[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF VIRGINIA, No. 63]

THE CONFIGURATIONS OF THE UNSATURATED DIBROMO 1,4-DIKETONES AND KETONIC ACIDS. SYNTHESIS AND STRUCTURE OF CIS AND TRANS BETA-BENZOYLDIBROMO-ACRYLIC ACIDS AND SOME OF THEIR DERIVATIVES.[1] STUDIES ON UNSATURATED 1,4-DIKETONES. V[2]

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RECEIVED MAY 21, 1930 PUBLISHED AUGUST 5, 1930

This investigation was undertaken in order to establish conclusively the configurations of the unsaturated 1,4-ketonic acids, and if possible to establish inter-relationships between this series and the unsaturated 1,4-diketones, the configurations of which in many cases have already been determined with a considerable degree of certainty.

β-Benzoylacrylic acid has long been known[3] and has been widely studied,[4] but in spite of this its configuration has not been experimentally established up to this time. The acid is prepared from maleic anhydride, but it undoubtedly possesses a *trans* configuration[4j,k] as is now shown by the results of some recent studies which I will discuss in detail in the next paper of this series.[5] The hypothetical labile (*cis*) isomer remains as yet unknown despite many attempts to synthesize it.[4d,k] The yellow ester of the *trans* acid[4d,e,f,g,h] has been rearranged by the absorption of light energy into a labile colorless isomer which corresponds to the *cis* form, and the stability or energy relationship of these two isomeric esters is exactly analogous to that of other known *cis–trans* stereoisomeric pairs such as maleic and fumaric acids. Both the *cis* and *trans* esters, however, give the same yellow stable (*trans*) acid whenever hydrolysis is successful.

In view of these facts it seemed desirable to prepare the hitherto unknown *cis* and *trans* β-benzoyldibromo-acrylic acids and their esters, since

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[1] Presented at the meeting of the American Chemical Society at Atlanta, April 9, 1930.

[2] The preceding paper, Lutz, THIS JOURNAL, **51**, 3008 (1929), entitled "1,6-Addition of Hydrogen to Unsaturated 1,4-Diketones," constitutes the fourth paper in this series.

[3] (a) H. v. Pechmann, *Ber.*, **15**, 881 (1882); (b) Koenigs and Wagstaffe, *ibid.*, **26**, 558 (1893); (c) Gabriel and Colman, *ibid.*, **32**, 395 (1899); (d) Kozniewski and Marchlewski, *Bull. Acad. Sci. Cracow*, **81** (1906); (e) Bougault, *Ann. chim. phys.*, [8] **15**, 296, 498 (1908).

[4] See also (a) Koenigs and Jaegle, *Ber.*, **28**, 1048 (1895); (b) Bougault, *Compt. rend.*, **146**, 140 (1908); **147**, 476 (1908); (c) Kohler and Engelbrecht, THIS JOURNAL, **41**, 768 (1919); (d) Rice, *ibid.*, **45**, 222 (1923); (e) **45**, 232 (1923); (f) **48**, 269 (1926); (g) **50**, 229 (1928); (h) **50**, 1481 (1928); (i) **52**, 2094 (1930); (j) Bogert and Ritter, *Proc. Nat. Acad. Sci.*, **10**, 363 (1924); THIS JOURNAL, **46**, 2871 (1924); (k) **47**, 526 (1925); (l) Cattelain, *Bull. soc. chim.*, **41**, 352 (1927).

[5] Lutz, THIS JOURNAL, **52**, 3423 (1930).

in these compounds the ethylenic hydrogen atoms, which in all probability are largely responsible for the lability, are replaced by two bromine atoms.

In this research I have been able to synthesize *cis* and *trans* β-benzoyldibromo-acrylic acids and the corresponding esters from dibromo maleic and fumaric acids. The reduction of both acids to the same β-benzoylpropionic acid confirms the structures that have been assigned. Both acids are stable and are not affected by the reagents usually employed to bring about direct stereochemical rearrangement.

The stereochemical stability of these acids was not unexpected in view of the fact that dibromo maleic and fumaric acids do not readily rearrange,[6] one into the other, whereas the unsubstituted maleic and fumaric acids are mutually interconvertible, from *cis* to *trans* by the action of hydrochloric acid, halogens, etc., and from *trans* to *cis* by the absorption of light energy.[7] Of course *trans* isomers may be converted into *cis indirectly* despite unfavorable energy relations, and this sometimes with great ease; but these transformations usually involve, as the driving force, the formation of ring compounds, as is illustrated by the conversion of fumaric and dimethylfumaric acids[8] into the corresponding maleic *anhydrides*, and of dibromofumaryl chloride into dibromomaleil *pseudo* chloride.[6d] Transformations of this sort are not pertinent to this discussion since the energy relations referred to above concern only inversions of the configuration of the double bond without other change in the molecule. This other phase of the subject will be treated in later papers.

The effect of substitution for ethylenic hydrogen in unsaturated 1,4-diketones on the stereochemical stability of the *cis–trans* isomeric pairs, is of interest in this connection. The labile *cis* forms of the unsaturated 1,4-diketones in which the ethylene double bond remains unsubstituted, are in general prepared by the action of sunlight on the trans forms,[9] and they are easily rearranged into the stable *trans* isomers by the action of catalysts such as iodine, hydrochloric acid, etc.[9] However, when halogens[10] or a methoxyl[11] are substituted for hydrogen on the ethylene double bond, it is no longer possible to prepare the *cis* isomers directly in this way. Furthermore, the *cis* isomers, obtained indirectly,[10] are considerably more stable than those in which the ethylene double bond is unsubstituted. The labile dibromo derivative, to be sure, is rearranged into the *trans* form

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[6] Compare: (a) Wislicenus, *Ann.*, **246**, 89 (1888); (b) Michael, *J. prakt. Chem.*, [2] **46**, 222 (1892); (c) **52**, 372 (1895); (d) Ott, *Ann.*, **392**, 267 (1912).

[7] Stoermer, *Ber.*, **42**, 4870 (1909); etc.

[8] Wislicenus, *Ann.*, **246**, 93 (1888); Volhard, *ibid.*, **268**, 256 (1892); Tanatar, *ibid.*, **273**, 31 (1893); Fittig and Kettner, *ibid.*, **304**, 165 (1898).

[9] (a) Paal and Schulze, *Ber.*, **35**, 168 (1902); (b) Conant and Lutz, THIS JOURNAL, **45**, 1303 (1923).

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

[11] Lutz, *ibid.*, **48**, 2905 (1926).

by the action of iodine and sunlight,[10] but it is perfectly stable toward the action of aluminum chloride as has now been shown, whereas the unsubstituted *cis* dibenzoylethylene itself is largely rearranged into the *trans* isomer under the same conditions.[5] The *cis* methoxy compound[12] is quite stable.

