p-diamino-diphenylthio-urea; it was identified by its qualitative reactions and by the mixed-melting-point method.

sym-p-**Diamino-diphenylthio-urea Dihydrochloride.**—A clarified solution of 30 g. of *p*-diamino-diphenylthio-urea in 270 cc. of water and 30 cc. of hydrochloric acid is poured into 7.5 liters of acetone; the voluminous precipitate is collected on a filter, washed with acetone and air-dried; yield, 37 g. The dihydrochloride is a slightly cream-colored powder that melts with decomposition and is very readily soluble in water.

Anal. Calcd. for $C_{13}H_{16}N_4SCl_2$: S, 9.67. Found: 9.47, 9.78.

The authors wish to thank Miss Hendry of the Department of Physiological Chemistry for making the nitrogen determinations reported in this paper. The expenses necessary for the pursuance of this investigation have been met from a fund for research in the Department of Tropical Medicine, given by a citizen of Boston.

Summary

1. Antimonyl tartrates of a number of organic bases have been studied but none of them is superior to tartar emetic (potassium antimonyl tartrate) toxicologically or trypanocidally.

2. When an aqueous solution of *sym-p*-diamino-diphenylthio-urea is refluxed, decomposition occurs whereby *p*-diphenylene-dithio-urea is formed.

BOSTON 17, MASSACHUSETTS

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF HARVARD UNIVERSITY]

UNSATURATED 1,4-DIKETONES

I. HALOGEN DERIVATIVES OF DIBENZOYL-ETHYLENE AND RELATED SUBSTANCES

BY JAMES B. CONANT AND ROBERT E. LUTZ

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The recently developed synthesis of dibenzoyl-ethylene from fumaryl chloride and benzene by the Friedel-Crafts reaction[1] makes readily accessible unsaturated 1,4-diketones of the general type, ArCOCH═CHCOAr. Such compounds are of interest because they contain the doubly conjugated system which is also characteristic of *para* quinones and because from them may be prepared substituted diaryl ethanes which readily pass into furanes and pyrroles. This paper deals primarily with the addition of chlorine and bromine to dibenzoyl-ethylene and the transformation of the resulting dihalogen compounds into a variety of substances; later papers will consider other addition reactions of unsaturated 1,4-diketones and the synthesis of certain substituted furanes and pyrroles.

Both the *cis* and *trans* forms of dibenzoyl-ethylene combine rapidly with bromine and chlorine; both isomers yield the same dibromide,[2] but

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

[2] Paal and Schulze, *Ber.*, **33**, 3800 (1900); **35**, 168 (1902).

with chlorine it is possible to obtain the two stereo-isomeric dichlorides. Each isomer gives principally one dichloride but the other is also obtained to some extent in each case. Both dichlorides form the same dichloro-diphenyl-furane on treatment with acetic anhydride and both on heating in alcoholic solution lose hydrogen chloride, yielding a high-melting dibenzoyl-chloro-ethylene. A stereo-isomeric chloro-ethylene is obtained by the addition of hydrogen chloride to dibenzoyl-acetylene,[3] and this may be converted into the high-melting isomer by the action of light *in the presence of iodine.*[4] These relationships are outlined below.

The two isomeric monochloro-ethylenes are undoubtedly *cis* and *trans* isomers, but we have no certain evidence at present on which to establish their configuration, and have therefore designated the labile isomer as alpha, the stable as beta, assuming that the change catalyzed by iodine and light represents a transformation from the labile to a stable form. Although one cannot assign final space formulas to the various compounds given above, certain interesting relationships may be pointed out. If one makes the probable assumption that the labile (α) chloro-ethylene has the *cis* configuration, then the stereochemical mode of addition of one molecule of hydrogen chloride to dibenzoyl-acetylene must be *cis.* Two molecules of hydrogen chloride unite with dibenzoyl-acetylene to form the high-melting dichloride (m. p., 167°). Since this reaction undoubtedly proceeds through the labile chloro-ethylene and the same dichloride is produced by the addition of chlorine to *trans*-dibenzoyl-ethylene, the mode of addition of the second molecule of hydrogen chloride to the acetylene compound and of the halogen to the ethylene compound must have taken place in the same stereochemical sense. If this mode of addition is also *cis,* the high melting dichloride would be the racemic compound. Since both dichlorides on prolonged heating yield the same (stable) monochloro-ethylene, no conclusions can be drawn in regard to their structure from their reactions.

Only one dibenzoyl-dibromo-ethane and only one dibenzoyl-bromo-ethylene were obtained. This latter substance is formed both by the elimination of hydrogen bromide from the dibromide and by the addition of hydrogen bromide to dibenzoyl-acetylene. It was not isomerized by the action of iodine in sunlight and appears to correspond to the stable chloro compound.

Further indications of *cis* addition to dibenzoyl-acetylene were obtained in our study of the action of halogens on this compound. The action of bromine on dibenzoyl-acetylene in chloroform solution at room tem-

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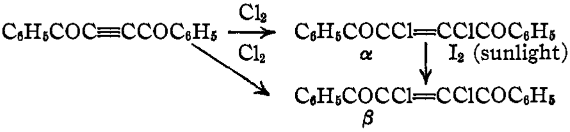
[3] Du Pont, *Compt. rend.,* **158,** 1349 (1914).

