Syntheses and Structures of Acetylformoin and Its Related Compounds. IV. Solvent Effects on a Tautomerism

By Yo Miyagi

(Received August 7, 1963)

A condensation of the benzoin type of an α-ketoaldehyde RCOCHO yields a formoin, the most primitive structure of which is RCOCH·(OH)COCOR:

$$2\ \mathrm{RCOCHO} \xrightarrow{\mathrm{CN^-}} \mathrm{RCOCH(OH)COCOR}$$

The formoins which had been synthesized were listed in a previous paper.[1] The conditions of the condensation of methylglyoxal were studied by Görlich,[2] while the products other than the formoin were isolated by Franzen.[3] The possible structures for the formoin are I—V.[4-7]

The present author and his co-workers have

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[1] Y. Miyagi and R. Goto, This Bulletin, **36**, 650 (1963).

[2] B. Görlich, *Ber.*, **89**, 2145 (1963).

[3] V. Franzen, ibid., **89**, 2154 (1963).

[4] P. W. Abenius and H. G. Söderbaum, ibid., **24**, 3033 (1891); **25**, 3468 (1892); P. W. Abenius, ibid., **27**, 706 (1894).

[5] A. H. Blatt, *J. Am. Chem. Soc.*, **57**, 1103 (1935); **58**, 1894 (1936).

[6] E. Steinbauer and E. Waldman, *Monat. Chem.*, **89**, 570 (1958).

[7] R. Nodzu and S. Kunichika, This Bulletin, **15**, 211 (1940).

studied the structures and the chemical behavior of several formoins. Acetylformoin⁸⁾ has been proved to have an enediol structure II ($R=CH_3$) in the solid state and in chloroform solution. Benzoylformoin,⁸⁾ neopentoylformoin¹⁾ and isobutyrylformoin⁹⁾ are furanones IV ($R=C_6H_5$, $C(CH_3)_3$ and $CH(CH_3)_2$ respectively) in the solid state. Isobutyrylformoin⁹⁾ has structure IV in tetrahydrofuran solution and structure II in chloroform solution.

Most of these conclusions have been deduced from infrared spectral data. Structure II is characterized by a broad, weak band of the OH stretching absorption and by an intense band of the C=O stretching absorption at a lower frequency, around 1620 cm^{-1}.¹⁰⁾ On the other hand, in structure IV, a rather broad but distinct band arises in the region of the OH stretching absorption, while the C=O and C=C stretching absorption bands are observed around 1690 and 1600 cm^{-1} respectively. Furthermore, these assignments are supported by some of the chemical behavior of formoins.

Results

The ultraviolet and infrared spectra of isobutyrylformoin was found to depend remarkably on the solvent in which it is measured, suggesting a tautomerism between structures II and IV in solution.⁹⁾ An ultraviolet absorption arises at 305 mμ ($\varepsilon=7350$) in tetrahydrofuran, and at 360 mμ, with a great enhancement of the intensity ($\varepsilon=14200$), in chloroform (Fig. 1). It has been concluded that the 305 mμ band is attributable to structure IV and the 360 mμ one to structure II, since the infrared spectra had established structure II for chloroform solution and structure IV for tetrahydrofuran solution.

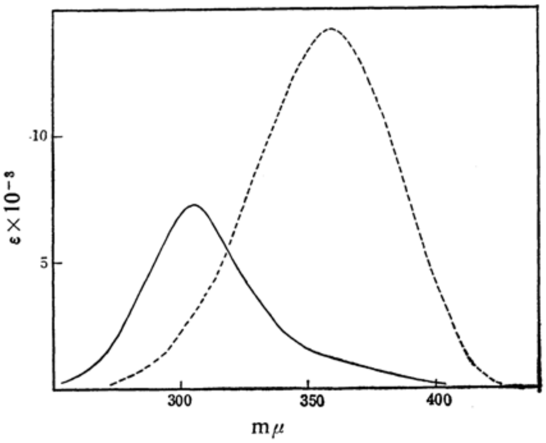

Fig. 1. Ultraviolet spectra of isobutyrylformoin in tetrahydrofuran (——) and chloroform (------).

The ultraviolet spectra of isobutyrylformoin were measured in some other solvents. Since the 305 mμ band arises in ethanol and ether (Fig. 2), structure IV may be considered to predominate in these solvents. A slight but distinct tailing beyond 350 mμ in tetrahydrofuran and ether indicates the existence of a

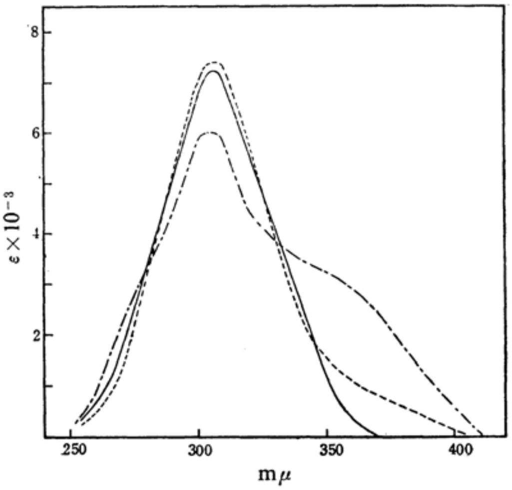

Fig. 2. Ultraviolet spectra of isobutyrylformoin in ethanol (——), acetonitrile (—–—) and ether (------).

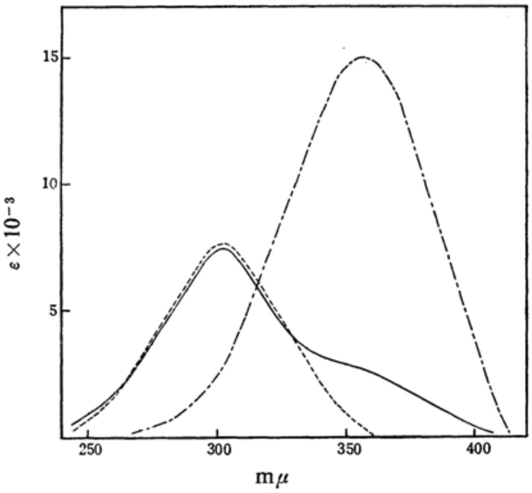

Fig. 3. Ultraviolet spectra of acetylformoin in tetrahydrofuran (——), chloroform (—–—) and ethanol (------).

