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THE SYNTHESIS AND CONFIGURATIONS OF UNSATURATED 1,4-DIKETONES AND KETONIC ACIDS, AND THE STEREOCHEMICAL MECHANISM OF THE ADDITION OF BROMINE. STUDIES ON UNSATURATED 1,4-DIKETONES. VI

BY ROBERT E. LUTZ

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Aryl substituted benzoylacrylic acids are readily prepared from maleic anhydride,[1] and dibenzoylethylenes from fumaryl chloride,[2] by the Friedel and Crafts reaction. The products thus obtained are yellow in color, are the stable forms as regards stereochemical rearrangements and undoubtedly possess the *trans* configuration.[1,2,3] The *cis* forms of many unsaturated 1,4-diketones are prepared by the action of sunlight on the *trans* isomers,[2,3] but the corresponding labile (*cis*) isomers of unsaturated 1,4-ketonic acids are known only in the form of their esters.[4] The present investigation was undertaken to add to the available information concerning these compounds, particularly as regards configurations and stereochemistry.

The configurations which were originally assigned to the unsaturated 1,4-diketones seem to be clearly established by the work which has been outlined in earlier papers.[2,3,5] The conclusions are based on two considerations: the relative ease with which the *cis* form reacts with hydrazine to give diphenylpyridazine,[3] and the close analogy between the stability (or rather energy) relationship of these *cis–trans* isomeric pairs[2,3] and that of maleic and fumaric acids.[6] In the preceding paper of this series[7] the validity of evidence based on energy relationship has been confirmed by the determination of the configuration of the analogously related *cis* and *trans* dibenzoyldibromo-ethylenes through the synthesis of the stable *trans* form from dibromofumaryl and *trans* benzoyldibromo-acrylyl chlorides by the Friedel and Crafts reaction, under conditions which preclude the possibility of rearrangements.

The configurations of the unsaturated 1,4-ketonic acids on the other hand are based on very meager evidence. The failure to form naphthoquinones

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[1] H. v. Pechmann, *Ber.*, **15**, 881 (1882), etc. See also Refs. 3 and 4, of the preceding paper.

[2] Conant and Lutz, THIS JOURNAL, **45**, 1303 (1923).

[3] Paal and Schulze, *Ber.*, **35**, 168 (1902).

[4] Rice, THIS JOURNAL, **45**, 222 (1923); see also *ibid.*, **45**, 232 (1923); **48**, 269 (1926); **50**, 229 (1928).

[5] Lutz, *ibid.*, **49**, 1106 (1927).

[6] Stoermer, *Ber.*, **42**, 4870 (1909); etc. (The labile (*cis*) isomer has the greater energy content, is formed by the absorption of light energy and rearranges under the influence of catalysts.)

[7] Lutz, THIS JOURNAL, **52**, 3405 (1930).

on dehydration has no bearing on the configuration because of the ease of formation of unsaturated lactones known as "Pechmann dyes"[1] in which the *cis-trans* asymmetry of the double bond is destroyed.[8] The acids, however, do appear to have the *trans* configuration,[1,4,8] and correspond to the yellow stable esters as has been shown by Mrs. Rice,[4] who esterified the silver salt of β-benzoylacrylic acid by means of methyl iodide under conditions which minimize the possibility of rearrangements. During hydrolysis of the isomeric esters, however, rearrangement occurs, since both esters give the same yellow and presumably *trans* acid. On the basis of the energy relationship of the two esters,[4] as compared with that of maleic and fumaric acids,[6] it is highly probable that the stable yellow isomeric esters and the corresponding acids have the *trans* configuration. The hypothetical labile (*cis*) acid must be extremely unstable, since, if it is formed in any reaction (as happens, presumably, in the Friedel and Crafts synthesis from maleic anhydride), it rearranges completely under the experimental conditions. The validity of this reasoning by analogy is now supported by the fact that the chemical reactions of the acid chloride of benzoylacrylic acid are entirely consistent with the conclusions drawn, as will be shown in the discussion to follow.

β-Benzoylacrylic methyl ester (V) has now been prepared from fumaric acid by partial alcoholysis of the acid chloride to the monomethyl ester monochloride (II) followed by a typical Friedel and Crafts reaction (see Diagram 1). Since benzoylacrylic methyl ester has been hydrolyzed to the acid (III),[4] this constitutes another synthesis of the acid from fumaric acid. Since the acid is thus obtainable from both maleic and fumaric acids, a rearrangement occurs in one case, and this undoubtedly in the synthesis from the labile maleic acid as soon as the stabilizing influence of the ring structure of the anhydride disappears in the course of reaction. It would seem highly improbable that the energy relationship would be reversed in going from fumaric acid to benzoylacrylic acid and the configurations must, therefore, correspond in the two cases. The independent evidence necessary to establish this point becomes available through a study of the acid chloride of benzoylacrylic acid.

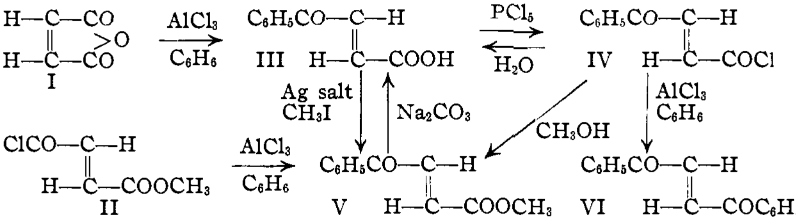

DIAGRAM 1

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[8] (a) Bogert and Ritter, THIS JOURNAL, **46**, 2871 (1924); (b) **47**, 526 (1925).

