BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN VOL. 42 3345—3348 (1969)

The Intramolecular Hemiacetal Structure of Benzoyl(2-hydroxybenzoyl)carbinol and Its Monobenzoate*1

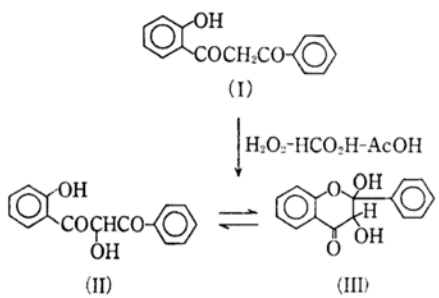
Heitaro OBARA and Jun-ichi ONODERA

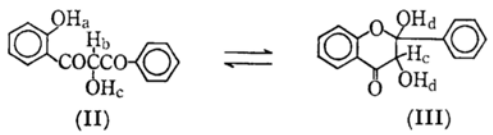
Department of Applied Chemistry, Faculty of Engineering, Yamagata University, Yonezawa

(Received May 6, 1969)

In previous studies, the present authors have reported that a ring-chain tautomerism exists between benzoyl(2-hydroxybenzoyl)methyl bromide and its cyclic intramolecular hemiacetal structure, *i. e.*, 2-hydroxy-3-bromoflavanone.[1] In the present investigation, we have found that a similar tautomerism exists between benzoyl(2-hydroxybenzoyl)-carbinol (II) and its monobenzoate (IV).

The carbinol (II) was prepared by Winicki *et al.*[2] from benzoyl(2-hydroxybenzoyl)methane (I) by oxidation with hydrogen peroxide in a mixed solution of formic and acetic acid; however, no investigation has been made concerning its hemiacetal structure (III). In order to ascertain the tautomerism between II and III, the NMR, IR, and UV spectra of this carbinol and the behavior of its monobenzoate (IV) will be discussed in the present paper.





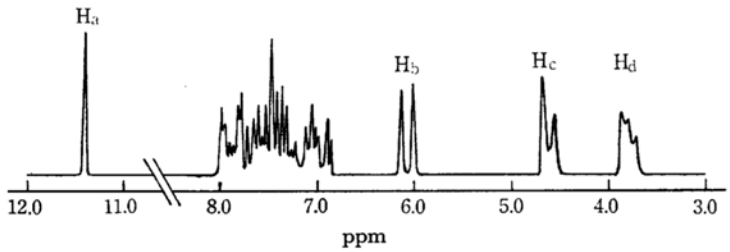


Fig. 1. NMR spectrum of II ⇋ III in $CDCl_3$.

Results and Discussion

The NMR spectrum of the carbinol (II) in $CDCl_3$ exhibits four groups of bands (a, b, c, and d) in addition to the aromatic protons (6.67 ppm—8.02 ppm), as Fig. 1 shows. These four bands were assigned as follows: 1) the a band on the low-field side of these bands is due to the hydrogen-bonding phenolic OH proton in II; 2) the b band (doublet), which changes to a singlet after deuterium exchange, is due to the methine proton of –COCH(OH)CO– in II, and the c band may be attributed to a mixture of the OH proton of –COCH(OH)CO– in II and the methine proton in III, which leaves after deuterium exchange. (They were determined by comparison with those of dibenzoylcarbinol.)*2

*1 Presented in part at the Tohoku Branch Meeting of the Chemical Society of Japan, Yonezawa, June, 1966.

1) H. Obara and J. Onodera, This Bulletin, **41**, 2798 (1968).

2) B. Winicki, C. Nofre, J. Chopin and A. Cier, *Bull. Soc. Chim. France*, **1962**, 1695.

*2 This carbinol was prepared by the oxidation of dibenzoylmethane with hydrogen peroxide in a mixture of formic and acetic acid; mp 110°C (lit mp 110°C[3]).

3) P. Karrer, J. Kebrle and R. M. Thakkar, *Helv. Chim. Acta*, **33**, 1711 (1950).

