

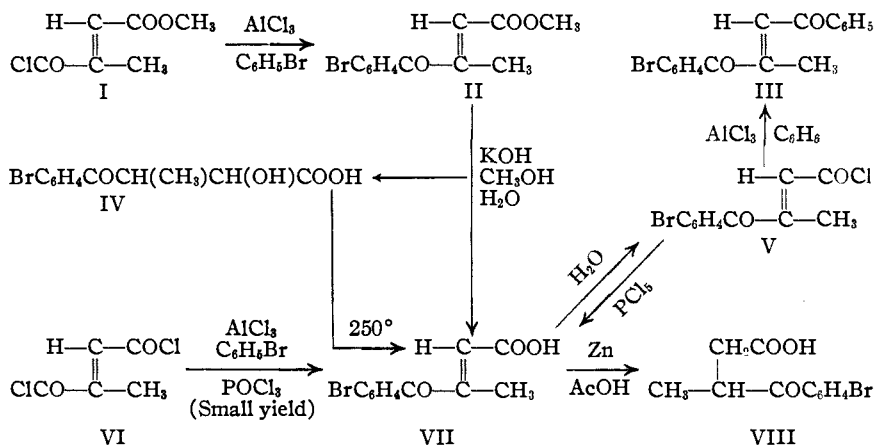
[CONTRIBUTION NO. 106 FROM THE COBB CHEMICAL LABORATORY OF THE UNIVERSITY OF VIRGINIA]

Studies on Unsaturated 1,4-Dicarbonyl Compounds. VII. Aryl Unsaturated 1,4-Diketones and Keticonic Acids Derived from Citraconic and Mesaconic Acids, with Particular Reference to the β -[*p*-Bromobenzoyl]-methylacrylic Acids

BY ROBERT E. LUTZ AND ROBERT J. TAYLOR

Two monomethyl unsaturated 1,4-keticonic acids have been described in the literature¹ but they have not been extensively studied and their configurations are not known. In an extension of our studies to this class of compounds we have utilized the bromophenyl analogs which are easily prepared, and have obtained three of the four possible isomers.

Trans- β -[*p*-Bromobenzoyl]-crotonic Acid (VII).—*Trans*- β -[*p*-bromobenzoyl]-crotonic methyl ester (II) was synthesized in good yield by the Friedel and Crafts reaction from mesaconyl α -methyl ester β -acid chloride (I), the structure of which is known.² From this synthesis the position of the methyl group is determined. The ester undergoes hydrolysis in dilute methanol to give two products, the expected *trans* acid (VII) (and also an addition compound, β -bromobenzoylhydroxybutyric acid (IV) which is described below). Under special conditions this *trans* acid is obtained also directly from mesaconyl chloride by the Friedel and Crafts reaction. The ester is easily regenerated.



The configuration of the acid and its derivatives must be *trans*, corresponding with that of the starting materials, since in Friedel and Crafts reactions of this type there is no reason to suppose that inversion in the

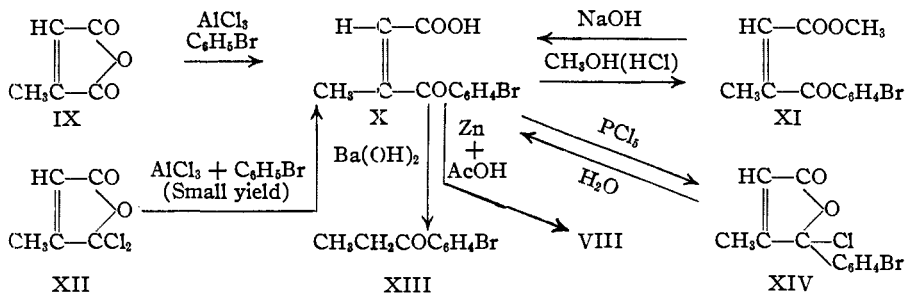
(1) (a) V. Pechmann, *Ber.*, **15**, 891 (1882); (b) Bogert and Ritter, *THIS JOURNAL*, **46**, 2871 (1924); **47**, 526 (1925).

(2) Anschütz, *Ann.*, **353**, 139 (1907).

direction *trans* to *cis* is likely.³ The acid chloride (V) reacts rapidly in the cold with methanol to form the ester and undergoes the Friedel and Crafts reaction with benzene and aluminum chloride to give the corresponding mixed diketone (III). It therefore reacts normally in contrast with the *cis* isomer described below. These facts are consistent with the *trans* formulation.