The synthesis of benzoylacrylic acid and its structural relationship to fumaric and maleic acids and the unsaturated 1,4-diketones are outlined in the above diagram. Fumaryl chloride reacts with one equivalent of methyl alcohol to give the monomethyl ester monochloride[9] (II), which may be separated by fractional distillation from unchanged dichloride and from the dimethyl ester which is formed in small amounts. Its structure is shown by its ready reaction with an excess of methyl alcohol to give dimethyl fumarate, and hydrolysis[9] to fumaric monomethyl ester.[10]

β-Benzoylacrylic acid, when treated with one equivalent of phosphorus pentachloride, reacts vigorously to give an oily acid chloride which is very unstable. When heated, or allowed to stand overnight, it decomposes with resinification and the evolution of hydrogen chloride. It could not be distilled or crystallized and, although not obtained in an analytically pure condition, it was isolated sufficiently pure for study by extracting the by-product phosphorus oxychloride with petroleum ether, in which the acid chloride is only slightly soluble.

The structure of β-benzoylacrylyl chloride (IV) and its configurational relationship to the acid and the ester are established by the following facts. The acid chloride is easily hydrolyzed to the original acid when shaken for a short time with water and reacts rapidly with methyl alcohol to give the yellow (stable) methyl ester (V). It is highly improbable that any reversal of configuration could occur in these transformations, and the configuration of the acid, acid chloride and stable (yellow) methyl ester must correspond. Furthermore, the acid chloride reacts readily with aluminum chloride and benzene to give a fair yield of *trans* dibenzoylethylene (VI). By these reactions it is shown that β-benzoylacrylyl chloride reacts in every way as does a typical normal and active acid chloride. *Cis* and *trans* β-benzoyldibromo-acrylyl chlorides have already been prepared;[7] the *cis* isomer fails to undergo hydrolysis and alcoholysis readily, and with aluminum chloride and benzene reacts exclusively in the pseudo or lactone form, whereas the *trans* acid chloride behaves in every way normally in these reactions. Inasmuch as β-benzoylacrylyl chloride is of the latter (normal) type, the functional groups must, therefore, lie in a *trans* relationship.

It is possible, though highly improbable, that benzoylacrylyl chloride, if it were *cis*, would rearrange in the course of the Friedel and Crafts reaction to give a product derived from the *trans* configuration, as undoubtedly happens in the preparation of benzoylacrylic acid from maleic anhydride. These two cases are not parallel since in the latter reaction the primary product should be the unstable *cis* ketonic acid, whereas in the former case, the acid chloride (if *cis*) should react in the pseudo form to give an unsymmetrical crotolactone as the product. The acid chlorides of succinic[10]

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[9] Anschütz and Baeumges, *Ann.*, **461**, 188 (1928).

[10] Sudborough and Roberts, *J. Chem. Soc.*, **87**, 1843 (1905).

and dichlorosuccinic[5] acids react tautomerically to give products derived from both the normal and the pseudo dichlorides, but when the functional groups are in actual *cis* relationship the pseudo or lactone form seems to react exclusively, as happens with phthalyl chloride,[11] *o*-benzoylbenzoic anhydrides,[12] and *cis* β-benzoyldibromo-acrylyl chloride.[7] Maleil chloride has been studied in this connection in a typical Friedel and Crafts reaction, and fails to yield significant amounts of the products to be expected from an acid chloride of normal structure. It seems clear, then, that if the configuration of benzoylacrylic acid were *cis*, its acid chloride would certainly react in the pseudo or lactone ring form and would not yield significant amounts of dibenzoylethylene in the Friedel and Crafts reaction.

As a consequence of the above considerations it follows that the configurations of the acid and esters as discussed above are confirmed. The stable yellow ester has been obtained from the acid by esterification of the silver salt[4] and is now prepared from the acid chloride by the action of methyl alcohol, and in neither case is rearrangement at all likely. Since the acid is now shown to be *trans*, it follows that the stable yellow ester is *trans*, that the labile colorless isomer is *cis*, and that the relation between stability (or energy content) and configuration corresponds to that for maleic and fumaric acids and the stereoisomeric unsaturated 1,4-diketones.

The synthesis of *trans* dibenzoylethylene from fumaryl chloride[2] and now from benzoylacrylyl chloride has been repeated under mild conditions and no trace of the labile isomer was isolated from the products. Undoubtedly, as has been shown independently, the configurations of the products correspond to that of the starting material, but this is not proved by the synthesis because the labile isomer (unlike *cis* dibenzoyldibromo-ethylene[7]) is unstable under the conditions of the Friedel and Crafts reaction and would be largely or completely rearranged if it were formed during the reaction. *Cis* dibenzoylethylene in benzene is partially isomerized when heated for a short time with aluminum chloride, with which it combines to form a dark red complex compound; however, when it is present during actual reaction between fumaryl chloride, benzene and aluminum chloride, it is practically completely isomerized, and only traces can be recovered. The rearrangement, then, would appear to be facilitated by the evolution of hydrogen chloride during the reaction; but the mechanism does not involve the formation of an intermediate hydrogen chloride addition compound followed by elimination of hydrogen chloride under the influence of aluminum chloride, because this addition compound is known, reacts to give a typical red halochromic salt when heated with aluminum chloride and benzene, and yet is recovered unchanged on subsequent hydrolysis.

The configurations of new derivatives synthesized from *trans* starting

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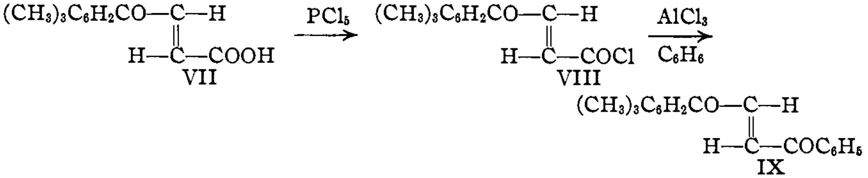
[11] Baeyer, *Ann.*, **202,** 50 (1880).