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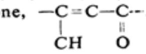
8) R. Goto, Y. Miyagi and H. Inokawa, This Bulletin, **36**, 147 (1963).

9) Y. Miyagi and R. Goto, ibid., **36**, 961 (1963).

10) The enol form of a β-diketone,  $\underset{\text{CH}}{\underset{|}{-\text{C}}}=\text{C}-\underset{\text{O}}{\underset{\|}{\text{C}}}-$, constitutes a conjugate chelation, which gives a broad, weak hydroxyl band and a widely shifted, intense carbonyl band: see, for example, L. J. Bellamy, "Infrared Spectra of Complex Molecules," Methuen, London (1958), pp. 104, 147.

small amount of structure II. In acetonitrile, isobutyrylformoin shows the 305 mμ band with a somewhat decreased intensity ($\varepsilon=6000$) and a shoulder at 360 mμ ($\varepsilon=2950$), suggesting an equilibrium between structures II and IV.

The above findings necessitate a reinvestigation of the structures of other formoins in solution. In the ultraviolet spectrum of acetylformoin in ethanol, the 303 mμ band is dominant (Fig. 3). In tetrahydrofuran there is an intense absorption at 303 mμ ($\varepsilon=7100$), with a shoulder around 360 mμ. Thus, in the former solvent, structure IV, and in the latter solvent, an equilibrium between IV and II, may be established. In chloroform an ultraviolet absorption also arises at 355 mμ with an enhancement of the intensity, indicating structure II.

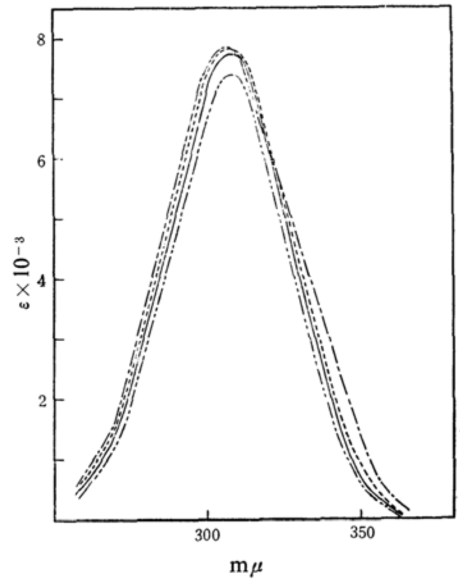


Fig. 4. Ultraviolet spectra of neopentoylformoin in tetrahydrofuran (——), acetonitrile (——-–), ethanol (—–––—) and ether (------).

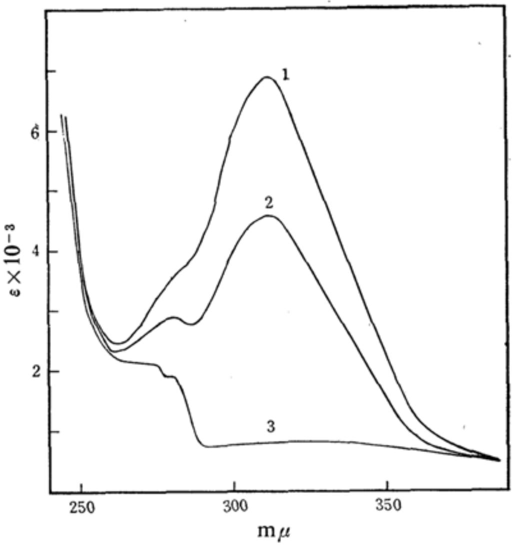


Fig. 5. Ultraviolet spectra of neopentoylformoin in chloroform: 1, in vacuo; 2, 5 hr. after breaking the seal; 3, 1 day after breaking the seal.

The infrared spectrum of isobutyrylformoin in chloroform (Fig. 8) is very similar to those of acetylformoin in chloroform and in the solid state (Fig. 9). As has been stated in previous papers,[8,9] these spectra are characteristic of structure II: a broad weak band of the OH stretching absorption and an intense one of the C=O stretching absorption at 1620 cm^{-1}. The infrared spectrum of acetylformoin in carbon tetrachloride makes these characteristics more distinct: it becomes more apparent that the OH absorption is broad and weak, because of the disappearance of the C–H stretching absorption of the solvent, which makes the OH band ambiguous. The insolubleness of isobutyrylformoin in this solvent fails to give such a characteristic spectrum as that of acetylformoin in this solvent.

Neopentoylformoin has spectral characteristics consistent with structure IV in ethanol, tetrahydrofuran, ether, acetonitrile and even in chloroform. In the first three solvents, neopentoylformoin shows an ultraviolet absorption at 308 mμ ($\varepsilon=$ca. 7000). In tetrahydrofuran and ether no such tailing beyond 350 mμ is observed as in acetyl- and isobutyrylformoin (Fig. 4). In acetonitrile an absorption arises also at 307 mμ without any shoulder around 360 mμ.

The infrared spectra in ether, tetrahydrofuran and acetonitrile are characteristic of structure IV: the C=O, C=C and OH stretchching absorptions are located at 1705, 1630 and ca. 3300 cm^{-1} respectively (Fig. 10).

Neopentoylformoin is rapidly oxidized in chloroform, so the ultraviolet spectrum in this solvent was measured in a cell sealed in vacuo. There occurs an absorption at 311 mμ with a slight shoulder around 275 mμ; when the sealed cell is opened, the 311 mμ band decreases and the shoulder at 275 mμ can be recognized as an absorption band (Fig. 5). Though the origin of this band has not been found, the dominating 311 mμ band suggests structure IV for neopentoylformoin in chloroform.