[4] As shown by the experiments with dibenzoyl-ethylene itself, this isomerization is in the reverse direction from that caused by light alone and is equivalent to heating with mineral acids; it is thus a change from a labile to a stable isomer, as in the case of the conversion of maleic to fumaric acid.

perature (the mixture being warmed to start the reaction) yielded a mixture of isomeric dibromo-dibenzoyl-ethylenes, the low-melting, labile isomer predominating. Similar results were obtained with chlorine. The labile isomers in both cases were readily converted into the stable isomers by the action of iodine in chloroform solution in sunlight. Considering the ease of this transformation, it seems most probable that the labile isomers in each instance were the primary products of the reaction and were partially isomerized into the stable isomers by the action of the halogen employed. If the *cis* configuration is assigned to the labile isomers, the addition of chlorine and bromine to dibenzoyl-acetylene must be regarded as primarily a case of *cis* addition.



$$\begin{tikzcd} C_6H_5COC{\equiv}CCOC_6H_5 \arrow[r, "Cl_2"] \arrow[dr, "Cl_2"'] & \underset{\alpha}{C_6H_5COCCl{=}CClCOC_6H_5} \arrow[d, "I_2\text{ (sunlight)}"] \\ & \underset{\beta}{C_6H_5COCCl{=}CClCOC_6H_5} \end{tikzcd}$$

When heated in a sealed tube in acetic acid solution dibenzoyl-acetylene combines with 4 atoms of bromine giving a tetrabromide.

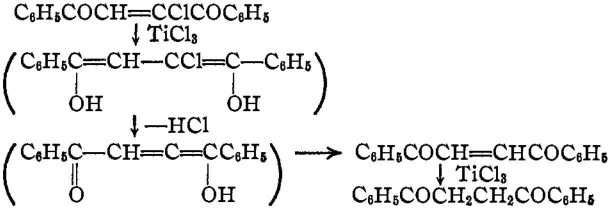
The configuration of the isomeric dibenzoyl-ethylenes rests on the ease of formation of a *ring compound with hydrazine*;[2] the *trans* compound is the stable isomer and is yellow, but contrary to the usual rule is lower-melting than the colorless *cis* isomer. In the case of the four other analogs of dibenzoyl-ethylene which have been obtained in both isomeric forms,[1] the stable isomer is in every case yellow and higher-melting than the labile isomer, which is colorless. The halogen derivatives of dibenzoyl-ethylene described above are colorless in both forms. In every case the labile isomer is lower-melting than the stable isomer, thus following the general rule to which dibenzoyl-ethylene itself seems to be the only known exception in the series of 1,4-diketones.

Reduction with Titanous Chloride

Dibenzoyl-ethane is formed by the action of titanous chloride at *room temperature* on acetone solutions of bromo-dibenzoyl-ethylene and dibromo-dibenzoyl-ethylene. Since the bromo-ethane, $C_6H_5COCHBrCH_2COC_6H_5$, is reduced to the ethane under the same conditions, this may well be an intermediate product in both reactions. Similar treatment of the chloro compounds yields the monochloro-ethane, $C_6H_5COCHClCH_2COC_6H_5$, which is not further reduced by the action of titanous chloride, either at room temperature or in boiling acetone. Strangely enough, however, chloro-dibenzoyl-ethylene is completely reduced to the ethane by *warming* with titanous chloride; since the chloro-ethane was not reduced in a parallel experiment, it cannot be an intermediate in this process. It seems probable that the reaction process first forms the di-enol,[5] and this substance

[5] Compare Conant and Lutz, THIS JOURNAL, 45, 1047 (1923).

at the temperature of boiling acetone then loses hydrogen chloride from the 1,4-position yielding dibenzoyl-ethylene which, of course, would be immediately reduced by the further action of titanous chloride.



$$\begin{array}{l} C_6H_5COCH{=}CClCOC_6H_5 \\ \quad\downarrow TiCl_3 \\ \left(C_6H_5\underset{\displaystyle OH}{\underset{|}{C}}{=}CH{-}CCl{=}\underset{\displaystyle OH}{\underset{|}{C}}{-}C_6H_5\right) \\ \quad\downarrow -HCl \\ \left(C_6H_5\underset{\displaystyle O}{\underset{\|}{C}}{-}CH{=}C{=}\underset{\displaystyle OH}{\underset{|}{C}}C_6H_5\right) \longrightarrow C_6H_5COCH{=}CHCOC_6H_5 \xrightarrow{TiCl_3} C_6H_5COCH_2CH_2COC_6H_5 \end{array}$$

