[CONTRIBUTION FROM THE COBB CHEMICAL LABORATORY, UNIVERSITY OF VIRGINIA]

RING-CHAIN TAUTOMERISM OF THE *cis*-β-BENZOYLPHENYLACRYLIC ACIDS

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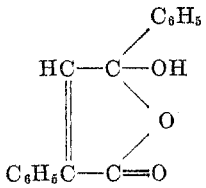
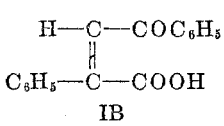
This investigation was undertaken to determine the effect of an α- or β-aryl substituent on the ring-chain tautomerism of β-aroylacrylic acids.[2] Previous publications from this laboratory have dealt with methyl- and bromo-substituted acids (*cf.* 1).

cis-β-BENZOYL-α-PHENYLACRYLIC ACID (I)

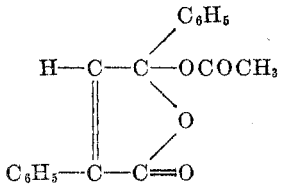
This compound and its *p*-chlorobenzoyl analog have been prepared and characterized by Kohler, *et al.* (3, 4) who reported them to be capable of reacting according to both the cyclic (IA) and acyclic (IB) formulations. The parent compound gave, for example, a cyclic acetoxy derivative (II) and the normal acyclic methyl ester (III).[3] The *p*-chlorobenzoyl analog gave, in addition to these types, a cyclic methyl ester.



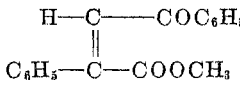
IA



IB



II



III

It can now be shown by analysis of ultraviolet absorption spectra that *cis*-β-benzoyl-α-phenylacrylic acid (I) exists in dilute 95% ethanol solution as an equilibrium mixture of the cyclic and acyclic forms (IA and B), in which the cyclic form predominates. This is in direct contrast with the corresponding saturated compound, β-benzoyl-α-phenylpropionic acid (IV), which is largely if not exclusively acyclic as indicated by its absorption peak of wavelength and molar absorptivity expected for a freely-functioning benzoyl group (ϵ = 12,800 at 242.5 mμ).

The strong absorption in the near ultraviolet (above 230 mμ) of the cyclic molecule (IA) must be due to the α-phenylacrylic system. The absorption characteristic of this system, a single peak in the 275 mμ region, has been deduced

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[2] For a list of references on this subject see (1).

[3] However, this ester (III) was reported as "too low-melting" and its properties were not given (4).