The spectra of benzoylformoin indicates structure IV for solution. In tetrahydrofuran it shows an infrared spectrum characteristic of structure IV (Fig. 11); the OH and C=O stretching absorptions arise at 3240 and 1705 cm^{-1} respectively, while the C=C stretching

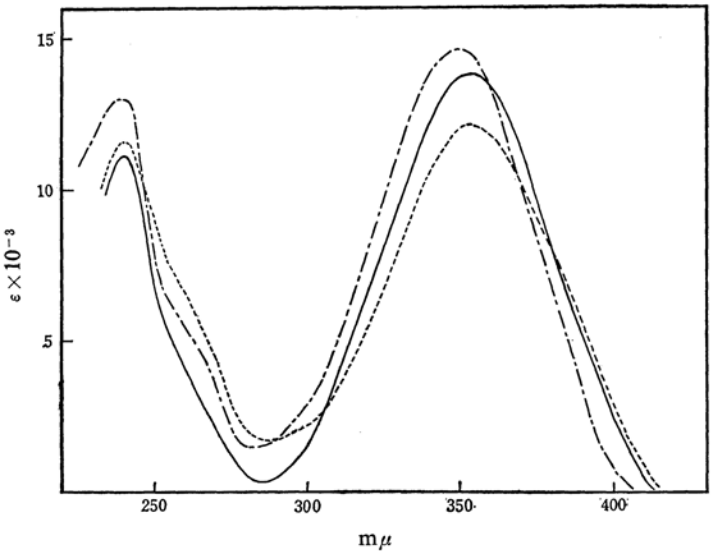


Fig. 6. Ultraviolet spectra of benzoylformoin in tetrahydrofuran (——), ether (–·–·–) and ethanol (------).

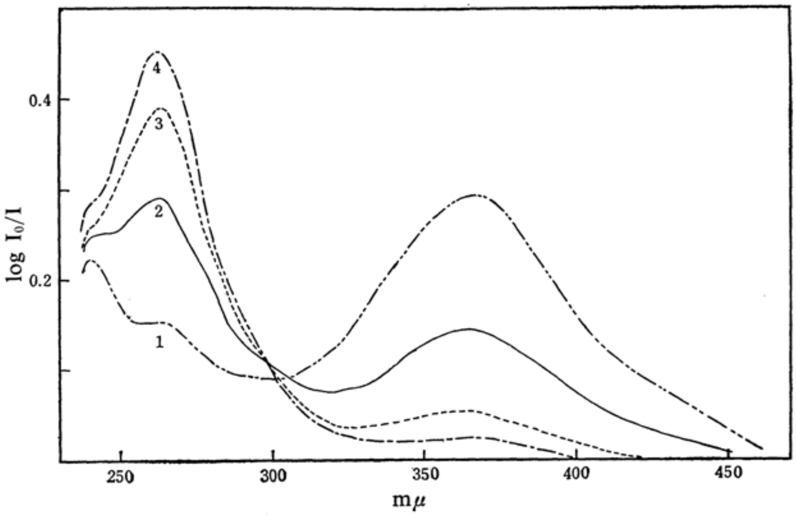


Fig. 7. Ultraviolet spectra of benzoylformoin' in chloroform: 1, in vacuo; 2, 2 hr. after breaking the seal; 3, 4 hr. after breaking the seal; 5, 1 day after breaking the seal.

absorptions are located at 1615 and 1595 cm^{-1}. The ultraviolet spectrum of benzoylformoin in tetrahydrofuran is quite identical with those in ether and ethanol (Fig. 6); the absorptions are observed at 354 and 240 mμ. Since structure IV is established for tetrahydrofuran solution by the infrared spectral evidence mentioned above, the two ultraviolet absorptions at 354 and at 240 mμ should be attributed to structure IV. It may be elucidated as follows: the absorption arising from the chromophore, C=C–C=O of IV, is shifted to longer wavelengths by conjugation with a phenyl group.

Benzoylformoin is also rapidly oxidized in chloroform; the ultraviolet spectrum in this solvent was measured in a sealed cell in vacuo. The absorption arises at 370 and at 240 mμ. The lapse of time does not change the spectrum. Opening the sealed cell decreases the 370 and 240 mμ bands. However, Eistert11) has pointed out a spectral change which might be attributed to a reaction of benzoylformoin with the ethanol present in chloroform as a stabilizer.

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11) B. Eistert, private communication.

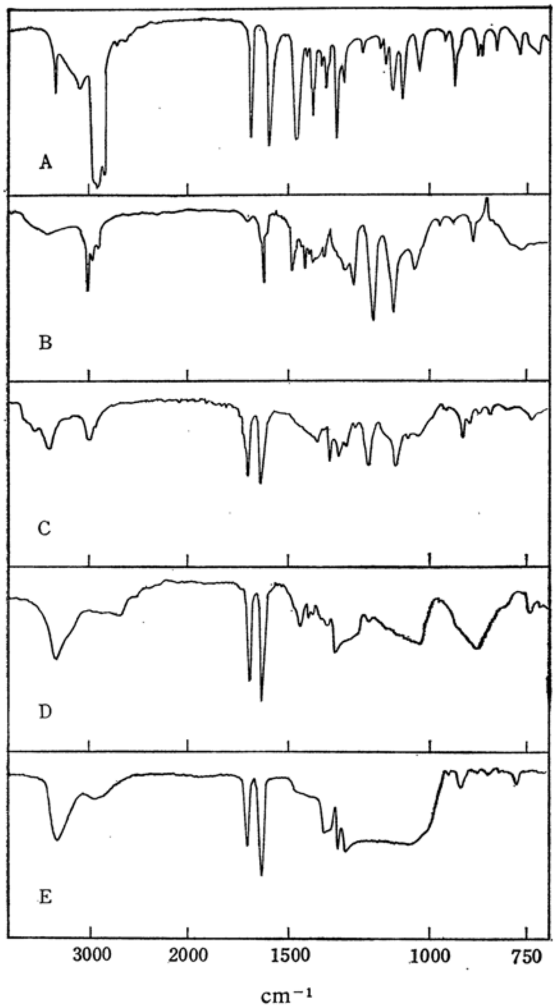

Fig. 8. Infrared spectra of isobutyrylformoin in Nujol (A), chloroform (B), acetonitrile (C), tetrahydrofuran (D) and ether (E).

Discussion

The above results are summarized in Table III. This tautomerism is apparently affected by two factors: the substituent R and the solvent. Some conclusions may be deduced as follows:

i) In benzoyl- and neopentoyl-formoin, structure IV is dominant in any solvent;

ii) In acetyl- and isobutyryl-formoin, a tautomerism between II and IV occurs in solution; in an A-type solvent,[*1] structure IV is dominant, while in a B-type[*1] solvent, structure II prodominates;

iii) In the solid state, benzoyl-, neopentoyl- and isobutyryl-formoin have structure IV; only acetylformoin has structure II.