The Action of Alkaline Reagents

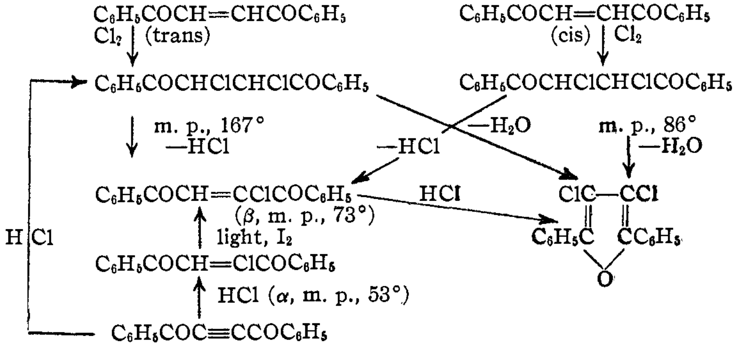
It was hoped that a convenient synthesis of dibenzoyl-acetylene might be realized by eliminating two molecules of halogen acid from dibromo- or dichloro-dibenzoyl-ethane. While there is no doubt that dibenzoyl-acetylene is formed by the action of alkaline reagents on the dihalides, we were unable to find conditions under which the acetylenic diketone could be isolated, as in every instance it immediately reacted with the reagent used for eliminating the halogen acid. Thus, with sodium ethylate or methylate in the corresponding alcohol, or sodium phenylate in ether, compounds of the type, $ArCOCH{=}\underset{\displaystyle OR}{\underset{|}{C}}COAr$ were obtained. Since dibenzoyl-acetylene itself when treated with the same reagents yielded identical products, there seems no doubt that the mechanism of the reaction was as follows.

$$ArCOCHXCHXCOAr \xrightarrow{-2HX} ArCOC{\equiv}CCOAr \xrightarrow{\substack{ROH \\ (RONa)}} ArCOC(OR){=}CHCOAr$$

We thus prepared a variety of unsaturated 1,4-diketones having alkoxyl or aroxyl groups in the α-position. A study of the "apparent reduction potentials" of these substances and of the chloro- and bromo-ethylenes discussed above will be reported in another paper. The only crystalline reduction product that could be isolated from methoxy-dibenzoyl-ethylene, ($C_6H_5COC(OCH_3){=}CHCOC_6H_5$) was the 1,4-diphenyl-2-methoxyfurane which was formed by the action of acetic acid and zinc. However, the reduction of α-(3-methylphenoxy)dibenzoyl-ethylene with chromous chloride proceeded normally yielding the crystalline ethane, $C_6H_5COCH_2$-$CH(OC_6H_4CH_3)COC_6H_5$.

Ammonia adds readily to dibenzoyl-acetylene, forming a yellow crystalline compound which is either α-amino-dibenzoyl-ethylene, C_6H_5COC-$(NH_2){=}CHCOC_6H_5$, or the isomeric imide, $C_6H_5COC({=}NH)CH_2CO$-C_6H_5. The same substance is obtained in good yields by the action of an alcoholic ammonia solution on dibenzoyl-dibromo-ethane, and the corresponding ditolyl compound was made in a similar fashion. Both substances are reduced by titanous chloride to the corresponding unsubstituted ethane, the amino group being eliminated, perhaps, by a mechanism such as that suggested above in connection with the reduction of chloro-dibenzoyl-ethylene. Because of the ease with which the substance is reduced to dibenzoyl-ethane, we prefer the amino-ethylene formula to the imide formula although further work will be necessary to decide definitely between the alternative structures.

The action of potassium acetate in alcoholic solution on dibenzoyl-acetylene or on dichloro- or dibromo-dibenzoyl-ethane yields a very unstable, yellow substance. Extreme difficulty was experienced in purifying the substance and the analyses were therefore not entirely satisfactory but indicated that the compound was an hydroxy-dibenzoyl-ethylene, $C_6H_5COC(OH)=CHCOC_6H_5$. The correctness of this formulation of its structure is further indicated by several reactions—it gives a deep color with ferric chloride, is a weak acid and forms an insoluble copper salt. So far we have been unable to transform it into any crystalline compounds and its structure therefore must be still regarded as somewhat problematical.



Besides the unsaturated 1,4-diketones described in our earlier paper we have now prepared and established the structure of the following compounds with a view to determine their apparent reduction potentials: di-(4-chloro-3-methyl-benzoyl)-ethylene, di-(2-chloro-5-methyl-benzoyl)-ethylene, di-(α - naphthoyl)-ethylene, di-(4-bromobenzoyl)-ethylene.

Experimental Part

Dibenzoyl-α,β-dichloro-ethane (HIGH-MELTING ISOMER), $C_6H_5COCHClCHClCOC_6H_5$.—Thirty g. of *trans*-dibenzoyl-ethylene was dissolved in acetic acid by warming the mixture slightly, and chlorine gas was passed into the solution until 9 g. had been added. The mixture was cooled, a small quantity of water added and the resulting crystalline precipitate filtered off. The yield was nearly quantitative and the crude product of high purity. Recrystallization from alcohol yielded a pure product melting at 167°; it was soluble in chloroform, ether, benzene, acetone and hot alcohol.

Anal. Calcd. for $C_{16}H_{12}O_2Cl_2$: Cl, 23.1. Found: 23.4.

The same compound was obtained by the action of dry hydrogen chloride on a chloroform solution of dibenzoyl acetylene; the solution was saturated with the gas at room temperature and allowed to stand for several hours. On evaporation, dibenzoyl-dichloro-ethane, m. p. 168°, was obtained and identified by mixed-melting-point determinations.