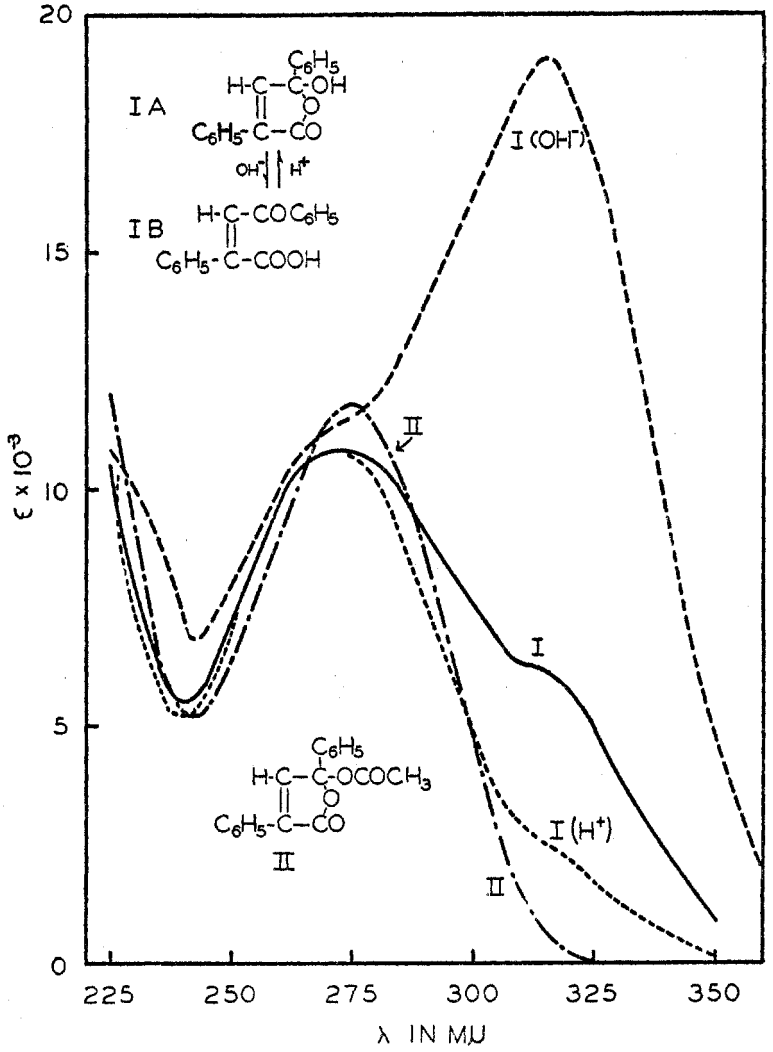
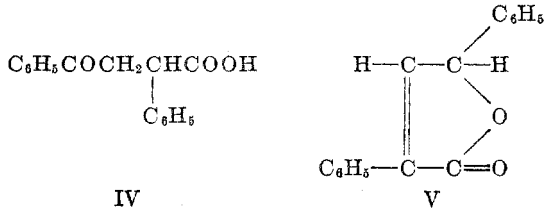


FIG. 1. SPECTRA OF β-BENZOYL-α-PHENYLACRYLIC ACID AND ITS CYCLIC ACETOXY DERIVATIVE. The acid; ethanol solution ————, NaOH added - - - -, HCl added -------, Cyclic acetoxy derivative —•—•—•

from the spectra of the related compounds containing this system, the cyclic acetoxy derivative (II) (Fig. 1) and α,γ-diphenylcrotolactone (V) (5). The



IV V

acyclic molecule (IB) on the other hand would possess in addition to the α-phenylacrylic acid system, a *trans*-benzalacetophenone system which is known to absorb strongly at 312 mμ (6).