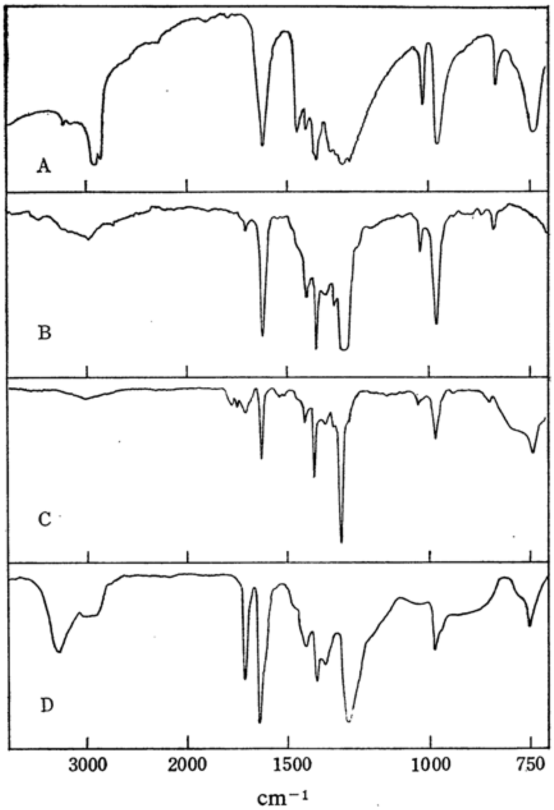

Fig. 9. Infrared spectra of acetylformoin in Nujol (A), chloroform (B), carbon tetrachloride (C) and tetrahydrofuran (D).

TABLE I. ULTRAVIOLET ABSORPTION BANDS OF FORMOINS

Formoin	Solvent	λ_{max}, mμ	ε_{max}
Acetyl	THF*	303	7300
	EtOH	303	7500
	$CHCl_3$	355	15000
Isobutyryl	EtOH	305	7200
	THF*	305	7350
	Et_2O	305	7400
	CH_3CN	305 360	6000 2950
	$CHCl_3$	360	14200
Neopentoyl	EtOH	308	7350
	THF*	308	7750
	Et_2O	308	7850
	CH_3CN	307	7750
	$CHCl_3$	311	ca. 6330
Benzoyl	EtOH	354 240	12000 10800
	THF*	354 240	13700 11300
	Et_2O	350 240	14600 13000
	$CHCl_3$	367 240	** —

* THF; tetrahydrofuran
** See Experimental.

[*1] A-type solvent: ethanol, ether and tetrahydrofuran. B-type solvent: chloroform and carbon tetrachloride.

The discussion of the cause of the tautomerism will be restricted here to the case of solution. It may be reasonable to consider that a tautomer predominating in a solvent is stabililized by a solvation. The most likely explanation is as follows: all A-type solvents have an oxygen atom carrying lone pair electrons, which may be supposed to take part in the formation of hydrogen bondings with the hydroxyl group of formoins, as in Fig. 17, and so the formoins are greatly stabilized. A B-type solvent has no such lone pair electrons with the ability to form a hydrogen bonding and structure IV can not be stabilized by such a solvation as above.*2 Consequently, in chloroform acetyl- and isobutyryl-formoin have more

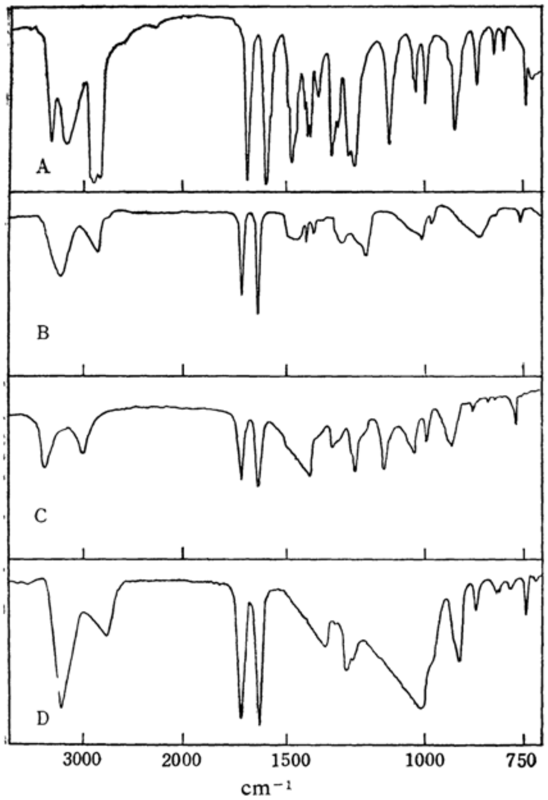

Fig. 10. Infrared spectra of neopentoylformoin in Nujol (A), tetrahydrofuran (B), acetonitrile (C) and ether (D); in ether, a 0.2 mm. cell was used.

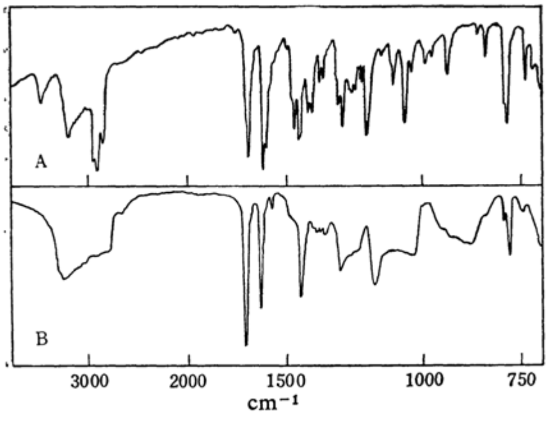

Fig. 11. Infrared spectra of benzoylfomoin in Nujol (A) and tetrahydrofuran (B).

