for the reaction of the former, may be explained by the increase in hyperconjugative resonance stabilization of the transition state with an increase in the number of available β-hydrogen atoms.[7] Differences in the rate constants for 1-bromopropane, 1-bromobutane, and 1-bromopentane, all of which have two β-hydrogen atoms, are very slight.

The rapid reaction of benzyl bromide is of course, explained by resonance stabilization of the transition state through participation of the phenyl group. In (2-bromoethyl)-benzene, the tendency of phenyl group to destabilize the transition state, presumably because of its electron-withdrawing inductive effect, is apparently not overcome significantly by the possible neighboring group interaction of the β-phenyl group.[11] From the heat of activation sequence, (2-bromoethyl)-benzene > (3-bromopropyl)-benzene > (4-bromobutyl)-benzene, it is seen that the electron-withdrawal effect of the phenyl group is diminished with an increase in the number of carbon atoms through which it must act, apparently disappearing altogether in the last-named compound. Even here, however, the phenyl-substituted bromide reacts more slowly than 1-bromobutane, indicating that the phenyl group inhibits the reaction through another mechanism, as well. It may be that mercuric ion, as was observed for silver ion, forms a loose complex[12] with the phenyl group in which its electrophilic character, and therefore the rate of its reaction with the bromides, is considerably decreased.

Acknowledgment.—The authors are grateful to the Research Corporation for a grant which made this and continuing work possible.

LAWRENCE, KANSAS

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(11) See D. J. Cram, THIS JOURNAL, **71**, 3863 (1949); S. Winstein and co-workers, *ibid.*, **74**, 1113, 1140 (1952).

(12) L. J. Andrews and R. M. Keefer, *ibid.*, **71**, 3644 (1949); **72**, 3113, 5034 (1950).

[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF THE UNIVERSITY OF TEXAS AND THE UNIVERSITY OF VIRGINIA]

The *cis*- and *trans*-β-Aroyl-α- and β-methylacrylic Acids and β-Aroyl-α-methylenepropionic Acids

BY ROBERT E. LUTZ,[1a] PHILIP S. BAILEY,[1b] CHI-KANG DIEN[1c,e] AND JAMES W. RINKER[1d,e]

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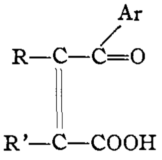
Ultraviolet absorption studies on the *cis*-β-aroyl-α- and β-methylacrylic acids and related compounds show that the *cis* compounds in solution are cyclic but are open-chain in the form of the anions. The *cis*-β-benzoyl-α- and β-methyl compounds and both β-aroyl-α-methylenepropionic acids have been made, respectively, from citraconic and itaconic anhydrides by Friedel–Crafts reactions. The structures and configurations have been demonstrated. The *trans* isomers are the stable forms; the *cis* isomers are labile; and the β-aroyl-α-methylenepropionic acids also are labile and the least stable of the three types. Interconversions of the various isomers are described.

This paper deals with the extension of earlier work and represents a joint effort which is basic to three fields of interest, the study of ring-chain tautomerism of compounds containing groups capable of interacting when sterically favorable circumstances are involved,[2] the influence of configuration and substitution on the effectiveness of the whole or parts of conjugated systems,[3] and the reactions and 1,3-hydrogen shifts during reactions of systems of the type —COCH=C(CH<)CO—.[4]

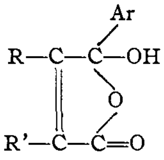
cis-β-Aroylacrylic acids (I) show no tendency to form cyclic derivatives.[2j] On the other hand, the *cis*-α[2b,f] and β[2b]-methyl, α,β[2c,g,h]-dimethyl and α,β-dibromo[2a] derivatives (II or III) give cyclic esters under acid-catalyzed esterification or methanolysis of the acid chloride, although they react with diazomethane and through the silver salts with methyl iodide to give open-chain esters.

$ArCOCH{=}CHCOOH$

I



II



III

The *cis*-acid of the β-(4-bromobenzoyl)-α-methylacrylic series (XIVb) was believed to be open-chained II because of its ready solubility in sodium bicarbonate and facile acid- or base-catalyzed rearrangement to the more stable *trans* isomer, whereas the structurally isomeric *cis*-β-methyl acid Vb which was not so easily rearranged and which was slow to dissolve in sodium bicarbonate, was presumed to be cyclic. Polarographic studies by Wawzonek, *et al.*,[2l] indicate that the latter compound Vb is cyclic to a considerable degree but open-chain in the form of the anion.

It has now become possible through determination of the ultraviolet absorption characteristics of the various compounds involved in both the α-