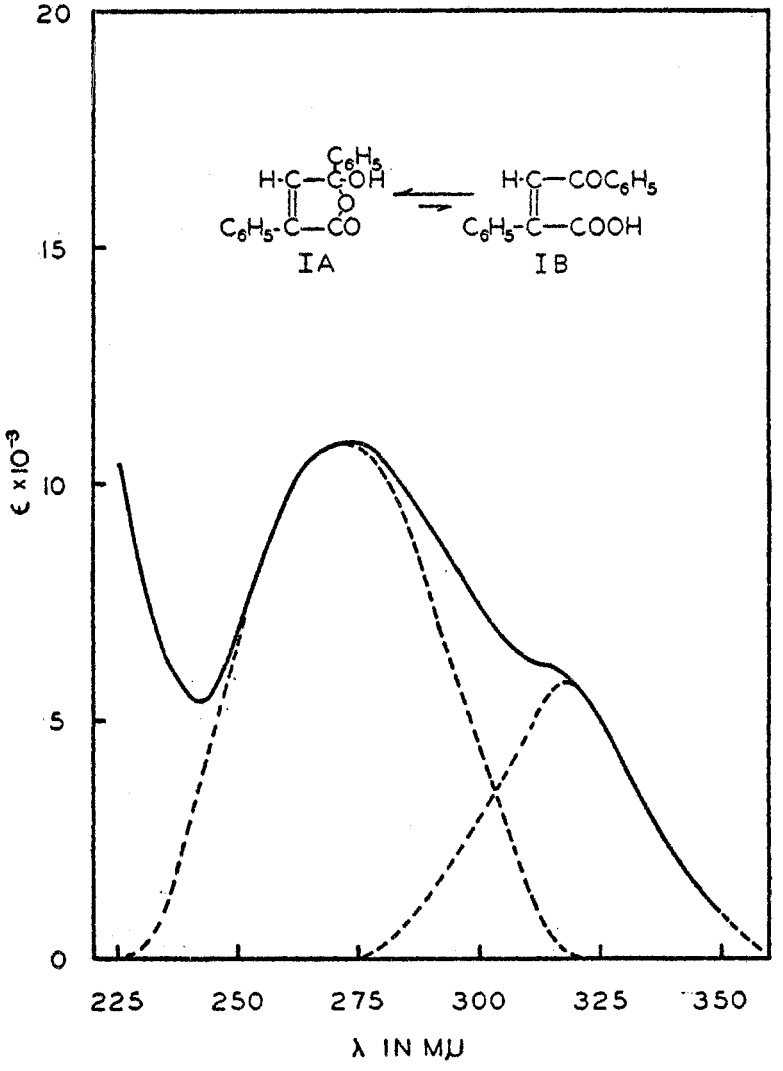


FIG. 2. GRAPHICAL RESOLUTION OF THE SPECTRUM OF β-BENZOYL-α-PHENYLACRYLIC ACID IN ETHANOL SOLUTION

The spectrum of an ethanol solution of the acid (Fig. 2) can be resolved graphically into two major component peaks, the one at 275 mμ which is due to the α-phenylacrylic acid system present in both the cyclic and acyclic molecules, and the other and smaller one at 315 mμ which can reasonably be attributed

only to the *trans*-benzalacetophenone system present in an equilibrium amount of acyclic molecules.

Figure 3 shows the spectrum of an alkalinized solution of the acid in which both forms have been converted into the more stable acyclic anion. Similarly,