[12] H. v. Pechmann, *Ber.*, **14,** 1865 (1881).

materials by the Friedel and Crafts reaction, to be sure, may now be assigned with considerable certainty, but in view of the foregoing discussion it is obvious that proof of configuration in these cases really rests on analogy with products the configurations of which have been determined independently. If the proof of configurations of the various compounds discussed in this and in the preceding paper is accepted, it is noteworthy that without exception the labile stereoisomers of the many and various unsaturated 1,4-dicarbonyl compounds in which the double bond is unsubstituted or is symmetrically disubstituted have the *cis* configuration. Therefore, one may now safely assign by analogy the configurations of all new derivatives of these types on the basis of synthesis from known stable *trans* compounds or on the basis of lability relationship as compared with that of maleic and fumaric acids. Undoubtedly these considerations apply also to simple unsymmetrically substituted products where hydrogen of the double bond is replaced by groups similar in character to halogen or methyl (*i. e.*, derivatives of citraconic and mesaconic acids, etc.). Experiments are being carried out to test this hypothesis further.

Mesitoylacrylic acid (VII)[13] was found to give a typical acid chloride (VIII) which reacted further with mesitylene and aluminum chloride to give small but significant yields of *trans* dimesitoylethylene. In a limited way it now becomes possible to prepare simple unsymmetrical unsaturated 1,4-diketones. Mesitoylacrylyl chloride (VIII) reacts readily with aluminum chloride and benzene to give benzoylmesitoylethylene (IX, Diagram 2); however, when benzoylacrylyl chloride is used in a similar synthesis with mesitylene and aluminum chloride, only non-crystalline products are obtained. Curiously enough the melting point of the new unsymmetrical product (61.5°) is considerably lower than that of either of the two related symmetrical products, dibenzoylethylene (m. p. 111°) and dimesitoylethylene (m. p. 174°). This phenomenon was noted also in the case of the similarly substituted dibromo derivatives,[7] and it would appear that the remarkably lowered melting point is concerned with the unsymmetrical character of the molecule.



$$\begin{array}{c}(CH_3)_3C_6H_2CO{-}C{-}H\\ \|\\ H{-}C{-}COOH\end{array} \xrightarrow{PCl_5} \begin{array}{c}(CH_3)_3C_6H_2CO{-}C{-}H\\ \|\\ H{-}C{-}COCl\end{array} \xrightarrow[C_6H_6]{AlCl_3} \begin{array}{c}(CH_3)_3C_6H_2CO{-}C{-}H\\ \|\\ H{-}C{-}COC_6H_5\end{array}$$

VII VIII IX

Diagram 2

The Stereochemical Mode of Addition of Bromine and the Configuration of the Dibromides.—In an earlier paper the stereochemical mecha-

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[13] Kozniewski and Marchlewski, *Bull. Acad. Sci. Cracow*, 81 (1906).

nism of addition of halogen under controlled conditions to dibenzoylethylene[5] was shown to be *trans*, and an important part of the evidence involved the determination of the configurations of the dihalides (XII and XVI) by relating them to the dibromosuccinic acids, the configurations of which are known.[14] In carrying this work further it has been possible to prepare these two dibromides from the two known stereoisomeric normal (X)[15] and iso (XIV)[8b] β-benzoyldibromopropionic acids. The iso acid is the sole product of the Friedel and Crafts reaction on *dl*-dibromosuccinic anhydride (XIII), and must correspond with it in configuration since there is no reason to suppose that any rearrangement related to the Walden inversion is possible when none of the groups attached to the asymmetric carbon atoms have been replaced in the reaction. The normal benzoyldibromopropionic acid is obtained as the main product of the addition of bromine to benzoylacrylic acid, and since it is the stereoisomeric racemic compound, it must have the opposite configuration (X) corresponding, therefore, to meso dibromosuccinic acid (from which, however, it has not been directly synthesized, although experiments are under way with this in view). The relationships are outlined in Diagram 3.

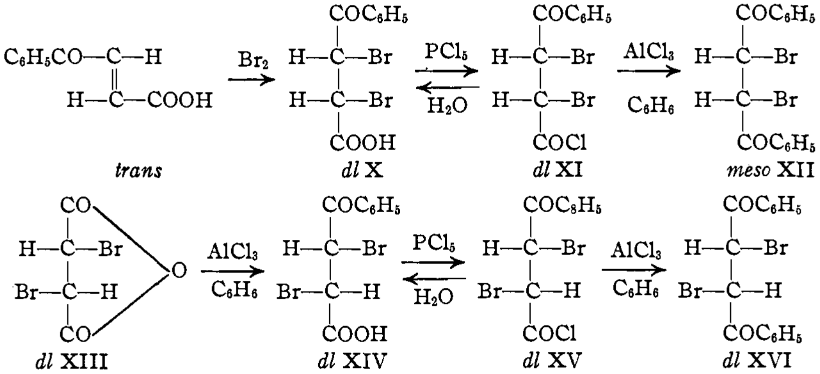

DIAGRAM 3

The two stereoisomeric benzoyldibromopropionic acids (X and XIV) react with phosphorus pentachloride to give oily acid chlorides (XI and XV) which are readily hydrolyzed back to the corresponding acids without change of configuration. These acid chlorides were not isolated in an analytically pure state, as they did not crystallize and decomposed when distilled under diminished pressure. Both acid chlorides reacted with aluminum chloride and benzene to give in each case exclusively a different dibenzoyldibromo-ethane, the chloride of the normal acid (XI) giving a good yield of the meso product (XII), and the iso acid chloride (XV) a

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[14] (a) McKenzie, *J. Chem. Soc.*, **101**, 1196 (1912); (b) Holmberg, *Svensk. Farm. Tid.*, **24**, 105 (1912).