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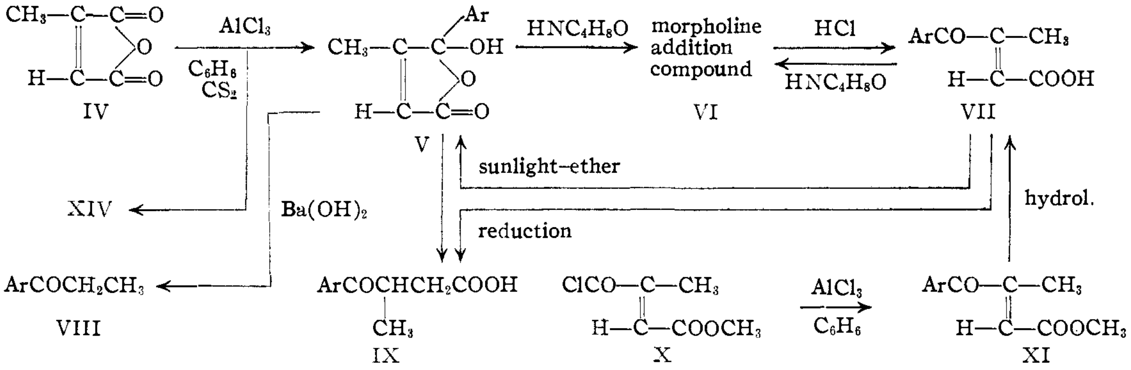
(1) (a) University of Virginia. (b) University of Texas. This work was supported in part by a grant-in-aid from the Research Corporation (to P.S.B.). (c) E. C. A. Scholarship from the State Department, University of Texas, 1952–1953. (d) Graduate Assistant, University of Virginia, 1952–1953. (e) Experimental contributions will be described in greater detail in doctoral dissertations to be completed shortly at the Universities of Texas and Virginia.

(2) (a) R. E. Lutz, THIS JOURNAL, **52**, 3405 (1930); (b) R. E. Lutz and R. J. Taylor, *ibid.*, **55**, 1168 (1933); (c) **55**, 1593 (1933); (d) R. E. Lutz and A. W. Winne, *ibid.*, **56**, 445 (1934); (e) R. E. Lutz, *ibid.*, **56**, 1378 (1934); (f) R. E. Lutz, D. T. Merritt and M. Couper, *J. Org. Chem.*, **4**, 95 (1939); (g) R. E. Lutz and M. Couper, *ibid.*, **6**, 77; (h) 91 (1941); (i) R. E. Lutz and F. B. Hill, *ibid.*, **6**, 175 (1941), (j) R. E. Lutz and G. W. Scott, *ibid.*, **13**, 284 (1948); (k) C. L. Browne and R. E. Lutz, *ibid.*, in press; (l) S. Wawzonek, H. W. Vaught, Jr., and J. W. Fan, THIS JOURNAL, **67**, 1300 (1945).

(3) (a) L. P. Kuhn, R. E. Lutz and C. R. Bauer, *ibid.*, **72**, 5058 (1950); (b) R. E. Lutz and C. R. Bauer, *ibid.*, **73**, 3456 (1951.

(4) (a) R. E. Lutz and P. S. Bailey, *ibid.*, **67**, 2229 (1945); (b) P. S. Bailey, G. Nowlin, S. H. Pomerantz, J. V. Waggoner and E. E. Kawas, *ibid.*, **73**, 5560 (1951); (c) P. S. Bailey and S. H. Pomerantz, *ibid.*, **75**, 281 (1952); (c) P. S. Bailey, Thomsen and Bath, a paper to be published shortly.

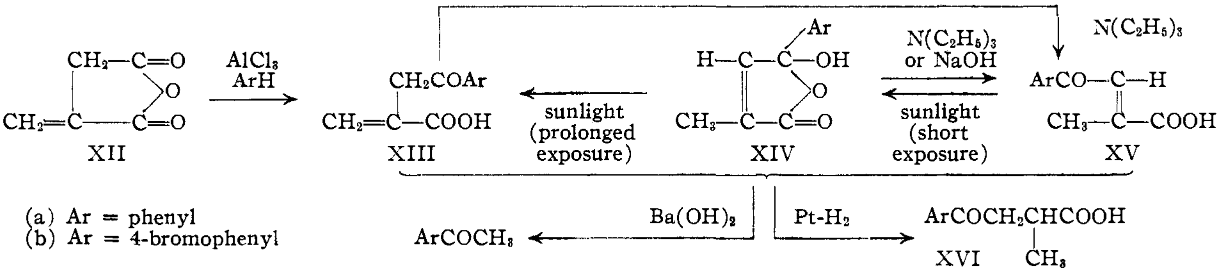


(a) Ar = phenyl; (b) Ar = 4-bromophenyl; HNC$_4$H$_8$O = morpholine

methyl and β-methyl series, to show conclusively that both of these *cis*-acids, and the parent β-benzoyl analogs as well, actually are largely cyclic (in alcohol solution). In the following discussion which precedes the presentation of the spectral evidence the cyclic formulations of the *cis*-acids will be used.

The parent *cis*-β-benzoyl-β-methylacrylic acid (Va, m.p. 79°) has now been obtained in 46% yield, along with a 14% yield of the α-methyl isomer (XIVa, m.p. 92°) by the Friedel–Crafts reaction between citraconic anhydride and benzene in carbon disulfide solution. The structure of this compound Va was established by a second synthesis from the appropriate mesaconyl monomethyl ester monoacid chloride X by the Friedel–Crafts reaction, hydrolysis of the resulting ester XI to the *trans*-acid VII, and sunlight inversion of the *trans* to the *cis* isomer. The *cis*-acid was converted back to the *trans* isomer by the addition and elimination of morpholine. Hydrolysis of both isomers by barium hydroxide produced propiophenone which substantiated conclusively the location of the methyl group. Reduction of both isomers gave the same saturated ketonic acid.