Cis-β-[p-Bromobenzoyl]-crotonic Acid (X).—The colorless *cis*-β-[bromobenzoyl]-crotonic acid (X) is prepared in a yield of 47% by the Friedel and Crafts reaction on citraconic anhydride with bromobenzene. It is obtained similarly from citraconyl chloride in a very small yield, but as the main product nevertheless.⁴ It is a stereoisomer and not a structural isomer of the *trans* acid described above, since both acids are reduced to the same β-[bromobenzoyl]-butyric acid (VIII). It is easily esterified,^{4a} and is regenerated in good yield from the ester by hydrolysis. The *cis* configuration follows from the synthesis since both stereoisomers are made, respectively, from starting materials of opposite and known configurations, and since no inversion from the one series into the other has been observed.

We have obtained independent proof of the position of the methyl group by the hydrolytic splitting of the *cis* acid at the double bond to give *p*-bromopropiophenone (XIII) which could only be formed if the methyl were alpha to the bromobenzoyl group. This degradation demonstrates that the Friedel and Crafts condensations occurred as expected para to the bromine in the benzene nucleus.



The acid chloride (XIV) of the *cis* isomer is easily prepared by the action of phosphorus pentachloride on the acid. It is a colorless solid which is hydrolyzed extremely slowly, and does not react readily with boiling methanol. The chlorine is therefore much less reactive than that of the

(3) Lutz, *THIS JOURNAL*, **52**, (a) 3405, (b) 3423 (1930).

(4) A relatively very minor yield of the *trans* structural isomer (XVI) was isolated as a by-product of the reactions with citraconic anhydride and chloride.

(4a) Since acceptance of this paper, Mr. A. W. Winne in this Laboratory has obtained the *cis*-β-[bromobenzoyl]-crotonic methyl esters in crystalline form (m. p. 62°, best prepared by alcoholysis of the acid chloride), and has obtained what appears to be an isomeric ester (m. p. 89°) by the silver salt method of esterification. These isomers correspond, we believe, to normal and cyclic types, and will be described in detail, together with analogs in the dimethyl and dihalogeno series in later papers.

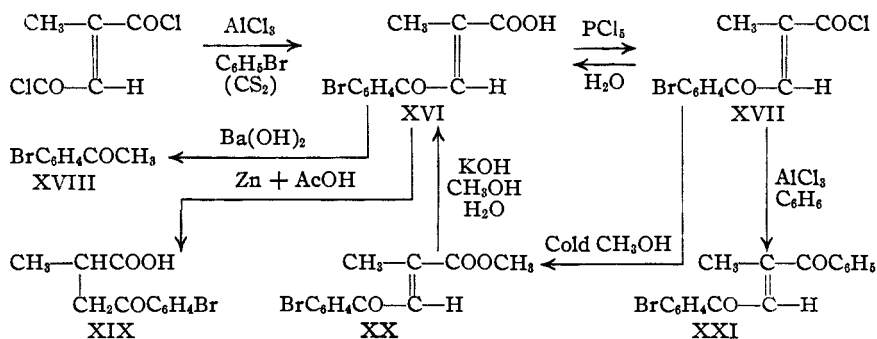
trans isomer. On the basis of these facts we have written the *cis* acid chloride as a γ -chlorocrotolactone. It is exactly analogous to *cis*- β -benzoyl-dibromoacrylyl chloride^{3a} (cf. also Ref. 4a).

The Friedel and Crafts reaction on the acid chloride gives a product in which, according to the analysis, chlorine has been replaced by bromophenyl. The product, however, is not a diketone, nor is it the expected γ,γ -di-[bromophenyl]-crotolactone, since it is an acid. We have not yet investigated its structure. It is clear, however, that the *cis* acid chloride has not reacted in a normal sense.

Trans- β -[*p*-bromobenzoyl]- α -methylacrylic Acid (XVI).—We have obtained only one of the two possible structural isomers of the β -methyl acids (VII and X) described above, namely, *trans*- β -[bromobenzoyl]- α -methylacrylic acid (XVI). This acid is yellow and is the sole crystalline product obtained in a 60% yield by the Friedel and Crafts reaction on mesaconyl chloride.^{4,5} The *trans* configuration follows from the synthesis.

Reduction yields a new acid which is isomeric with β -[bromobenzoyl]-butyric acid (VIII) and must therefore be β -[bromobenzoyl]- α -methylpropionic acid (XIX). Proof of the position of the methyl group and also that of the bromine atom was accomplished by the hydrolytic splitting of the parent *trans* acid (XVI) at the double bond to yield *p*-bromoacetophenone (XVIII).

The acid chloride, obtained by the action of phosphorus pentachloride, is a brilliant yellow solid which reacts rapidly with cold methanol to form the ester, is hydrolyzed rapidly in hot water, and reacts readily with benzene and aluminum chloride to give a mixed diketone (XXI) in good yield. It is therefore a normal acid chloride. These reactions are consistent with the *trans* formulation, and would not be expected of a *cis* isomer.