The lability of the *cis* isomers is undoubtedly due in part at least to a lack of balance of forces within the molecule, which is accentuated when relatively light and mobile hydrogen atoms occupy two positions on the ethylene double bond opposite and also alpha to much larger groups of an unsaturated character such as benzoyl and carboxyl. The ethylenic hydrogens of benzoylacrylic acid, for instance, are labile, as is shown by the mechanism[4j,k] and ease of formation of "Pechmann dyes" in which enolization of alpha hydrogen destroys the *cis–trans* asymmetry of the ethylene double bond. The substitution of bromine probably alters the difference in energy content of the *cis* and *trans* forms but undoubtedly it also increases the stereochemical stability by sheer inactivation of the molecule, for it is well known that a highly substituted double bond is often very unreactive. The hypothetical *cis* benzoylacrylic acid undoubtedly possesses a high degree of lability, and if ever formed it always rearranges to the stable (*trans*) isomer under the experimental conditions involved in any synthesis. On the other hand, the elimination of mobile groups by the substitution of bromine for the ethylene hydrogens certainly increases the stereochemical stabilities to such an extent that both *cis* and *trans* isomers are easily obtained and defy rearrangement, even under the drastic conditions of a Friedel and Crafts reaction.

Cis β-Benzoyldibromo-acrylic Acid and its Derivatives.—*Cis* β-benzoyldibromo-acrylic acid (II) was prepared by the Friedel and Crafts reaction from dibromomaleic anhydride using benzene and aluminum chloride. The synthesis, structures and reactions are outlined in Diagram I. The *cis* acid, as will be shown, is not isomerized in the course of the Friedel and Crafts reaction as happens in the analogous preparation of β-benzoylacrylic acid from maleic anhydride,[3,4,5] and it is stable toward the reagents that are ordinarily effective in rearranging labile isomers. It is readily reduced by zinc and acetic acid to the known benzoylpropionic acid (VI), and it is esterified by the action of methyl alcohol saturated with dry hydrogen chloride. Hydrolysis of the ester with cold alcoholic sodium hydroxide produces the *cis* acid in good yield, but when aqueous sodium hydroxide is used the molecule undergoes cleavage, and a nearly theoretical yield of benzoic acid is obtained. In these experiments there was found no evidence of rearrangement of the sort that takes place under similar conditions in the hydrolysis of the unsubstituted labile esters of β-benzoylacrylic acid.[4d]

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[12] Both forms of dibenzoylmethoxyethylene are known, and both are stable, but the configurations have not as yet been established (see Ref. 11).

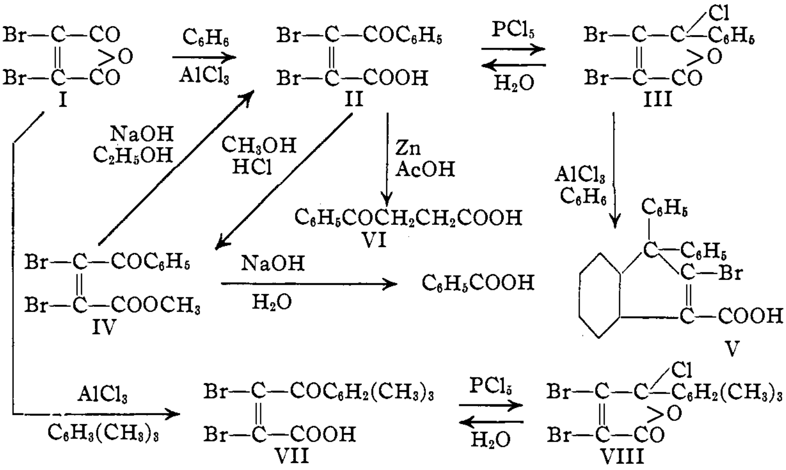


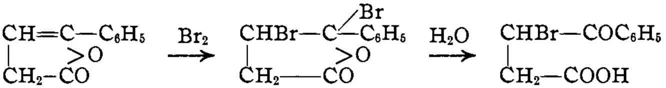
DIAGRAM I

A number of mesitoyl analogs of the compounds described above have been prepared and studied; the results are described in the experimental part, and are referred to also in Diagram I.

The β-benzoyldibromo-acrylic acid, prepared from dibromomaleic anhydride, has the *cis* configuration as is shown by the following facts. The ester of the isomeric *trans* acid has been prepared by a synthesis from dibromofumaric acid, which leaves no doubt as to its structure, and from this ester by hydrolysis is obtained the corresponding and isomeric *trans* acid. No inter-transformations between the two series have been observed, and the various configurations, therefore, must be stable, and must correspond to those of the starting materials. Furthermore, the acid chloride obtained from the *cis* acid behaves as if it were of the pseudo or chloro lactone type (III), in contrast to the normal behavior of the acid chloride obtained from the *trans* acid (XXI).

The acid chloride of *cis* benzoyldibromo-acrylic acid (III) is formed readily by the action of phosphorus pentachloride on the free acid and is a colorless solid melting at 82.5°. The possibility of rearrangement in the process is excluded since on hydrolysis with water the original acid is recovered unchanged. This hydrolysis, however, takes place extremely slowly as compared with the relative ease of hydrolysis of the *trans* acid chloride and acid chlorides in general (one week in contact with moisture was required for this hydrolysis). For this reason it may be separated from the by-product phosphorus oxychloride by shaking the crude mixture with water, a procedure which is without effect on the product but by which the phosphorus oxychloride is rapidly hydrolyzed. It dissolves in boiling methyl alcohol and crystallizes unchanged on cooling, and must therefore possess an inactive halogen atom since acid chlorides, the structures of which are known to be normal, react immediately with methyl alcohol to form esters, as actually does *trans* β-benzoyldibromo-acrylyl chloride. The pseudo or lactone structure (III) which I have assigned in Diagram I, and the *cis* relationship of carboxyl and carbonyl groups required on stereochemical grounds for this formulation, would therefore appear to be fully established. Further studies on this problem are being undertaken to confirm the above conclusion and to extend the work in a number of directions.

The pseudo or lactone forms of the acid chlorides of *o*-benzoylbenzoic acid[13] and ortho benzil mono and dicarboxylic acids[14] are known. The latter are characterized chemically by their inertness toward alcoholysis.[14] These compounds constitute excellent analogs of the pseudo acid chloride described above. No open-chain analog, so far as I know, has yet been made, but a closely related compound has been prepared by the addition of bromine to the internal anhydride of β-benzoylpropionic acid (IX).[15] The product is a substance which has the characteristics of a pseudo β-benzoyl-β-bromopropionyl bromide (X) since it hydrolyzes very slowly to β-benzoyl-β-bromopropionic acid (XI, see Diagram II). Diphthalyl, in the aromatic series, adds halogen similarly to give a di-pseudo acid chloride.[16]



IX X XI

Diagram II

The Friedel and Crafts Reaction on Cis (ψ)-β-Benzoyldibromo-acrylyl Chloride.—*Cis* pseudo β-benzoyldibromo-acrylyl chloride was treated with aluminum chloride and benzene in a typical Friedel and Crafts reaction. It was hoped when the work was originally started that the acid chloride might react in part normally to give some *cis* dibenzoyldibromoethylene, for as is now shown this latter product is stable under the conditions of the experiment. No trace of such a product was isolated, however, nor was there obtained the expected unsymmetrical 4,4-diphenyl-1,2-dibromocrotolactone (XII) analogous to the similar products obtained from succinyl chloride,[17] meso dichlorosuccinyl chloride,[18] and phthalyl chloride.[19] This hypothetical lactone (XII) may be formed as an inter-

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[13] (a) Haller and Guyot, *Bull. soc. chim.*, [3] **25**, 54 (1901); (b) Meyer, *Monatsh.*, **25**, 475, 1181 (1904); **28**, 1235 (1907). See also (c) Martin, This Journal, **38**, 1142 (1916); (d) McMullen, *ibid.*, **38**, 1228 (1916); (e) Hantzsch, *Ber.*, **52**, 1572 (1919).