Low-melting Isomer.—Two g. of *cis*-dibenzoyl-ethylene was suspended in 30 cc. of chloroform, and chlorine gas was passed in at a temperature of —20° until the yellow color of chlorine persisted. The solvent was evaporated in a current of air and the residue recrystallized from a mixture of chloroform and petroleum ether; 0.15 g. of high-melting dichloride and 2.1 g. of low-melting dichloride (m. p., 86°) were obtained.

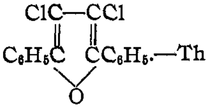
Anal. Calcd. for $C_{16}H_{12}O_2Cl_2$: Cl, 23.1. Found: 22.8.

Addition of Halogens to Other Unsaturated 1,4-Diketones

The compounds listed below were prepared by the action of bromine or chlorine on a solution of the *trans* isomer of the corresponding unsaturated 1,4-diketone in acetic acid or chloroform.

TABLE I

Name	Formula	M. p. °C.	Analysis Calcd.	Found
Ditoluyl-dichloro-ethane	$CH_3C_6H_4COCHClCHClCOC_6H_4CH_3$	210	Cl, 21.2	21.3
Di-(4-Chlorobenzoyl)dibromo-ethane	$ClC_6H_4COCHBrCHBrCOC_6H_4Cl$	201	0.1936 g. gave 0.2710 g. of mixed silver halides; calcd., 0.2744 g.	
Di-(4-Chloro-3-methylbenzoyl) dibromo-ethane	 $(Cl)(CH_3)C_6H_3COCHBrCHBrCOC_6H_3(Cl)(CH_3)$	207	0.1166 g. gave 0.1579 g. of mixed silver halides; calcd., 0.1571 g.	
Di-(2,4,6-Trimethylbenzoyl)-dibromo-ethane	$(CH_3)_3C_6H_2COCHBrCHBrCOC_6H_2(CH_3)_3$	207	Br, 33.2	33.3

1,4-Diphenyl-2,3-dichloro-furane,  —The high-melting dichloride was treated with acetic anhydride and a few drops of concd. sulfuric acid. After four hours the mixture was diluted with water and the solid thus obtained recrystallized from alcohol. From 0.2 g., 0.13 g. of the furane was thus obtained; m. p., 91°. The low-melting dichloride in a parallel experiment yielded the same substance. It was also formed by saturating an alcoholic solution of the beta isomer of dibenzoyl-chloro-ethylene with hydrogen chloride at 0° and allowing the mixture to stand for several hours. The product was obtained by diluting with water and recrystallizing from alcohol.

Anal. Calcd. for $C_{16}H_{10}OCl_2$: Cl, 24.5. Found: 24.3.

Monochloro-dibenzoyl-ethylene, $C_6H_5COCH{=}CClCOC_6H_5$ Labile Isomer (α).—To an absolute alcoholic solution of 1.5 g. of dry hydrogen chloride, 1 g. of dibenzoyl-acetylene was added.[3] The mixture was shaken until solution was complete and then allowed to stand for one hour. The reaction product was obtained by adding water, extracting the solution with ether, drying the extract with calcium chloride and evaporating it. The resulting oil solidified, and on recrystallizing from a mixture of alcohol and ether the substance was obtained as colorless crystals; m. p., 53°; yield, 0.6 g.

Anal. Calcd. for $C_{16}H_{11}O_2Cl$: Cl, 13.3. Found: 13.4.

STABLE ISOMER (β).—Ten g. of the high-melting dibenzoyl-dichloro-ethane (m. p., 167°) was heated with 600 cc. of 95% alcohol under a return condenser for 21 hours. The mixture was diluted with water and the oil that precipitated was allowed to crystallize slowly. It was purified by recrystallization from a mixture of ether and petroleum ether; 4 g. of nearly pure product, m. p. 74°, and 2 g. of a somewhat less pure material were obtained. By repeated crystallization the melting point was raised to 75°.

Anal. Calcd: for $C_{16}H_{11}O_2Cl$: 13.2. Found: 13.0.

The same compound was obtained by carrying out the same reaction with the low-melting dibenzoyl-dichloro-ethane.

ISOMERIZATION OF THE ALPHA TO THE BETA ISOMER.—A chloroform solution of the alpha isomer (m. p., 53°) containing a trace of iodine was exposed to strong sunlight for two hours. The product obtained after evaporation of the solvent and recrystallization of the residue melted at 73° and was identified as the beta isomer by mixed-melting-point determinations.

REDUCTION.—The alpha isomer was dissolved in acetone containing a little mineral acid and the solution treated with an excess of titanous chloride solution. After a short time, water was added and the product was recrystallized from alcohol. It was identified as dibenzoyl-chloro-ethane.[2]

The beta isomer in a similar experiment also yielded dibenzoyl-chloro-ethane. However, when the titanous chloride was added in excess to the acetone solution at its boiling point, the product was dibenzoyl-ethane. Several parallel experiments with dibenzoyl-chloro-ethane in hot acetone and titanous chloride yielded only unchanged material. Zinc and acetic acid, however, reduce dibenzoyl-chloro-ethane to dibenzoyl-ethane and also dibenzoyl-chloro-ethylene to the same substance.