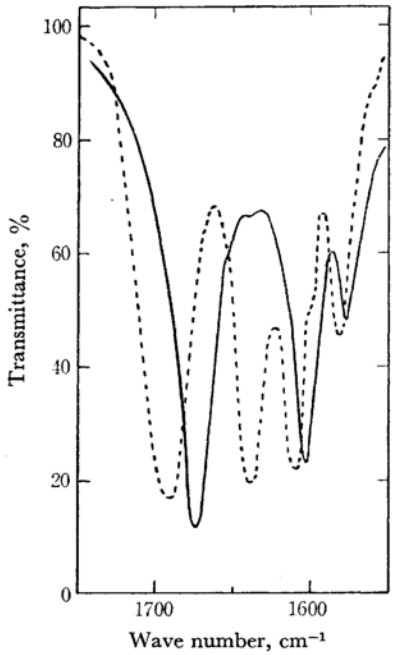


Fig. 2. IR spectra of benzoyl(2-hydroxybenzoyl)-carbinol.
——: in KBr disk, ------: in $CHCl_3$.

3) The remaining d band is due to the two OH protons in III, which disappears after the deuterium exchange. From the relative areas of the a, b, c, and d bands, the molar ratio of the tautomers II and III in this case was found to be approximately 2 : 1.

The IR spectrum of this carbinol showed a strong carbonyl absorption band at 1674 cm^{-1} in the KBr disk, while two carbonyl absorption bands at 1690 cm^{-1} and 1638 cm^{-1}, corresponding to free and bonded carbonyl groups,[4] were observed in the chloroform solution, as is shown in Fig. 2.

From the results of these NMR and IR spectral analyses, the cyclic hemiacetal structure, *i. e.*, 2,3-dihydroxyflavanone (III), rather than II must be given for this carbinol in the crystalline state; in the chloroform solution, this carbinol exists as an equilibrium state between II and III, analogous to benzoyl(2-hydroxybenzoyl)methyl bromide and its hemiacetal structure.[1] However, when this carbinol was dissolved in chloroform, no variation in the absorption band with the lapse of time has been observed in the IR spectrum. It is considered that this carbinol immediately reaches equilibrium between II and III in a solution.

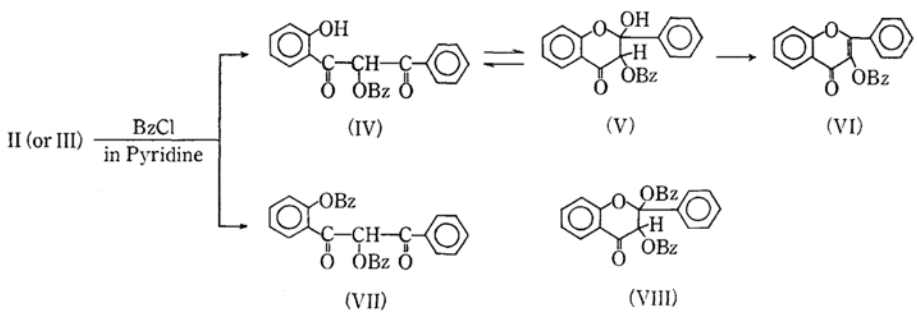
The UV spectrum of this carbinol exhibits its absorption maxima at 253 mμ and 321 mμ in ethanol; the absorption curve is very similar to those of flavanone and 3-hydroxyflavanone.

Finally, the existence of a ring-chain tautomerism between II and III was ascertained by the chemical method.

Two benzoates were obtained from this carbinol by benzoylation with benzoyl chloride in pyridine. One was dibenzoate (mp 159—160°C), which had previously been reported in the literature,[2] and the other was a new monobenzoate (mp 102—104°C). The structure of this monobenzoate was identified as benzoyl(2-hydroxybenzoyl)benzoyloxymethane (IV) because it is converted into 3-benzoyloxyflavone[5] (VI) with acid or heat.