It is to be noted that in the Friedel–Crafts synthesis from citraconic anhydride and benzene, as with bromobenzene,[2b] both α- and β-methyl-β-aroylacrylic acids were obtained with the β-methyl isomers predominant. While the mode of ring opening of citraconic anhydride has been consistent, the (4-bromobenzoyl)-α-methyl compound, in contrast with the parent β-benzoyl analog, underwent stereochemical inversion to the stable *trans* form.



(a) Ar = phenyl
(b) Ar = 4-bromophenyl

Earlier investigators carried out the Friedel–Crafts reaction between citraconic anhydride and benzene,[5a,b] and had reported the preparation in very poor yields of a compound of m.p. 155° which they supposed was one of the possible isomeric β-benzoyl-α-methylacrylic acids. More recently Dixon, *et al.*,[5c] have obtained this acid in 78% yield from itaconic anhydride using benzene as the solvent, and shortly before the appearance of this paper we had obtained essentially the same result. This compound, believed by Dixon, *et al.*,[5c] to be *trans*-β-benzoyl-α-methylacrylic acid (XVa), is now shown to be β-benzoyl-α-methylenepropionic acid (XIIIa) which is produced by a straightforward reaction without rearrangement. The anomalous isolation of this compound in the earlier experiments from citraconic anhydride, in very small yields it should be noted, is explained by the very reasonable assumption that the citraconic anhydride used contained itaconic anhydride as an impurity; using purified citraconic anhydride we were unable to isolate any of this acid in repeated trials.

The analogous β-(4-bromobenzoyl)-α-methylenepropionic acid (XIIIb) has been made by a similar Friedel–Crafts condensation between itaconic anhydride and bromobenzene. Evidence for the position of the methylene group and the direction of ring opening in these Friedel–Crafts reactions is the ready isomerization of the β-(4-bromobenzoyl) compound XIIIb by the action of triethylamine to the stable *trans* isomer XVa the structure of which has already been established,[2b] and by catalytic reduction to the known β-(4-bromobenzoyl)-α-methylpropionic acid.[2b]

As stated above, the parent *cis*-β-benzoyl-α-methylacrylic acid (XIVa) (new) is obtained along with the β-methyl isomer Va in the Freidel–Crafts reaction on citraconic anhydride. It is labile and is converted by prolonged exposure to sunlight into the methylenepropionic acid (XIIIa); it undergoes base-catalyzed conversion into the new *trans* isomer (XVa, stable) by the action of triethyl-

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[5] (a) F. Mayer and G. Stamm, *Ber.*, **56B**, 1424 (1923); (b) M. J. Bogart and J. H. Ritter, This Journal, **47**, 526 (1925); (c) S. Dixon, H. Gregory and L. F. Wiggins, *J. Chem. Soc.*, 2139 (1949).

amine; and it is regenerated from the *trans* isomer by short exposure of a solution to sunlight. Reduction of the three isomers (XIII, XIV and XV) gave the corresponding β-benzoyl-α-methylpropionic acid, and hydrolytic cleavage by barium hydroxide[2b] gave in each case acetophenone and thus demonstrated conclusively that the methyl group in this series is alpha to the carboxyl.

Although from the foregoing outline of the completed chemical relationships it is obvious that the assigned structures and configurations of the compounds involved are correct, these conclusions were not so apparent in the earlier stages of the work in the light of the interpretations of Dixon.[5c] It should therefore be pointed out that the β-aroyl-α-methylenepropionic acid structures (XIII) and the *cis*-β-aryl-α-methylacrylic acid configurations (XIV) logically follow from the syntheses from itaconic and citraconic anhydrides, respectively, on the principle of minimum structural change because these products are labile and because they are independently stable during their formation in the respective Friedel–Crafts reactions.

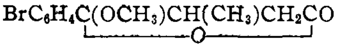
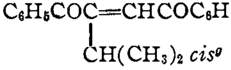
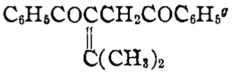
In this connection it is interesting to note that the two α-methylenepropionic acids (XIII) are not reduced normally to the saturated ketonic acid XVI by zinc and acetic acid but give instead high-melting and presumably dimolecular products. These results are consistent with the fact that these two compounds do not have the easily reducible quinone-like unsaturated 1,4-ketonic acid systems.

As a base for reference for ultraviolet absorption studies of the various compounds described above, determinations were made of the absorptions of the saturated compounds, the β-benzoyl- and β-(4-bromobenzoyl)-α- and β-methylpropionic acids (IX, XVI). The results show that (as had been presumed) these acids have open-chain structures because they absorb strongly in the ranges 240–245 mμ and 250–260 mμ which are characteristic for the benzoyl and 4-bromobenzoyl groups, respectively. Only one cyclic derivative has been obtained among these types, and this indirectly through cyclization of the enol ether[2e] of β-(4-bromobenzoyl)-β-methylpropionic acid; this compound, the intrinsically unstable cyclic ("pseudo") ester shows no significant absorption in the near ultraviolet.

