analogous to those used in the preparation of phenylstearic acid, oleic acid also reacts with toluene and with naphthalene. In the latter case, carbon disulfide was used as solvent. The nature of the reaction appears to be the same in all these cases, but the products were not further studied.

Summary

1. Phenylstearic acid has been prepared from benzene and oleic acid. Its derivatives show a rather surprising reluctance to crystallize.

CHICAGO, ILLINOIS

[CONTRIBUTION FROM THE HAVEMEYER CHEMICAL LABORATORY OF NEW YORK UNIVERSITY]

STUDIES ON UNSATURATED 1,4-DIKETONES. III. THE MODE OF ADDITION OF HALOGEN TO DIBENZOYLETHYLENE

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Two stereo-isomers of dibenzoylethylene, $C_6H_5COCH{=}CHCOC_6H_5$, are known[1] and each adds halogen readily and quantitatively in acetic acid as the solvent to give almost exclusively the same (high-melting) dihalide, $C_6H_5COCHXCHXCOC_6H_5$. Two such dihalides are possible and as I have shown in the first paper[2] of this series, the lower-melting stereo-isomers are formed simultaneously but only in small amounts. When halogen adds to certain other unsaturated 1,4-diketones, in each case a similar pair of stereo-isomeric dihalides is obtained, the relative yields of which more nearly approach equality when the reactions proceed in chloroform at ordinary or somewhat elevated temperatures. On the basis of consistent physical relationships, these stereo-isomers may be classified as lower-melting or alpha, and higher-melting or beta, but there has been available practically no evidence to indicate which of these isomers corresponds to the *dl* and which to the *meso* forms.[3]

It is known that at —20° in chloroform, chlorine adds to the stereo-isomers of dibenzoylethylene to give almost exclusively in each case a different dichloride, the colorless *cis* modification yielding the alpha dichloride and the yellow *trans* isomer yielding the beta dichloride.[1c] In this research I have added bromine to the two isomers of dibenzoylethylene at —12° in chloroform and in each case, also, I have obtained almost exclusively a different dibromide; the colorless *cis* isomer yields (as with chlorine) the alpha dihalide, and the yellow *trans* isomer the beta dihalide.

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[1] (a) Paal and Schulze, *Ber.*, **33**, 3800 (1900); (b) **35**, 168 (1902). (c) Conant and Lutz, THIS JOURNAL, **47**, 881 (1925).

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

[3] Dibenzoyldibromo-ethane(β), $C_6H_5COCHBrCHBrCOC_6H_5$, was prepared, however, from *meso*dibromosuccinyl dichloride by Meyer and Marx [*Ber.*, **41**, 2469 (1908)]. A question has been raised concerning the identity of the acid chloride used [Ing and Perkin, *J. Chem. Soc.*, **125**, 1814 (1924)].

These isomeric dihalides yield the same products with reducing agents, ammonia, sodium acetate, sodium alcoholates, etc., and must correspond to *dl* and *meso* forms.

Since the addition of chlorine at low temperatures to the two isomers of dibenzoylethylene gives a different dihalide in each case, the addition must have taken place in the same stereochemical sense. This is likewise true of bromine addition. If the alpha dichloride and dibromide have the same configuration, and the beta isomers the reverse, then the mode of addition must be the same in all cases. In order to confirm this point and to decide whether halogen has added symmetrically (*cis*) or unsymmetrically (*trans*), one must know the configurations of the two isomers of dibenzoylethylene and the isomeric dihalides produced. The configurations of the colorless *cis*- and yellow *trans*-dibenzoylethylenes were assigned by Paal and Schulze[1b] on the basis of the relative ease with which they react with hydrazine to give diphenylpyridazine. Smedley,[4] because of evidence based on refractive indices and because of the higher melting point and lesser solubility of the colorless labile isomer, reversed these configurations; however, a number of unsaturated 1,4-diketones and their labile, colorless isomers have since been prepared[5] and their differences in melting points and solubilities show dibenzoylethylene to be an exception in this relation. Since in each case the colorless isomer is the labile form, requiring a definite absorption of light energy for its formation,[6] I shall assume that the configurations originally assigned are correct, although the evidence is perhaps not as complete as could be desired.