[14] Hantzsch and Schwiete, *ibid.*, **49**, 213 (1916).

[15] Fittig and Ginsberg, *Ann.*, **299**, 19 (1898).

[16] Ador, *ibid.*, **164**, 246 (1872); see also Ref. 14.

[17] Auger, *Ann. chim. phys.*, [6] **22**, 310 (1891); *Bull. soc. chim.*, [2] **49**, 345 (1888).

[18] Lutz, This Journal, **49**, 1106 (1927).

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

mediate product in the reaction, however, but the lactone ring opens with the introduction of a third phenyl group into the 4-position (see XIII), accompanied or followed by an internal condensation with the loss of hydrogen bromide between the alpha bromine and an ortho hydrogen of one phenyl group, to close an indene ring. The suggested mechanism of this reaction is outlined in Diagram III.

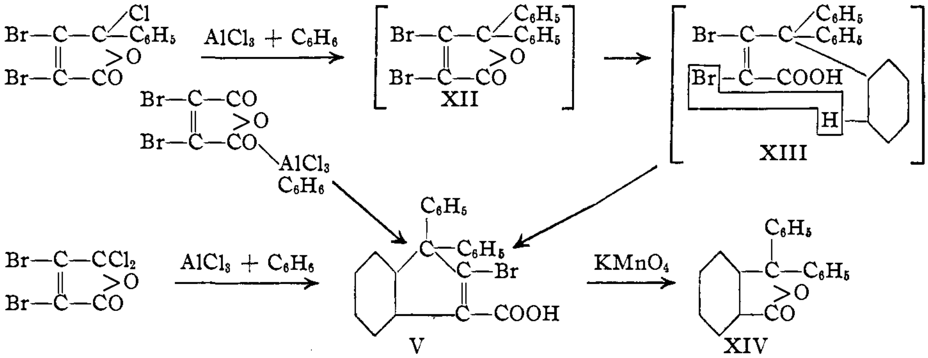

Diagram III

It is interesting to note also in this connection that this same product can be obtained in small yields directly from dibromomaleic anhydride and from dibromomaleil chloride by the Friedel and Crafts reaction. In the former case possibly some of the *cis* β-benzoyldibromo-acrylic acid formed reacts further in the same general way that *o*-benzoylbenzoic acid reacts with aluminum chloride and benzene to give diphenylphthalide.[20] In the latter case dibromomaleil chloride reacts in the pseudo form as does phthalyl chloride.[19]

The structure of this new substance, 1,1-diphenyl-2-bromo-3-carboxyindene (V), is evident from analysis, properties and its oxidation product. It is an acid with one carboxyl group, forms salts readily, is dissolved by approximately one equivalent of sodium hydroxide, and loses carbon dioxide when heated above its melting point. On oxidation in alkaline solution with potassium permanganate it gives a good yield of diphenylphthalide (XIV), the structure of which is known.[19] The carbon skeleton of diphenylphthalide must therefore be present in the new compound, and it seems clearly established, at least, that three phenyl groups are attached to the 4-carbon and that one of them is attached to another position on the chain through loss of an ortho hydrogen and the alpha or beta bromine as hydrogen bromide. For obvious steric reasons the alpha bromine is undoubtedly the one which reacts since the formation of the five-membered indene ring would be the more likely result. The drastic oxidation of such a structure as is suggested would be expected to yield diphenylphthalide.

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

If the above conclusions as regards structure and mechanism are correct, and if one assumes that the indene ring is a *cis* ring, then the stereochemical mode of closing the ring by the Friedel and Crafts reaction would appear to be *trans*, since the bromine atom is *trans* with respect to the phenyl group with which it reacts, and since rearrangement preceding reaction seems unlikely in view of the general stability of the *cis* dibromo compounds under these conditions. This idea is illustrated by Formula XIII in Diagram III. However, since the mechanism of this peculiar step in the reaction is not clear, little significance can be attached to this point.

That *cis* β-benzoyldibromo-acrylyl chloride has the pseudo structure is evident (though perhaps not conclusively proved) by its failure to react readily with methyl alcohol. It is clearly shown that there exists a *cis* relationship between the acid chloride and benzoyl radicals, whether the compound actually exists in the pseudo form or not, because the acid chloride undergoes the Friedel and Crafts reaction as if the pseudo form either did actually exist or was potentially available through a tautomerism possible only in a *cis* compound, and because the stereoisomeric acid chloride behaves in every way normally, as will be shown in the folowing section.

Trans β-Benzoyldibromo-acrylic Acid and its Derivatives.—All efforts to prepare the *trans* derivatives of β-benzoyldibromo-acrylic acid by rearranging the corresponding *cis* isomers have failed. The action of halogens and sunlight, of boiling concentrated hydrochloric acid, and of cold alcoholic sodium hydroxide, were without effect. The compounds of this series, then, despite the fact that they possess a *cis* configuration, are extremely stable.

The synthesis of *trans* β-benzoyldibromo-acrylic acid and its derivatives was accomplished through the use of dibromofumaric acid as the starting material. The reactions and structures are outlined in Diagrams IV and V.

Dibromofumaryl chloride reacts with aluminum chloride and benzene to give *trans* dibenzoyldibromo-ethylene (XVIII, known as the "high melting beta" stable isomer[10]). Dibromofumaric monomethyl ester monochloride (XX) was obtained from the above dichloride by partial alcoholysis of one acid chloride group by means of one equivalent of methyl alcohol. Subsequent condensation with benzene and aluminum chloride gave fair yields of β-benzoyldibromo-acrylic methyl ester (XXII), which was converted readily into the corresponding *trans* acid (XIX) by hydrolysis with cold alcoholic sodium hydroxide. Hydrolysis of the ester by means of aqueous sodium hydroxide, however, gave nearly theoretical yields of benzoic acid through cleavage of the molecule.

The relationships established between the various new derivatives of dibromofumaric acid confirm the structures and configurations assigned in Diagram (IV). The acid chloride (XVI) is easily hydrolyzed to the original acid, and may be alcoholized, partially to dibromofumaric monomethyl