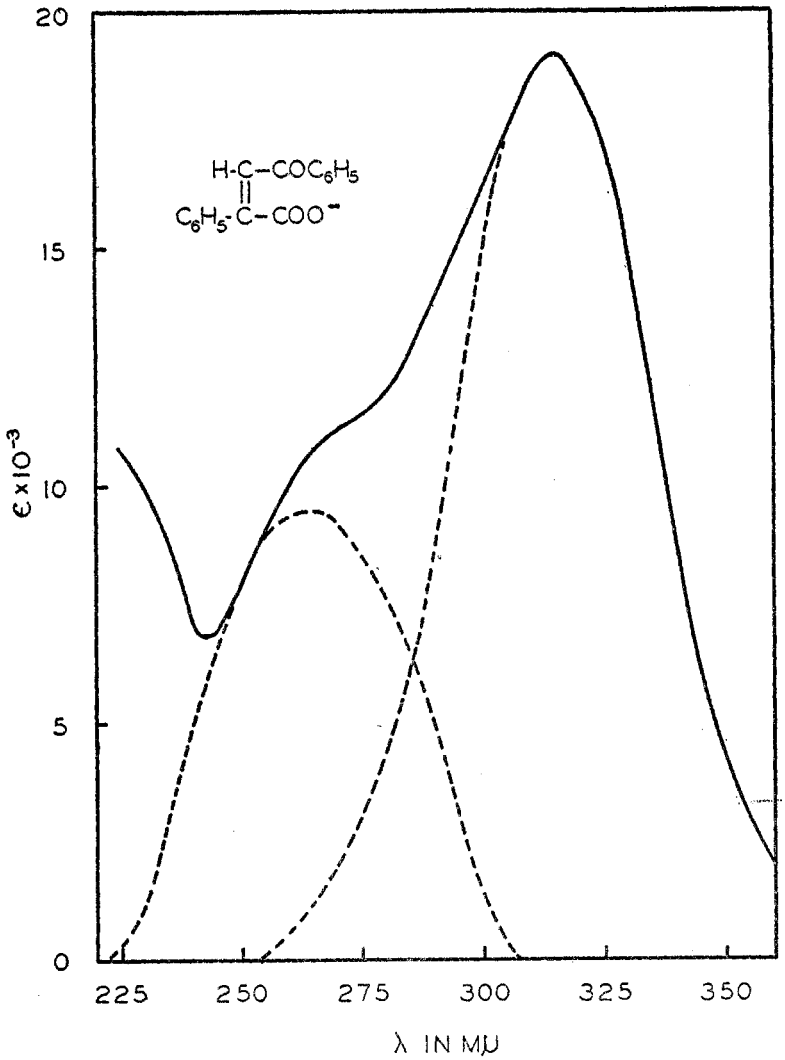


FIG. 3. GRAPHICAL RESOLUTION OF THE SPECTRUM OF β-BENZOYL-α-PHENYLACRYLIC ACID IN ALKALINE SOLUTION (β-Benzoyl-α-phenylacrylate ion).

this curve can be resolved graphically into two peaks, one at 265 mμ which is due to the α-phenylacrylate ion, and the other at 315 mμ which is again attributed to the *trans*-benzalacetophenone system now present in all molecules, and which now has the expected high molar absorptivity characteristic of *trans*-

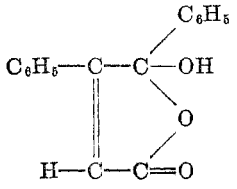
benzalacetophenone itself. The shift of the absorption peak of the α-phenylacrylic acid system from 275 mμ to 265 mμ in alkaline solution may be considered analogous to a similar shift observed in the case of *trans*-cinnamic acid in alkaline solution (7).

If one considers that the molar absorptivity of the 315 mμ peak of the spectrum taken in alkaline solution (Fig. 3) represents the molar absorptivity when all molecules are present in an acyclic form, and that there is no significant absorption in this region when the molecules are all cyclic as they are in the cyclic acetoxy derivative (Fig. 1), then the reality of an equilibrium between cyclic and acyclic forms in the neutral solution is shown by the small but significant absorption at 315 mμ (Fig. 2). On this basis it is possible to calculate from the molar absorptivities of the 315 mμ peaks in Figures 2 and 3 that the equilibrium consists of approximately 70% of the cyclic and 30% of the acyclic forms.

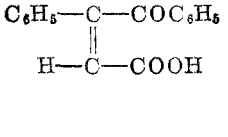
When a simple or alkalinized solution of the acid is acidified with excess strong acid (hydrochloric), the longer wavelength peak is depressed below that of the original simple solution (Fig. 1); this shows a shift in the equilibrium in favor of the less acidic (cyclic) form of the acid. This is consistent with the fact that alkali converts the acid into the anion of the more acidic (acyclic) form.

cis-β-BENZOYL-β-PHENYLACRYLIC ACID (VI)

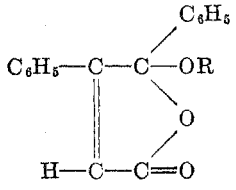
This acid has been prepared by the decarboxylation of the aldol condensation product of benzil and malonic ester (8), the hydrolysis of γ-bromo-β,γ-diphenylcrotolactone (9), and more recently by the Friedel-Crafts reaction between phenylmaleic anhydride and benzene (10, 11). It is known to react in the cyclic (VIA) and acyclic (VIB) senses giving derivatives of both types. The cyclic methyl ester (VIIA) and the acetoxy derivative (VIIB) were prepared by the reaction of γ-bromo-β,γ-diphenylcrotolactone (which may be regarded as the cyclic acid bromide of VI) with absolute methanol and with silver acetate, respectively (9). The normal acyclic methyl ester (VIII) was prepared by the