The very broad ultraviolet absorption bands of the parent (unsubstituted) *cis*- and *trans*-β-benzoylacrylic acids (I) with maxima at 245 and 238 mμ, respectively (ε 11–12 × 10^3) indicate benzoyl type conjugation and show conclusively that the *cis* isomer is open-chain and not cyclic (see Table I).[6]

TABLE I

ULTRAVIOLET ABSORPTION DATA IN 95% ETHANOL[a]

Compound	Ref.	λmax. mμ	$\epsilon \times 10^{-3}$
$ArCOC(CH_3){=}CHCOOH$			
Ar = C_6H_5 *cis*-acid	...	(246)[b]	3.6[b]
cis-anion	...	246	11.8
trans-acid	...	245	11.0
trans-anion	...	250	11.3
Ar = 4-BrC_6H_5 *cis*-acid	2b	(260)[b]	2.4[b]
cis-anion	...	260	14.2
cis-methyl ester[c]	2b	262	13.2
trans-acid	2b	275	14.8
trans-anion	...	275	17.2
trans-methyl ester	2b	267	13.2
$ArCOCH{=}C(CH_3)COOH$			
Ar = C_6H_5 *cis*-acid	...	(267)[b]	2.0[b]
cis-anion	...	267	14.4
trans-acid	...	258	13.4
trans-anion	...	262	13.8
Ar = 4-BrC_6H_4 *cis*-acid	2f	(275)[b]	3.2[b]
cis-anion	...	275	16.8
trans-acid	2b	273	14.6
trans-anion	...	275	16.8
trans-methyl ester	2b	277	13.8
$ArCOCH(CH_3)CH_2COOH$			
Ar = C_6H_5	...	242	10.9
Ar = 4-BrC_6H_4	2b	255	16.2
$ArCOCH_2CH(CH_3)COOH$			
Ar = C_6H_5	...	242	11.5
Ar = 4-BrC_6H_4	2b	255	17.6
$ArCOCH_2C({=}CH_2)COOH$			
Ar = C_6H_5 (*cf.* ref. 5c)	5c	243	11.6
Ar = 4-BrC_6H_5	...	255	16.0
 $BrC_6H_4\overset{}{C}(OCH_3)CH(CH_3)CH_2CO$ (C and CO joined through O)	2e	260	1.6
$BrC_6H_4C(OCH_3){=}C(CH_3)CH_2COOH$	2e	260	9.8
$C_6H_5COCH{=}CHCOOH$			
cis (*cf.* ref. 6)	6	245[d]	10.7[a]
trans (*cf.* ref. 5, 6)	5, 6	238[d]	11.7[d]
$C_6H_5COC(CH_3){=}CHCOC_6H_5$			
cis isomer	2b	258[e]	22.1[e]
trans isomer	2b	260[e]	21.7[e]
$C_6H_5COC({=}CH_2)CH_2COC_6H_5$	4b	246[f]	22.0[f]
 $C_6H_5CO\underset{CH(CH_3)_2}{\underset{\vert}{C}}{=}CHCOC_6H_5$ *cis*[g]	4d	258[f]	23.0[f]
 $C_6H_5CO\underset{C(CH_3)_2}{\underset{\Vert}{C}}CH_2COC_6H_5$[g]	4d	247[f]	24.4[f]

[a] Taken with a Beckman DU quartz spectrophotometer at 0.00005 *M* concentration. [b] Showed low but significant and decreasing absorption with no maximum in the range 230–310 mμ. [c] Open-chain (normal) ester. [d] For actual curves see ref. 5 and 6, and work to be published shortly from this Laboratory. The figures given here represent our determinations. Although the maxima for the parent benzoylacrylic acids fall close to those of a normal isolated benzoyl group (present in the saturated α- and β-methyl acids), it should be pointed out that the peaks are relatively broad, and that the total areas under the curves are relatively large, whereas the peaks for the α- and β-methylaroylacrylic acids are much narrower and sharper. [e] Data taken from ref. 3b. [f] Determination by Dr. C. R. Bauer. [g] Compounds to be reported in a separate paper by P. S. B. (see ref. 4c).

In the β-(4-bromobenzoyl)-β-methylacrylic acid series (Vb, VIIb) neither the *cis*-acid nor its cyclic ester show a significant absorption maximum in the 255–275 mμ range characteristic for a conjugated 4-bromobenzoyl group. The *cis*-acid is therefore largely cyclic in solution III. The *cis*-α-methyl acid (XIVb) originally believed to be open-chain,[2b] and the new *cis*-β-benzoyl-α- and β-methylacrylic acids (XIVa, Va) are also shown to be cyclic by the absence of significant absorption maxima in the near ultraviolet. In contrast both of the *trans*-β-(4-bromobenzoyl)-α- and β-methyl acids (VIIb, XVb) and the ester of the *trans*-β-methyl com-

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(6) R. L. McConnell, Dissertation, University of Virginia, 1952.