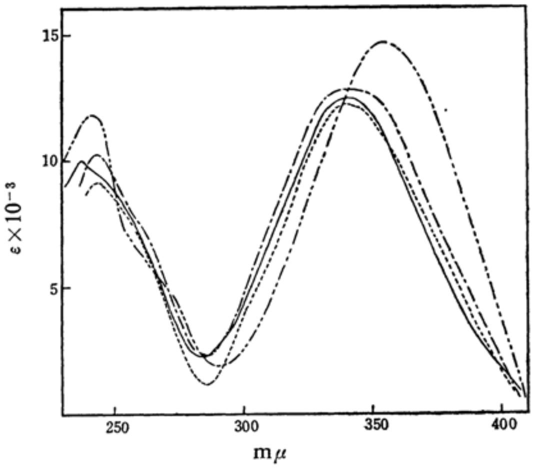

Fig. 12. Ultraviolet spectra of derivatives of benzoylformoin: 1st mono-*O*-methyl benzoylformoin in ethanol (—–––—); di-*O*-methyl benzoylformoin in ethanol (——–—-); 2nd mono-*O*-methyl benzoylformoin in tetrahydrofuran (——) and chloroform (------).

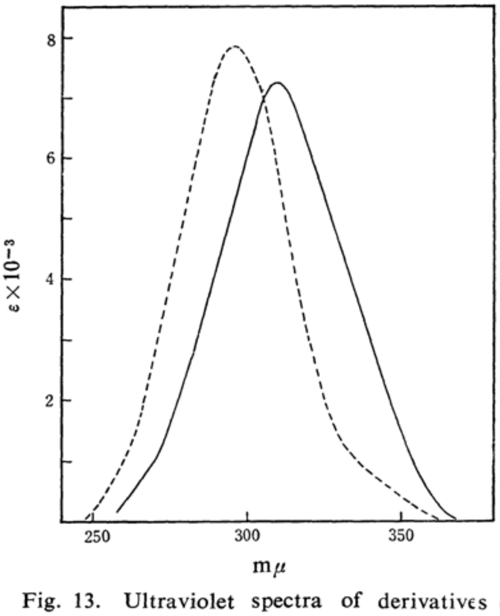

Fig. 13. Ultraviolet spectra of derivatives of neopentoylformoin in ethanol: mono-*O*-methyl neopentoylformoin (——); di-*O*-methyl neopentoylformoin (------).

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*2 The B-type solvent may also stabilize formoins by a solvation, but the effect is not so great as in the above-depicted case.

stable tautomer II. In benzoyl- and neopentoylformoin, structure II seems to be unstable, and both formoins have structure IV even in a B-type solvent, chloroform. However, in this solvent structure IV can not be stabilized so much as in an A-type solvent because of the absence of the solvation,[*2] so both formoins are easily oxidized.

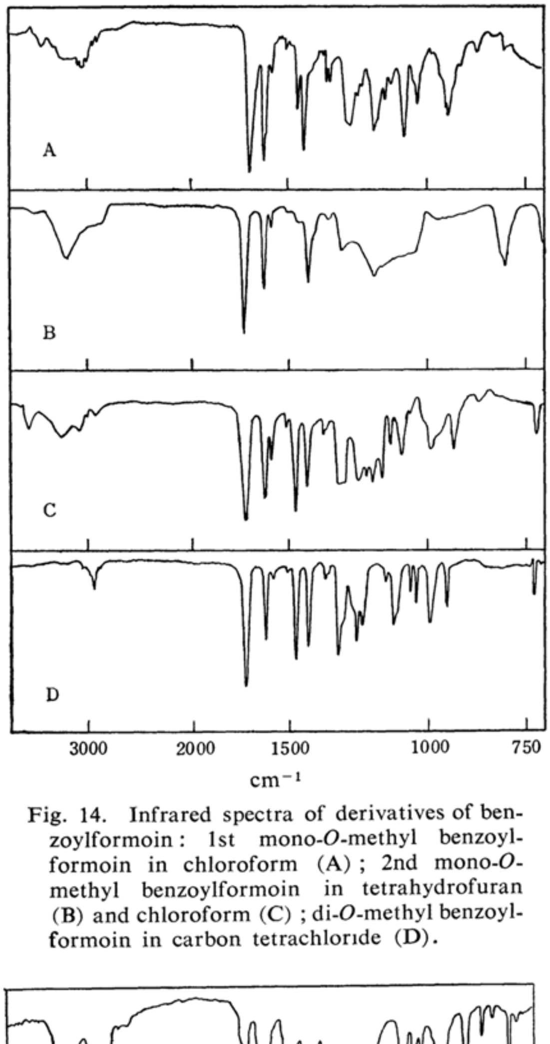

Fig. 14. Infrared spectra of derivatives of benzoylformoin: 1st mono-*O*-methyl benzoylformoin in chloroform (A); 2nd mono-*O*-methyl benzoylformoin in tetrahydrofuran (B) and chloroform (C); di-*O*-methyl benzoylformoin in carbon tetrachloride (D).

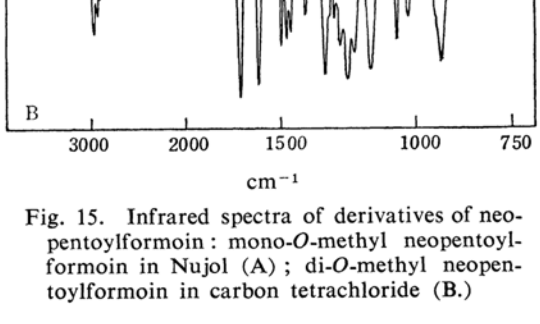

Fig. 15. Infrared spectra of derivatives of neopentoylformoin: mono-*O*-methyl neopentoylformoin in Nujol (A); di-*O*-methyl neopentoylformoin in carbon tetrachloride (B.)

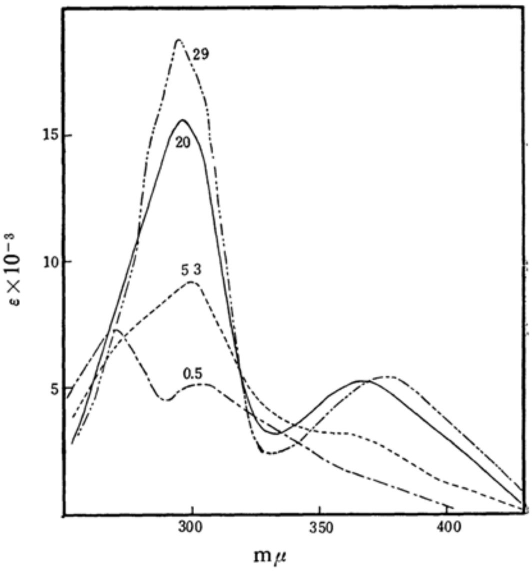

Fig. 16. Ultraviolet spectra of isobutyrylformoin in methanolic hydrogen chloride: numbers are the weight per cent of hydrogen chloride.