I have attempted in this research to determine the configurations of the products of the addition of halogen to these isomers of dibenzoylethylene by relating the resulting dihalides to the *dl*- and *meso*dichloro- and dibromosuccinic acids, the configurations of which are known.[7] By converting these acids with phosphorus pentachloride into the acid chlorides and treating them with aluminum chloride and benzene, it has been possible to obtain consistently in each case a different dihalide of dibenzoylethylene; the *meso*dichloro- and dibromosuccinic acids yield the beta (higher-melting) dibenzoyldichloro- and dibromo-ethanes, and the *dl* acids give the alpha (lower melting) dihalides. Assuming that the con-

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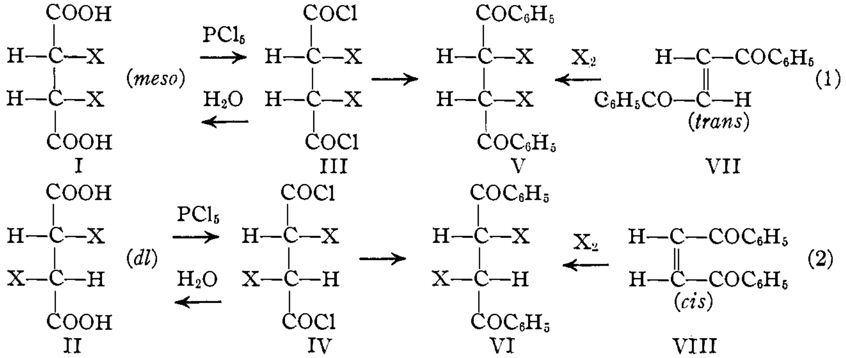
[4] Smedley, *J. Chem. Soc.*, **95**, 219 (1909).

[5] (a) Conant and Lutz, THIS JOURNAL, **45**, 1303 (1923). (b) Oddy, *ibid.*, **45**, 2156 (1923).

[6] The colorless modification, when allowed to stand with iodine or when heated with hydrochloric acid, passes readily into the yellow isomer. The reverse transformation is brought about in solution by the action of ultraviolet light. The inter-transformations of maleic and fumaric acids are exactly analogous [Stoermer, *Ber.*, **42**, 4870 (1909)].

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

figurations have remained unaltered, the following relationships are determined (X = Cl or Br).

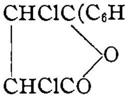


I III V VII

II IV VI VIII

That the configurations of the dihalides of dibenzoylethylene (V and VI) correspond to those of the halogen succinic acids (I and II) seems evident from the following considerations. Each halogen succinic acid passes readily into the acid chloride and back into the acid by hydrolysis, without reversing the configurations. The Friedel-Crafts reactions on the acid chlorides give consistently in each case a different dihalide of dibenzoylethylene in yields varying from 43 to 66%, and in no case were there isolated significant amounts of the isomer of reverse configuration.

Isomerization, unsymmetrical reaction and reaction with the alpha halogen atoms are possible. No evidence of the latter reaction was observed. There always remained oils which failed to crystallize and which resembled those often obtained with fumaryl chloride.[5a] These oils could not have contained significant quantities of isomeric dihalides because mixtures of these are easily separated. It is possible that traces of the low-melting isomers remained in the oils but this is probably not true of the higher-melting dihalides which are difficultly soluble and crystallize readily. In only one isolated experiment was there obtained evidence of isomerization; a trace of the beta dibromide was formed during the reaction with *dl*-dibromosuccinyl dichloride. Isomerization is, therefore, a negligible factor. When the Friedel-Crafts reaction upon *meso*dichlorosuccinyl dichloride was carried out under special conditions (the order of adding reagents being reversed), there was obtained a by-product corresponding to α,β-dichloro-γ,γ-diphenylbutyrolactone[8] (IX). This indicates that the acid chlorides are to a minor extent capable of reacting unsymmetrically.



IX

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[8] Analogous reactions are known to occur with (*a*) succinyl chloride [Auger, *Ann. chim. phys.*, [6] **22**, 310 (1891); *Bull. soc. chim.*, [2] **49**, 345 (1888)], and (*b*) phthalyl chloride [Baeyer, *Ann.*, **202**, 50 (1880)].

While the yields of dihalides in these Friedel-Crafts reactions are not all that could be desired, nevertheless the direction of the reactions is consistent, and it seems clear that the products bear a definite stereochemical relation to the halogen succinic acids from which they were synthesized. Walden inversions are known to occur in certain transformations of optically active, substituted succinic acids. The derivatives studied in this research (I and II) are symmetrically disubstituted; therefore, if such an inversion were to occur, it would affect both of the asymmetric carbon atoms, since they are similar, and the configurations would remain unchanged. A reversal of configuration (from *dl* to *meso*) can only occur if a partial inversion were to affect consistently but one of the two similar asymmetric carbon atoms, but there is at present no reason to suppose that this is possible.