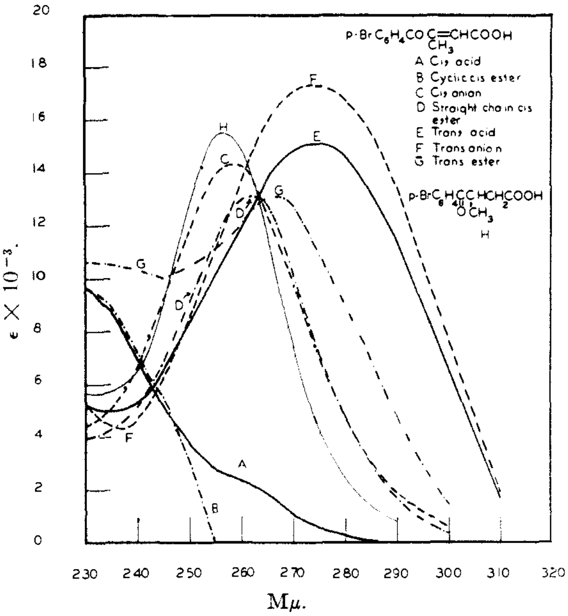


Fig. 1.—The β-(4-bromobenzoyl)-β-methylacrylic acids and related compounds: A, *cis*-acid (Vb); B, cyclic *cis*-methyl ester; C, *cis*-anion; D, straight chain *cis*-methyl ester; E, *trans*-acid (VIIb); F, *trans*-anion; G, *trans*-methyl ester (XIb); H, β-(4-bromobenzoyl)-β-methylpropionic acid (IXb).

pound XIb, which are necessarily open-chain, absorb strongly (at 275, 275 and 267 mμ, respectively) and also the *cis* open-chain ester (of Vb) absorbs strongly in this region but at slightly lower wave length (262 mμ) which is consistent with the fact that this isomer is the labile form and involves an appreciably greater steric interference with effective planarity of the conjugated system. The parent *trans*-β-benzoyl-α- and β-methylacrylic acids show strong and characteristic absorptions at 258 and 245 mμ, respectively. Incidentally it is interesting to note that *cis*- and *trans*-β-benzoyl-β-methylacrylic acids and the *trans* anion have markedly lower absorption wave lengths and extinction coefficients than do the α-methyl analogs, whereas in the main no such general displacement is to be noted in the case of the β-(4-bromobenzoyl) compounds.

Alcohol solutions of all four of the *cis*-β-aroyl-α- and β-methylacrylic acids immediately upon treatment with sufficient sodium hydroxide to effect conversion into the anions, absorb strongly at wave lengths and with extinction coefficients similar to those of the corresponding *trans*-aroylacrylic systems, and the solutions revert back to their original absorptions upon acidification with hydrochloric acid. It is thus shown that the anions have the open-chain structures II, and that upon acidification immediate reversion occurs to the original cyclic acids. On the other hand, the strong and characteristic absorptions of the *trans*-acids, which are necessarily open-chain, are not altered significantly by conversion to the anions by bases or upon acidification with hydrochloric acid, although the extinction coefficients are raised in some cases. The facile ring-chain interchange between the *cis*-acids and their anions is thus demonstrated.

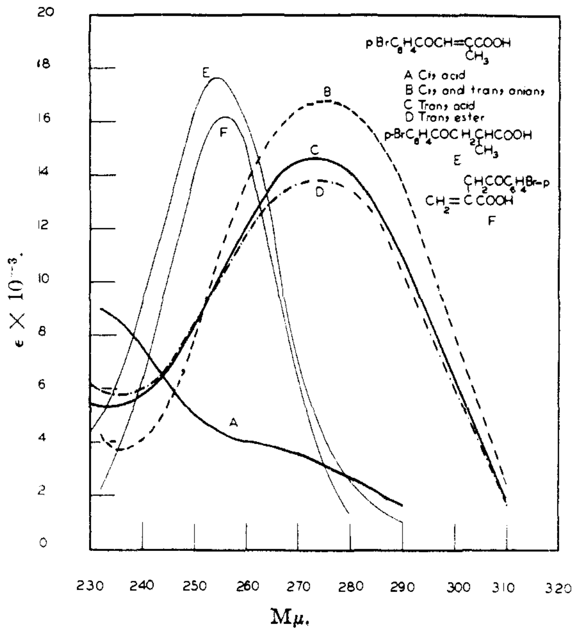


Fig. 2.—The β-(4-bromobenzoyl)-α-methylacrylic acids and related compounds: A, *cis*-acid (XIVb); B, *cis*- and *trans*-anions (curves practically coincidental); C, *trans*-acid (XVb); D, *trans*-methyl ester; E, β-(4-bromobenzoyl)-α-methylpropionic acid (XVIb); F, β-(4-bromobenzoyl)-α-methylenepropionic acid (XIIIb).

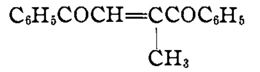
It should be noted that all four *cis*-acids show some absorption over the range of the absorption maxima of the corresponding anions. Acidification with a small excess of hydrochloric acid does not drastically suppress these absorptions although it does reduce them somewhat. The presence of small proportions of the open-chain forms at equilibrium is therefore probable. In this connection the absorption characteristics of the cyclic methyl ester in one case has been measured, and here there can be no open-chain form present; the absorption is very close to that of the corresponding acid Vb, but there is enough difference to suggest that in the case of the acid there is some open-chain form present in equilibrium. Estimating from the extinction coefficients of the four *cis*-acids at the wave length of the $\gamma_{\max}$ of their anions, assuming negligible absorption at these points for the cyclic forms, and assuming the anions to be completely open-chain, the following are the approximate percentages of open-chain form at equilibrium in dilute 95% ethanol: Va, 30%; Vb, 17%; XIVa, 14%; XIVb, 19%.