Dibenzoyl-bromo-ethylene, $C_6H_5COCH{=}CBrCOC_6H_5$.—Twenty g. of dibenzoyl-dibromo-ethane[2] was heated in a mixture of 1 liter of 95% alcohol, 300 cc. of acetone and 20 cc. of water for 20 hours. After the solution had cooled, 9 g. of unchanged dibromide was recovered. The addition of water to the filtrate yielded an oil that slowly crystallized and from which by fractional crystallization from alcohol two compounds were obtained melting at 88° and 126°, respectively. The high-melting compound was difficult to purify and its structure has not yet been definitely established. The substance melting at 88° was also obtained in good yields by the action of hydrogen bromide on dibenzoyl-acetylene. This synthesis, together with the fact that it is readily reduced by titanous chloride in acetone (hot or cold) to dibenzoyl-ethane, proves that it is dibenzoyl-bromo-ethylene.

Anal. Calcd. for $C_{16}H_{11}O_2Br$: Br, 25.4. Found: 25.7.

The substance was unchanged after exposure to sunlight in a chloroform solution containing iodine. Attempts to prepare the labile isomer corresponding to the chloro compound by the action of the stoichiometric amount of hydrogen bromide in alcohol solution on dibenzoyl acetylene yielded only the same substance melting at 88°.

In connection with the mechanism of the reduction of dibenzoyl-bromo-ethylene, the action of titanous chloride on dibenzoyl-bromo-ethane in acetone solution was investigated. The action of this reagent at room temperature readily reduces the bromo-ethane to dibenzoyl-ethane in contrast to the chloro compound which is unaffected even at the boiling point of acetone.

Dibenzoyl-dichloro-ethylene, $C_6H_5COCCl{=}CClCOC_6H_5$ LABILE ISOMER (*α*).—A solution of 2 g. of dibenzoyl-acetylene in chloroform was treated with a small quantity of a chloroform solution of chlorine and the mixture warmed slightly to start the reaction. The remainder of the calculated quantity of the chloroform solution of chlorine was then added to the mixture cooled in an ice-bath. After 30 minutes the solution was evaporated to small volume and the crystalline material was filtered off; yield, 0.5 g.; m. p., 147–155° (see below, beta isomer). The filtrate was evaporated to dryness and the residue recrystallized from alcohol, yielding 1.2 g. of colorless crystals; m. p., 63–65°. After several recrystallizations the substance melted sharply at 66°.

Anal. Calcd. for $C_{16}H_{10}O_2Cl_2$: Cl, 23.3. Found: 23.3.

A small quantity of this substance was dissolved in acetone containing a little mineral acid and treated with an excess of titanous chloride solution. After one hour water was added and the product recrystallized from alcohol. It melted at 143° and was identified as dibenzoyl-chloro-ethane.

STABLE ISOMER (*β*).—The high-melting, less soluble substance that first separated from the reaction mixture described above, was recrystallized from alcohol; m. p., 162°. It was also obtained by exposing a chloroform solution of the alpha isomer containing a trace of iodine to strong sunlight for two hours.

Anal. Calcd. for $C_{16}H_{10}O_2Cl_2$: Cl, 23.3. Found: 23.4.

Dibenzoyl-dibromo-ethylene, $C_6H_5COCBr{=}CBrCOC_6H_5$ LABILE ISOMER (*α*).—A chloroform solution of 1 g. of dibenzoyl-acetylene was treated with a chloroform solution of the equivalent quantity of bromine, a small portion of the bromine being first added and the mixture warmed to start the reaction. After the reaction had once started the mixture was cooled in ice during the addition of the remainder of the bromine. The solution was evaporated to small volume and the first crystals which separated were filtered off. The less soluble material thus obtained weighed 0.4 g. and melted at 207–208°; it was the stable beta isomer described below. The filtrate on evaporation yielded a solid that after recrystallization from alcohol melted at 108°. A sample of it was treated in acetone solution with titanous chloride; after one hour water was added and the solid precipitate recrystallized. It melted at 138° and was identified as dibenzoyl-ethane.

Anal. Calcd. for $C_{16}H_{10}O_2Br_2$: Br, 40.6. Found: 40.7.

STABLE ISOMER (*β*).—The less soluble, high-melting compound mentioned above was purified by recrystallization from alcohol and melted at 213° when pure. It was also obtained from a chloroform solution of the alpha isomer to which a trace of iodine had been added and which had been exposed to sunlight for two hours.

Anal. Calcd. for $C_{16}H_{10}O_2Br_2$: Br, 40.6. Found: 41.0.

Dibenzoyl-tetrabromo-ethane, $C_6H_5COCBr_2CBr_2COC_6H_5$.—Dibenzoyl-acetylene does not combine with bromine readily in acetic acid, but when the mixture is heated for some time at 100° a tetrabromide can be formed. Thus, a solution of 2 g. of dibenzoyl-acetylene and 1.5 g. of bromine in acetic acid was heated in a sealed tube for ten hours at 100°. On working up the product, 1.1 g. of fine colorless needles, m. p. 150–157°, was obtained, together with some non-crystalline material. Recrystallization of the crystalline material from benzene yielded a pure compound; m. p., 188–188.5°.