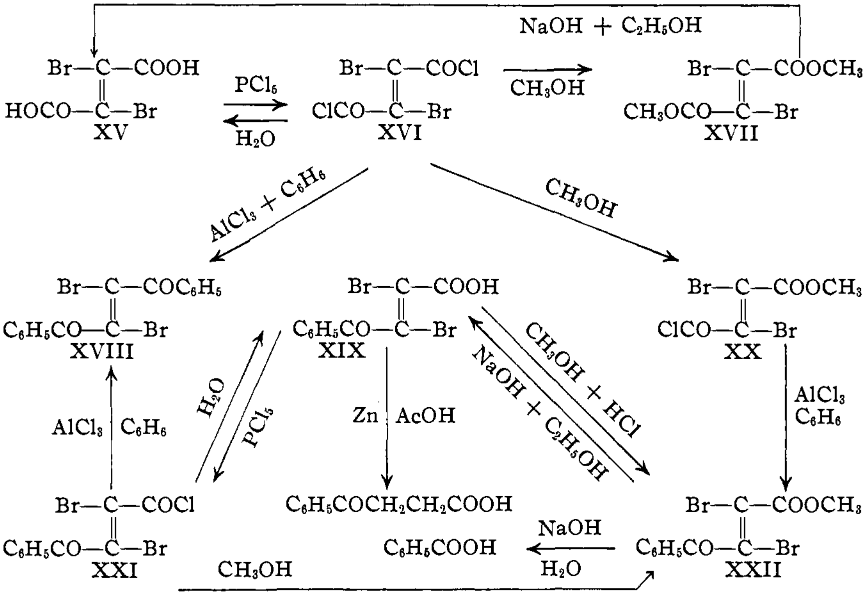

DIAGRAM IV

ester monochloride (XX), and completely to dimethyldibromofumarate (XVII). Dibromofumaric monomethyl ester monochloride has not as yet been isolated in a pure state free from dibromofumaryl chloride and dimethyl dibromofumarate. That it exists and has the character of a normal acid chloride is shown by the Friedel and Crafts reaction described above, and by the fact that an excess of methyl alcohol, acting on the original dichloride, gives the dimethyl ester. Furthermore, the analogous mono acid chloride monomethyl ester of fumaric acid has been isolated in a pure state and studied.[21,5] Dimethyl dibromofumarate is readily hydrolyzed by means of cold alcoholic sodium hydroxide and dibromofumaric acid is regenerated. Thus it is shown that the configurations have remained unchanged throughout these transformations, and that the new derivatives belong indeed to the *trans* series.

Trans β-benzoyldibromo-acrylic acid is easily esterified by saturating a methyl alcohol solution with dry hydrogen chloride. It is reduced readily by zinc and acetic acid to the known β-benzoylpropionic acid.[22] It is converted by the action of phosphorus pentachloride into an acid chloride which is of the normal type, as is shown by the ease with which it is hydrolyzed to the acid by water, and is alcoholized to the ester by methyl alcohol. The acid chloride reacts normally in the Friedel and Crafts reaction to give the known "high melting" (*trans*) dibenzoyldibromo-ethylene.[10]

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

[22] H. v. Pechmann, *Ber.*, **15**, 881 (1882).

The mesitoyl analogs of *trans* β-benzoyldibromo-acrylic acid, its ester and acid chloride, have been made (see Diagram V). This acid chloride (XXV), and also dibromofumaryl chloride, are readily converted by means of aluminum chloride and mesitylene into *trans* dimesitoyldibromo-ethylene (XXIV).

The *trans* configurations of the acids of this series derived from dibromofumaric acid, are clearly established by their synthesis alone, because there is no reason to suppose that rearrangement in the course of the reaction is possible, even under the drastic conditions of the Friedel and Crafts reaction and of hydrolysis (the isomers of opposite configuration are prepared by other methods from dibromomaleic anhydride, and are stable; and no inter-transformations between the two series have been observed). The above conclusion is strikingly confirmed by the normal character of the *trans* acid chloride as contrasted with the pseudo character of the *cis* isomer.

Synthesis and Configuration of Unsaturated Dibromo 1,4-Diketones.— In the course of the experiments described above, *trans* dibenzoyl-[10] and dimesitoyldibromo-ethylenes have been synthesized, respectively, from *trans* benzoyl- and mesitoyl-dibromo-acrylyl chlorides and also from dibromofumaryl chloride, by the Friedel and Crafts reaction. The structure of *trans* dimesitoyldibromo-ethylene was shown by reducing it with zinc and acetic acid to the known dimesitoylethane (XXVII).[23]

The configuration of dibenzoyldibromo-ethylene is evidently *trans* since it is the stable isomer, as has already been shown[10] by the rearrangement of the *cis* isomer. The *trans* configuration is now confirmed by the above syntheses, as is evident from the following considerations. Both of the starting materials are known to have the *trans* configuration and are stable. There is no reason to suppose that inversion could occur at any point in the syntheses because the double bond is inactive and does not appear to enter into the reaction in any way, and because no group attached directly to the double bond undergoes replacement. The only conceivable way for rearrangement to occur would be through the change from a labile intermediate to a stable isomer by the catalytic action of the reagents involved, as undoubtedly happens[5] in the preparation of the stable (*trans*) benzoylacrylic acid from maleic anhydride. The labile dibenzoylethylene (unsubstituted) is actually rearranged[5] under the conditions involved in the Friedel and Crafts synthesis. If such a rearrangement were to occur in the reaction in question, it would mean that the final stable product (actually obtained exclusively) would have the *cis* configuration (opposite that of the starting materials), and that the intermediate labile isomer necessarily assumed, would be *trans*, a relationship which is highly improbable since it is opposite that of maleic and fumaric acids and of *cis* and *trans* dibenzoylethylenes. In the reaction in question the labile dibromo isomer

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[23] Conant and Lutz, This Journal, **45**, 1303 (1923).

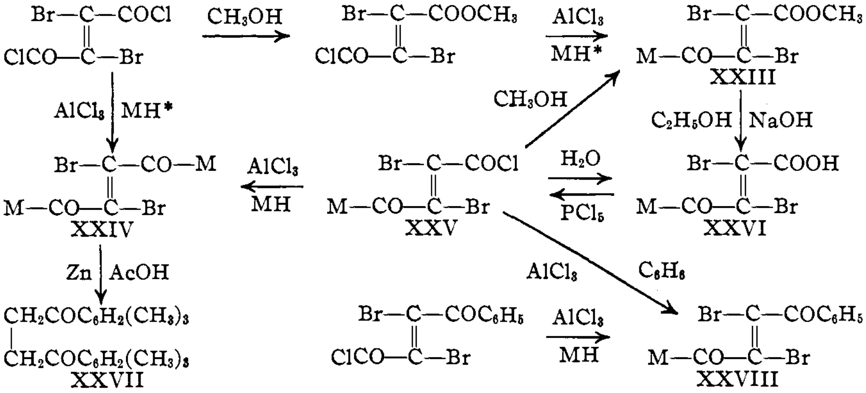
is not formed in the reaction as an intermediate product because (contrary to the analogous unsubstituted labile dibenzoylethylene) it is perfectly stable under the conditions of the experiment, as is now shown, and it would have been isolated among the reaction products if it had been formed in significant amounts. Therefore, the stable isomer only is produced in the reaction, and it must correspond in configuration to dibromofumaric acid and *trans* benzoyldibromo-acrylic acid from which it was synthesized.

The above statement concerning the stability of the known labile (*cis*) dibenzoyldibromo-ethylene under the conditions of the Friedel and Crafts reaction is based on the complete recovery of a sample of the labile isomer after it was subjected to the action of the reagents in a typical experiment. The colorless *cis* dibenzoyldibromo-ethylene reacts immediately with aluminum chloride in benzene to give the same sort of highly colored complex product as that obtained in the Friedel and Crafts reaction itself on dibromofumaryl chloride and on *trans* benzoyldibromo-acrylyl chloride; but on hydrolysis the *cis* product may be recovered unchanged. Furthermore, when dibromofumaryl chloride is added to a mixture of *cis* dibenzoyldibromo-ethylene, aluminum chloride and benzene, the normal Friedel and Crafts reaction takes place with the formation of the usual yield of *trans* dibenzoyldibromo-ethylene, and the bulk of the *cis* isomer introduced at the start can be recovered. Qualitatively the properties of these complex halochromic compounds correspond exactly in every way. The complex compound from the *cis* isomer apparently does not involve the ethylene double bond (at least as regards the major valence forces), since otherwise the asymmetry of the double bond would be destroyed and the stable form produced, a point of some significance, perhaps, in connection with theories of halochromism. It seems reasonably certain, then, that the conditions in these tests are nearly enough identical with those existing in actual experiment to justify the conclusion that *cis* dibenzoyldibromo-ethylene is stable under the conditions involved in the Friedel and Crafts reaction.