[15] Ref. 1 and also Bougault, *Ann. chim. phys.*, [8] **15**, 491 (1908).

rather low yield of the *dl*-isomer (XVI). In each case no trace of the compound of opposite configuration was isolated. The two possible products crystallize well and are easily separated. If both had been formed in a reaction in significant amounts they would have been detected. It seems clear, therefore, that in each series of compounds there is a correspondence of configuration, as is indicated in Diagram 3.

The mechanism of the addition of bromine to unsaturated 1,4-ketonic acids may be deduced from these relationships because the configurations of both starting material and addition products are now reasonably well established. Benzoylacrylic acid has been shown to add bromine to give mainly the normal dibromide (X), which has a melting point nearly identical with that of the isomeric iso benzoyldibromopropionic acid (XIV), which is obtained from *dl*-dibromosuccinic anhydride. Since the bulk of the product is the normal dibromide and since this dibromide corresponds in configuration to meso dibenzoyldibromo-ethane, then the stereochemical mode of addition of bromine would appear to be *trans*. However, in view of the fact t hat mixtures of isomeric dibromides are invariably obtained (contrary to Bogert and Ritter[8b]), and since the iso dibromide is obtained under some conditions in very considerable yield (see experimental part and also the recent work of Mrs. Rice[16]), no conclusion can be drawn as yet. *Cis* and *trans* dibenzoylethylenes undergo *trans* addition of bromine only under certain controlled conditions,[5] and ordinarily give mixtures of stereoisomeric dibromides, as is the case with benzoylacrylic acid. The results of this paper, through the determination of configurations of the substances concerned, open the way to further profitable study, and experiments are in progress on the acid and on the esters where both *cis* and *trans* isomers are available, in order to gain further information on the mechanism of addition under conditions which will permit consistent stereochemical orientation during reaction.

Stereochemical Mode of Addition of Halogen to Dibenzoylacetylene.—In an earlier research[17] halogens were found to add to dibenzoylacetylene to give in each case largely the labile stereoisomeric dihalide. It was pointed out that if these labile isomers were *cis*, then the stereochemical mechanism of the addition to dibenzoylacetylene is *cis*. The configurations hypothesized have now been shown to be correct[7] by the synthesis of *trans* dibenzoyldibromo-ethylene from *trans* benzoyldibromo-acrylic acid and from dibromofumaric acid. As a consequence the *cis* mechanism of addition is definitely substantiated. It would seem, then, that the normal mode of addition of halogen to the acetylene linkage, *when conditions are such as to permit molecular orientation during reaction*, is *cis*, and opposite in a stereochemical sense to the normal (*trans*) mode of addition of halogen

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[16] Rice, THIS JOURNAL, **52**, 2098 (1930).

[17] Conant and Lutz, *ibid.*, **47**, 881 (1925).

to the ethylene double bond. Problems in this field are being actively investigated in this Laboratory.

Experimental Part

Fumaryl Chloride.—Boiling point 59° under 16 mm. pressure (Anschütz and Wirtz[18] found 60° at 14 mm.).

Fumaric Monomethyl Ester Monochloride.—The method of Anschütz and Baeumges[9] was modified. A slight excess of one equivalent of methyl alcohol (13 g.) in 200 cc. of benzene was added slowly to 60 g. of well-stirred fumaryl chloride, and the mixture was allowed to stand for five hours. During the addition of methyl alcohol heat and hydrogen chloride were evolved. The bulk of the product distilled at 76° under 22 mm. pressure; crude yield, 30 g. The residue in the flask solidified and was identified as dimethyl fumarate. The crude product was fractionally distilled under diminished pressure using a 10-inch Vigreaux column. A small amount of fumaryl chloride distilled first. The bulk of the material was collected in a series of fractions which solidified on cooling in ice, and which melted at points ranging from 13 to 16°. The two fractions melting sharply at 16° were chosen for analysis.

They gave colorless needles; melting point 16° (corr.); boiling point 69.5° (corr.) at 14 mm. pressure; insoluble in cold petroleum ether.

Anal. Calcd. for $C_5H_5O_3Cl$: Cl, 23.87. Found: 23.62.

Fumaric Acid Monomethyl Ester.—Fumaric monomethyl ester monochloride was shaken with water. The emulsion which formed quickly crystallized to give a nearly quantitative yield of fumaric acid monomethyl ester[9,18] which was recrystallized from benzene and obtained as feathery white crystals melting at 144.5° (corr.) and was identified by analysis.

Anal. Calcd. for $C_5H_6O_4$: C, 46.92; H, 4.62. Found: C, 47.04; H, 4.20.

Trans **β-Benzoylacrylic Acid Methyl Ester (V).**—The ester was prepared by the Friedel and Crafts reaction with aluminum chloride and benzene on pure fumaric monomethyl ester monochloride, or directly on the crude mixture obtained by the action of one equivalent of methyl alcohol on fumaryl chloride.

In a typical experiment 1.5 g. of fumaric monomethyl ester monochloride in 5 cc. of benzene was treated with 3 g. of aluminum chloride.[19] The mixture was heated on a water-bath for ten minutes and was then decomposed in ice and hydrochloric acid. The benzene layer was distilled under diminished pressure and gave 1.5 g. of nearly pure benzoylacrylic acid methyl ester melting at 29° and boiling at 168° under 17 mm. pressure.

In another experiment a benzene solution of 5.5 g. of methyl alcohol was added slowly over a period of one hour to 25 g. of fumaryl chloride. After standing for four hours the mixture was refluxed for three minutes. It was then treated directly with 75 g. of aluminum chloride added in small portions with vigorous mechanical stirring. After the addition of the first third of the aluminum chloride the mixture turned brown. Heat and hydrogen chloride were evolved up to the addition of the last portion of aluminum chloride. The mixture was then decomposed in the usual way, and the benzene layer was distilled under diminished pressure. Some dimethyl fumarate was obtained in the first fraction; then 20.5 g. of benzoylacrylic methyl ester melting at 28–29° distilled; yield, 67%. A red tarry residue remained. When, in another experiment,

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[18] Anschütz and Wirtz, *Ber.*, **18**, 1947 (1885).