Anal. Calcd. for $C_{16}H_{10}O_2Br_4$: Br, 59.9. Found: 59.9.

Dibenzoyl-methoxy-ethylene,[6] $C_6H_5COC(OCH_3){=}CHCOC_6H_5$.—A suspension of 24 g. of dibenzoyl-dibromo-ethane in absolute methyl alcohol was treated with the cal-

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[6] We are indebted to Mr. C. R. Kinney for the first preparation and analysis of this compound.

culated quantity of sodium methylate solution (made by dissolving metallic sodium in absolute methyl alcohol) and the mixture heated under a return condenser until all the dibromide had dissolved. Water was added to the solution and the precipitated organic substance recrystallized from alcohol. There was thus obtained 15 g. of material, m. p., 108.5°; yield, 93%. Similar results were obtained using dibenzoyl-dichloroethane in place of the dibromo compound.

A solution of dibenzoyl-acetylene in absolute methyl alcohol was treated with a drop of sodium methylate solution. The dibenozyl-methoxy-ethylene, m. p., 108.5°, crystallized from the solution.

Anal. Calcd. for $C_{17}H_{14}O_3$: C, 76.7; H, 5.3. Found: C, 76.4; H, 5.3.

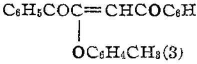
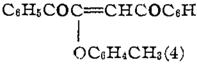
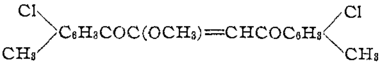
Dibenzoyl-phenoxy-ethylene, $C_6H_5COC(OC_6H_5){=}CHCOC_6H_5$.—A calculated amount of metallic sodium (2 equivalents to one of dibenzoyl-dibromo-ethane) was dissolved in an absolute ether solution of phenol, the mixture being heated under return condenser until all the sodium had dissolved. Dibenzoyl-dibromo-ethane was then added and an immediate reaction took place with the evolution of considerable heat; after a few minutes' further heating the reaction was complete. The ether solution was washed with water, dried and evaporated; the residue was recrystallized from alcohol and melted at 92°.

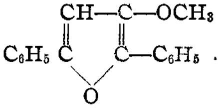
Anal. Calcd. for $C_{22}H_{16}O_3$: C, 80.0; H, 5.2. Found: C, 80.0; H, 5.2.

Other Alkoxy and Aroxy Unsaturated 1,4-Diketones.—A number of alkoxy and aroxy unsaturated 1,4-diketones were prepared from the corresponding dibromides and sodium alcoholate or sodium phenolate solutions according to the procedure outlined above for the methoxy and phenoxy compounds. They are listed in the following table; they were all colorless.

TABLE II

OTHER ALKOXY AND AROXY UNSATURATED 1,4-DIKETONES

			Analysis			
			Calcd.		Found	
Name of ethylene	Formula	M. p. °C.	C %	H %	C %	H %
Ditoluyl-methoxy-	$CH_3C_6H_4COC(OCH_3){=}CHCOC_6H_4CH_3$	100	77.0	6.1	77.1	6.3
Dibenzoyl-ethoxy-	$C_6H_5COC(OC_2H_5){=}CHCOC_6H_5$	103	76.7	5.8	77.0	5.7
Dibenzoyl-[3-methylphenoxy]-	 $C_6H_5COC(OC_6H_4CH_3(3)){=}CHCOC_6H_5$	104.5	80.7	5.3	80.4	5.5
Dibenzoyl-[4-methylphenoxy]-	 $C_6H_5COC(OC_6H_4CH_3(4)){=}CHCOC_6H_5$	165	80.7	5.3	80.6	5.7
Di-[4-chlorobenzoyl]methoxy-	$ClC_6H_4COC(OCH_3){=}CHCOC_6H_4Cl$	131	Cl =	21.2	Cl =	21.1
Di-[4-chloro-3-methylbenzoyl]-methoxy-	 $(Cl)(CH_3)C_6H_3COC(OCH_3){=}CHCOC_6H_3(Cl)(CH_3)$	123.5	Cl =	19.0	Cl =	19.4
Di-[2,4-dimethylbenzoyl]methoxy-	$(CH_3)_2C_6H_3COC(OCH_3){=}CHCOC_6H_3(CH_3)_2$	117.5	78.2	6.8	77.7	6.5
Di-[2,4,6-trimethylbenzoyl]methoxy-	$(CH_3)_3C_6H_2COC(OCH_3){=}CHCOC_6H_2(CH_3)_3$	120	79.0	7.2	78.7	7.6

1,4-Diphenyl-3-methoxyfurane,  .—A small quantity of dibenzoyl-methoxy-ethylene was reduced by heating with zinc and acetic acid. On diluting the mixture with water, a solid was obtained which after several recrystallizations from alcohol melted at 115°. With chromous chloride, vanadous chloride and sodium hydrosulfite only non-crystalline products were obtained.

Anal. Calcd. for $C_{17}H_{14}O_2$: C, 81.6; H, 5.6. Found: C, 81.0, 81.2; H, 5.9, 5.9.