VIA

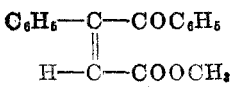


VIB

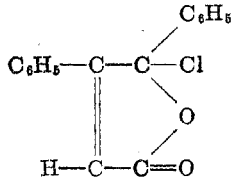


VII

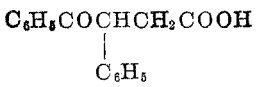
R = (a)CH_3; (b) $COCH_3$



VIII



IX



X

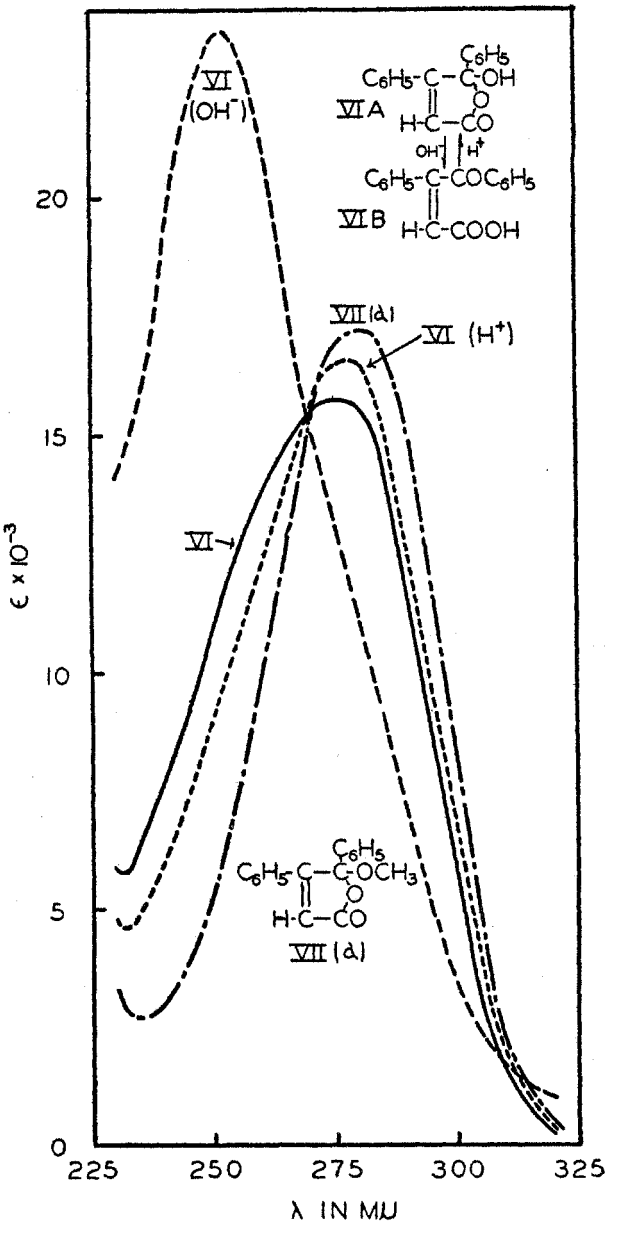


FIG. 4. SPECTRA OF β-BENZOYL-β-PHENYLACRYLIC ACID AND ITS CYCLIC METHYL ESTER. The acid; ethanol solution ————, NaOH added - - - -, HCl added ------, Cyclic methyl ester —•—•—•

silver salt-methyl iodide synthesis (9). The preparations of these derivatives have been repeated using in the case of the cyclic compounds the chlorolactone (IX) which was prepared from the acid by the action of thionyl chloride.

Following the method of spectral analysis described in the foregoing section, the acid (VI) can also be shown to exist in dilute 95% ethanol solution as an equilibrium mixture of cyclic (VIA) and acyclic (VIB) forms in which the cyclic