[19] In this and in similar experiments a high grade of finely ground anhydrous aluminum chloride was used.

the benzene solution was evaporated and diluted with petroleum ether, a small yield of *trans* dibenzoylethylene was obtained. The benzoylacrylic methyl ester was identified by a mixed melting point with known material, by conversion into the *cis* isomer in the sunlight,[4] and by its reaction with semicarbazide.[4]

Trans **β-2,4,6-Trimethylbenzoylacrylic Acid Methyl Ester,** $(CH_3)_3C_6H_2COCH=CHCOOCH_3$.—A solution of fumaric monomethyl ester monochloride, prepared by the action of 6.5 g. of methyl alcohol in 75 cc. of carbon disulfide and 24 g. of mesitylene on 30 g. of fumaryl chloride, was treated directly with 90 g. of aluminum chloride, added in small portions with efficient stirring. The red pasty mass was heated for ten minutes and decomposed in ice and hydrochloric acid. The carbon disulfide layer was diluted with ligroin, cooled and seeded. There was deposited 2 g. of nearly pure *trans* dimesitoylethylene. The filtrate was distilled under diminished pressure. The first fraction consisted of mesitylene, dimethyl fumarate and a small amount of unchanged fumaric monomethyl ester monochloride; 8 g. of yellow oil then distilled at 152–160° under 18 mm. pressure, and solidified on cooling; yield, 18%; pale yellow, rectangular, truncated tablets; melting point 53° (corr.) after repeated crystallization from petroleum ether; soluble in alcohol, ether, benzene, acetone, ethyl acetate, acetic acid and chloroform.

Anal. Calcd. for $C_{14}H_{16}O_3$: C, 72.40; H, 6.94. Found: C, 72.22; H, 6.93.

β-2,4,6-Trimethylbenzoylchloropropionic Methyl Ester, $(CH_3)_3C_6H_2COCH_2CHClCOOCH_3$.—A solution of 2 g. of *trans* β-mesitoylacrylic acid in methyl alcohol was saturated with dry hydrogen chloride, and allowed to stand overnight. On decomposing in ice and sodium carbonate an oil was obtained which quickly crystallized; yield, 2 g. The position of the chlorine atom was not determined.

It forms colorless crystals; melting point 78° (corr.) after repeated crystallization from ligroin.

Anal. Calcd. for $C_{14}H_{17}O_3Cl$: C, 62.56; H, 6.38; Cl, 13.20. Found: C, 62.29; H, 6.38; Cl, 12.72.

Trans **β-Benzoylacrylyl Chloride (IV),** $C_6H_5COCH=CHCOCl$.—Benzoylacrylic acid, when treated with one equivalent of phosphorus pentachloride, reacts vigorously with the evolution of heat and hydrogen chloride. The product is a yellow oil. If the temperature of the reaction is not moderated the product is dark in color. If the reaction is carried out in solvents, the hydrogen chloride evolved adds to unchanged benzoylacrylic acid to form benzoylchloropropionic acid. This happens also when thionyl chloride is used. The reaction proceeds smoothly on a small scale when the acid and phosphorus pentachloride are mixed with thorough cooling in an ice-bath. When the crude mixture is shaken with water, the phosphorus oxychloride is quickly removed and the acid chloride separates as an oil which may be drawn off. On standing with water it soon hydrolyzes to benzoylacrylic acid hydrate, which was identified in a typical experiment. The crude acid chloride may be separated from the phosphorus oxychloride by extracting the latter with several portions of petroleum ether, but the yield of oily acid chloride is small because it is somewhat soluble in the petroleum ether–phosphorus oxychloride layer.

Benzoylacrylyl chloride is a pale yellow oil. If it is allowed to stand overnight, or is warmed, it decomposes with the evolution of hydrogen chloride and the formation of a hard resinous mass. For this reason it has not been possible to distil it under diminished pressure. Because of its instability it is always freshly prepared for each experiment and is used immediately, usually without removing the phosphorus oxychloride.

Alcoholysis.—The crude benzoylacrylyl chloride from 9 g. of the acid and one equivalent of phosphorus pentachloride was poured into methyl alcohol. Heat was evolved. The mixture was immediately decomposed in ice and the oil was extracted with chloroform and distilled under diminished pressure. The yield of *trans* benzoylacrylic methyl ester boiling at 150° under 5 mm. pressure was 5 g. (52%).

Dibenzoylethylene (VI).—A crude mixture of benzoylacrylyl chloride and phosphorus oxychloride from 2.64 g. of the acid and 3.5 g. of phosphorus pentachloride was treated with 30 cc. of benzene and 15 g. of aluminum chloride. Heat and hydrogen chloride were evolved. The red mixture was decomposed immediately in ice and the mixture was stirred with water to decompose the phosphorus oxychloride. The dark colored benzene layer was allowed to evaporate and the black residue was taken up in alcohol. A black crystalline deposit was filtered off, washed with alcohol and crystallized from benzene and then from alcohol. The dark color was largely removed and 0.8 g. of pale yellow needles melting at 110° was obtained and identified by a mixed melting point as dibenzoylethylene. From the filtrates 0.75 g. of very dark colored crystals was obtained and identified as nearly pure material melting at 107–108°. The total yield of nearly pure dibenzoylethylene was 1.55 g. (44%).

The experiment was repeated several times and the results were thoroughly substantiated. A black tar was obtained as by-product.

Action of Aluminum Chloride on *Cis* Dibenzoylethylene.—One gram of *cis* dibenzoylethylene was treated with 10 cc. of benzene and 2 g. of aluminum chloride. A red gummy mass formed immediately and gave a deep red solution when the mixture was heated to boiling. The product was decomposed in ice and fractionally crystallized by successive additions of petroleum ether to the benzene solution, followed by cooling and evaporating. The first two fractions (0.35 g.) proved to be unchanged *cis* dibenzoylethylene, and the third fraction and the residue (0.55 g.) consisted mainly of *trans* dibenzoylethylene.

