops of piperidine were then added to the solution at a temperature below  $-10^{\circ}\text{C}$ . After the solution had stood in a refrigerator for several days, the resulting yellow solid was collected and recrystallized from dilute ethanol to give 11.2 g (55.8%) of pale yellow needles; mp  $125\text{--}127^{\circ}\text{C}$ .

Found: C, 70.86; H, 5.96%. Calcd for C<sub>12</sub>H<sub>12</sub>O<sub>3</sub>: C, 70.58; H, 5.92%.

This compound is hydrolyzed to its original components by repeated recrystallizations from dilute ethanol.

**3-(*m*-Hydroxybenzylidene)-2,4-pentanedione (MOBAA).** *m*-Hydroxybenzaldehyde was used in place of *p*-hydroxybenzaldehyde; otherwise the procedure was the same as in POBAA synthesis. The product was recrystallized from ethanol to give 16.7 g (83.2% yield) of colorless crystals; mp  $128\text{--}129^{\circ}\text{C}$ .

Found: C, 70.68; H, 6.07%. Calcd for C<sub>12</sub>H<sub>12</sub>O<sub>3</sub>: C, 70.58; H, 5.92%.

**Thallous Salt of POBAA and MOBAA.** To a solution of POBAA or MOBAA in absolute ethanol we added an equimolar amount of freshly prepared thallous ethoxide<sup>2)</sup> in absolute ethanol at room temperature. The resulting orange or yellow crystals were filtered and washed with absolute ethanol and dried over P<sub>2</sub>O<sub>5</sub> at  $50^{\circ}\text{C}$  in a vacuum.

POBAA-Tl (I), Found: C, 35.14; H, 2.77%. MOBAA-Tl (I), Found: C, 35.08; H, 2.75%. Calcd for C<sub>12</sub>H<sub>11</sub>O<sub>3</sub>Tl: C, 35.34; H, 2.72%.

### Results and Discussion

According to the molecular model of 3-benzylidene-2,4-pentanedione (BAA),<sup>3)</sup> it seems to be impossible that all the double bonds including the two carbonyl groups are in one conjugated system, because the planarity of the molecule is impaired by the steric hindrance between the benzene ring and the *syn*-acetyl group. The methine proton exhibits a PMR peak in the low magnetic field at  $\tau$  2.51. This indicates that the proton and the benzene ring are coplanar.

There are two singlets, at  $\tau$  7.72 and  $\tau$  7.60, which are due to the two acetyl groups. The peak in the higher magnetic field can be assigned to the conjugation-free acetyl group which is at the *syn*-position to the phenyl group, and the lower one, to another acetyl group which is conjugated with the styryl moiety. In the region of carbonyl and olefinic stretching vibrations, BAA exhibits IR absorptions at 1711 (strong), 1662 (strong), 1620 (medium), and 1576 (weak)  $\text{cm}^{-1}$ . The absorption at 1711  $\text{cm}^{-1}$  is assigned to the conjugation-free acetyl carbonyl, while the others are due to another acetyl carbonyl, an olefinic bond, a benzene ring, or their conjugated stretching vibrations.

In the cases of POBAA and MOBAA, the PMR spectra are shown in Fig. 1. The assignments of the peaks can be understood in the same way as those of BAA; the coplanar methine proton resonance appears at  $\tau$  2.60 in the former and at  $\tau$  2.50 in the latter. The singlets at  $\tau$  7.66 and  $\tau$  7.60 for POBAA and the singlets at  $\tau$  7.69 and  $\tau$  7.60 for MOBAA are assigned to the conjugation-free and the conjugated acetyl groups. The peak due to hydroxyl proton appears at  $\tau$  2.89 and at around  $\tau$  2.8 respectively. The infrared spectra of POBAA and MOBAA are shown in Fig. 2, in which the stretching vibration of the conjugation-free acetyl carbonyl appears at 1705  $\text{cm}^{-1}$  for the former and at 1702  $\text{cm}^{-1}$  for the latter; in addition, the OH stretching vibrations are at 3350  $\text{cm}^{-1}$  and at 3230  $\text{cm}^{-1}$  respectively.

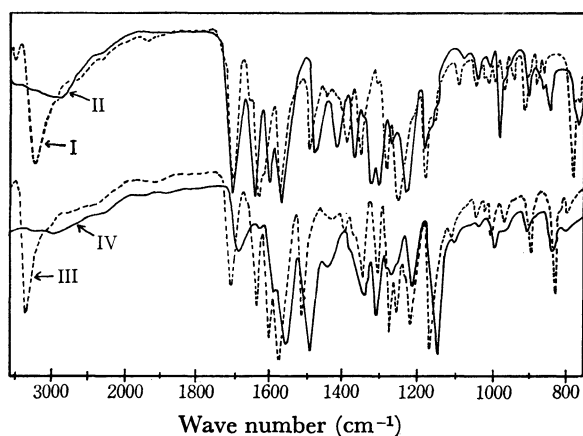


Fig. 1. IR spectra of I: MOBAA, II: MOBAA-Tl(I), III: POBAA, and IV: POBAA-Tl(I).