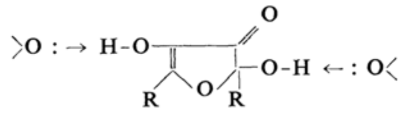

Fig. 17

The solubility[*3] of the formoins seems to have a correlation with their structures. While acetylformoin is very soluble in chloroform and carbon tetrachloride (B-type solvents), the other three formoins are only slightly soluble in chloroform and quite insoluble in carbon tetrachloride. This difference may be explained in terms of the solvation energy and the interaction of molecules in the solid state.[*4]

All the formoins except acetylformoin show slight but definite discrepancies (about 20 cm⁻¹) in the C=O and C=C stretching absorption bands of structure IV between the solid state and solutions in A-type solvents. On the other hand, the C=O stretching absorption of

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[*3] This investigation often encounters a difficulty with low solubilities of the formoins in solvents desirable for the spectroscopic measurement (carbon tetrachloride, heptane, cyclohexane; i. e., B-type solvents).

[*4] In general, the solubility is proportional to $e^{-\Delta H/RT}$, where ΔH is the energy change in dissolving and is further expressed:

$\Delta H = \Delta H_V - \Delta H_S$
ΔH_V; heat of vaporization
ΔH_S; solvation energy

TABLE II. INFRARED ABSORPTION BANDS OF FORMOINS, cm^{-1}

Formoin	Phase	ν_{OH}		$\nu_{C=O}$	$\nu_{C=C}$	
Acetyl	Nujol	broad and weak		1620		
	$CHCl_3$			1625		
	CCl_4			1630		
	THF*	3280		1705	1640	
Isobutyryl	Nujol	3340	3100	1685	1605	
	$CHCl_3$	broad and weak		1630		
	THF*	3290		1705	1630	
	CH_3CN	3380		1705	1630	
	Et_2O	3320		1710	1635	
Neopentoyl	Nujol	3330	3180	1690	1605	
	THF	3280		1705	1630	
	CH_3CN	3400		1705	1630	
	Et_2O	3240		1703	1627	
Benzoyl	Nujol	3500	3210	1685	1608	1595 (shoulder)
	THF*	3240		1705	1615	1595 (shoulder)

* THF: Tetrahydrofuran

TABLE III. STRUCTURES OF FORMOINS

Formoin	R	Solid state	Solution	
			A-Type solvent	B-Type solvent
Acetyl	CH_3	II	IV	II
Isobutyryl	$CH(CH_3)_2$	IV	IV	II
Neopentoyl	$C(CH_3)_3$	IV	IV	IV
Benzoyl	C_6H_5	IV	IV	IV

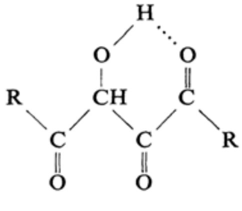
TABLE IV. ULTRAVIOLET AND INFRARED ABSORPTION BANDS OF *O*-METHYL DERIVATIVES OF BENZOYL- AND NEOPENTOYL-FORMOIN

	UV absorption band			IR absorption band, cm^{-1}			
	Solvent	λ_{max}, mμ	ε_{max}	Phase	ν_{OH}	$\nu_{C=O}$	$\nu_{C=C}$
1st mono-*O*-methyl benzoylformoin	EtOH	355 241	14500 11800	$CHCl_3$	3530 3340～3100	1705	1625 1585
Di-*O*-methyl benzoylformoin	EtOH	342 243	12800 10300	CCl_4		1710	1612 1690
2nd mono-*O*-methyl benzoylformoin	EtOH	342 237	12400 10100	THF*	3580～3600 3240	1710	1614
	$CHCl_3$	342 244	12200 9200	$CHCl_3$	3580 3260	1705	1610
Mono-*O*-methyl neopentoylformoin	EtOH	309	7250	Nujol	3310	1690	1610
Di-*O*-methyl neopentoylformoin	EtOH	296	7850	CCl_4		1710	1610

* THF: Tetrahydrofuran

acetylformoin in the solid state (structure II) arises at the same position as that in a B-type solvent. In other words, the positions of the infrared absorptions of structure IV are different in the solid state and in the solution, while that of structure II is identical in both states. It means that the intermolecular bonding in the solid state is strong in structure IV, but not so strong in structure II. This is easily understandable, because the intermolecular chelation is very intense in structure II. A large intermolecular bonding in the solid state suggests a large value of the heat of vaporization (ΔH_v): the ΔH_v value of structure IV is larger than that of structure II. As has been mentioned previously, the solvation to structure IV is large in an A-type solvent. This means that the ΔH_s value of structure IV is large in the A-type solvent but small in B-type solvents, while that of structure II in B-type solvents is small.

In spite of its small ΔH_s value, acetylformoin has a large solubility in the B-type solvent because it has structure II in the solid state; in other words, it has a small ΔH_v value. A combination of a large ΔH_v value and a small ΔH_s value results in low solubilities of the other three formoins in B-type solvents.



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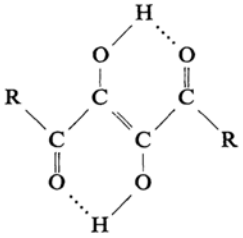

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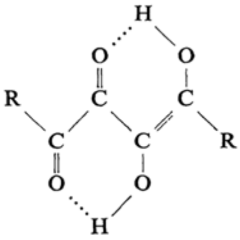

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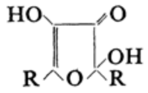
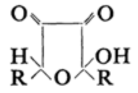


IV

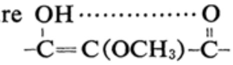


V

Further Results

O-Alkyl Derivatives of Benzoylformoin.—Benzoylformoin undergoes a series of reactions as follows: it suffers methanolysis with methanolic hydrogen chloride to give a mono-O-methyl benzoylformoin, which is further methylated with dimethyl sulfate to give di-O-methyl benzoylformoin. A hydrolysis of the latter compound yields a second mono-O-methyl benzoylformoin, which is soluble in chloroform.