The experiment was repeated using 20 cc. of benzene and 3 g. of aluminum chloride, and refluxing for ten minutes. The product was found to be largely the *trans* isomer, but an appreciable amount of the *cis* isomer (about 10%) was recovered.

A synthesis of *trans* dibenzoylethylene was carried out in which the fumaryl chloride was added to a cooled mixture; the temperature was not allowed to go above 50° and the total time of reaction was about one minute. The yield (65%) was low because the reaction was not complete, as was shown by the odor of fumaryl chloride after decomposing in ice. No *cis* isomer was isolated or detected among the products. In two similar experiments to which samples of *cis* dibenzoylethylene had been added, the *cis* isomer was completely isomerized in one case, and very nearly so in the other (a trace being recovered).

***Trans* β-2,4,6-Trimethylbenzoylacrylyl Chloride (VIII),** $(CH_3)_3C_6H_2COCH{=}CHCOCl$.—Equivalent amounts of *trans* β-mesitoylacrylic acid and phosphorus pentachloride were mixed with cooling in an ice-bath. Hydrogen chloride was evolved and the mixture liquefied. The heat of reaction was moderated to prevent the formation of a dark colored product. In the experiments to follow (hydrolysis, alcoholysis, and the Friedel–Crafts reaction) the acid chloride was not separated from the by-product phosphorus oxychloride. The acid chloride is an unstable yellow oil which resembles benzoylacrylyl chloride in its properties.

The crude acid chloride from 0.5 g. of acid was shaken for several hours with water and the resulting yellow solid was filtered, washed with petroleum ether and identified as mesitoylacrylic acid; yield, 0.4 g.

The crude acid chloride from 1 g. of acid was added to methyl alcohol. The solution was immediately decomposed in ice and extracted with ether. On evaporating the solvent, treating the oily residue with petroleum ether and cooling, 0.15 g. of yellow crystals was obtained and identified as *trans* mesitoylacrylic methyl ester.

***Trans* Di(2,4,6-trimethylbenzoyl)ethylene.**—In a typical experiment 2.18 g. of β-mesitoylacrylic acid was treated with 2.1 g. of phosphorus pentachloride. The mixture containing the crude acid chloride was then treated directly with 1.5 g. of mesitylene, 10 cc. of carbon disulfide, and 6 g. of aluminum chloride, and was decomposed in ice and worked up in the usual manner. A small yield (0.15 g.) of yellow crystals was isolated and identified as dimesitoylethylene. The reaction was repeated several times without bettering the yield. The principal product was an orange colored resinous oil.

In a similar experiment benzene was used as the solvent in place of carbon disulfide. The product was separated from an orange colored resin by taking up in petroleum ether. The crystalline product was warmed with methyl alcohol and on cooling 0.55 g. of yellow crystals was isolated and identified as nearly pure *trans* dimesitoylethylene (yield, 16.5%). The methyl alcohol filtrate was diluted with water and gave 0.35 g. of colorless crystals melting at 217°. The new substance dissolved in sodium carbonate and was precipitated by acids. The experiment was repeated and the yield of *trans* dimesitoylethylene was confirmed, but only 0.1 g. of the colorless acid was isolated. The latter substance will be investigated further.

Normal and Iso β-Benzoyldibromopropionic Acids (X and XIV).—The iso acid was prepared by the method of Bogert and Ritter[8b] by adding aluminum chloride to a cooled mixture of benzene and dibromosuccinic anhydride.

The normal acid was prepared by adding one equivalent of bromine to *trans* benzoylacrylic acid, in acetic acid as the solvent. Recrystallization from toluene gave a product melting at 148° (decomp.).

In two experiments one equivalent of bromine in 6 cc. of chloroform was added to 1 g. of benzoylacrylic acid in 5 cc. of chloroform. In the first case the reaction mixture was kept at the boiling point of chloroform. On evaporating the solvent and crystallizing the somewhat oily residue from benzene a yield of 1.3 g. of pure acid melting at 148° was obtained. In the second experiment the reaction mixture was cooled in an ice-bath. Upon evaporation of the solvent, the residue completely crystallized, melted at 108–135° (yield 1.8 g.) and was shown to consist of a mixture of the two isomeric benzoyldibromopropionic acids as follows. A dilute chloroform–benzene solution of the mixture was allowed to evaporate slowly overnight, and a deposit of large crystals was obtained from which the mother liquor was decanted. The crystalline layer adhering to the bottom of the dish was washed with ligroin. The large opaque granules of twinned rhombic plates were dislodged and rolled out of the thin layer of smaller, clear, rhombic plates which adhered firmly to the bottom of the vessel. Thus complete separation of the pure components was effected; the former melted with decomposition at 149° and was identified as the iso acid; the latter, melting at 148° (decomp.), was shown to be the normal acid; a mixture of the two melted at 108–135°. The disagreement as to the melting points[20] is perhaps not surprising since both products decompose at their melting points.

Normal and Iso β-Benzoyldibromopropionyl Chlorides (XI and XV), C_6H_5-COCHBrCHBrCOCl.—The acid chlorides were obtained as oils by the action of an excess of phosphorus pentachloride on the acids. They decomposed with the evolution of hydrogen chloride when distillation under diminished pressure was attempted. Samples of the oily acid chlorides, suspended in water, were allowed to stand overnight and hydrolyzed to give nearly quantitative yields of the original acids.

