The Intramolecular Hemiacetal Structure of Benzoyl-(2-hydroxybenzoyl)methyl Bromide*[1]

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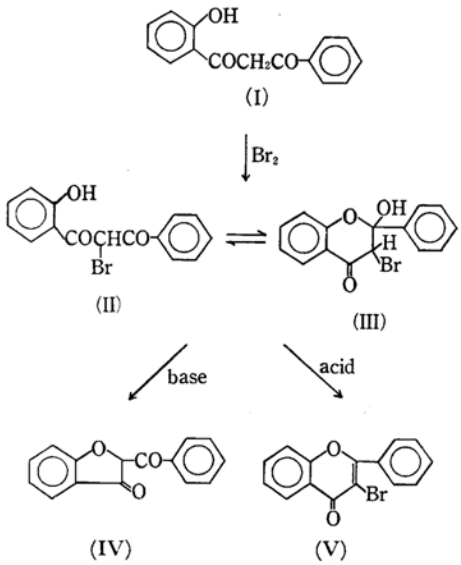
During the course of their studies of the properties of benzoyl(2-hydroxybenzoyl)methyl bromide (II), which was afforded from benzoyl(2-hydroxybenzoyl)methane (I) by bromination in a chloroform solution in the presence of potassium carbonate, the present authors found that a ring-chain tautomerism exists between II and its cyclic hemiacetal structure (III). II was prepared by Hlavka,[1] in 1965, from I by bromination with *N*-bromosuccinimide in a chloroform solution for the purpose of its photolysis, and it has been reported that this bromide converts easily into 3-benzoylcoumaranone (IV)[2] and 3-bromoflavone (V)[3] with a base or an acid respectively.

However, no investigation has been made concerning its cyclic hemiacetal structure. In order to ascertain this tautomerism, the NMR, IR and UV spectra of this bromide and its homologue will be discussed in the present paper.



Results and Discussion

The NMR spectrum of this bromide in $CDCl_3$ exhibits four groups of signals (a, b, c, and d) in addition to the aromatic proton groups (6.65 ppm—8.20 ppm), as is shown Fig. 1. From the fact that the a and d bands disappear after the D_2O exchange, the a peak on the lowfield side of these bands was attributed to the hydrogen bonding phenolic OH proton in II, while the d peak was attributed to the hemiacetal OH proton in III. The c band was assigned by comparing it with the signal due to the -COCHBrCO- proton in dibenzoyl methyl bromide,*[2] and the b band was assigned to the -COCHBr- proton in the hemiacetal (III).

From the relative peak areas of a, b, c, and d, the molar ratio of the tautomer II and III in this case was found to be approximately 3 : 11.

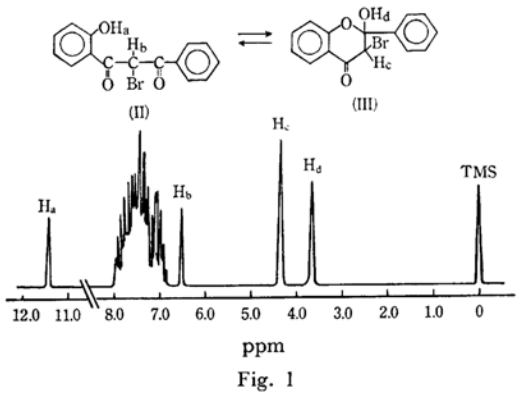


Fig. 1

The IR spectrum of this bromide in a chloroform solution gave an interesting result in the 1600 cm^{-1}—1700 cm^{-1} region. It showed a strong carbonyl absorption band at 1678 cm^{-1} immediately after it had been dissolved in chloroform; however, this absorption band decreased slowly with the lapse of time, and a new absorption band appeared at 1634 cm^{-1} and then remained unchanged for at least 4 hr (Fig. 2). It is considered that this new band is a characteristic absorption band due to the intramolecular chelated carbonyl group in the structure II which is observed in aromatic *o*-hydroxyketones.[4]

*1 Presented at the Tohoku Local Meeting of the Chemical Society of Japan, Hirosaki, October, 1967.