On the basis of these considerations, then, I have drawn the following conclusions. The configurations of the alpha and beta isomers of the dihalides of dibenzoylethylene correspond to those of the *dl* and *meso* dihalogen succinic acids from which they were synthesized; the alpha dihalides are therefore *dl* and the beta are *meso*. As a consequence of this the mode of addition of halogens to *cis*- and *trans*-dibenzoylethylene is clearly consistent. Since the *cis* isomer adds halogen to give the *dl* dihalides which are unsymmetrical, and since the *trans* isomer yields the *meso* dihalides which are symmetrical, addition has in every case reversed the symmetry relations. The mode of addition is, therefore, unsymmetrical and *trans*, and is exactly analogous to the mode of addition of halogen to maleic and fumaric acids and their derivatives.[9]

Further studies in this field are in progress in this Laboratory.

Experimental Part

Addition of Bromine to *cis*-Dibenzoylethylene.—Thirty-four hundredths g. of bromine in chloroform as the solvent was added at —12° to a chloroform solution of 0.5 g. of *cis*-dibenzoylethylene. The color of bromine slowly disappeared, and after standing at —12° for one and one-half hours the solvent was evaporated in a current of air. A residue of 0.80 g. of α-*dl*-dibenzoyldibromo-ethane was obtained and identified; m. p., 108°. Upon fractional recrystallization from alcohol, 0.03 g. of β-*meso*dibenzoyldibromo-ethane was isolated and identified.

Addition of Bromine to *trans*-Dibenzoylethylene.—In an exactly similar experiment 0.34 g. of bromine was added to 0.5 g. of *trans*-dibenzoylethylene in chloroform at —12°. A yield of 0.84 g. of β-*meso*dibenzoyldibromo-ethane was obtained and identified; m. p., 178°. By fractional recrystallization from alcohol the amount of α-*dl* isomer was found to be less than 0.02–0.03 g.

Acid Chlorides of Substituted Succinic Acids.—*meso*-Dichloro- and dibromosuccinyl dichlorides were prepared[9] by adding halogens to fumaryl chloride. The *dl* acid chlorides were newly prepared in this research by treating the corresponding acids

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[9] Fumaryl chloride adds halogen practically quantitatively to give the acid chlorides of *meso*dihalogen succinic acid, and maleic anhydride to give the anhydride of the *dl* acid, etc. [Michael, *J. prakt. Chem.*, **46**, 392 (1892); **52**, 292 (1895)].

with phosphorus pentachloride. In some cases thionyl chloride was tried but the reactions were complicated by the formation of anhydrides. The *dl* acids were prepared by adding halogens to maleic anhydride and hydrolyzing the product.[9]

***dl*-Dichlorosuccinyl Dichloride** (IV).—Thirty-five g. of *dl*-dichlorosuccinic acid was treated with two equivalents of phosphorus pentachloride. In a short time the mixture melted; the liquid was decanted from a small amount of residue and separated from phosphorus oxychloride by distillation in a vacuum; yield, 37 g.; b. p., 78.5°, at 7 mm. The acid chloride crystallized readily; m. p., 39°. A sample was hydrolyzed and the crude product identified by mixed melting point as nearly pure *dl*-dichlorosuccinic acid.

Anal. Calcd. for $C_4H_2O_2Cl_4$: Cl, 63.4. Found: 63.5.

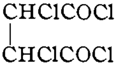
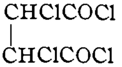
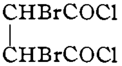
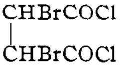
***dl*-Dibromosuccinyl Dichloride** (IV).—The preparation was exactly similar to the foregoing; b. p., 85°, at 4 mm. The acid chloride did not solidify on cooling. Upon hydrolysis a nearly pure sample of *dl*-dibromosuccinic acid was obtained and identified.

Anal. Calcd. for $C_4H_2O_2Br_2Cl_2$: Ag halide, 0.2511 g. Found: 0.2501 g.

Syntheses of the Dihalides of Dibenzoylethylene.—In a general procedure a solution of the acid chloride in benzene was added over a period of five minutes to a mechanically stirred mixture of finely ground aluminum chloride and benzene. The weight of aluminum chloride was twice that of the acid chlorides. The temperature rose and was moderated by cooling. Stirring was continued for another five minutes and the mixture was decomposed with ice. The *meso* dihalides usually crystallized at this point. The benzene layer was separated, washed and evaporated; the resulting oil was taken up in alcohol and caused to crystallize. The crude product was then fractionally recrystallized to isolate any by-products. Several experiments were carried out upon each acid chloride, and (with a minor exception, as noted) only one of the two possible dihalides was obtained as the product of each reaction.