The Directing Influence of the Methyl Group.—The Friedel and Crafts reaction with citraconic anhydride proceeds in two senses structurally; it involves mainly the carbonyl adjacent to the methyl, and to a very minor

(5) When the reaction is carried out in phosphorus oxychloride and bromobenzene, however, a 10% yield of the structural isomer (VII) is the only crystalline product isolated.

extent the other carbonyl (giving, respectively, X and XVI). Citraconyl chloride reacts similarly, but since the yields are very much smaller it is of course questionable whether or not the ratio of the two products (X and XVI) is a true measure of the two different reaction tendencies.

Mesaconyl chloride, in contrast with the *cis* isomer, reacts largely in the opposite sense⁵ (to give XVI) involving the carbonyl chloride which is farthest removed from the methyl. A similar directing influence has been noted in the reaction with aromatic amines.²

Inversion from Cis to Trans during the Friedel and Crafts Reaction.—In the Friedel and Crafts reaction with bromobenzene and citraconic anhydride the methyl group on the ethylene linkage has stabilized the configuration since the principal product is a *cis* acid (X).⁶ In the minor reaction involving the carbonyl to which the methyl is beta, complete inversion results (to give XVI). The expected fourth isomer, *cis*- β -[bromobenzoyl]- α -methylacrylic acid, has not been found and possibly is too labile to exist under the reaction conditions.⁷

The governing factor in inversion during the reaction is clearly the position of the methyl group, or, as is probably more significant, the position of the mobile hydrogen atom with respect to the carbonyl group involved: in the reactions with maleic anhydride^{3b} and in the minor reactions of citraconic anhydride and chloride, where *hydrogen is alpha* to the reacting carbonyl, inversion occurs; but when *methyl is alpha* as in the main course of the reaction with citraconic anhydride and bromobenzene (and also with dimethyl maleic anhydride and benzene),⁸ no inversion occurs.

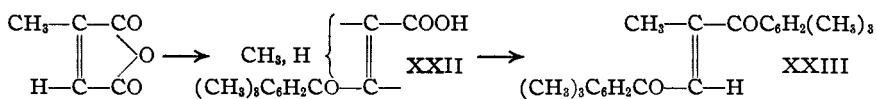
A Trans-trimethylbenzoylmethylacrylic Acid (XXII).—Mesitylene reacts with citraconic anhydride in the Friedel and Crafts reaction to give only one crystalline product in a 36% yield. This trimethylbenzoylmethylacrylic acid is brilliant yellow, a fact which indicates the *trans* configuration. Its acid chloride is unstable, but when treated cautiously in a Friedel and Crafts reaction with mesitylene, it gives a very small but significant yield of di-[2,4,6-trimethylbenzoyl]-methylethylene (XXIII), which is obtained also directly from mesaconyl chloride by the same reaction. Such a result is hardly to be expected of a *cis* acid chloride⁸ and may be regarded as evidence that the configuration is *trans*, and that inversion during the synthesis has taken place. The position of the methyl group has not been determined. It might be assigned on the basis of the observation noted above that inversion during the preparation of the bromobenzoyl analog occurs only when hydrogen is alpha to the carbonyl involved in the reaction; but on the other hand bromobenzene reacts largely in the opposite sense structurally; furthermore, in the

(6) In the analogous preparation of aroylacrylic acids from maleic anhydride, inversion is complete.^{3b}

(7) Cf. the unknown *cis*- β -benzoylacrylic acid (Ref. 3b).

(8) Lutz and Taylor, ninth paper of this series, to be published later.

analogous reaction with dimethylmaleic anhydride and mesitylene inversion has apparently occurred where no alpha hydrogen exists.⁸



β -[Bromobenzoyl]- α (?)-hydroxybutyric Acid (IV).—In the hydrolysis of β -[bromobenzoyl]-crotonic methyl ester (II), a side reaction takes place involving the addition of the elements of water, probably by a 1,4-addition followed by hydrolysis, to give β -[bromobenzoyl]- α (?)-hydroxybutyric acid (IV). The greater the percentage of water in the hydrolytic solvent, the better the yield of the expected *trans* acid, whereas in nearly absolute methanol no *trans* acid was isolated. The nature of this addition compound was shown by pyrolysis, water being eliminated to give *trans* β -bromobenzoylcrotonic acid (VII). The position of the hydroxyl group is undoubtedly alpha to the carboxyl, since addition to the more active conjugated system, favored also by the steric hindrance of the methyl group, would be expected. β -Benzoylacrylic methyl ester reacts in this sense during hydrolysis.⁹ Addition compounds of this type were not isolated in the hydrolysis of either the *cis* ester or the structurally isomeric *trans* ester, but were probably present in the oily by-products of these reactions.