***dl*-Dibenzoyldibromo-ethane (XII).**—The crude acid chloride from 3 g. of iso β-

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[20] For the normal acid H. v. Pechmann[1] gives 135°, Bougault [*Ann. chim. phys.*, [8] **15**, 491 (1908)] 148°, Mrs. Rice[16] 150°, my finding 150° (corr.) with decomposition; for the iso acid Bogert and Ritter[8b] give 142°, Mrs. Rice[16] 148°; my finding 150° (corr.) with decomposition.

benzoyldibromopropionic acid and 3 g. of phosphorus pentachloride was treated directly with benzene and 15 g. of aluminum chloride. Heat and hydrogen chloride were evolved. The mixture was then decomposed in ice. The benzene layer was evaporated and the residue taken up in methyl alcohol; 0.8 g. of crystals was isolated and identified by a mixed melting point as nearly pure *dl*-dibenzoyldibromo-ethane. The tar obtained by diluting the filtrate with water was taken up in petroleum ether. The solution deposited 0.4 g. of colorless crystals of a new substance melting at 155–160° which was soluble in sodium carbonate and was precipitated by acids. The yield of *dl*-dibenzoyldibromo-ethane was confirmed in several experiments, but only traces of the new acid were obtained. The latter will be investigated further.

Meso Dibenzoyldibromo-ethane (XVI).—The crude acid chloride from 1.5 g. of β-benzoyldibromopropionic acid and phosphorus pentachloride was treated directly with benzene and 6 g. of aluminum chloride; the mixture was then decomposed in ice. The benzene layer was cooled and diluted with a little petroleum ether. The crystalline deposit was washed with sodium carbonate solution. The product melting at 176° (decomp.) was identified as meso dibenzoyldibromo-ethane; yield, 1.0 g. (57%).

A Third Isomeric β-Benzoylbromo-acrylic Acid, $C_6H_5COCH{=}CBrCOOH$ or $C_6H_5COCBr{=}CHCOOH$.—In an attempt to prepare benzoylpropiolic acid, a mixture of 25 g. of β-benzoyldibromopropionic acid, 30 g. of sodium acetate, 7 g. of sodium carbonate, 150 cc. of acetone and 10 cc. of methyl alcohol was refluxed for four and one-half hours. After cooling, the crystalline solid was filtered off and acidified. The crystalline product obtained was identified as nearly pure β-benzoyl-β-bromo-acrylic acid (known[8b,16]) melting at 106–107°. The acetone filtrate was acidified and diluted with water, and gave 1.5 g. of a new isomeric β-benzoylbromo-acrylic acid. This new substance gave a considerable melting point depression when mixed with the β-bromo isomer prepared by Bogert and Ritter,[8b] differs in melting point from the α-bromo derivative obtained by Mrs. Rice,[16] and is undoubtedly a stereoisomer of one of these; colorless needles; melting point 105° (corr.) after several crystallizations from benzene and petroleum ether.

Anal. Calcd. for $C_{10}H_7O_3Br$: Br, 31.34. Found: 31.65.

A small sample reacted with zinc and acetic acid with the evolution of heat. On filtering, diluting with water, extracting with ether, evaporating and crystallizing from water, shiny plates of benzoylpropionic acid were isolated and identified.

The position of the bromine atom and the configuration have not been determined.

On the Preparation of Some Unsaturated 1,4-Diketones and their Derivatives.—In the Friedel and Crafts reactions used in the foregoing work it was often found desirable to use the crude acid chloride without removing the phosphorus oxychloride obtained as a by-product of the action of phosphorus pentachloride on the acids. Experiment showed that in the synthesis of dibenzoylethylene from fumaryl chloride the yield was in no way affected by the presence of phosphorus oxychloride, providing that a large excess of aluminum chloride was used. It was necessary, however, to insure complete hydrolysis of the phosphorus oxychloride after decomposing in ice, before evaporating the benzene solution of the product; otherwise a dark color developed. It was also found that an excess of aluminum chloride in general gives a better yield and a purer product, and that the reaction is complete in a very short time. The dark red color that often develops in the final product seems to be due to the action of unchanged or partly reacted acid chloride or phosphorus oxychloride which escapes hydrolysis and remains in the benzene solution of the final product. Two typical experiments follow in outline.

(a) Fumaryl chloride (15 g.) was added rapidly drop by drop to a well-stirred mixture of 200 cc. of benzene and 45 g. of aluminum chloride. Considerable heat and hydrogen chloride were evolved. In a few minutes the reaction subsided and the red pasty mass was decomposed and the product isolated in the usual manner; the yield of pure *trans* dibenzoylethylene melting at 108–108.5° was 21 g. (89%).

(b) In a similar experiment 15 g. of fumaryl chloride in 20 g. of phosphorus oxychloride was added to a mixture of 60 g. of aluminum chloride in benzene. After decomposing in ice, the mixture was stirred for half an hour with water to decompose completely the phosphorus oxychloride; the yield of pure *trans* dibenzoylethylene was 21.5 g. (93%).

The use of carbon disulfide as the solvent in these Friedel and Crafts reactions often gives very poor results, and in many cases the yields are very considerably improved by using benzene instead. This method was applied successfully in some reactions between fumaryl chloride and certain aromatic hydrocarbons possessing a much greater reactivity than benzene, namely, mesitylene and naphthalene. When technical benzol, which contains as much as 20% of toluene, is used in the reaction, the product is exclusively *trans* ditoluylethylene. The use of benzene as the solvent is particularly good in the preparation of *trans* dimesitolylethylene, whereby a yield of 74% was obtained in a typical experiment. The yield of *trans* dinaphthoylethylene is very low when carbon disulfide is used as the solvent,[17] but it has been raised to 41% in a typical experiment when the reaction was carried out in benzene as the solvent, under somewhat moderated conditions. Curiously, however, the method failed to improve the yield of *trans* dianisoylethylene. Furthermore, in certain experiments using dibromofumaryl, β-benzoyl- and β-mesitoyl-dibromo-acrylyl chlorides[7] it was found that the benzene used as the solvent reacted instead of the mesitylene, a result contrary to that which was expected from the above results with fumaryl chloride.