As a consequence of the relationships discussed above the configurations of the *cis* ("low-melting alpha") and *trans* ("high-melting beta") isomers of dibenzoyldibromo-ethylene (and by analogy those of the corresponding dichloro compounds) are established. Furthermore, since the stability relationship between these *cis–trans* isomeric pairs corresponds to that between maleic and fumaric acids, the validity of conclusions regarding the configurations of various other symmetrical unsaturated 1,4-diketones based on exactly analogous stability or energy relationships and upon the synthesis from fumaryl chloride, is confirmed.

It now becomes possible to prepare unsymmetrical unsaturated dibromo 1,4-diketones. The synthesis of a typical derivative is outlined in Diagram V. *Trans* benzoyldibromo-acrylyl chloride reacts with aluminum chloride and mesitylene to give *trans* benzoylmesitoyldibromo-ethylene (XXVIII);

the same product is obtained from *trans* mesitoyldibromo-acrylyl chloride (XXV) by the action of benzene and aluminum chloride.



* M = Mesityl, —$C_6H_2(CH_3)_3$. MH = Mesitylene, $C_6H_3(CH_3)_3$.

DIAGRAM V

Several points of interest arise in connection with this synthesis. First, the melting point of dibenzoyldibromo-ethylene is 213°, but when one mesityl group is substituted for phenyl, the melting point drops to 102.5°, then rises again to 198.5° upon substitution of the second mesityl group.

A second point of interest concerns the use of benzene in place of carbon disulfide as the solvent in the Friedel and Crafts reaction utilizing a more active aromatic hydrocarbon such as, for example, mesitylene. In the reaction between fumaryl chloride, mesitylene and aluminum chloride, with benzene as the solvent, mesitylene reacts exclusively.[5] Curiously enough, benzene reacts exclusively under similar conditions when dibromofumaryl chloride or *trans* benzoyl- or mesitoyl-dibromo-acrylyl chlorides are used in place of fumaryl chloride.

Conclusion

The evidence for the configurations assigned the two stereoisomeric benzoyldibromo-acrylic acids and their derivatives may be briefly summarized as follows. In every preparation of a compound in either the *cis* or *trans* series, there is formed exclusively one of the two possible stereoisomers and in no case has stereochemical rearrangement been observed. The configurations, therefore, correspond, respectively, to those of the two starting materials, dibromo maleic and fumaric acids, and are confirmed by the fact that the acid chlorides of the series derived from dibromomaleic acid are of the pseudo type, whereas those derived from dibromofumaric acid are normal in character.

The configurations of the unsaturated dibromo 1,4-diketones are established by the synthesis of the *trans* forms from compounds of known configurations under conditions which preclude the possibility of rearrangement.

Experimental Part

Dibromomaleic acid was prepared by the bromine oxidation of furoic acid to mucobromic acid[24] followed by further oxidation with fuming nitric acid.[25] The anhydride (I) was prepared by passing a stream of dry carbon dioxide over the molten acid at 130–140°. In an alternative method 80 g. of dibromomaleic acid was refluxed with an excess of thionyl chloride. After distilling the excess of reagent, 70 g. of sufficiently pure anhydride was obtained. An attempt was made to prepare the acid chloride by treating dibromomaleic acid with phosphorus pentachloride, but there was obtained only dibromomaleic anhydride, which resisted further action of the reagents.

Dibromofumaric acid (XV)[26,6d] was prepared by the action of bromine vapor on a concentrated aqueous solution of acetylene dicarbonic acid, and was isolated by evaporating the solvent in vacuum desiccators and filtering off successive crops of crystals. The low-melting end fractions containing dibromomaleic acid were discarded. The acid chloride[6d] (XVI) was prepared by the action of phosphorus pentachloride.

Dibromofumaric Monomethyl Ester Monochloride (XX), $CH_3OCOCBr{=}CBrCOCl$.—Dibromofumaryl chloride was partially alcoholized with one equivalent of methyl alcohol in carbon disulfide or benzene as the solvent. The mixture was allowed to stand for five to six hours and was refluxed for a short time. When used in a reaction the product was not isolated. In one experiment the product was subjected to a series of fractional distillations under diminished pressure using a Vigreux column, but a pure sample was not obtained. Small amounts of maleic anhydride were isolated, formed possibly by decomposition and rearrangement. The unchanged dichloride present in considerable amounts was rearranged nearly completely by the long continued heating involved (80–120° at 7 mm. pressure), as was shown by the fact that dibromomaleic acid was obtained in considerable amounts on hydrolysis of some of the fractions (compare Ref. 6d). The best sample isolated was a nearly colorless oil; boiling point 83–86° at 3.5 mm. pressure.

Anal. Calcd. for $C_5H_3O_3Br_2Cl$: C, 19.59; H, 1.24; Br_2Cl, 63.77. Found: C, 20.93; H, 1.13; Br_2Cl, 64.67.

Dimethyl Dibromofumarate (XVII), $CH_3OCOCBr{=}CBrCOOCH_3$.—Dibromofumaryl chloride (15 g.) dissolved in methyl alcohol with the evolution of heat. The solution was decomposed in ice and sodium carbonate and was extracted with chloroform. The solution thus obtained was fractionally distilled under diminished pressure using a Vigreux column; 13.5 g. of colorless oil was obtained which finally solidified on cooling; yield 93%; colorless needles; melting point 41.5° (corr.) after several crystallizations from petroleum ether; boiling point 113–114° (corr.) at 5 mm.

Anal. Calcd. for $C_6H_6O_4Br_2$: C, 23.86; H, 2.00; Br, 52.93. Found: C, 23.95; H, 1.70; Br, 53.40, 53.44, 53.34.

Dimethyl dibromofumarate (0.5 g.) was dissolved in a solution of 0.15 g. of sodium in 10 cc. of alcohol and 1 cc. of water. After standing for eighteen hours, the solution was diluted with water, extracted with ether, acidified and again extracted with ether. This latter ether extract, on evaporation and vacuum desiccation, gave 0.4 g. of dibromofumaric acid.

***Cis* β-Benzoyldibromo-acrylic Acid (II), $C_6H_5COCBr{=}CBrCOOH$.**—A mixture of 150 g. of dibromomaleic anhydride, 120 g. of finely ground aluminum chloride[27] and

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[24] Jackson and Hill, *Ber.*, **11**, 1671 (1878).

[25] Salmony and Simonis, *ibid.*, **38**, 2584 (1905).

[26] Lossen and Treibich, *Ann.*, **384**, 324 (1911).

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

300 cc. of benzene was warmed gently for thirty minutes with mechanical stirring, and was then heated on a boiling water-bath for fifteen minutes. The dark colored pasty mass was decomposed in ice and hydrochloric acid, and the benzene layer separated and allowed to evaporate. The residue was crystallized from carbon tetrachloride; the yield of crude product melting at 78° was 124 g. (63%). A small amount of unchanged dibromomaleic anhydride was recovered from the filtrates.

The compound forms colorless crystals, melting point 92° (corr.) after repeated crystallizations from carbon tetrachloride; soluble in alcohol, ether, acetone; insoluble in ligroin; crystallizes from chloroform, and crystallizes from benzene and ethylene dibromide with solvent of crystallization.