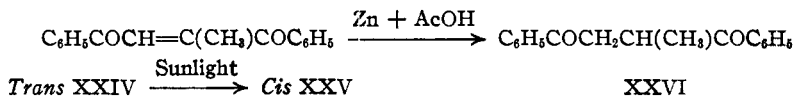
Methyl Unsaturated 1,4-Diketones.¹⁰—The *trans* methyl unsaturated 1,4-diketones were prepared from mesaconyl chloride by the Friedel and Crafts reaction. Bromobenzene, however, failed to give a diketone in an analogous experiment, mesaconyl chloride reacting only part way under a variety of conditions to give the intermediate *trans*- β -[bromobenzoyl]-methylacrylic acids. The acid chlorides of these latter substances appear to give only complex resinous products when the Friedel and Crafts reaction with bromobenzene is forced under more drastic conditions; yet benzene reacts readily enough in both cases to give the corresponding mixed diketones, III and XXI. This failure of bromobenzene to react in the second stage of the Friedel and Crafts reaction is surprising since the analogous reaction with fumaryl chloride gives the corresponding diketone in excellent yield.¹¹

The configurations of the diketones follow from the synthesis.³ *Trans* dibenzoylmethylethylene (XXIV) on exposure to the sunlight in a solvent gives the *cis* isomer in a fair yield, apparently irreversibly, together with resinous decomposition products. Both stereoisomers are reduced to the same 1,2-dibenzoylpropane (XXVI).

(9) Rice, *THIS JOURNAL*, **45**, 222 (1923).

(10) The preparation of the diketones from mesaconyl chloride was first carried out by Mr. W. W. Huang under the direction of the senior author, in the Nichols Chemical Laboratory of New York University. We have repeated and extended this work.

(11) Conant and Lutz, *THIS JOURNAL*, **47**, 881 (1925).



The *cis* isomer could not be rearranged back to the *trans* by the action of iodine and sunlight. Overlong exposure to the sunlight converts either form into intractable oils, and it is possible that the transformation *cis* to *trans* does occur, but that the *trans* isomer is the more easily resinified by the action of sunlight and is destroyed as fast as it is formed. It is obvious in any case that the *cis* isomer results from the *trans* by the absorption of light energy, and although not rearranged back is nevertheless to be regarded as potentially the labile form with the higher energy content.

The Effect of the Methyl Group on Color.—The unsubstituted *trans* aryl unsaturated 1,4-diketones and ketonic acids are all to some degree yellow, and the *cis* isomers colorless. The aryl group is undoubtedly responsible for the shift of absorption into the visible region, fumaric acid types being colorless. The color is diminished if not destroyed by ethylenic substituents such as halogen and aroyl. The methyl group in the diketone series diminished the color very markedly. Of the two *trans* β -[bromobenzoyl]-methylacrylic acids, the one in which the methyl is adjacent to the aroyl group (VII) is almost colorless, the other (XVI) is bright yellow.

Experimental Part

Citraconic and Mesaconic Acids

The conversion of citraconic to mesaconic acid¹² by the action of sunlight on a chloroform-ether solution containing bromine proceeds best in large scale runs on 700 g. of material to give yields as high as 85%.

Mesaconyl chloride was prepared according to Petri.¹³ In one large scale preparation from 650 g. of acid the fractionation at atmospheric pressure involved long heating of the bulk of the material. An end fraction of 82 g. of pure citraconyl chloride was collected and identified by its boiling point (96–97° corr. at 15 mm.), and by nearly quantitative hydrolysis to citraconic acid (no mesaconic acid being detected). Similar results were obtained when mesaconyl chloride was refluxed for three hours or was heated at 100° with 20% of its weight of aluminum chloride, but when allowed to stand in diffused light for one year, or heated for one hour at 50° (the conditions of the average Friedel and Crafts reaction) no such inversion was detected.

A sample of mesaconyl chloride was hydrolyzed completely upon standing twenty-four hours with water. In a similar experiment citraconyl chloride was not completely hydrolyzed until about five days had elapsed. We regard this abnormally slow hydrolysis in the latter case as possible evidence in favor of the cyclic formulation (XII).

Partial alcoholysis of mesaconyl chloride with one equivalent of methanol gave a mixture consisting largely of unchanged material and dimethyl ester.

Mesaconyl α -methyl acid ester (I) was prepared by the method of Anschütz,² but longer standing (fifty hours) gave a better yield (74%); b. p. 122° (corr.) under 4 mm.

Dimethyl ester,² b. p. 99.5° (corr.) at 18 mm.

(12) Fittig and Landolt, *Ann.*, **188**, 72 (1877). See also Cummings, Hopper and Wheeler, "Systematic Organic Chemistry," 1931, pp. 243, 406, 414.

(13) Petri, *Ber.*, **14**, 1635 (1881).