Di(α-naphthoyl)ethane, $C_{10}H_7COCH_2CH_2COC_{10}H_7$.—Dinaphthoylethylene (2 g.) was reduced in the usual way with zinc and acetic acid; the yield of ethane was 1.5 g.; shining, colorless leaflets (microscopic scales); melting point 130–131° (corr.); difficultly soluble in boiling alcohol; soluble in chloroform, acetone, benzene, ethyl acetate, and acetic acid; insoluble in ether and ligroin.

Anal. Calcd. for $C_{24}H_{18}O_2$: C, 85.12; H, 5.36. Found: C, 85.02; H, 5.39.

dl-**Di(4-methylbenzoyl)dibromo-ethane,**[21] $CH_3C_6H_4COCHBrCHBrCOC_6H_4CH_3$.—*Trans* ditoluylethylene adds bromine in acetic acid to give mainly the high-melting meso[22] dibromide melting at 198°. The low-melting (*dl*)[22] isomer was isolated in a small yield from the acetic acid mother liquors by diluting with water. It forms fine colorless crystals; melting point 138° (corr.) after repeated crystallization from alcohol and from benzene; soluble in chloroform and hot acetic acid; insoluble in ligroin.

Anal. Calcd. for $C_{18}H_{16}O_2Br_2$: Br, 37.70. Found: 37.55.

Trans **Di(4-phenoxybenzoyl)ethylene,**[21] $C_6H_5OC_6H_4COCH{=}CHCOC_6H_4OC_6H_5$.—Diphenyl ether was allowed to react in the usual way with aluminum chloride and fumaryl chloride in carbon disulfide as the solvent. The product was isolated from a crude resinous tar by crystallizing from acetone and refluxing in solvents with animal charcoal.

It gives orange crystals; melting point 170.5–171° (corr.), after eight crystallizations from an alcohol–benzene mixture; soluble in chloroform, benzene and in hot acetone and acetic acid; insoluble in hot alcohol.

Anal. Calcd. for $C_{28}H_{20}O_4$: C, 80.00; H, 4.80. Found: C, 79.88; H, 4.89.

Trans **Di(4-phenoxybenzoyl)ethane,**[21] $C_6H_5OC_6H_4COCH_2CH_2COC_6H_4OC_6H_5$.—The corresponding ethylene was reduced in the usual way with zinc and acetic acid.

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[21] Prepared and analyzed in this Laboratory by Mr. Ernly Estes.

[22] The configuration is based on analogy (see Ref. 5).

It forms colorless crystals; melting point 160° (corr.) after repeated crystallization from acetone; soluble in chloroform and benzene; insoluble in alcohol.

Anal. Calcd. for $C_{28}H_{22}O_4$: C, 79.57; H, 5.76. Found: C, 79.45; H, 5.11.

Trans **1-Benzoyl-2-(2,4,6-trimethylbenzoyl)ethylene (IX)**, $C_6H_5COCH{=}CHCO{-}C_6H_2(CH_3)_3$.—The crude acid chloride from 2.18 g. of *trans* mesitoylacrylic acid and 2.1 g. of phosphorus pentachloride was treated directly with benzene and 8 g. of aluminum chloride. Heat and hydrogen chloride were evolved. The red mass was decomposed in ice. The benzene layer was evaporated and the residue was dissolved in methyl alcohol. On cooling 0.9 g. of pure product was obtained, a yield of 32%.

Anal. Calcd. for $C_{19}H_{18}O_2$: C, 82.00; H, 6.52. Found: C, 82.10; H, 6.62.

Benzoylacrylyl chloride when treated with mesitylene and aluminum chloride in carbon disulfide failed to yield a crystalline product.

Reduction with zinc and acetic acid gave a nearly colorless oil which has not yet been obtained in a crystalline form.

Maleil chloride[18] was prepared by the action of phosphorus pentachloride on maleic acid, and was isolated by fractional distillation under reduced pressure. On redistillation it boiled at 65° under 2 mm. pressure.

Trans **4,4-Diphenyl-4-hydroxybutenoic Acid**, $(C_6H_5)_2C(OH)CH{=}CHCOOH$.—Maleil chloride was used in the Friedel and Crafts reaction with aluminum chloride and benzene under a variety of conditions. Resins were obtained from which small amounts of an acid were isolated as white powdery deposits from carbon tetrachloride solutions. It was soluble in sodium carbonate and precipitated by acids. It formed colorless, microscopic, blade-shaped scales; melting point (decomp.), 224° (corr.) after several crystallizations from acetic acid; very soluble in alcohol; insoluble in ethyl acetate benzene, ethyl bromide and ligroin.

Anal. Calcd. for $C_{16}H_{14}O_3$: C, 75.59; H, 5.55. Found: C, 75.27; 75.90; H, 5.07, 5.61.

The *trans* structure is suggested because the product is not the lactone that was expected. The free hydroxy acid, once formed, undoubtedly rearranges under these conditions to the stable *trans* state as happens in the preparation of benzoylacrylic acid from maleic anhydride.

Summary

The configurations of benzoyl and mesitoylacrylic acids are shown to be *trans* by the normal character of their acid chlorides which have been synthesized and converted into the unsaturated 1,4-diketones by the Friedel and Crafts reaction.

Syntheses of unsaturated 1,4-ketonic esters from fumaric monomethyl ester, and new developments in the synthesis of symmetrical unsaturated 1,4-diketones are described.

The configurations of the dibromides of benzoylacrylic acid are determined by the synthesis of one of them from *dl*-dibromosuccinic acid, and by their conversion through the acid chlorides into the known dibenzoyldibromomethanes.

The stereochemical mode of addition of bromine to ethylene and acetylene linkages is discussed.

UNIVERSITY, VIRGINIA