Anal. Calcd. for $C_{10}H_6O_3Br_2$: Br, 47.87. Found: Br, 47.87.

When the above reaction mixture was heated for a greater length of time a small amount of colorless solid (m. p. 237.5–238°) was filtered from the benzene layer and was identified by a mixed melting point as 1,1-diphenyl-2-bromo-3-carboxyindene.

Samples of *cis* benzoyldibromo-acrylic acid in various solvents were subjected to the action of iodine or bromine and sunlight. Another sample was boiled with hydrochloric acid (20%) for several hours. In every case the acid was recovered unchanged.

Cis benzoyldibromo-acrylic acid (1 g.) was reduced with 2 g. of zinc dust and acetic acid. Considerable heat was evolved. The product was isolated by filtering, diluting with water, extracting with ether, evaporating and crystallizing the residue from water. A yield of 0.4 g. (80%) of β-benzoylpropionic acid melting at 114–115° was obtained and identified by a mixed melting point.

***Cis*-β-[2,4,6-trimethylbenzoyl]dibromo-acrylic Acid (XXVI)**, $(CH_3)_3C_6H_2COCBr{=}CBrCOOH$.—A mixture of 40 g. of dibromomaleic anhydride, 22 g. of mesitylene, 80 cc. of carbon disulfide, and 48 g. of aluminum chloride was refluxed for twenty minutes with efficient mechanical stirring. The red mass was decomposed in ice and hydrochloric acid. The carbon disulfide layer was separated and on cooling deposited 46.5 g. of nearly pure product melting at 153–154°; yield, 79%.

It forms pale yellowish rhombic crystals; melting point 157° (corr.) after three crystallizations from benzene: soluble in acetone, alcohol, ether, ethyl acetate and acetic acid; insoluble in cold chloroform and hot ligroin.

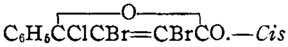
Anal. Calcd. for $C_{13}H_{12}O_3Br_2$: C, 41.52; H, 3.22; Br, 42.50. Found: C, 41.74; H, 3.23; Br, 42.43, 42.72.

***Cis* β-Benzoyldibromo-acrylic Methyl Ester (IV)**, $C_6H_5COCBr{=}CBrCOOCH_3$.—A solution of 25 g. of *cis* β-benzoyldibromo-acrylic acid in 40 cc. of methyl alcohol was saturated with dry hydrogen chloride and allowed to stand overnight. The solution was decomposed in ice and sodium carbonate, extracted with ether, dried with anhydrous potassium carbonate and distilled under diminished pressure. The crude ester boiled at 162–164° under 3.5 mm. pressure and solidified on cooling; yield, 19 g. (73%).

It gives colorless crystals; melting point 71.5° (corr.) after several crystallizations by dissolving in ethyl bromide, diluting with a little petroleum ether, seeding and allowing the solution to stand.

Anal. Calcd. for $C_{11}H_8O_3Br_2$: C, 38.04; H, 2.32. Found: C, 38.22; H, 2.37.

Hydrolysis.—The ester was allowed to stand overnight in a solution of a small excess of one equivalent of sodium in 95% ethyl alcohol. On diluting with water. acidifying, extracting with ether and crystallizing the product from carbon tetrachloride a sample of the *cis* acid was obtained and identified.

***Cis* β-(ψ)-Benzoyldibromo-acrylyl Chloride (III)**,  $C_6H_5\overset{\frown O \frown}{CClCBr{=}CBrCO}$.—*Cis* β-benzoyldibromo-acrylic acid (15 g.) was treated with 9 g. of phosphorus pentachloride.

The liquid product was diluted with petroleum ether, cooled and stirred until the acid chloride crystallized; yield, 12 g. (76%).

It forms colorless crystals; melting point 82.5° (corr.) after several crystallizations from chloroform and petroleum ether mixtures; soluble in chloroform and benzene; insoluble in ligroin; crystallizes unchanged from methyl alcohol, but gives an oil on long continued boiling.

Anal. Calcd. for $C_{10}H_5O_2Br_2Cl$: Cl, Br, 55.26. Found: 55.00.

A sample of the acid chloride was very slowly hydrolyzed upon standing in a moist condition for one week. The regenerated acid was isolated and identified.

In one experiment the crude acid chloride was shaken with water to remove the phosphorus oxychloride by hydrolysis. In a short time the acid chloride crystallized, was filtered, dried, recrystallized and identified.

Cis **β-(ψ)-[2,4,6-trimethylbenzoyl]dibromo-acrylyl Chloride (XXV),** $(CH_3)_3C_6H_2$-$\overbrace{\mathrm{CClCBr{=}CBrCO}}^{\mathrm{O}}$.—*Cis* β-mesitoyldibromo-acrylic acid (7.5 g.) was treated with 4.2 g. of phosphorus pentachloride. The mixture liquefied with the evolution of hydrogen chloride. On diluting with petroleum ether, cooling and subsequently evaporating, several crops of crystals were obtained; yield, 6.7 g. (85%).

It forms long colorless needles; melting point 76° (corr.) after three crystallizations from ligroin; soluble in hot methyl alcohol and crystallizes unchanged on cooling; soluble in hot ligroin, and in cold chloroform, acetone, benzene, ethyl acetate and acetic acid.

Anal. Calcd. for $C_{13}H_{11}O_2Br_2Cl$: C, 39.63; H, 2.81; Br, Cl, 49.52. Found: C, 39.76, 40.09, 39.63; H, 3.09, 3.10, 2.63; Br, Cl, 49.20.

Hydrolysis was accomplished by heating a sample of the acid chloride with water for five hours. The crude acid thus obtained was recrystallized from benzene and identified.

The above acid chloride was treated in several experiments with mesitylene, carbon disulfide and aluminum chloride, but only scarlet resinous products were obtained from which in a few cases small amounts of a colorless solid were isolated; melting point 240–242° after recrystallizing from alcohol; insoluble in chloroform and benzene; soluble in sodium carbonate and precipitated by acids.

Anal. Calcd. for $C_{21}H_{22}BrO_3$: C, 62.68; H, 5.51; Br, 19.87. Found: C, 63.01, 63.06; H, 5.56, 5.48; Br, 20.12, 20.36.

1,1-Diphenyl-2-bromo-3-carboxyindene (V), $\overline{\mathrm{C_6H_4C(COOH){=}CBrC}}(C_6H_5)_2$.—*Cis* (ψ)-benzoyldibromo-acrylyl chloride was treated with 50 cc. of benzene and 10 g. of aluminum chloride, and the mixture was stirred until it became a red pasty mass. Benzene (50 cc.) was added and the mixture was stirred and heated on a water-bath for fifteen minutes. After decomposing in ice the product was precipitated from the benzene layer by diluting with petroleum ether; yield, 9 g. (71%).

It gives colorless microscopic prisms; melting point (decomp.) 242–243° (corr.) after three crystallizations from benzene; when heated above its melting point carbon dioxide was evolved and was detected qualitatively; soluble in cold acetone, and hot alcohol and chloroform; insoluble in ligroin.

Anal. Calcd. for $C_{22}H_{15}O_2Br$: C, 67.53; H, 3.84; Br, 23.73. Found: C, 67.66; 67.50; H, 3.87, 3.99; Br, 25.71.