The ultraviolet absorption maxima of BAA, MOBAA, and POBAA in ethanol are: BAA: 208 nm ( $\log \epsilon$ : 3.99), 220 (3.92), 284 (4.24); MOBAA: 217 (4.11), 245 (3.98), 287 (4.21), around 330 (shoulder); POBAA: 218 (3.88), 235 (3.96), 327 (4.35). These strong absorptions due to  $\pi$ - $\pi^*$  transitions indicate the presence of a long conjugated system. Judging from the highest degree of red shift in POBAA, the electronic contribution of the *p*-hydroxyl group is included in the conjugated system.

The Tl(I) salts of POBAA and MOBAA are soluble in polar solvents; however, their electronic absorption spectra in solution resemble those of the parent compounds. It is, therefore, assumed that POBAA-Tl(I) and MOBAA-Tl(I) both dissociate incompletely into

the Tl(I) ion and the anion of POBAA or MOBAA in the solution. The PMR spectra of POBAA-Tl(I) and MOBAA-Tl(I) in  $\text{D}_2\text{O}$  are shown in Fig. 2. The PMR pattern of MOBAA-Tl(I) is nearly equal to that of MOBAA except for the absence of the peak due to a hydroxyl proton and the induced chemical shifts of the methine and phenyl peaks by the Tl(I) ion in MOBAA-Tl(I); it also exhibits the methine proton resonance at  $\tau$  2.31 and the two acetyl proton resonances at  $\tau$  7.67 and  $\tau$  7.56 respectively. It can be said that there is no fundamental difference in structure between MOBAA and MOBAA-Tl(I).

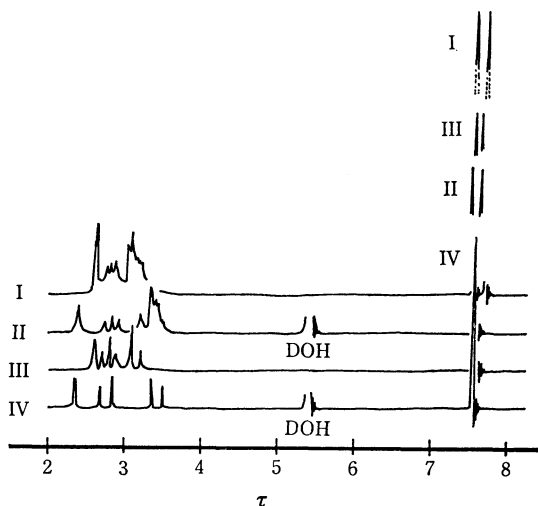
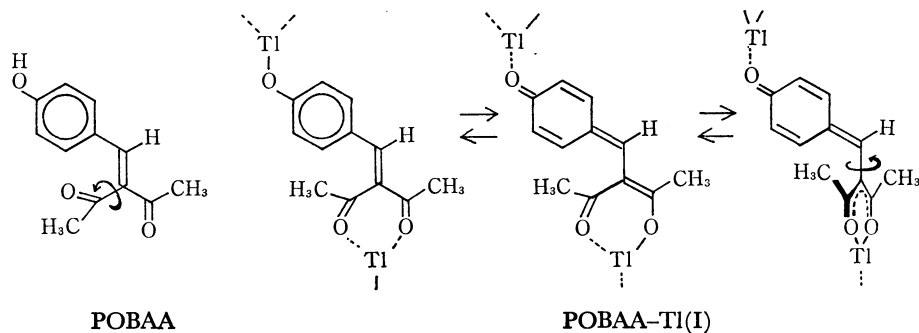


Fig. 2. PMR spectra of I: MOBAA and III: POBAA in  $\text{CDCl}_3$ , and II: MOBAA-Tl(I) and IV: POBAA-Tl(I) in  $\text{D}_2\text{O}$ .

Between the PMR spectrum of POBAA and that of POBAA-Tl(I), a marked difference was observed. Two peaks due to the two kinds of acetyl protons in POBAA became one sharp peak at  $\tau$  7.59 in the Tl(I) salt in  $\text{D}_2\text{O}$ , while the methine proton peak shifted to the lower magnetic field and appeared at  $\tau$  2.37. The formation of such a singlet at around  $\tau$  7.5 was observed in methanol and dimethylsulfoxide as well as in  $\text{D}_2\text{O}$ . This means that all the acetyl protons of POBAA-Tl(I) are equivalent. Judging from the low  $\tau$  value of the methine peak, the methine proton and the benzene ring are maintained in a coplanar configuration. If the molecule is fixed as a phenolate structure, the steric situation of the two acetyl groups, one of which is in the same plane as the benzene ring, while the other is out of the plane, can not differ from that of POBAA. The equivalence of the acetyl protons can be understood provided the acetyl groups are rapidly interconverted by a flip rotation of the 2,4-pentanedione moiety, as is shown in Scheme II. This explanation leads to the conclusion that the benzylidene C=C bond must have a single-bond character; hence, a long-range anionotropy should exist in the anion of POBAA.