Dibenzoyl-[3-methylphenoxy]-ethane, $C_6H_5COCH(OC_6H_4CH_3)CH_2COC_6H_5$.—An acetone solution of 2 g. of dibenzoyl-[3-methylphenoxy]-ethylene was treated with a solution of chromous chloride freshly prepared by reducing 3 g. of chromic chloride with zinc and hydrochloric acid. The reduction was very rapid. On diluting the mixture with water and recrystallizing the material from alcohol, a colorless crystalline solid was obtained; m. p., 111°.

Anal. Calcd. for $C_{23}H_{20}O_3$: C, 80.0; H, 6.0. Found: C, 80.0; H, 6.3.

Dibenzoyl-amino-ethylene, $C_6H_5COC(NH_2){=}CHCOC_6H_5$. — Twenty g. of dibenzoyl-dibromo-ethane was added to an alcoholic solution of ammonia and the mixture heated for 15 to 20 minutes until all the dibromide had dissolved. After the liquid had cooled, 12.5 g. of pale yellow crystals, m. p., 134°, was obtained; yield, 98%. Recrystallization from alcohol yielded a yellow substance; m. p., 137.5°. A qualitative test showed the presence of nitrogen. The substance has no basic properties.

Anal. Calcd. for $C_{16}H_{14}O_2N_2$: C, 76.5; H, 5.2. Found: C, 76.3; H, 5.2.

Dibenzoyl-amino-ethylene was also formed by heating dibenzoyl-dibromo-ethane with an alcoholic solution of ammonium acetate and by the action of the same reagent on dibenzoyl-acetylene at room temperature.

Reduction of dibenzoyl-amino-ethylene with vanadous chloride in acetone solution yielded dibenzoyl-ethane.

Ditoluyl-amino-ethylene, $CH_3C_6H_4COC(NH_2){=}CHCOC_6H_4CH_3$.—This yellow substance was obtained by the action of an alcoholic solution of ammonia on ditoluyl-dichloro-ethane; yield, 88%; m. p., 136°. Reduction with zinc and acetic acid or sodium hydrosulfite in alcohol yielded ditoluyl-ethane.

Anal. Calcd. for $C_{18}H_{17}O_2N_2$: C, 77.4; H, 6.2. Found: C, 77.1; H, 6.3.

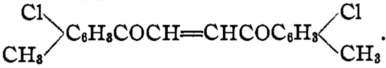
Dibenzoyl-hydroxy-ethylene.—To a solution of 30 g. of potassium acetate in ethyl alcohol was added 20 g. of dibenzoyl-dibromo-ethane and the mixture was heated under a return condenser until the reaction was complete as evidenced by the fact that the solid precipitate (potassium bromide) dissolved completely in water, showing the absence of the dibromo-ethane. Water and ice were then added to the dark-colored solution, and then dil. hydrochloric acid. The addition of acid precipitated an intensely yellow solid which was filtered off, washed and dried. It weighed 14 g. It was not found possible to purify this material completely, as when it was treated with most solvents only non-crystalline products were obtained. A certain amount of purification could be accomplished, however, either by dissolving it in cold dil. sodium hydroxide solution and precipitating with acid or adding petroleum ether to a benzene solution. Various samples showed different indefinite melting points between 60° and 100°. They all gave a characteristic dark color with ferric chloride and yielded a green copper salt when shaken in ether with aqueous copper acetate solution. The copper salt was soluble in hot alcohol and hot benzene.

Anal. Calcd. for $C_{16}H_{12}O_3$: C, 76.2; H, 4.8. Found: C, 78.0, 77.3, 77.8; H, 4.9, 4.9, 4.9.

COPPER SALT, *Anal.* Calcd. for $C_{32}H_{22}O_6Cu$: C, 68.0; H, 3.9; Cu, 11.2. Found: C, 68.6, 69.9; H, 4.4, 4.4; Cu, 10.7.

The same substance was formed by the action of potassium acetate on a hot alcoholic solution of dibenzoyl-dichloro-ethane and by heating dibenzoyl-acetylene with potassium acetate in alcoholic solution. The material was identified by its color, acidic properties, and the formation of the green, insoluble copper salt.

Di-(4-chloro-3-methylbenzoyl)-ethylene,



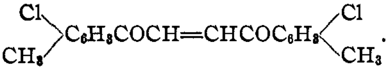
$${}^{\mathrm{Cl}}_{\mathrm{CH_3}}\!>\!\mathrm{C_6H_3COCH{=}CHCOC_6H_3}\!<^{\mathrm{Cl}}_{\mathrm{CH_3}}$$

.—To a well-stirred mixture of 40 g. of finely ground aluminum chloride and 40 g. of *o*-chlorotoluene diluted with carbon disulfide, 20 g. of fumaryl chloride was slowly added and the mixture then heated at 50–60° for two hours. The reaction mixture was treated in the usual manner, the product being recrystallized from alcohol; 20 g. of pale yellow crystals, m. p. 167°, was thus obtained; yield, 51%. The structure was established by oxidation with aqueous alkaline permanganate to chlorobenzene-2,4-dicarboxylic acid (m. p. above 250°; insoluble in water) and by fusion of the dibromide (see above) with sodium hydroxide. The latter reaction yielded 4-chloro-3-methylbenzoic acid; m. p., 209–210°.