1) J. J. Hlavka, *Chem. Ind.*, **1965**, 1500.

2) T. A. Geissman and Ardy Armen, *J. Am. Chem. Soc.*, **77**, 1623 (1955).

3) Hrishikesh Krishna Pendse, *Rasâyanam.*, **2**, 121 (1956); *Chem. Abstr.*, **51**, 5063 (1957).

*2 This bromide was prepared by the bromination of dibenzoylmethane, mp 92—93°C.

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

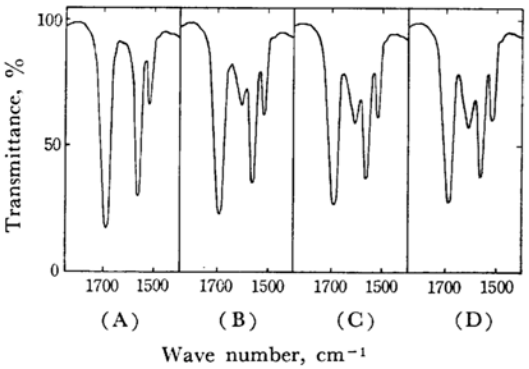


Fig. 2. The variation of the IR spectra of (II) with time in $CHCl_3$.
A: Immediately after dissolving. B: After 10 min. C: After 30 min. D: After 4 hr.

From the results of these IR spectra measurements, it is expected that this bromide has the structureIII before dissolving, and that it reaches equilibrium between II and III in a solution. It seems to be a very valuable result that the variation in such ring-chain tautomerism between II and III was observed in the IR spectrum measurements. On the other hand, the IR spectrum of this bromide in a KBr disk is similar to those of flavanone (VI) and 3-hydroxyflavanone (VII), and there is no chelated carbonyl absorption band near 1634 cm^{-1}, which would be expected if the structure of this bromide were II (Fig. 3).

From these observations, the cyclic hemiacetal structure III rather than II must be given for this bromide in the crystalline state. Accordingly, it is presumed that the strong peak of this bromide shown at 3270 cm^{-1} in Fig. 3 is not a phenolic OH peak but a hemiacetal OH-stretching peak.

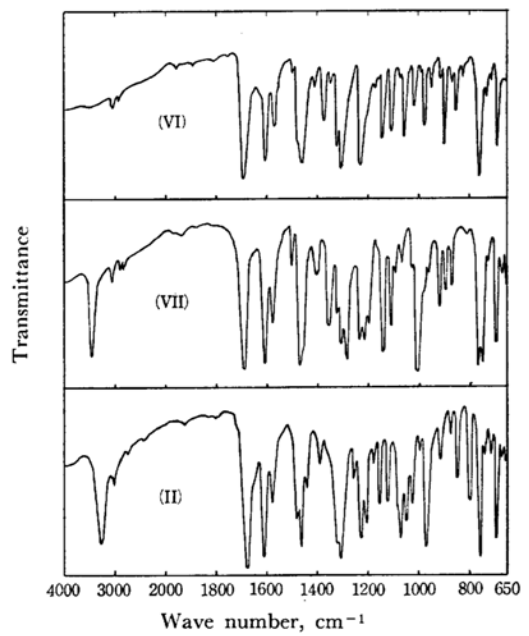


Fig. 3. The IR spectra of flavanone (VI), 3-hydroxyflavanone (VII) and benzoyl(2-hydroxybenzoyl)methyl bromide (II) in KBr disks.