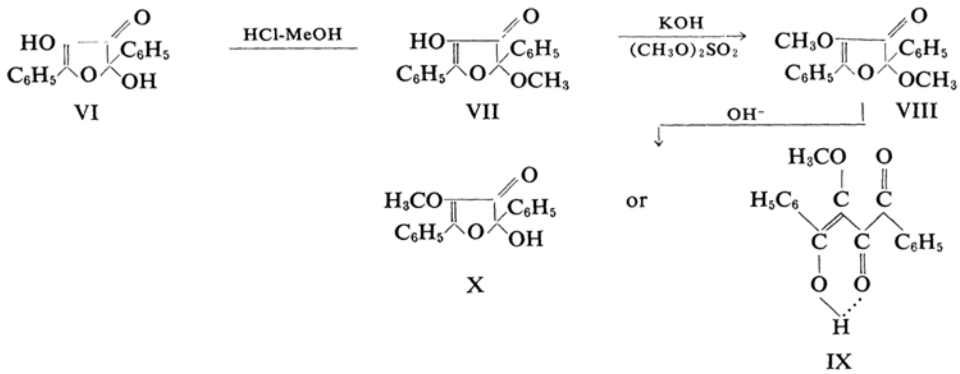
Blatt[5a] has stated that second mono-O-methyl benzoylformoin was IX. However, structure X may also be possible. A careful study of the ultraviolet and infrared spectra of this compound was undertaken (Figs. 12 and 14). Its ultraviolet spectrum in chloroform is almost identical with that in ethanol and is similar to that of di-O-methyl benzoylformoin,*5 the structure of which was established as VIII by chemical evidences. Moreover, there have been found no differences between the infrared spectrum in chloroform (a B-type solvent) and that in tetrahydrofuran (an A-type solvent): the C=O and C=C stretching absorptions arise around 1705 and 1610 cm^{-1} respectively. In structure IX, a partial structure



$\overset{\displaystyle OH\cdots\cdots\cdots\cdots O}{-\overset{|}{C}=C(OCH_3)-\overset{\|}{C}-}$

constitutes a conjugate chelation. If second mono-O-methyl benzoylformoin were IX, it would show a broad weak band of the OH stretching absorption and of the C=O stretching absorption around 1620 cm^{-1} and the ultraviolet absorption at 340 mμ would be shifted to longer wavelengths. For instance, 1-benzoyl-2-α-pyridylethenediol (XII)[12] shows a broad band of the OH stretching absorption, the C=O stretching absorption band at 1603 cm^{-1}, and an ultraviolet absorption at 405 mμ (ε=15940).

These results indicate that the structure of second mono-O-methyl benzoylformoin is X in both types of solvents. Here again a tautomerism between IX and X does not arise.



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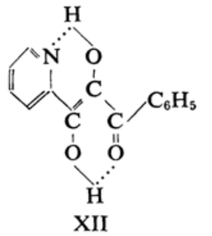
*5 The introduction of a glycosidic ether linkage does not bring about a shift of the ultraviolet absorption. However, that of an enol ether linkage results in a shift of the 354 mμ band to 340 mμ. A similar shift was observed in di-O-methyl neopentoylformoin (Fig. 13).

[12] B. Eistert and H. Munder, *Ber.*, **91**, 1415 (1958).

Alcoholysis of Isobutyrylformoin.—There is an interesting experimental observation: neopentoylformoin and benzoylformoin undergo methanolysis with methanolic hydrogen chloride to give quantitatively mono-*O*-methyl derivatives. On the other hand, the color of the methanolic hydrogen chloride solutions of isobutyryl- and acetyl-formoin is yellow at first; it turns black while the alcohol and the acid being evaporated under reduced pressure. The residues are black syrups, from which the isolation of mono-*O*-methyl derivatives failed.[*6]


XII

No differences were observed between the ultraviolet spectrum of neopentoylformoin in ethanol and those in methanolic hydrogen chloride (the concentration of hydrogen chloride, 8 and 17 wt. %), and the latter spectra show no absorptions beyond 350 mμ. On the other hand, the ultraviolet spectra of isobutyrylformoin in methanolic hydrogen chloride (Fig. 16) differ greatly from those of neopentoylformoin. In 0.5% methanolic hydrogen chloride, a band arises at 269 mμ besides the 304 mμ band of a slightly decreased intensity ($\varepsilon = 5100$). The absorption band of 7% methanolic hydrogen chloride, arising at 300 mμ, seems to be a overlapping band of the two above bands of a 0.5% solution. In a greatly concentrated solution, the absorption has a remarkably increased intensity. It may be considered that the band located at 269 mμ in 0.5% solution is shifted to longer wavelengths and that its intensity is remarkably enhanced to overlap with the 304 mμ band of 0.5% solution, which may be attributed to the enone chromophore of the formoin.

In methanolic hydrogen chloride solutions of acetyl- and isobutyryl-formoin, it may be considered that some chemical reaction other than etherification occurs, probably a condensation involving C-H bonds of the substituent R. The ultraviolet absorption at 269 mμ arising in the 0.5% methanolic hydrogen chloride solution of isobutyrylformoin may be attributed to this condensation product, the amount of which may increase with the increment in concentration of hydrogen chloride, thus enhancing the intensity of the ultraviolet absorption. Though the attempts to isolate the condensation product have not been successful, the above explanation may be reasonable, because a condensation of a ketone having hydrogen atoms attached to α-carbon atoms occurs under acidic conditions.[*7]

Isobutyrylformoin in methanolic hydrogen chloride shows at 360 mμ an additional absorption band, the intensity of which increases also with the increment in the concentration of hydrogen chloride. This band may be ascribed to the condensation product or to the shift of the equilibrium toward structure II upon the decrease in the solvation of methanol: in methanolic hydrogen chloride the proton forms an oxonium ion, $CH_3\text{-}O^+H_2$, to deprive methanol of the ability to solvate.

In an alcoholic solution of an acid, the protonated ketone shows an additional absorption band at a longer wavelength.[13] However, the 360 mμ band arising in a methanolic hydrogen chloride solution of isobutyrylformoin is not attributable to the protonated ketone. If this were the case, neopentoylformoin would show an absorption at 360 mμ in methanolic hydrogen chloride.