TABLE I

PREPARATION OF DIHALIDES OF DIBENZOYLETHYLENE. TYPICAL DATA

Acid chloride		Wt., g.	Product	Yield G.	%
 $\begin{array}{l}\mathrm{CHClCOCl}\\ \vert\\ \mathrm{CHClCOCl}\end{array}$	*meso*	5	α-$C_6H_5COCHClCHClCOC_6H_5$ (*meso*)[a]	3.8	60
 $\begin{array}{l}\mathrm{CHClCOCl}\\ \vert\\ \mathrm{CHClCOCl}\end{array}$	*dl*	10	α-$C_6H_5COCHClCHClCOC_6H_5$ (*dl*)	8.4	66
 $\begin{array}{l}\mathrm{CHBrCOCl}\\ \vert\\ \mathrm{CHBrCOCl}\end{array}$	*meso*	5	β-$C_6H_5COCHBrCHBrCOC_6H_5$ (*meso*)	3.5	50
 $\begin{array}{l}\mathrm{CHBrCOCl}\\ \vert\\ \mathrm{CHBrCOCl}\end{array}$	*dl*	10	α-$C_6H_5COCHBrCHBrCOC_6H_5$ (*dl*)[b]	6.0	43

[a] A trace of α,β-dichloro-γ,γ-diphenylbutyrolactone was isolated in one of two experiments.

[b] A trace of the *meso* isomer was isolated in one of two experiments.

α,β-Dichloro-γ,γ-diphenylbutyrolactone (IX).—When aluminum chloride is added to *meso*dichlorosuccinyl dichloride in benzene (the reverse of the usual order of adding reagents), a small but significant yield of α,β-dichloro-γ,γ-diphenylbutyrolactone (IX) is obtained, whereas the yield of the normal product (V) is considerably below that obtained when the reagents are added in the usual order.

Forty g. of finely ground aluminum chloride was added in small portions to a solution of 20 g. of *meso*dichlorosuccinyl dichloride in benzene. After standing for 15 minutes the mixture was decomposed in ice, the benzene washed, separated and evaporated, and the product was fractionally recrystallized from alcohol; yields, 7.0 g. of *meso*-dibenzoyldichloro-ethane and 4.0 g. of α,β-dichloro-γ,γ-diphenylbutyrolactone. The latter crystallized from alcohol in balls of colorless radiating needles; m. p., 141–142°.

Anal. Calcd. for $C_{16}H_{12}O_2Cl_2$: Cl, 24.0. Found: 23.8.

Chromous chloride, zinc and acetic acid, zinc amalgam and sodium hydrosulfite failed to reduce the lactone to the γ,γ-diphenylbutyrolactone, although partial reduction in several cases was believed to have occurred. Further study is in progress on this and related substances.

The melting point of the lactone (141–142°), when mixed with different amounts of *meso*dibenzoyldibromo-ethane (m. p., 168°, with decomposition), is never lowered by more than 1.5–2.0° and not at all by small proportions of the latter substance although a large excess gives a melting point intermediate between the two. A slight turbidity results at the melting point and is followed by decomposition when completely melted. The mixtures reduce chromous chloride (in acetone) instantly, the dibenzoyldichloro-ethane being reduced to dibenzoylethane, whereas a pure sample of the lactone remains unchanged.

Preparation of γ,γ-Diphenylbutyrolactone.—Because of the analogy of the foregoing to the Friedel-Crafts reaction on succinyl chloride, the work was repeated and the method previously used was improved. Auger[8a] added aluminum chloride to a well cooled benzene solution of succinyl chloride, and allowed the mixture to stand for five hours. By slowly adding the acid chloride to well stirred benzene and aluminum chloride (the reverse order), I have obtained similar yields at a much higher temperature (40–50°), in a shorter time (15 minutes) and without the formation of significant amounts of β-benzoylpropionic acid; yields (from 14.5 g. of succinyl chloride), 3.5 g. of dibenzoylethane, 14.5 g. of γ,γ-diphenylbutyrolactone and 0.3 g. of β-benzoylpropionic acid.

Summary

Bromine adds very nearly quantitatively at low temperatures to *cis*- and *trans*-dibenzoylethylene to give exclusively in the first case α-, and the second case β-dibenzoyldibromo-ethane.

The alpha dihalides of dibenzoylethylene are obtained exclusively from *dl*-dichloro- and dibromosuccinic acids by the Friedel-Crafts reaction upon the acid chlorides, and the beta dihalides are obtained from the *meso* acids. The *dl* acid chlorides were newly prepared and revert to the *dl* acids upon hydrolysis.

Conclusions are drawn that the configurations of the dihalides of dibenzoylethylene correspond to those of the halogen succinic acids from which they were prepared, that the alpha dihalides are therefore *dl*, and the beta *meso*, and that the mode of addition of halogen to the two isomers of dibenzoylethylene is *trans*.

In a special procedure α,β-dichloro-γ,γ-diphenylbutyrolactone is obtained as a by-product in the Friedel-Crafts reaction upon *meso*dichlorosuccinyl dichloride.

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