The IR spectrum of this monobenzoate in a chloroform solution gave an interesting result, as much as in the case of benzoyl(2-hydroxybenzoyl)-methyl bromide[1] in the 1600—1750 cm^{-1} region. It showed two strong carbonyl absorption bands at 1713 cm^{-1} and 1728 cm^{-1} immediately after it had been dissolved in chloroform, but the former band slowly decreased with the lapse of time; a new absorption band appeared at 1643 cm^{-1}, and then it remained unchanged for at least 1 hr (Fig. 3).

This new band is considered to be a characteristic absorption band due to the intramolecular chelated carbonyl group in the structure IV which is observed in aromatic *o*-hydroxyketones.[4] On the other hand, the IR spectrum of this monobenzoate in a KBr disk showed no chelated carbonyl absorption band near 1630—1640 cm^{-1}; such a band would appear if the structure were IV (Fig. 4).



4) L. J. Bellamy, "The Infra-red Spectra of Complex Molecules," John Wiley & Sons, New York (1958), p. 143.

5) J. E. Gowan, P. M. Hayden and T. S. Wheeler, *J. Chem. Soc.*, **1955**, 862.

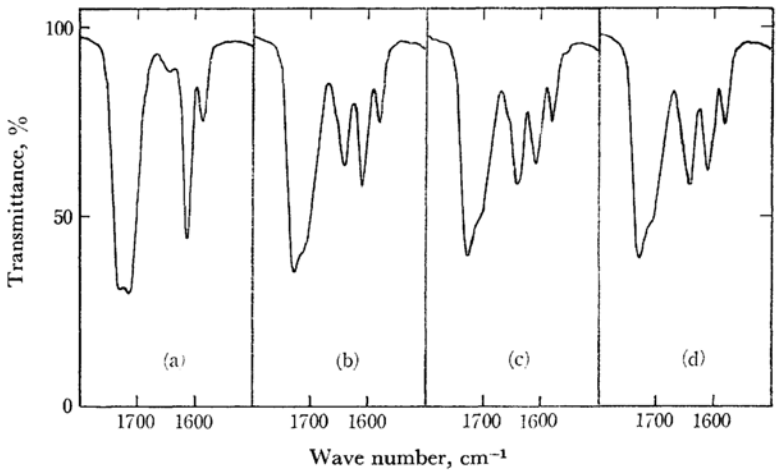


Fig. 3. The variation of IR spectra of benzoyl(2-hydroxybenzoyl)-benzoyloxymethane (IV) with the time in $CHCl_3$ solution. (a): Immediately after dissolving. (b): After 10 min. (c): After 25 min. (d): After 1 hr.

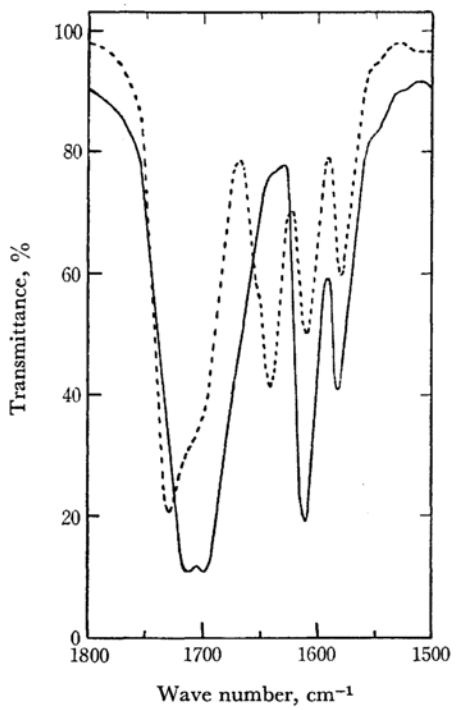


Fig. 4. IR spectra of benzoyl(2-hydroxybenzoyl)-benzoyloxymethane (IV).
——: in KBr disk, ------: in $CHCl_3$.