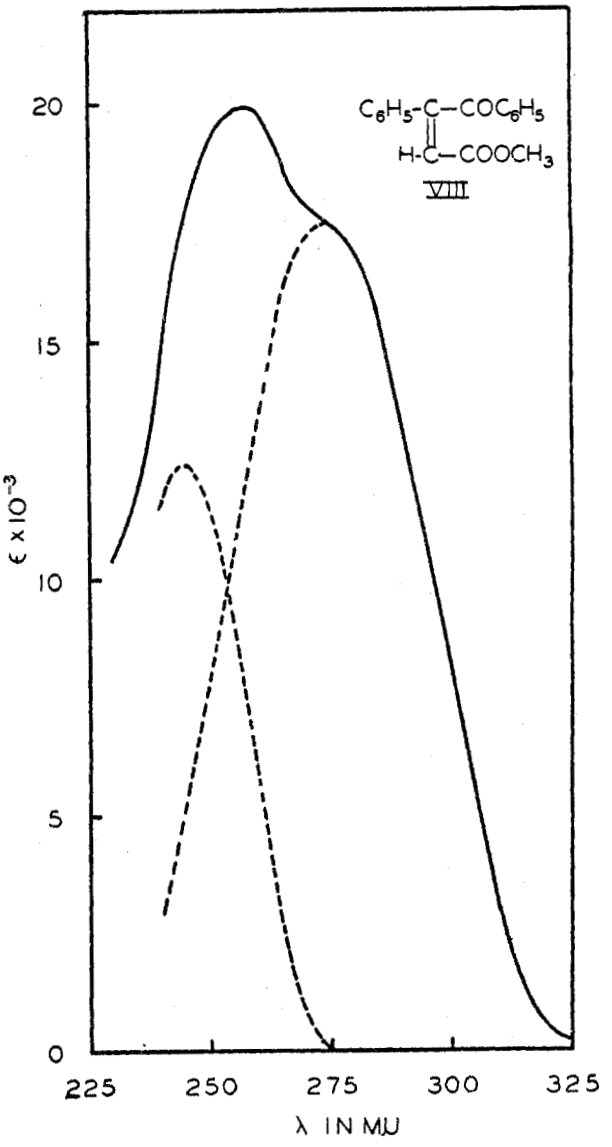


FIG. 5. SPECTRUM OF METHYL β-BENZOYL-β-PHENYLACRYLATE AND ITS GRAPHICAL RESOLUTION.

form predominates. As was also true in the case of the α-phenyl analog, the corresponding saturated acid, β-benzoyl-β-phenylpropionic acid (X), in contrast with the unsaturated (*cis*) acid (VI), is shown to be largely if not exclusively

acyclic by the presence in its spectrum of a normal benzoyl-type peak (ϵ = 12,200 at 245 mμ).

One would expect the principal absorption peak of the cyclic molecule (VIA) to be very similar to that of *trans*-cinnamic acid. This is borne out by the spectrum of the cyclic methyl ester (VIIA) (Fig. 4) whose single peak actually has wavelength and molar absorptivity similar to that of *trans*-cinnamic acid (7).

On the basis of the spectrum of *cis*-phenyldibenzoylethylene (XI) (12) which shows a benzoyl group and a *trans*-benzalacetophenone system functioning independently due to group interferences, the spectrum of the acyclic molecule

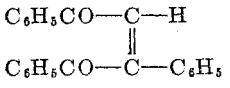
TABLE I

ABSORPTION MAXIMA AND MOLAR ABSORPTIVITIES IN 95% ETHANOL

COMPOUND	λ_{max} IN mμ	$\epsilon \times 10^{-3}$
cis - β - Benzoyl - α - phenylacrylic acid (Fig. 1)		
Ethanol solution	275	10.9
	312.5[a]	6.3
NaOH added	315	19.1
	275[a]	11.5
HCl added	272.5	11.0
Cyclic acetoxy derivative	275	11.7
cis - β - Benzoyl - β - phenylacrylic acid (Fig. 4)		
Ethanol solution	275	15.9
NaOH added	252.5	23.6
HCl added	277.5	16.6
Cyclic methyl ester	280	17.4
Cyclic acetoxy derivative[b]	282.5	16.9
Acyclic methyl ester (Fig. 5)	257.5	20.0
	272.5[a]	17.7
α,γ-Diphenylcrotolactone[b](5)	277.5	—[c]
trans-Cinnamic acid[b]	275[d]	20.1[d]
trans-Benzalacetophenone[b](6)	312	26.7
Phenylmaleic anhydride[b]	275	14.3

[a] Inflection points. [b] Not given in figure. [c] Compound too insoluble to obtain quantitative figure. [d] Our figures (*cf.* ref. 7).