Aryl α,β -Unsaturated 1,4-Ketonic Acids

Trans- β -[*p*-bromobenzoyl]-crotonic Acid (VII).—The methyl ester (4 g.) was dissolved in 30 cc. of hot methanol and the mixture chilled to give a mass of fine crystals: 15 cc. of water containing 1.2 g. of potassium hydroxide was then added, and the mixture shaken (machine) until complete solution took place (about twenty minutes). The mixture was diluted with water and extracted with ether from which a small amount of unchanged ester was recovered. The aqueous solution was acidified and the product extracted into ether and isolated on subsequent evaporation as an oil. This gave a total of 1.9 g. (50%) of nearly pure crystalline *trans* acid from a benzene-ligroin mixture. The filtrate yielded the addition product (see below); crystallized as thin rectangular scales from benzene; m. p. 144.5–145° (corr.).

Anal. Calcd. for $C_{11}H_9O_3Br$: C, 49.07; H, 3.37. Found: C, 49.07; H, 3.72.

Several attempts were made to prepare the corresponding diketone from mesaconyl chloride with two equivalents of phosphorus oxychloride, bromobenzene, and aluminum chloride, heating the mixture on a steam-bath for five minutes. Small yields (5–10% in several runs) of the above acid were isolated and identified.

A small sample was reduced with zinc and acetic acid in the usual way, and a small yield of β -[bromobenzoyl]-butyric acid was isolated and identified by a mixed melting point.

β -[*p*-Bromobenzoyl]- α (?)-hydroxybutyric Acid (IV).—The benzene-ligroin mother liquor from the above preparation was evaporated to an oil which began to crystallize on standing several days. It was taken up again in benzene and ligroin, cooled and filtered to give 0.9 g. (22%) of nearly pure material; crystallized as thin hexagonal or boat-shaped scales from benzene-ligroin mixtures: m. p. 85–86° (corr.); soln. in sodium bicarbonate.

Anal. Calcd. for $C_{11}H_{11}O_4Br$: C, 45.99; H, 3.86. Found: C, 46.14; H, 4.42.

A small sample of the above acid was heated quickly to 250° in an oil-bath and allowed to cool. As the temperature reached 150° the molten product boiled and moisture condensed in the delivery tube. The orange colored oily residue was dissolved in benzene, ligroin was added, and on seeding a good yield of *trans*-bromobenzoylcrotonic acid crystallized and was identified by mixed m. p. with known material.

Trans β -[*p*-Bromobenzoyl]-crotonic Methyl Ester (II).—Ten grams of mesaconyl α -methyl acid ester was allowed to react with 16 g. of phosphorus pentachloride. The liquid mixture containing two equivalents of phosphorus oxychloride was filtered from a small amount of unchanged phosphorus pentachloride, rinsing with carbon disulfide. This solution was then added slowly to a well-stirred mixture of 20 g. of bromobenzene and 60 g. of aluminum chloride in 100 cc. of carbon disulfide. The reaction mixture was refluxed for two hours and decomposed in the usual way. The carbon disulfide solution was evaporated. The oily residue partly crystallized on standing, and was diluted with petroleum ether and filtered; yield of nearly pure product, 11.5 g. (66%); crystallized as almost colorless (yellowish tinted), long, thin rectangular scales from alcohol; m. p. 75.5° (corr.). It dissolves to give a deeply yellow solution. It gives a sharp mixed melting point depression with the isomeric α -methylacrylic ester.

Anal. Calcd. for $C_{12}H_{11}O_3Br$: C, 50.88; H, 3.92. Found: C, 51.07; H, 4.08.

Hydrolysis in dilute methanolic potassium hydroxide gave mixtures of the acid and the addition product, bromobenzoyl- α -hydroxybutyric acid. The latter was the sole product isolated when pure methanol (without added water) was used as the solvent. The yield, however, was not good.

Trans- β -[*p*-bromobenzoyl]-crotonyl Chloride (V).—Obtained as a yellow oil by the action of phosphorus pentachloride on the acid, with vacuum desiccation to remove

phosphorus oxychloride. A droplet was hydrolyzed to the acid when heated for two minutes with water. It reacted rapidly in the cold with methanol, the ester crystallizing quickly from the solution. A separate Friedel and Crafts reaction with bromobenzene was not carried out directly on this acid chloride, but β -[bromobenzoyl]-crotonic acid was isolated from typical reactions between mesaconyl chloride, bromobenzene, and aluminum chloride, in which the crotonyl chloride was undoubtedly present as an intermediate under conditions which would normally have led to the formation of the diketone.

Cis- β -[*p*-bromobenzoyl]-crotonic Acid (X).—Citraconic anhydride (50 g.) was added slowly over a period of one hour to a well stirred mixture of 134 g. of finely ground aluminum chloride in 140 g. of bromobenzene and 100 cc. of carbon disulfide, the reaction mixture being kept at 50°, subsequently heated for half an hour, and allowed to stand overnight. It was decomposed in ice and hydrochloric acid. Upon separating and evaporating the carbon disulfide layer the crude product crystallized; yield, nearly pure 57.2 g. (47%); cryst. as colorless, square or octahedral prisms, m. p. 142.5° (corr.).