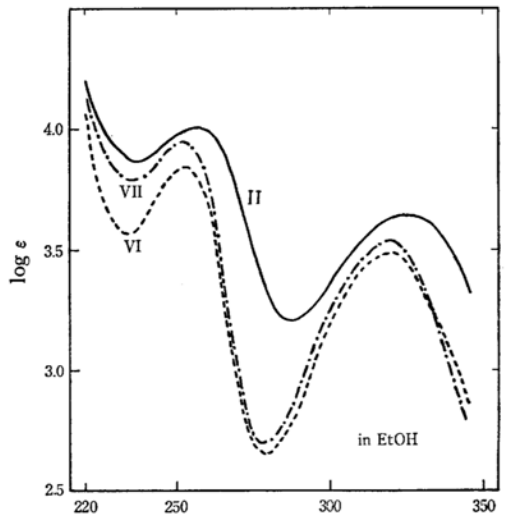


Fig. 4. The UV spectra of benzoyl(2-hydroxybenzoyl)methyl bromide (II); flavanone (VI) and 3-hydroxyflavanone (VII).

The UV spectrum of this bromide exhibits its absorption maxima at 257 mμ and 324 mμ in ethanol; the similarity of the absorption curve with those of flavanone (VI) and 3-hydroxyflavanone (VII) was observed.

Finally, the existence of ring-chain tautomerism in II and III was ascertained by the chemical

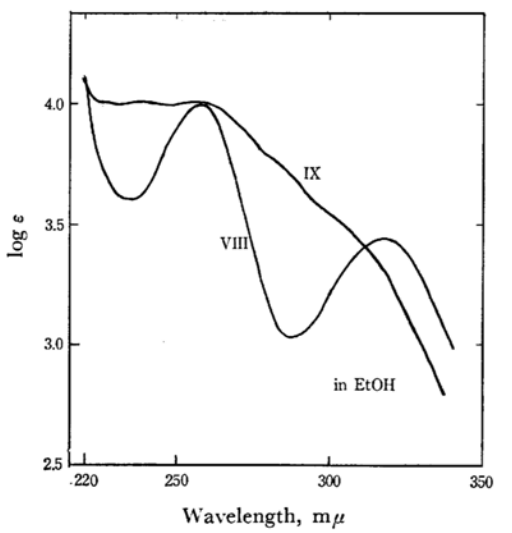
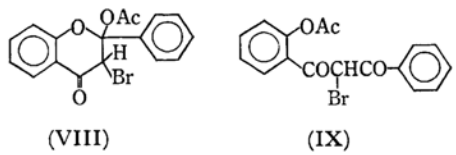


Fig. 5. The UV spectra of benzoyl(2-acetoxybenzoyl)methyl bromide (IX) and 2-acetoxy-3-bromoflavanone (VIII).

method. Two acetates were obtained from this bromide by acetylation with acetic anhydride in pyridine; one was crystalline (mp 151—152°C), and the other was a viscous oil, while both were analyzed as acetates of II or III.

The UV spectrum of the crystal acetate exhibits its absorption maxima at 257 mμ and 318 mμ, and its absorption curve is similar to those of flavanones (VI and VII); however, the oily acetate is not. (Fig. 5). The IR spectra of both acetates showed the same CO bands due to the acetyl groups at 1766 cm^{-1} and 1767 cm^{-1}, but two different CO bands were observed in the 1670 cm^{-1}—1700 cm^{-1} region (Fig. 6).



(VIII) (IX)

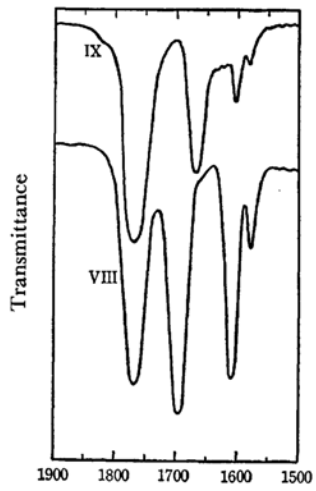


Fig. 6. The IR spectra of benzoyl(2-acetoxybenzoyl)methyl bromide (IX) and 2-acetoxy-3-bromoflavanone (VIII) in $CHCl_3$.