Both β-aroyl-α-methylenepropionic acids (XIII) are shown by their characteristic ultraviolet absorptions to be open-chain, like the *trans*-aroylmethylacrylic compounds XV and like the saturated acids XVI. The observed narrow-banded absorptions at the slightly shorter wave lengths are consistent with the absence of full conjugation of the free functional groups, aroyl, ethylenic double bond and carboxyl, and are characteristic of compounds containing only the simple aroyl group. They match closely the absorptions of the saturated acids which have isolated aroyl groups, and they are to be contrasted with the longer wave lengths and broader areas of absorptions of the *trans* compounds XV and of the anions of the *cis* compounds, all of which contain the aroylacrylic conjugation.

Ultraviolet absorption measurements made at different time intervals proved to be of practical value in following the sunlight isomerizations of the *trans*-α-methyl acids XV, which proceed stepwise to give first the *cis* (rapidly), and finally (slowly) the methylenepropionic acids XIII. In a typical experiment the high maximum of the *trans*-acid rapidly diminished, but at each time interval the addition of potassium hydroxide to the samples revealed the presence of the cyclic *cis* isomer by the resulting immediate development of the high absorption of the open-chain anion. On further exposure the solution lost its power to develop this band upon addition of alkali and the lower wave length absorption band of the methylenepropionic acid appeared at its characteristic maximum. From solutions irradiated for appropriate lengths of time, the two products could each be isolated and identified.

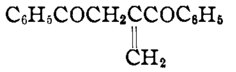
In summation of the above results it should be pointed out that all of the *cis*-β-aroyl-α- and β-methylacrylic acids studied so far are largely cyclic and give cyclic derivatives, whereas the related compounds, *cis*-β-benzoylacrylic acid itself, the β-aroyl-α-methylenepropionic acids and the β-aroyl-α- and β-methylpropionic acids are open-chained and do not show any tendency to react in the cyclic forms. The *cis*-α- and β-methyl-β-aroylacrylic acids in respect to cyclization are in some contrast to the α- and β-phenyl analogs which, although largely cyclic, have been shown at equilibrium to involve a sizeable proportion of the open-chain forms.[2k]

In connection with the above studies it seems important to consider at this time the *cis*- and *trans*-methyldibenzoylethylenes (XVII) and the structurally isomeric methylenedibenzoylethane (1,2-dibenzoylpropene) (XVIII) where the normal *cis*–*trans* stability relationships are reversed. The *trans* isomer is labile and rearranged by triethylamine, first to the *cis* isomer and then to a mixture



$C_6H_5COCH{=}C(CH_3)COC_6H_5$

XVII *cis* and *trans*



$C_6H_5COCH_2C({=}CH_2)COC_6H_5$

XVIII

of the *cis* isomer and the seemingly more stable methylene compound.[4b] These stability relationships are what one might expect from a study of molecular models,[3b] and they are to be contrasted with the relative stabilities in the β-aroyl-α- and β-methylacrylic and α-methylenepropionic acid series which correspond to those of itaconic, citraconic and mesaconic acids and their derivatives. The methylene diketone XVIII is unique, as would be expected, and in comparison with the more highly conjugated *cis* and *trans* isomers XVII its absorption maximum is displaced 12–14 mμ toward the shorter wave length. In the case of the analogous isomeric pair (new),[4c] *cis*-isopropyldibenzoylethylene and its more stable isomer, isopropylidinedibenzoylethane (see Table I) the similar, small but significant difference in the ultraviolet absorption maxima of 11 mμ supports the structures assigned.

An extension of these studies is under way to obtain more information on the effect of substituents on cyclization tendencies and on the stabilities of conjugations and configurations.

Experimental[7]

The Friedel–Crafts Reaction between Itaconic Anhydride and Benzene.[8] β-Benzoyl-α-methylenepropionic Acid (XIIIa).—To a well-stirred mixture of 140 g. of anhydrous aluminum chloride, 80 ml. of dry benzene and 150 ml. of dry carbon disulfide, at 45°, was added 50 g. of itaconic anhydride[9] over a period of one hour. After stirring for an additional hour at 50–55° and 10 hours at room temperature, the mixture was hydrolyzed in ice and concd. hydrochloric acid. Filtration of the resulting colorless crystals gave 59 g. of XIIIa (m.p. 138–140°) [the benzene–carbon disulfide layer (A) was retained] which upon trituration with 500 ml. of boiling benzene left 40 g. (m.p. 148–152°) [the filtrate (B) was retained]. This product was shown by mixture melting points to be identical with the products obtained by repetition of the older experiments.[5]

In repetition of the Dixon, *et al.*,[5c] experiment, which uses no carbon disulfide, we obtained only XIIIa. In the Bogart and Ritter[5b] experiment, using moderately pure citraconic anhydride, we obtained a 10% yield, but using carefully fractionated citraconic anhydride we were not able to isolate any of this acid from the resinous products.

By cooling filtrate B (above) 12.5 g. of material melting at 125–128° was obtained [the filtrate from this (C) was retained]. Recrystallization from benzene (m.p. 130–131°) and elaborate fractional crystallization from 60% ethanol gave 7 g. of XIIIa, and 4 g. (5%) of a *new isomer* of m.p. 146–147° (mixture melting point with XIIIa, 130–133°); this compound failed to undergo reduction and hydrolytic cleavage analogous to those reactions described below for XIIIa, and related compounds, and it underwent permanganate oxidation to phthalic acid. It therefore appears to be a nuclear cyclization product (this will be reported in a later paper by P. S. B. and C. K. D.).