Conclusion

When R is methyl or isopropyl (i. e., acetyl- or isobutyryl-formoin), a tautomerism between structures II and IV occurs in solution. When R is phenyl or *t*-butyl (i. e., benzoyl- or neopentoyl-formoin), structure IV predominates in both types of solvents. In a B-type solvent, acetyl- and isobutyryl-formoin have structure II, the more stable tautomer. In an A-type solvent, they have structure IV, a tautomer stabilized by the solvation depicted in Fig. 17.

The above sequence of investigation suggests two assumptions: structure IV is generally more stable than structure II, although when R is methyl or isopropyl, the latter becomes more stable than the former; structure II is, in general, more stable than structure IV, although the former structure becomes unstable when R is phenyl or *t*-butyl. The former assumption is apparently reasonable because γ-

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[*6] Steinbauer and Waldman[6] isolated mono-*O*-methyl acetylformoin in a 30% yield. The author isolated a trace of a solid product by pouring a methanolic hydrogen chloride solution of isobutyrylformoin into cold water. The product is probably the mono-*O*-methyl derivative because it shows ν_{OH} at 1960, and $\nu_{C=C}$ at 3160, $\nu_{C=O}$ at 1620 cm^{-1} in Nujol.

[*7] For example, diacetyl gives a trimer when shaken with concentrated hydrochloric acid at 0°C (R. M. Cresswell, W. R. D. Smith and H. L. S. Wood, *J. Chem. Soc.*, **1961**, 4882). The self-condensation of acetone in the presence of hydrochloric acid gives mesityl oxide, phorone and isophorone (J. B. Conant and N. Tuttle, "Organic Syntheses," Coll. Vol. I, 346 (1948)).

13) See, for example, J. F. Thomas and G. Branch, *J. Am. Chem. Soc.*, **75**, 4793 (1953); M. H. Palmer and D. S. Urch, *J. Chem. Soc.*, **1963**, 174.

and δ-oxy-aldehydes or ketones prefer hemiacetal or hemiketal forms; for example, aldoses and ketoses exist as pyranoses and furanoses. However, structures II and IV involve conjugation, so that the above analogy may not always hold true.

Experimental

Formoins.—All formoins were prepared by the usual method of the benzoin condensation described in previous papers.

*Acetylformoin.*8)—Yellow needles, purified by vacuum sublimation; m. p. 82∼83°C.

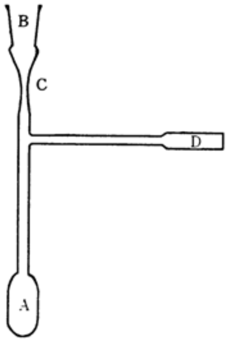

Fig. 18

*Isobutyrylformoin.*9)—Colorless needles, recrystallized by adding water to an alcoholic solution; m. p. 87∼93°C.

*Neopentoylformoin.*1)—Colorless needles, recrystallized from isopropanol; m. p. 170∼171°C.

*Benzoylformoin.*8)—yellow needles, recrystallized from ethanol; m. p. 186∼188°C.

First Mono-*O*-methyl Benzoylformoin (VII).—Benzoylformoin (4 g.) was dissolved in ca. 10% methanolic hydrogen chloride (80 ml.) (slightly warmed). After they had stood overnight, the solvent and the acid were evaporated off under reduced pressure. The residue was washed with cold water and dried in vacuo. The recrystallization was carried out from 50 ml. of ethanol: yellow needles; 3 g.; m. p. 180∼182°C.

Found: C, 72.15; H, 4.91. Calcld. for $C_{17}H_{14}O_4$: C, 72.33; H, 5.00%.

By the addition of 10 ml. of water to the mother liquor, 1 g. of the product was collected; m. p. 176∼182°C.

Di-*O*-methyl Benzoylformoin (VIII).—First mono-*O*-methyl benzoylformoin (2.5 g.) was dissolved in a solution of 0.7 g. of sodium methoxide in 50 ml. of methanol. After the addition of 15 g. of methyl iodide, the solution was refluxed for 3 hr. After it had stood overnight, the solvent was evaporated off under reduced pressure. Water and ether were added to the residue. The product was obtained as yellow needles by evaporating ether from the ethereal layer and then recrystallized from 2 ml. of methanol: 2.1 g.; m. p. 79.5∼80.5°C.

Found: C, 72.85; H, 85.29. Calcd. for $C_{18}H_{16}O_4$: C, 72.96; H, 5.44%.

Second Mono-*O*-methyl Benzoylformoin (X).—This compound was prepared by the method of Blatt:5a) m. p. 120∼124°C.

Found: C, 72.19; H, 5.01. Calcd. for $C_{17}H_{14}O_4$: C, 72.33; H, 5.00%.

Mono-*O*-methyl Neopentoylformoin.1)—Colorless needles; recrystallized from isopropanol; m. p., 100.5∼101°C.

Di-*O*-methyl Neopentoylformoin.1) — Colorless liquid; b. p., 107∼108°C/5 mmHg.

The Ultraviolet Spectra of Neopentoyl- and Benzoyl-formoin in Chloroform.—A definite quantity (3 ml.) of a tetrahydrofuran solution of neopentoylformoin (ca. 5×10^{-5} M) was placed in bottle A, which was then attached to a vacuum line through ground joint B. The solvent was distilled off under 10^{-4} mmHg. Chloroform (3 ml.) was placed in a flask attacthed to the vacuum line, and chloroform was distilled into bottle A which was cooled by liquid air under 10^{-4} mmHg. The thin glass tube C was sealed. After the contents of bottle A reached room temperature, it was poured in cell D and the spectrum was recorded. Consequently, the molecular extinction coefficient was nearly correct. In the case of benzoylformoin, about 0.5 mg. of crystals was placed in bottle A and chloroform was distilled in by the same method as above: the intensity in Fig. 7 is arbitrary.

Spectra.—The infrared spectra were recorded with a Koken model DS-301 and IR-S spectrophotometer. The ultraviolet spectra were recored with a Shimadzu model QR-50 spectrophotometer.

The author wishes to express his thanks to Professor Ryozo Goto of Kyoto University for his kind guidance and encouragement throughout the work, and to Professor Saburo Nagakura of The University of Tokyo and Dr. Yoshiki Matsui of Shionogi & Co. for their discussions.

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