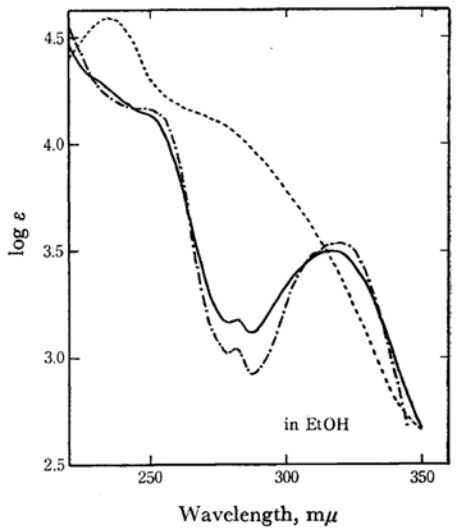


Fig. 5. UV spectra of benzoyl(2-hydroxybenzoyl)-benzoyloxymethane (IV) (——), 3-benzoyloxyflavanone (IX) (·—·—·) and benzoyl(2-benzoyloxybenzoyl)benzoyloxymethane (VII) (------).

From these results, it is expected that this monobenzoate has the structure V before dissolving and that it reaches equilibrium between IV and V in a solution; the cyclic hemiacetal structure V rather than IV must be given for this monobenzoate in the crystalline state. The isomeric monobenzoate, *i.e.*, benzoyl(2-benzoyloxybenzoyl)carbinol, was not isolated in this benzoylation.

The UV spectrum of the monobenzoate in ethanol, which exhibits absorption maxima at 248 mμ (inflect.), 283 mμ, and 316 mμ, is very similar to that of 3-benzoyloxyflavanone (IX) (Fig. 5).

On the other hand, two isomeric structures, *i. e.*, VII or VIII, must be considered for the dibenzoate. Structure VII was, however, supported by its UV spectrum, because the absorption curve does not resemble that of flavanones (Fig. 5). Another dibenzoate (VIII) has not been isolated in this benzoylation of this carbinol.

Experimental

Benzoyl(2-hydroxybenzoyl)carbinol (II). This carbinol was prepared from benzoyl(2-hydroxybenzoyl)-methane (I) in a 53% yield as has been described by Winicki *et al.*[2] Mp 101.5—103.5°C, (lit[2] mp 104°C) UV λ_{max}^{EtOH} mμ (log ε) 253 (4.00) 321 (3.50).

Found: C, 70.24; H, 4.68%. Calcd for $C_{15}H_{12}O_4$: C, 70.30; H, 4.72%.

Benzoylation of Benzoyl(2-hydroxybenzoyl)-carbinol (II). Into a solution of II (520 mg) in 2 m*l* of pyridine, there was added a 600 mg portion of benzoyl chloride. After it had been heated on a water bath for 10 min, the reaction mixture was poured into cold 3 N hydrochloric acid; the resulting pale yellow oil was extracted with ether. The ether layer was washed with water and dried over anhydrous sodium sulfate. The filtrate was concentrated to about 8 m*l*, and 4 m*l* of petroleum ether were added. After the solution had then been allowed to stand overnight in an ice-box, the resulting crystal (A) was filtered out and the filtrate was chromatographed on a column of silica gel. Elution with benzene-ethyl acetate (20 : 1) gave benzoyl-(2-hydroxybenzoyl)benzoyloxymethane (IV), which was recryltallized from carbon tetrachloride. Yield, 35 mg; mp 102—104°C. UV λ_{max}^{EtOH} mμ (log ε) 248 (inflect.) (4.14), 283 (3.18), 316 (3.50).

Found: C, 73.22; H, 4.80%. Calcd for $C_{22}H_{16}O_5$: C, 73.33; H, 4.48%.

The recrystallization of (A) from ethanol gave 235 mg of benzoyl(2-hydroxybenzoyl)carbinol dibenzoate (VII) as colorless prisms; mp 159—160°C (lit[3] mp 159°C), UV λ_{max}^{EtOH} mμ (log ε) 235 (4.59).

The authors wish to express their thanks to Professor Koji Nakanishi of Tohoku University and the members of his laboratory for their measurement of the NMR spectra.