In a qualitative experiment a sample of dibromomaleil chloride was prepared by heating dibromofumaryl chloride with an excess of aluminum chloride at 100° for three hours.[6d] The crude mixture was treated directly (without isolating the acid chloride) with benzene and refluxed for half an hour. On decomposition in ice, a large amount of resinous amorphous product was obtained from which a small yield of 1,1-diphenyl-2-bromo-3-carboxyindene was isolated and identified.

A sample of the acid dissolved in one equivalent of dilute sodium hydroxide. The sodium salt crystallized as shining leaflets upon the addition of an excess of sodium ion. When dissolved in water, the sodium salt gave precipitates with salts of silver, copper, calcium, barium, lead and magnesium. The acid is stable in boiling sodium hydroxide solution.

Oxidation.—A solution of 6 g. of 1,1-diphenyl-2-bromo-3-carboxyindene, 3 g. of sodium hydroxide and 7.5 g. of potassium permanganate (a slight excess of the calculated amount) was boiled for a short time. The purple color persisted. In another run, using slightly less than the calculated amount of permanganate, the color was quickly discharged. The mixture was decomposed with hydrochloric acid and sulfur dioxide, and gave 3.75 g. (85%) of nearly pure diphenylphthalide, which was identified by analysis and by a mixed melting point with a known sample prepared from phthalyl chloride by the Friedel and Crafts reaction.

Anal. Calcd. for $C_{20}H_{14}O_2$: C, 83.90; H, 4.93. Found: C, 84.04, 83.69; H, 5.14, 5.06.

Trans **β-Benzoyldibromo-acrylic Methyl Ester (XXII),** $C_6H_5COCBr{=}CBrCOOCH_3$.—Methyl alcohol (10.5 g.) in 300 cc. of benzene was added over a period of two hours to 93 g. of well-stirred dibromofumaryl chloride. The mixture after standing for two hours was refluxed for five minutes. Aluminum chloride (120 g.) was then added in small portions to the effectively stirred mixture. Color appeared only after about one-third of the aluminum chloride had been added; hydrogen chloride ceased to be evolved after the addition of the last portion. The brown mass was stirred for ten minutes and was decomposed in ice and hydrochloric acid. The benzene layer was cooled and 15 g. of the very insoluble dibenzoyldibromo-ethylene melting at 203–206° was filtered off and identified. The benzene solution was fractionally distilled under diminished pressure. The fraction boiling at 110° under 3 mm. pressure rapidly solidified in the side arm and receiver and was identified as dimethyl dibromofumarate; yield, 8 g. An intermediate fraction (6 g.) was collected, and then 52 g. of *trans* benzoyldibromo-acrylic acid methyl ester distilled at 170–180° under 3 mm. pressure and solidified on cooling.

It forms colorless prisms; melting point 80.5° (corr.) after four crystallizations from a mixture of ligroin and ethyl bromide; soluble in acetone, chloroform, benzene, ether, ethyl acetate and acetic acid; crystallizes from alcohol in thin scales.

Anal. Calcd. for $C_{11}H_8O_3Br_2$: C, 38.04; H, 2.32; Br, 45.94. Found: C, 37.96; H, 2.32; Br, 45.93, 46.31, 45.78.

A sample of the ester was suspended in boiling 20% hydrochloric acid for several hours and was recovered unchanged. It was sensitive to boiling aqueous alkaline solutions, sodium carbonate yielding dark colored solutions, and sodium hydroxide cleaving the molecule to give a nearly theoretical yield of benzoic acid and a low-melting acid containing halogen which has not yet been investigated.

Trans **β-Benzoyldibromo-acrylic Acid (XIX),** $C_6H_5COCBr{=}CBrCOOH$.—*Trans* benzoyldibromo-acrylic methyl ester (30 g.) was dissolved in a solution of 3 g. of sodium in 300 cc. of ethyl alcohol and 15 cc. of water, and the mixture was allowed to stand overnight. The solution was then diluted with water, extracted with ether and acidified. A second extraction with ether removed the organic acid which was liberated. The product was isolated by evaporating the ether solution and inducing the oily residue to crystallize; yield 20 g. (70%).

It forms colorless prisms; melting point 108° (corr.) after four crystallizations from chloroform by adding ligroin and seeding; soluble in acetone, alcohol, ether, benzene, ethyl acetate and acetic acid.

Anal. Calcd. for $C_{10}H_6O_3Br_2$: C, 35.95; H, 1.81; Br, 47.87. Found: C, 35.91; H, 1.92; Br, 47.81.

Reduction in the usual way by means of zinc and acetic acid gave a good yield of β-benzoylpropionic acid. The acid was partially converted to the methyl ester on standing in methyl alcohol saturated with dry hydrogen chloride.

Trans **β-Benzoyldibromo-acrylyl Chloride (XXI),** $C_6H_5COCBr{=}CBrCOCl$.—*Trans* benzoyldibromo-acrylic acid (3.3 g.) reacted with 2.2 g. of phosphorus pentachloride to give a liquid product which was fractionally distilled under diminished pressure. The acid chloride distilled at 164° at 7 mm. pressure and solidified in the receiver; yield 2.5 g. (72%).

It forms colorless prisms; melting point 37° (corr.) after two crystallizations from petroleum ether; very soluble in chloroform and benzene.

Anal. Calcd. for $C_{10}H_5O_2Br_2Cl$: C, 34.02; H, 1.43; Br, Cl, 55.26. Found: C, 34.09; H, 1.70; Br, Cl, 55.50.

Hydrolysis by shaking a sample of the acid chloride with water gave a nearly quantitative yield of benzoyldibromo-acrylic acid.

Alcoholysis with methyl alcohol took place with the evolution of heat and with the formation of benzoyldibromo-acrylic methyl ester which was isolated and identified by a mixed melting point.

Trans **β-[2,4,6-Trimethylbenzoyl]dibromo-acrylic Methyl Ester (XXIII),** $(CH_3)_3C_6H_2COCBr{=}CBrCOOCH_3$.—A mixture of 6.5 g. of methyl alcohol, 25 g. of mesitylene and 160 cc. of carbon disulfide was allowed to run into 56 g. of well stirred dibromofumaryl chloride over a period of half an hour. The mixture, after standing for four hours was refluxed for a few minutes; seventy-five grams of aluminum chloride was then added in small portions. The mixture was finally decomposed in ice and hydrochloric acid. The carbon disulfide solution was successively cooled, evaporated and diluted with petroleum ether. Two crystalline products were isolated: 5.6 g. of the difficultly soluble *trans* dimesitoyldibromo-ethylene, and 25 g. of the more soluble *trans* mesitoyldibromo-acrylic methyl ester; yield, 36%.

It gives pale yellow, short, thick prisms; melting point 115.5–116° (corr.) after three crystallizations from benzene by the addition of petroleum ether, and one crystallization from ligroin; soluble in acetone, ether, ethyl acetate, acetic acid and hot alcohol.

Anal. Calcd. for $C_{14}H_{14}O_3Br_2$: C, 38.04; H, 2.32; Br, 40.97. Found: C, 37.99; H, 2.45; Br, 40.86, 41.05.

Trans **β-[2,4,6-Trimethylbenzoyl]dibromo-acrylic Acid (XXVI),** $(CH_3)_3C_6H_2COCBr{=}CBrCOOH$.—*Trans* mesitoyldibromo-acrylic methyl ester was hydrolyzed with cold alcoholic sodium hydroxide; 9.5 g. of the ester gave 2.5 g. of nearly pure acid; yield, 27%; pale yellow crystals; melting point 139° (corr.) after crystallizing twice from benzene and ligroin, and once from benzene; soluble in chloroform, acetone, ether, ethyl acetate, acetic acid and alcohol.