In these experiments, the ring-chain tautomerism between II and III was confirmed by NMR, IR and UV spectra measurements, and by the formation of two isomeric acetates; furthermore, it was proved that this bromide exists as the cyclic hemiacetal structure (III) *i. e.*, 2-hydroxy-3-bromoflavanone in the crystalline state.

Experimental

Benzoyl(2-hydroxybenzoyl)methyl Bromide (II). A solution of 1.0 g of bromine in 8 m*l* of chloroform was stirred into a mixture of 1.40 g of benzoyl(2-hydroxybenzoyl)methane (I) and 2.5 g of anhydrous potassium carbonate in 60 m*l* of chloroform at 0°C. After the addition was completed, the reaction mixture was filtered, and the filtrate was evaporated *in vacuo*. Ligroin was added to the oily residue, which was then allowed to stand overnight in an ice box. By the recrystallization of the resulting pale yellow solid from chloroform-ligroin, 1.29 g of II were afforded as colorless needles. Mp 141°C. Reported mp 145—146°C[1] IR (KBr), 3270 cm^{-1} (ν OH), 1678 cm^{-1} (ν CO). UV λ_{max}^{EtOH} mμ (log ε), 257 (4.01), 324 (3.65).

Found: C, 56.63; H, 3.70%. Calcd for $C_{15}H_{11}O_3Br$: C, 56.45; H, 3.47%.

Formation of 2-Benzoylcoumaranone (IV) and 3-Bromoflavone (V). a) II was converted to yellow crystals by heating it with pyridine at 75°C for 5 min. Recrystallization from methanol gave IV as yellow needles melting at 79—81°C. Reported mp 79—80°C.[2] IR (KBr), 1616 cm^{-1} (ν CO). UV λ_{max}^{EtOH} mμ (log ε), 241(4.05) 258(4.02) 348(4.21). b) To a solution of II in acetic acid, a drop of concentrated sulfuric acid was added, and the mixture was heated for 10 min at 100°C. It was then poured into water. The recrystallization of the resulting crystals from ethanol gave V as colorless needles melting at 124—125°C. Reported mp 126.5°C.[3] IR (KBr), 1660 cm^{-1} (ν CO). UV λ_{max}^{EtOH} mμ (log ε) 249 (4.27) 309 (4.09).

Acetylation of Benzoyl(2-hydroxybenzoyl)-methyl Bromide (II). To a solution of 500 mg of II in 5 m*l* of acetic anhydride, 2 drops of pyridine were added, after which the mixture was allowed to stand at room temperature for 2 days. The resulting yellow solution was poured into cold water, and the oily product was extracted with ether. The ether layer was washed with a dilute sodium hydrogencarbonate solution and water, and was dried over anhydrous sodium sulfate. The ether was removed by distillation, and the residue was chromatographed on a column of silica gel. Elution with ether-petroleum ether (2 : 1) gave 10 mg of 2-acetoxy-3-bromoflavanone (VIII) as colorless prisms. Mp 151—152°C. IR ($CHCl_3$), 1695, 1767 cm^{-1}. UV λ_{max}^{EtOH} mμ (log ε) 257 (4.01) 318 (3.45).

Found: C, 56.62; H, 3.68%. Calcd for $C_{17}H_{13}O_4Br$: C, 56.53; H, 3.63%.

Continuing elution with the same eluents yielded 23 mg of white crystals, which were identified as 3-bromoflavone (V) by means of their IR spectra, their melting points, and a mixed melting point determination with an authentic sample (mp 124—125°C). Using the same procedure from the last eluents 234 mg of benzoyl-(2-acetoxybenzoyl)methyl bromide (IX) were afforded as viscous oil. IR ($CHCl_3$) 1672, 1766 cm^{-1} (ν CO). UV λ_{max}^{EtOH} mμ (log ε) 237 (4.04) 257 (4.03).

Found: C, 56.63; H, 3.91%. Calcd for $C_{17}H_{13}O_4Br$: C, 56.53; H, 3.63%.

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