Anal. Calcd. for $C_{18}H_{14}O_2Cl_2$: Cl, 21.3. Found: 21.5.

This substance is presumably the *trans* isomer.

Di(2-chloro-5-methylbenzoyl)ethylene,



$${}^{\mathrm{Cl}}_{\mathrm{CH_3}}\!>\!\mathrm{C_6H_3COCH{=}CHCOC_6H_3}\!<^{\mathrm{Cl}}_{\mathrm{CH_3}}$$

.—This substance was prepared exactly as was the 4-chloro-3-methyl compound, except that *p*-chlorotoluene was substituted for the *ortho* compound. A low yield (about 25%) was obtained, apparently because the reaction did not go to completion in the length of time employed (two hours at 50–60°); the odor of fumaryl chloride was evident in the reaction mixture. The product was purified by recrystallization from alcohol. It melted at 158° and was pale yellow. Its structure was established by oxidation with potassium permanganate, chlorobenzene-2,4-dicarboxylic acid, m. p. 286° (uncorr.) being obtained. Since *para*-chlorotoluene was used in the synthesis, the substance must be the 2-chloro-5-methyl compound to yield this acid on oxidation.

Anal. Calcd. for $C_{18}H_{14}O_2Cl_2$: Cl, 21.3. Found: 21.4.

Di(α-naphthoyl)ethylene, $C_{10}H_7COCH{=}CHCOC_{10}H_7$.—No satisfactory procedure for obtaining this compound was developed. Black tars were formed when the Friedel-Crafts reaction was carried out in the usual way and in every variation of the conditions that was tried. By extracting these tars with boiling alcohol, a small amount of yellow substance was obtained. Repeated crystallization from alcohol yielded a pale yellow crystalline powder; m. p., 140°. On oxidation with potassium permanganate this yielded α-naphthoic acid.

Anal. Calcd. for $C_{24}H_{16}O_2$: C, 85.5; H, 4.8. Found: C, 85.1; H, 5.2.

Di(4-bromobenzoyl)ethylene.[7]—This compound can be prepared in the usual manner from bromobenzene, fumaryl chloride and aluminum chloride, a 73% yield being obtainable without difficulty. It is very insoluble in cold water or alcohol, slightly soluble in hot acetone and fairly soluble in hot chloroform from which it crystallizes in yellow leaflets; m. p., 188.5°. It was reduced to the known di-(bromobenzoyl)-ethane by zinc and acetic acid or sodium hydrosulfite.[8]

Anal. Calcd. for $C_{16}H_{10}O_2Br_2$: Br, 40.6. Found: 40.5.

Summary

1. Two isomeric dichlorides can be obtained by the action of chlorine on the *trans* and *cis* forms of dibenzoyl-ethylene. Both yield a dichlorofurane when treated with dehydrating agents.

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[7] We are indebted to Mr. L. F. Lea for the preparation of this substance.

[8] Hale and Thorp, THIS JOURNAL, **35**, 272 (1913).

2. A labile and a stable dibenzoyl-chloro-ethylene can be prepared by the addition of hydrogen chloride to dibenzoyl-acetylene and by the loss of hydrogen chloride from the dichlorides of dibenzoyl-ethylene.
3. A labile and a stable dichloro- and dibromo-dibenzoyl-ethylene can be prepared by the addition of chlorine and bromine to dibenzoyl-acetylene.
4. The action of alcoholates and phenolates on dibenzoyl-dibromo-ethane first forms dibenzoyl-acetylene which then immediately adds a molecule of alcohol or phenol. Similar reactions can be carried out with the dibromides and dichlorides prepared from other unsaturated 1,4-diketones.
5. The action of ammonia on dibenzoyl-acetylene or dibenzoyl-dibromo-ethane yields dibenzoyl-amino-ethylene. The action of potassium acetate in alcohol on the same substances forms dibenzoyl-hydroxy-ethylene, an unstable acidic substance.
6. The action of reducing agents on certain substituted unsaturated 1,4-diketones is discussed.

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NOTE

Does Nicotine Combine with Calcium Ions?—The existence of a calcium-nicotine combination has been claimed in a recent paper by Graham and Carr.[1] From their experimental data it may be inferred that the reputed combination is not of the nature of nicotine of crystallization but rather a union between nicotine and calcium ions which is readily formed and which is difficultly soluble in water and in the ordinary organic solvents. Such a compound would be of decided practical interest, for its properties would need consideration in analytical methods for the determination of nicotine, in commercial methods for the extraction of nicotine, in formulas for dusting powders and in the selection or preliminary treatment of waters employed for preparing nicotine sprays and dipping baths.

Thatcher[2] already has criticized the report on general principles and for its possible failure to allow for the notable volatility of nicotine under certain conditions, but has not examined all the evidence in the detail that the importance of the matter appears to demand. Graham and Carr present three lines of evidence for the existence of their hypothetical combination, which will here be discussed in their original order.

First, they failed to obtain quantitative recovery of nicotine by the Kissling method in the presence of calcium compounds, even if only the powdered calcium carbonate regularly added as an absorbent. The pres-

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[1] Graham and Carr, THIS JOURNAL, **46**, 695 (1924).

[2] Thatcher, *ibid.*, **46**, 1539 (1924).