(VIB) in which the same kind of interferences are present, would be expected to possess a characteristic benzoyl peak in addition to the cinnamic acid type peak. It can be seen from Fig. 5 that this actually is the case; the spectrum of the acyclic methyl ester (VIII) is resolvable graphically into a benzoyl peak at 245 mμ and a *trans*-cinnamic acid peak at 275 mμ.



XI

The spectrum of the solution of the acid (VI) (Fig. 4), as in the case of the isomeric acid (I), is intermediate between those expected for the cyclic and acyclic forms; again this indicates an equilibrium mixture. No attempt was made to determine the position of this equilibrium from the varying amounts of absorption in the benzoyl region because other unidentifiable absorptions appearing in this region introduce a much larger uncertainty than in the case of the isomeric acid where both extremes of absorption were more apparent.

The presence of two peaks in the spectrum of an alkalized solution of the acid where both forms of the acid may be considered to have been converted to the stabler acyclic anion, is not so apparent. The cinnamic acid system has now become a cinnamate-ion system with its peak shifted from 275 mμ to 265 mμ (ϵ = 15,400) (7) which is closer to the benzoyl peak at 245 mμ (ϵ = 12,600); hence a smoother curve is obtained than in the case of the acyclic methyl ester (Fig. 5) where the peaks are further separated and are more distinct.

The sharpening of the absorption peak of the solution when it is acidified with strong acid (Fig. 4) points to a favoring of the cyclic form (VIA) in strongly acid solution for the reasons already stated in the case of the α-phenyl compound.

EXPERIMENTAL

cis-β-Benzoyl-α-phenylacrylic acid (I) and its *cyclic acetoxy derivative* (II) were prepared by the method of Kohler, *et al.* (3) starting from benzalacetophenone. The acid (I) melted at 123–124°.

Anal. Calc'd for $C_{16}H_{12}O_3$: C, 76.18; H, 4.80.
Found: C, 76.16; H, 4.48.

The cyclic acetoxy derivative (II) melted at 92.5–93.5°.

Anal. Calc'd for $C_{18}H_{14}O_4$: C, 73.40; H, 4.80.
Found: C, 73.37; H, 4.48.

cis-β-Benzoyl-β-phenylacrylic acid (VI) was prepared from phenylmaleic anhydride (13) and benzene by a Friedel-Crafts reaction (10, 11); m.p. 141–142°.

γ-Chloro-β,γ-diphenylcrotolactone (IX) was prepared from VI in almost quantitative yield by the action of refluxing thionyl chloride (overnight), evaporating under reduced pressure, and recrystallizing from isoöctane; m.p. 122.5–123.5°.

Anal. Calc'd for $C_{16}H_{11}ClO_2$: C, 70.99; H, 4.10; Cl, 13.10.
Found: C, 71.06; H, 4.10; Cl, 12.99.

The *cyclic methyl ester* (VIIA) (9) was obtained by shaking IX with absolute methanol for 15 minutes. From the resulting acid solution the ester was precipitated by addition of water and was recrystallized from isoöctane; m.p. 103–104°.

Anal. Calc'd for $C_{17}H_{14}O_3$: C, 76.67; H, 5.30.
Found: C, 76.49; H, 5.17.

The *cyclic acetate* (VIIB) (9) resulted when IX was added to a suspension of silver acetate in hot glacial acetic acid. The suspension was filtered and diluted with water, and the precipitate was recrystallized from a benzene-isoöctane mixture; m.p. 116–117°.

Anal. Calc'd for $C_{18}H_{14}O_4$: C, 73.46; H, 4.80.
Found: C, 73.36; H, 4.78.

The *acylcic methyl ester* (VIII) (9) was prepared by the standard silver salt-methyl iodide procedure, m.p. 91–92°.

Anal. Calc'd for $C_{17}H_{14}O_3$: C, 76.67; H, 5.30.
Found: C, 76.27; H, 5.15.

α,γ-Diphenylcrotolactone (V) was prepared by heating IV with acetic anhydride (5). It is so insoluble in most solvents that its spectrum could be determined only qualitatively from a saturated 95% ethanol solution.