Anal. Calcd. for $C_{11}H_9O_3Br$: C, 49.07; H, 3.37. Found: C, 49.35; H, 3.47.

From the oily residues of the above experiment a crystalline product was isolated, recrystallized from chloroform, and identified as *trans*- β -[bromobenzoyl]- α -methylacrylic acid; yield 2 g. (2%).

When 10 g. of citraconyl chloride was used in a Friedel and Crafts reaction under approximately the same conditions as above, a total of 2 g. (12.5%) of the above described *cis* acid (X) was isolated, together with a very small amount (0.05 g.) of the *trans*- α -methylacrylic acid (XVI). It is very unlikely that this α -methyl isomer came from mesaconyl chloride present as an impurity in the starting material. The sample of acid chloride used gave only citraconic acid on hydrolysis.

A benzene solution of the *cis* acid with aluminum chloride was heated on the steam-bath for one hour. Only unchanged material was recovered.

A suspension of 3 g. of the *cis* acid in water with 10 g. of barium hydroxide was distilled, and the steam distillate (0.5 g.) of m. p. 43–44° (corr.) was identified as *p*-bromobenzophenone by a mixed melting point with a known sample.

Cis- β -[*p*-bromobenzoyl]-crotonic Methyl Ester (XI).—The ester was prepared by allowing the acid to stand for one week in saturated methanolic hydrochloric acid. It was isolated by decomposing the mixture in iced sodium carbonate solution, extracting into ether, drying with anhydrous sodium carbonate, and distilling under reduced pressure; yield 4.1 g. (78%); colorless oil of b. p. 156–158° at 4 mm.

Anal. Calcd. for $C_{12}H_{11}O_3Br$: C, 50.88; H, 3.92. Found: C, 50.79; H, 4.15.

Hydrolysis of 1 g. by allowing it to stand for twenty-four hours in 10 cc. of 95% ethanol containing 0.1 g. of dissolved sodium, gave a yellow oil from which 0.82 g. of crude *cis* acid crystallized and was identified.

Cis- γ -[*p*-bromophenyl]- γ -chloro- β -methyl Crotolactone (Cis-(ψ) β -[*p*-bromobenzoyl]-crotonyl Chloride) (XIV).—The acid (2 g.) was allowed to react with 1.56 g. of phosphorus pentachloride, the mixture being warmed gently to start the reaction. The acid chloride crystallized from the phosphorus oxychloride solution and was filtered; yield 1.96 g. (91%); colorless; crystallized from benzene; m. p. 82.5° (corr.).

Anal. Calcd. for $C_{11}H_9O_2BrCl$: C, 45.92; H, 2.81. Found: C, 45.89; H, 2.91.

A small sample required one week, standing in contact with water to undergo complete hydrolysis. The reaction was quantitative. The acid chloride dissolves in hot alcohol and crystallizes on cooling unchanged.

The Friedel and Crafts reaction in a number of experiments under a variety of conditions gave only one product. In a typical experiment on 1.4 g. of the acid chloride, 1.38 g. (69%) of a colorless solid was isolated; crystallized from bromobenzene; m. p.

208° (corr.). It is soluble in cold dilute sodium carbonate with effervescence, and is precipitated crystalline by acids and by an excess of sodium ion.

Anal. Calcd. for $C_{17}H_{12}O_2Br_2$: C, 50.01; H, 2.96; Br, 39.18. Found: C, 50.06; H, 3.00; Br, 39.39, 39.54.

β -[*p*-Bromobenzoyl]-butyric Acid (VIII).—The above *cis* acid (2 g.) was reduced with zinc and boiling acetic acid in the usual way; yield 1.35 g. of pure product; crystallized from chloroform and petroleum ether; m. p. 95.5° (corr.).

Anal. Calcd. for $C_{11}H_{11}O_2Br$: C, 48.71; H, 4.09. Found: C, 48.39; H, 4.18.

Trans- β -[*p*-bromobenzoyl]- α -methylacrylic Acid (XVI).—Mesaconyl chloride (25 g.) was added slowly to a well-stirred mixture of 70 g. of bromobenzene and 45 g. of aluminum chloride, heated on a steam-bath. Upon decomposing in ice and concentrating the carbon disulfide layer, 25 g. of crude product (60%) was isolated;¹⁴ crystallized as yellow needles from chloroform or benzene; m. p. 188° (corr.).

Anal. Calcd. for $C_{11}H_9O_2Br$: C, 49.07; H, 3.37. Found: C, 49.03, 49.16; H, 3.45, 3.47.

Steam distillation of a suspension of the acid in water with barium hydroxide gave *p*-bromopropiophenone which was identified by a mixed melting point with a known sample prepared from propionyl chloride and bromobenzene, and by the characteristic melting point of its oxime.