Anal. Calcd. for $C_{11}H_{10}O_3$: C, 69.5; H, 5.3. Found: C, 69.3; H, 5.4.

From filtrates A and C (above) 6.7 g. of XIIIa was obtained, bringing the total yield to 53.7 g. (63%). This acid is readily soluble in sodium carbonate, very slowly dissolved in sodium bicarbonate, and readily decolorizes an acetone solution of potassium permanganate.

β-(4-Bromobenzoyl)-α-methylenepropionic Acid (XIIIb).—This compound was obtained as the only product in 91% yield from itaconic anhydride and bromobenzene by a procedure analogous to that described in the preceding experiment. Purification was from ethanol, m.p. 163–164°.

Anal. Calcd. for $C_{11}H_9BrO_3$: C, 49.1; H, 3.4. Found: C, 49.1; H, 3.2.

The Friedel–Crafts Reaction between Pure Citraconic Anhydride and Benzene to give *cis*-β-Benzoyl-α- and β-methylacrylic Acids (Va and XIVa).—Fifty grams of pure citraconic anhydride was added to a well-stirred mixture of 130 g. of anhydrous aluminum chloride, 100 ml. of benzene and 150 ml. of carbon dioxide over a period of one hour at 50°. After 30 min. additional heating and stirring overnight, the mixture was hydrolyzed with ice and hydrochloric acid. The organic layer was evaporated in a stream of air, and the residue, which did not crystallize, was extracted with 400 ml. of 10% sodium carbonate. This extract was washed with benzene, acidified with hydrochloric acid and extracted with benzene. Concentration of the benzene extract to 100 ml. and cooling gave 39 g. (46%) of material melting at 65–75° (the filtrate (A) was retained). Recrystallization gave pure *cis*-β-benzoyl-β-methylacrylic acid (Va) melting at 79–80%.

Anal. Calcd. for $C_{11}H_{10}O_3$: C, 69.5; H, 5.3. Found: C, 69.5; H, 5.2.

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[7] Some of the microanalyses were by Clark Microanalytical Laboratory.

[8] Carried out first by Dr. Gene Nowlin at the University of Texas.

[9] Prepared from itaconic acid (kindly furnished by Charles F. Pfizer Co.) by refluxing a mixture of the acid and acetyl chloride; yield 80%, m.p. 66–68°.

Dilution of filtrate A with petroleum ether and cooling gave 12 g. (14%) of *cis*-β-**benzoyl**-α-**methylacrylic acid** (XIVa), m.p. 70–80°, recrystallized from carbon tetrachloride, m.p. 92–93°.

Both acids are readily soluble in hot water and cold sodium bicarbonate solution, and decolorize an acid solution of potassium permanganate.

Anal. Calcd. for $C_{11}H_{10}O_3$: C, 69.5; H, 5.3. Found: C, 69.5; H, 5.1.

***trans*-β-Benzoyl-α-methylacrylic Acid (XVa).**—A solution of 1 g. of β-benzoyl-α-methylenepropionic acid (XIIIa) and 5 ml. of triethylamine in 15 ml. of ether was allowed to stand for 24 hours. After evaporation and extraction with dilute hydrochloric acid the oily residue crystallized; 0.85 g. (yellow); recrystallized from ethanol, m.p. 109–110°. The compound was readily soluble in sodium bicarbonate and quickly decolorized an acetone solution of potassium permanganate.

Anal. Calcd. for $C_{11}H_{10}O_3$: C, 69.5; H, 5.3. Found: C, 69.4; H, 5.3.

The above isomerization also occurred slowly when XIIIa was dissolved in sodium hydroxide solution, and occurred in ten minutes when XIIIa was heated at 175°.

***trans*-β-Benzoyl-β-methylacrylic Acid (VIIa).**—This acid was obtained by the method used to prepare its *p*-bromo analog.[2b] The oily ester (XIa) (not characterized) was immediately hydrolyzed at room temperature over a period of two hours. The resulting mixture was washed with ether, acidified and extracted with ether; evaporation of the ether extract, and crystallization of the residue from a benzene–carbon tetrachloride mixture gave a 41% yield of material melting at 90–94°; recrystallized from dilute ethanol, m.p. 102–103°. The substance is similar to XIVa in solubility and unsaturation properties.

Anal. Calcd. for $C_{11}H_{10}O_3$: C, 69.5; H, 5.3. Found: C, 69.4; H, 5.3.

Reductions.—(a) **Catalytic reduction of the** β-**aroyl**-α-**methylenepropionic acids (XIII)** were carried out in ethanol solution using platinum oxide for XIIIa and Raney nickel for XIIIb at atmospheric pressure. The yield of β-benzoyl-α-methylpropionic acid (XVIa, m.p. 138–140°; semicarbazone, m.p. 220–223°) from XIIIa was 81%. From XIIIb the bromo analog[2b] (XVIb, m.p. 120–122°) was obtained in 88% yield. Zinc and acetic acid reduction gave high melting and presumably dimolecular substances in each case which were not given further study (m.p. 204–212° from XIIIa and above 350° for XIIIb).