α- and β-Phenyl-β-benzoylpropionic acids (IV and X) were both obtained from the Friedel-Crafts reaction of phenylsuccinic anhydride with benzene. This reaction had been reported previously as giving only IV (14).

To a suspension of 8 g. of aluminum chloride in 25 ml. of dry benzene was added over a period of 10–15 minutes a solution of 5 g. of phenylsuccinic anhydride in 25 ml. of benzene. The reaction was allowed to proceed for a half hour at 45–50° after which it was poured over a conc'd hydrochloric acid-ice mixture; the benzene layer was separated, washed, dried and evaporated. The solid residue which melted at 80–110° was treated with 10% sodium hydroxide in which it all dissolved; soon an insoluble salt of X separated. After filtering the pure acids were obtained, one from the filtrate by acidification and the other by dissolving the alkali-insoluble salt in water and acidifying. Both were recrystallized from benzene-isoöctane and melted at 151–152° and 165–166°, respectively (identified by mixture melting points with known samples). The acid IV had been obtained as an intermediate in the synthesis of I (2, 3) and X was made by a zinc-acetic acid reduction of VI (9).

All *absorption spectra* were taken at room temperature in 4–5 × 10^{-5} *M* 95% ethanol solutions using a Beckman DU quartz spectrophotometer.

In graphically resolving the absorption curves, it was assumed that these curves are composed of only two symmetrical peaks and that the effect of lesser peaks in the region is negligible and constant (*cf.* 15). The component peaks were arrived at by (a) arbitrarily constructing one likely symmetrical peak from one portion of the area under the curve, and then (b) obtaining the heights of the second peak at the various wavelengths by subtracting the heights of the first peak at those wavelengths from the heights of the original curve.

SUMMARY

Graphical resolution of the ultraviolet absorption spectra of their cyclic and acyclic derivatives show that α- and β-phenyl-β-benzoylacrylic acids exist in dilute 95% ethanol solutions as equilibrium mixtures of their cyclic and acyclic forms in which the cyclic forms predominate. In the case of α-phenyl-β-benzoylacrylic acid it has been estimated that the equilibrium mixture consists of 70% of the cyclic and 30% of the acyclic forms. In alkaline solution both acids exist as the anions of their more acidic (acyclic) forms while in strongly acidic solution the equilibria lies in favor of the less acidic (cyclic) forms.

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REFERENCES

(1) LUTZ, BAILEY, DIEN, AND RINKER, *J. Am. Chem., Soc.*, **75**, 5039 (1953).
(2) KOHLER AND KIMBALL, *J. Am. Chem. Soc.*, **56**, 729 (1934).
(3) KOHLER, PETERSON, AND BICKEL, *J. Am. Chem. Soc.*, **56**, 2000 (1934).
(4) KOHLER AND PETERSON, *J. Am. Chem. Soc.*, **56**, 2192 (1934).
(5) ROBERTSON AND STEPHEN, *J. Chem. Soc.*, 863 (1931).
(6) SZMANT AND BASSO, *J. Am. Chem. Soc.*, **74**, 4397 (1952).
(7) BODFORSS, *Ann.*, **534**, 238 (1938).
(8) JAPP AND DAVIDSON, *J. Chem. Soc.*, **67**, 132 (1895).
(9) THIELE AND STRAUS, *Ann.*, **319**, 174 (1901).
(10) BAUER AND LUTZ, *J. Am. Chem. Soc.*, paper in press.
(11) BAUER, Doctoral Dissertation, University of Virginia (1950).
(12) KUHN, LUTZ, AND BAUER, *J. Am. Chem. Soc.*, **72**, 5058 (1950).
(13) MILLER, STALEY, AND MANN, *J. Am. Chem. Soc.*, **71**, 374 (1949).
(14) ANSCHÜTZ, WALTER, AND HAHN, *Ann.*, **354**, 148 (1907).
(15) BRODE, *Bur. Standards J. Research*, **2**, 520 (1929).