Trans- β -[*p*-bromobenzoyl]- α -methylacrylic Methyl Ester (XX).—Prepared by the interaction of the acid chloride and methanol; crystallized from ethanol as long, thin, square-ended needles of a very pale yellowish color; m. p. 86° (corr.). A mixed melting point with the stereoisomer showed a sharp depression.

Anal. Calcd. for $C_{12}H_{11}O_2Br$: C, 50.88; H, 3.92. Found: C, 51.18; H, 4.05.

Hydrolysis of 0.11 g. of the ester with potassium hydroxide in 80% methanol gave 0.03 g. of pure acid. This is to be regarded as a fair yield since difficulty in handling the sample resulted in some losses.

Trans- β -[*p*-bromobenzoyl]- α -methylacrylyl Chloride (XVII).—The acid (3 g.) reacted with 3 g. of phosphorus pentachloride to give an oil which crystallized. On diluting with petroleum ether, cooling and filtering, 2.2 g. was isolated; crystallized from ligroin as brilliant yellow, thin, diamond-shaped plates of m. p. 66° (corr.), turning bright red at 100 to 150°. On standing for two days the solid was transformed into a brown resinous mass with the evolution of considerable hydrogen chloride.

Anal. Calcd. for $C_{11}H_9O_2ClBr$: C, 45.92; H, 2.81. Found: C, 45.77; H, 2.99.

A small sample was hydrolyzed completely when heated for ten minutes with water in a steam-bath. It dissolved quickly in cold methanol, and almost immediately the ester crystallized and was filtered off and identified by a mixed melting point. In a typical Friedel and Crafts reaction in bromobenzene at 70–80° the *trans* acid was recovered, but no other crystalline product was found.

β -[*p*-Bromobenzoyl]- α -methylpropionic Acid (XIX).—The *trans* acid (1 g.) was reduced by zinc and acetic acid in the usual way, and gave 0.8 g. (80%) of nearly pure product; crystallized from benzene; m. p. 124° (corr.); colorless.

Anal. Calcd. for $C_{11}H_{11}O_2Br$: C, 48.71; H, 4.09. Found: C, 49.09; H, 4.08.

Trans- β -[2,4,6-trimethylbenzoyl]-methylacrylic Acid (XXII).—Prepared by a typical Friedel and Crafts reaction on citraconic anhydride with mesitylene in carbon disulfide, but with short heating (ten minutes) to minimize resinification. The product was isolated by steam distillation to remove mesitylene and carbon disulfide, and crys-

(14) From the mother liquors a small amount of a colorless solid (not an acid) of m. p. 140.5° (corr.) was isolated. It crystallizes from benzene and has not yet been identified.

tallizing the oily residue from benzene-petroleum ether mixtures. From 10 g. of anhydride, a total of 7.4 g. (36%) of crude product was obtained, the rest of the material going into intractable oils; bright yellow crystals from benzene; m. p. 142° (corr.).

Anal. Calcd. for $C_{14}H_{16}O_3$: C, 72.37; H, 6.95. Found: C, 72.53; H, 6.87.

The acid gave an unstable oily acid chloride which decomposed when purification was attempted. On standing with water it was hydrolyzed back to the *trans* acid. The Friedel and Crafts reaction under ordinary conditions gave only resinous products, but when the reaction was controlled and allowed to run for only one minute a small yield of crystals (0.075 g. from 0.5 g. of the acid) was isolated and identified by a mixed melting point as trimethylbenzoylmethylethylene. The large amounts of oily by-products interfere seriously with the isolation of the product.

Trans- β -[2,4,6-trimethylbenzoyl]-methylacrylic Methyl Ester.—Prepared by the action of saturated methanolic hydrogen chloride on the acid (standing for one week), and isolated in the usual way; yield 4.5 g. from 5 g. of acid (85%); yellow oil; b. p. 144.5° (corr.) at 5 mm.

Anal. Calcd. for $C_{15}H_{18}O_3$: C, 73.13; H, 7.37. Found: C, 72.82; H, 7.42.

The Diaroyl Methylethylenes¹⁰

Trans-1,2-dibenzoylpropene-1 (Dibenzoylmethylethylene) (XXIV).—Mesaconyl chloride (25 g.) was added dropwise to a well-stirred mixture of aluminum chloride in 45 g. of benzene and 50 cc. of carbon disulfide over a period of twenty minutes. The red reaction mixture was then stirred at room temperature for two hours, heated for ten minutes, and decomposed in ice and hydrochloric acid. The carbon disulfide solution was dried over sodium sulfate and upon concentrating and cooling gave 27 g. of crude crystalline diketone (72%); crystallized from benzene or alcohol; very pale yellow; m. p. 52° (corr.).

Anal. Calcd. for $C_{17}H_{14}O_2$: C, 81.56; H, 5.64. Found: C, 81.27; H, 5.70.