(b) **Reductions of** *cis*- **and** *trans*-β-benzoyl-α-methylacrylic **acids (XIVa and XVa)**, carried out with zinc and acetic acid over a steam-bath for 10 min., gave 79 and 81% yields of the corresponding propionic acid (XVIa, m.p. 138–140°). The product was isolated by filtration, evaporation and crystallization of the residue from dilute ethanol.

(c) **Reductions of** *cis*- **and** *trans*-β-benzoyl-β-methylacrylic **acids (Va and VIIa)** by the method described in the preceding experiment, except that the heating period was extended to 20 min., gave 63 and 71% yields, respectively, of β-benzoylbutyric acid (IXa), m.p. 59–60°; semicarbazone, m.p. 177–178°.

Hydrolyses.—(a) **Hydrolyses of** β-benzoyl-α-methylene**propionic acid (XIIIa) and** *cis*- **and** *trans*-β-benzoyl-α-meth**acrylic acids (XIVa and XVa)** gave high yields of crude acetophenone. In each case the acetophenone was steam distilled from the reaction mixtures (1 g. of acid, 6–8 g. of barium hydroxide and 50–100 ml. of water, refluxed for 4 hours) and was identified as the semicarbazone by mixture melting points; m.p. 197–198°.

(b) *cis*- **and** *trans*-β-**benzoyl**-β-**methylacrylic acids (Va and VIIa)**, upon similar hydrolysis gave 71 and 50% yields, respectively, of propiophenone, identified as the semicarbazone by mixture melting points, m.p. 172–173°.

(c) **Similar hydrolyses of** β-(4-bromobenzoyl)-α-methyl**enepropionic acid (XIIIb) and** *cis*-β-(4-bromobenzoyl)-α-**methylacrylic acid (XIVb)** gave 69 and 51% yields, respectively, of *p*-bromoacetophenone, m.p. 51–52°, oxime, m.p. 127–129°.

(d) **The** *trans*-β-**(4-bromobenzoyl)**-β-**methylacrylic acid (VIIb)**, hydrolyzed similarly, gave a 57% yield of *p*-bromopropiophenone (m.p. 46–48°; oxime, m.p. 88–89°).

Base-catalyzed Isomerizations.—By the method described above for the conversion of β-benzoyl-α-methylenepropionic acid (XIIIa) to *trans*-β-benzoyl-α-methylacrylic acid (XVa), the following isomerizations were carried out: β-(4-bromobenzoyl)-α-methylenepropionic acid (XIIIb) to *trans*-β-(4-bromobenzoyl)-α-methylacrylic acid (XVb, m.p. 182–184°) in 90% yield; *cis*-β-(4-bromobenzoyl)-α-methylacrylic acid (XIVb) to its *trans* isomer (XVb, m.p. 182–184°) in 70% yield; *cis*-β-benzoyl-α-methylacrylic acid (XIVa) to its *trans* isomer (XVa, m.p. 104–106°) in 88% yield. Also, XIVa was isomerized slowly to XVa when dissolved in sodium hydroxide or bicarbonate; the isomerization was also brought about by heat alone (10 min. at 175°). Triethylamine failed to cause the isomerization of *cis*-β-benzoyl-β-methylacrylic acid (Va) to its *trans* isomer VIIa; starting material was always recovered; heat also failed to produce isomerization. Isomerization was brought about by adding morpholine to the *cis* isomer in ether solution (addition compound, m.p. 138–140°)[10] and decomposing the addition compound with warm 10% hydrochloric acid; yield of *trans* isomer 40%, m.p. 100–102°. Triethylamine also failed to isomerize Vb to VIIb. All products obtained above were identified by mixture melting points.

Sunlight Isomerization. (a) **Conversion of** ***trans*-β-Benzoyl-α-methylacrylic Acid (XVa) to *cis* Isomer (XIVa).**—A solution containing 1 g. of XVa in 50 ml. of dry ether was exposed to sunlight until the yellow color disappeared (2 days). Evaporation and crystallization of the residue from hot benzene gave 0.9 g., m.p. 80–85°; recrystallized from benzene, m.p. 89–92°; identified as XIVa by mixture melting point with the material prepared from citraconic anhydride.

(b) **Conversion of** ***cis*- or *trans*-β-Benzoyl-α-methylacrylic Acid (XIVa and XVa) into β-Benzoyl-α-methylenepropionic Acid (XIIIa).**—When an ether solution of XVa was exposed to sunlight for one week or an ether solution of XIVa for four days, 40–50% yields of XIIIa were obtained, m.p. 152–154° (from dilute ethanol), identified by the mixture melting point method.

(c) **Conversion of XIVb to XIIIb** by the method described in (a) and (b) occurred in 30% yield, m.p. 160–162° (from benzene). Likewise, XVb was converted to XIIIb. Identifications were by mixture melting point.

(d) **Conversion of** *trans*-β-benzoyl-β-**methylacrylic acid (VIIa) to the** *cis* **isomer (Va)** was carried out by two-day exposure to sunlight of an ether solution; yield of Va, 80%, m.p. 68–76°; recrystallized from carbon tetrachloride, m.p. 78–80°; no depression in a mixture melting point with a sample obtained from citraconic anhydride.

(e) **Conversion of VIIb to Vb** was carried out as in (d); 64% yield, m.p. 130–135°; recrystallized from carbon tetrachloride, m.p. 138–141°; identified by mixture melting point.

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[10] To be described in detail in another paper by P.S.B. and C.K.D.