Anal. Calcd. for $C_{13}H_{12}O_3Br_2$: C, 41.52; H, 3.22; Br, 42.50. Found: C, 41.65, 41.69; H, 3.05, 3.61; Br, 42.25.

Trans **β-(2,4,6-Trimethylbenzoyl)dibromo-acrylyl Chloride (XXV),** $(CH_3)_3C_6H_2COCBr{=}CBrCOCl$.—*Trans* β-mesitoyldibromo-acrylic acid (1.05 g.) reacted with 0.65 g. of phosphorus pentachloride to give an oil. On adding petroleum ether 0.6 g. of the acid chloride crystallized; yield, 60%; very pale yellow crystals; melting point 73–73.5° (corr.) after several crystallizations from ligroin.

Anal. Calcd. for $C_{13}H_{11}O_2Br_2Cl$: BrCl, 49.52. Found: 50.06.

A sample of the acid chloride, when allowed to stand in water, was hydrolyzed to the acid.

When treated in the usual way with aluminum chloride, mesitylene and carbon disulfide, a good yield of *trans* dimesitoyldibromo-ethylene was obtained and identified by a mixed melting point.

A sample of the acid chloride was warmed with a little methyl alcohol. On cooling a crystalline product melting at 113° was isolated and identified by a mixed melting point as *trans* mesitoyldibromo-acrylic methyl ester.

Trans **Dibenzoyldibromo-ethylene (XVIII).**—*Trans* benzoyldibromo-acrylic acid (0.33 g.) was treated with one equivalent of phosphorus pentachloride and the product, without removing the phosphorus oxychloride formed, was treated directly with 5 cc. of benzene and 1.5 g. of aluminum chloride. The reaction mixture was heated to boiling and when the evolution of hydrogen chloride subsided it was decomposed in ice. The benzene layer, on cooling, deposited 2.5 g. of pure *trans* dibenzoyldibromo-ethylene; yield, 64%.

In a second experiment 10 g. of dibromofumaryl chloride was added to a well-stirred mixture of 50 cc. of benzene and 12 g. of aluminum chloride. The product was isolated as above. The yield of pure *trans* dibenzoyldibromo-ethylene was 10.5 g. (85%).

In a third experiment one equivalent of bromine was added to a boiling chloroform solution of dibenzoylacetylene. The yield of *trans* dibenzoyldibromo-ethylene was raised to about 60%, nearly twice that previously obtained[10] when the mixture was cooled. The *cis* isomer in this case was isolated in a relatively small yield.

Cis **Dibenzoyldibromo-ethylene.**[10]—A sample of *cis* dibenzoyldibromo-ethylene (1 g.) was treated with benzene and aluminum chloride. A red-brown mass was obtained. The mixture was heated to boiling, and was allowed to stand for one minute. The deep red mixture was decomposed in ice and the product isolated by extracting with ether and evaporating the solvent; 0.9 g. of nearly pure *cis* dibenzoyldibromo-ethylene melting at 102–104° was recovered and identified by a mixed melting point. No traces of the *trans* isomer were isolated.

In another experiment 0.5 g. of *cis* dibenzoyldibromo-ethylene in 10 cc. of benzene and 1 g. of dibromofumaryl chloride was treated with 4 g. of aluminum chloride. The red pasty mixture was heated for several minutes and was then decomposed in ice. On cooling and diluting the benzene layer with petroleum ether 0.95 g. of *trans* dibenzoyldibromo-ethylene was obtained. On evaporating the filtrate an oil was obtained which crystallized when taken up in alcohol to give 0.4 g. of unchanged *cis* dibenzoyldibromo-ethylene.

Trans **Di-(2,4,6-trimethylbenzoyl)dibromo-ethylene (XXIV),** $(CH_3)_3C_6H_2COCBr{=}CBrCOC_6H_2(CH_3)_3$.—Dibromofumaryl chloride (10 g.) was added slowly to a well-stirred mixture of 16 g. of aluminum chloride, 10 g. of mesitylene and 25 cc. of carbon disulfide. The product was decomposed in ice. The carbon disulfide layer, on cooling, deposited 7.5 g. of nearly pure product; yield, 49%; very pale yellowish crystals; melting point 198.5° (corr.) after four crystallizations from benzene; difficultly soluble in hot alcohol.

Anal. Calcd. for $C_{22}H_{22}O_2Br_2$: C, 55.25; H, 4.64; Br, 33.44. Found: C, 55.24; H, 4.64; Br, 33.53.

When benzene was used in place of carbon disulfide in the above experiment only the corresponding dibenzoyldibromo-ethylene was obtained as the product.

A sample (1 g.) reacted with zinc dust and acetic acid with the evolution of considerable heat. From the filtrate 0.57 g. of nearly pure dimesitoylethane melting at 135–136.5° was isolated and identified by a mixed melting point; yield, 95%.

Trans **1-Benzoyl-2-[2,4,6-trimethylbenzoyl]dibromo-ethylene (XXVIII)**, C_6H_5CO-$CBr{=}CBrCOC_6H_2(CH_3)_3$.—Benzoyldibromo-acrylic acid (1 g.) was treated with 0.67 g. of phosphorus pentachloride and the crude acid chloride was treated directly with carbon disulfide, 1 cc. of mesitylene and 2 g. of aluminum chloride. The red-brown mass was decomposed with ice, and the carbon disulfide layer was steam distilled. The oily residue was dissolved in methyl alcohol and on seeding deposited 0.15 g. of product; very pale yellowish crystals; melting point 102.5° (corr.) after two crystallizations from methyl alcohol, in which the substance dissolves when hot to give a yellow solution.

Anal. Calcd. for $C_{19}H_{16}O_2Br_2$: C, 52.30; H, 3.70. Found: C, 52.94; H, 3.86.

In a second experiment benzene was used as the solvent in place of carbon disulfide, but benzene reacted instead of mesitylene to give a good yield of *trans* dibenzoyldibromo-ethylene.

In a third experiment in which 0.1 g. of *trans* mesitoyldibromo-acrylyl chloride was treated with 1 cc. of benzene, 0.1 cc. of mesitylene and 0.6 g. of aluminum chloride, a yield of 0.06 g. of *trans* benzoylmesitoyldibromo-ethylene was isolated and identified by a mixed melting point.

Summary

Cis β-Benzoyldibromo-acrylic acid and a number of derivatives have been synthesized from dibromomaleic anhydride. The acid chloride is of the pseudo type and undergoes the Friedel and Crafts reaction to give 1,1-diphenyl-2-bromo-3-carboxyindene. The structure and mechanism of formation of the latter are discussed.

Trans β-Benzoyldibromo-acrylic acid and a number of derivatives have been synthesized from dibromofumaric acid. Incidental to the syntheses some new derivatives of dibromofumaric acid are described.

The unsaturated dibromo 1,4-diketones are prepared by the Friedel and Crafts reaction on the *trans* aroyl dibromo-acrylyl chlorides and on dibromofumaryl chloride. A method of preparing unsymmetrical, unsaturated dibromo 1,4-diketones is described.

The configurations of the unsaturated 1,4-diketones and ketonic acids are discussed.

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