The IR spectra of POBAA-Tl(I) and MOBAA-Tl(I) were compared with those of POBAA and MOBAA (Fig. 1). The band due to a hydroxyl group is necessarily absent in the Tl(I) compounds. Most remarkable is the difference between the IR peaks of POBAA-Tl(I)



Scheme II

and those of POBAA in the double-bond stretching region. The peaks of POBAA-Tl(I) are found to be broad and to shift to lower wave numbers compared with those of POBAA. This difference in the absorption pattern clearly reveals a change in the bond character from POBAA to POBAA-Tl(I), in which the electron delocalization or coordination of the diketone moiety to the Tl(I) ion takes part. The structure of POBAA-Tl(I) seems to consist of the planes of the anions of POBAA chained together by the Tl(I) ions. On the contrary, these situations are not observed in MOBAA-Tl(I).

It can thus be concluded that MOBAA-Tl(I) is a simple phenolate, while in POBAA-Tl(I), as a result of a long-range anionotropy, the diketone moiety interacts in part with the Tl(I) ion, as in acetylacetonates.

We also attempted to prepare transition-metal chelates of POBAA. When POBAA was heated in ethanol with each acetate of copper(II), nickel(II), and cobalt(II), or each chloride of cobalt(II) and iron(III), no complexes were obtained, and the hydrolysis of the ligand took place slowly in every case. The metal-ion-exchange reaction with POBAA-Tl(I) was thus examined. A mixture of POBAA-Tl(I) and anhydrous cobalt(II) chloride or anhydrous ferric chloride in absolute ethanol gave white precipitates of thallos chloride; however, all attempts to isolate the desired complex from the resulting filtrate were unsuccessful.

During the course of the PMR investigation of

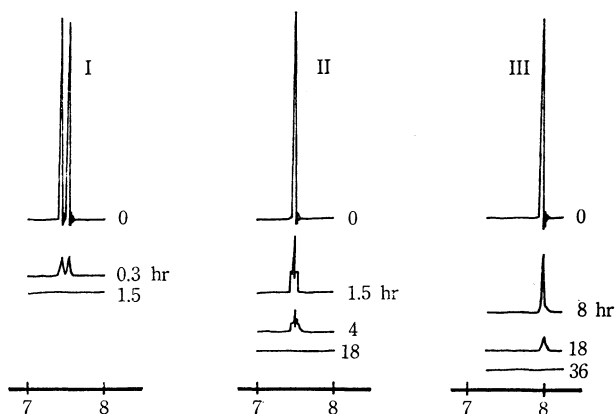
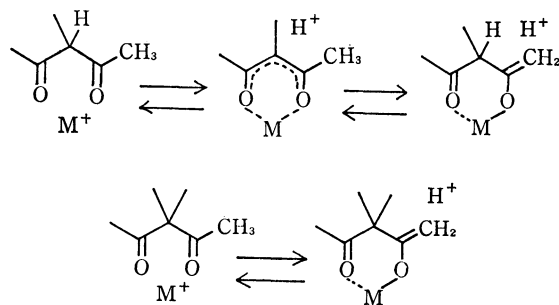


Fig. 3. PMR peaks due to acetyl protons of I: MOBAA-Tl(I), II: POBAA-Tl(I) and III: Tl(I)-acetylacetonate recorded at 35.5 °C at appropriate time intervals (hour) after being dissolved in D<sub>2</sub>O.



Scheme III

POBAA-Tl(I) in D<sub>2</sub>O, a decrease in the intensity of the peak due to acetyl protons were observed with the time. This is clearly due to a hydrogen-deuterium exchange reaction in solution. The exchange rate was, therefore, compared with those of MOBAA-Tl(I) and Tl(I)-acetylacetonate;<sup>4</sup> the results are shown in Fig. 3. The decreasing order of the rate of the acetyl proton exchange is: MOBAA-Tl(I) > POBAA-Tl(I) > Tl(I)-acetylacetonate. This order is opposite to that of the stability of the complexes. From an inspection of the mechanism of the proton dissociation shown in Scheme III, it can readily be understood that the proton dissociation from the methyl group is necessary for MOBAA to form a chelate. In other words, the methyl proton of MOBAA is activated by the neighboring metal ion. On the other hand, acetylacetonate forms stable metal chelates by the dissociation of the methylene proton at the 3-position. The methyl-proton activation, therefore, is inhibited by metal-chelate formation. The situation of POBAA-Tl(I) is in between, since the chelate ring stabilization is possible but incomplete because it can take place only with the long-range anionotropy, as has been discussed above. Since the relationship between such a proton exchange rate and the degree of activation of methyl protons has not yet been investigated, the systematic investigation of various thallos compounds is now in progress.

#### References

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