The diketone reacts with bromine under a variety of conditions but gives largely oils, with the evolution of hydrogen bromide and the formation of lachrymatory by-products. Bromination in chloroform at boiling temperature, however, gave a product which crystallized from chloroform and petroleum ether; m. p. 130° (corr.).

Cis-1,2-dibenzoylpropene-1 (Dibenzoylmethylethylene) (XXV).—The *trans* isomer (5 g.) in 25 cc. of alcohol was exposed to direct sunlight for four days. The solution upon concentrating and cooling gave 3 g. of colorless crystals of the *cis* isomer (yield 60%). Resinous by-products remained in solution; colorless needles; cryst. from alcohol; m. p. 68.5° (corr.).

Anal. Calcd. for $C_{17}H_{14}O_2$: C, 81.56; H, 5.64. Found: C, 81.54; H, 5.58.

Solutions of the *cis* isomer in alcohol, chloroform and benzene, containing a trace of iodine, were exposed to direct sunlight for lengths of time varying between five hours and two days. Only unchanged material and resinous by-products were isolated.

One gram of the *cis* isomer was reduced with zinc and acetic acid to give 0.9 g. (89%) of 1,2-dibenzoylpropane.

1,2-Dibenzoylpropane (XXVI).—*Trans*-dibenzoylmethylethylene (5 g.) in 150 cc. of hot acetic acid was treated with 20 g. of zinc dust and the mixture boiled for fifteen minutes. Upon filtering, cooling and diluting with water, an oily product separated which soon crystallized; yield of crude product, 4.1 g. (81%); crystallized from alcohol; colorless; m. p. 105° (corr.).

Anal. Calcd. for $C_{17}H_{16}O_2$: C, 80.91; H, 6.40. Found: C, 80.76; H, 6.32.

Trans-1,2-di-[2,4,6-trimethylbenzoyl]-propene-1 $(CH_3)_3C_6H_3COC(CH_3)=CHCO-C_6H_3(CH_3)_3$.—Mesaconyl chloride (50 g.) was added to a well-stirred mixture of 80 g.

of aluminum chloride in 75 g. of mesitylene and 200 cc. of carbon disulfide, and the red reaction mixture heated for fifteen minutes. The nearly pure diketone was isolated in the usual way; yield 68 g. (68%); crystallized from alcohol; yellow; m. p. 96° (corr.).

Anal. Calcd. for $C_{22}H_{20}O_2$: C, 82.58; H, 7.84. Found: C, 82.27; H, 7.96.

A number of attempts under a variety of conditions to prepare the *cis* isomer from the *trans* by exposure of the latter to sunlight failed, either unchanged material or intractable oils being obtained. Reduction under a variety of conditions failed to give a crystalline product.

Bromination under a variety of conditions gave largely non-crystalline products, and hydrogen bromide was liberated. Bromination at 0° in chloroform gave a mixture of products from which two substances were isolated. Analysis indicated one of these (m. p. 176°) to be a *dibromide*, and the other (m. p. 134°) a *monobromoethylene*.

Trans-1-benzoyl-2-bromobenzoylpropene-1 (III).—*Trans*-bromobenzoylcrotonyl chloride from 0.5 g. of the acid and 0.5 g. of phosphorus pentachloride was treated directly (without separating from phosphorus oxychloride) with 3 cc. of benzene and 3 g. of aluminum chloride. A deep red solution formed. After standing for four minutes the mixture was decomposed in ice and the benzene layer separated, extracted with sodium carbonate, dried and evaporated to yield an oil which crystallized from alcohol; yield 0.35 g. (59%); crystallized from ethanol as pale yellow, thin, elongated, rectangular leaflets; m. p. 73–74° (corr.). It is yellow in solution.

Anal. Calcd. for $C_{17}H_{13}O_2Br$: C, 62.00; H, 3.97. Found: C, 62.30, 62.27; H, 4.13, 4.07.

Trans-1-bromobenzoyl-2-benzoylpropene-1 (XXI).—Prepared in exactly the same way as the above isomer; yield 0.85 g. (72%) from 1 g. of the acid; crystallized from ethanol as pale cream-tinted, almost colorless, thin, diamond-shaped leaflets; m. p. 56° (corr.).

Anal. Calcd. for $C_{17}H_{13}O_2Br$: C, 62.00; H, 3.97. Found: C, 62.20; H, 3.95.

Summary

Cis and *trans* β -bromobenzoylcrotonic acids and *trans*- β -[bromobenzoyl]- α -methylacrylic acid, and a number of derivatives, have been prepared and their structures and configurations elucidated. The effect of the substituted methyl group in the various reactions concerned is discussed.

The synthesis of methyl unsaturated 1,4-diketones is described.

UNIVERSITY, VIRGINIA

RECEIVED SEPTEMBER 8, 1932

PUBLISHED MARCH 7, 1933