in a crystalline condition. This is the first acylthionamino acid to be described in the chemical literature. Acetylthionamino-acetate or its corresponding acid could not be separated.

NEW HAVEN, CONNECTICUT

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

STUDIES ON UNSATURATED 1,4-DIKETONES. I. SYNTHESIS AND STRUCTURE OF 1,2-DI(2,4,6-TRIMETHYLBENZOYL)-ETHENOL

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An interesting substance assumed to be an hydroxy-dibenzoyl-ethylene, $C_6H_5COC(OH){=}CHCOC_6H_5$ (dibenzoyl-ethenol), a tautomer of the hypothetical dibenzoyl-ethanone, $C_6H_5COCOCH_2COC_6H_5$, was described in a previous paper[1] dealing with certain derivatives of dibenzoyl-ethylene; it was prepared by the action of sodium acetate both on dibenzoyl-dibromoethane and on dibenzoyl-acetylene, which was considered to be an intermediate in the reaction. It was extremely difficult to purify the substance and the analyses were unsatisfactory; although a copper salt was prepared, no other crystalline derivatives were obtained from it and therefore the structure was not clearly established. Experiments were undertaken in an attempt to obtain more evidence concerning the structure of this substance and to prepare some derivative possessing somewhat modified properties, which could be more easily studied and in which the system, $ArCOC(OH){=}CHCOAr$, could definitely be shown to be present. It has been possible to prepare the dimesityl derivative, di(2,4,6-trimethylbenzoyl)-ethenol, $(CH_3)_3C_6H_2COC(OH){=}CHCOC_6H_2(CH_3)_3$, which has been successfully studied. This paper deals primarily with the synthesis and structure of this compound and its ketonic modification, and with the general reaction,

$$ArCOCHBrCHBrCOAr \xrightarrow{CH_3COONa} ArCOC(OH){=}CHCOAr \qquad (1)$$

A preliminary study was made of derivatives of di(bromobenzoyl)-ethylene,[2] $BrC_6H_4COCH{=}CHCOC_6H_4Br$, and a yellow substance was obtained which was difficult to purify but which gave a characteristic copper derivative and yielded satisfactory analyses. The substance was undoubtedly di(bromobenzoyl)-ethenol, $BrC_6H_4COC(OH){=}CHCOC_6H_4Br$.

When the mesityl group was substituted for phenyl the desired derivatives proved to be more crystalline in character, more easily purified

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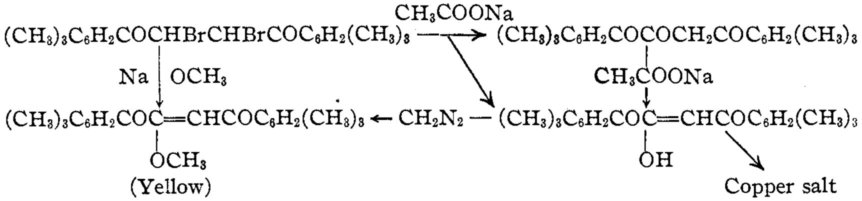
[1] Conant and Lutz, THIS JOURNAL, 47, 881 (1925).

[2] The Friedel and Crafts reaction with aluminum chloride, fumaryl chloride and aryl hydrocarbons has made easily accessible many derivatives of dibenzoyl-ethylene. Conant and Lutz, THIS JOURNAL, 45, 1303 (1923). See also Ref. 1.

and less sensitive to the action of solvents and chemical reagents. Bromine was added to di(2,4,6-trimethylbenzoyl)-ethylene to give simultaneously two stereo-isomers which varied considerably in relative yields under different experimental conditions. The dibromides, when treated with an alcoholic solution of various amounts of sodium acetate and under different thermal conditions, yielded two isomeric, yellow, crystalline substances. When an excess of sodium acetate was used and the period of heating was limited, a mixture of products was obtained from which small yields of di(2,4,6-trimethylbenzoyl)-ethanone, $(CH_3)_3C_6H_2COCOCH_2COC_6H_2(CH_3)_3$, was isolated, and the residual oils were shown to contain considerable amounts of the enolic modification. When a large excess of sodium acetate was used in alcohol with prolonged heating the dibromides (and also the triketone under these conditions) were converted in excellent yields into di(2,4,6-trimethylbenzoyl)-ethenol.

Analyses showed that these two substances were isomeric; their relation to each other was shown by the ready conversion of the ketonic modification into the enolic by the action of sodium acetate. The ketonic modification was the higher melting, reacted very slowly with bromine, and gave no copper salt even on long continued shaking with copper acetate solution. The enolic form was distinguished by its rapid and complete conversion into the copper salt and by the great speed with which it decolorizes bromine solutions.

The position of enolization was established by methylation of the enolic modification with diazomethane. A yellow monomethoxy derivative was obtained which proved to be the stereo-isomer of the normal, colorless di(2,4,6-trimethylbenzoyl)-methoxy-ethylene, $(CH_3)_3C_6H_2COC(OCH_3){=}CHCOC_6H_2(CH_3)_3$, which had been previously prepared from di(2,4,6-trimethylbenzoyl)-dibromo-ethane by the action of sodium methylate. This important relationship was shown by repetition of the preparation of the colorless isomer and the discovery and identification of the yellow stereo-isomer as a second though minor product of the reaction.



$$\begin{tikzcd}
(CH_3)_3C_6H_2COCHBrCHBrCOC_6H_2(CH_3)_3 \arrow[r, "CH_3COONa"] \arrow[d, "Na\ OCH_3"'] \arrow[dr] & (CH_3)_3C_6H_2COCOCH_2COC_6H_2(CH_3)_3 \arrow[d, "CH_3COONa"] \\
(CH_3)_3C_6H_2CO\underset{\substack{|\\ OCH_3\\ \text{(Yellow)}}}{C}=CHCOC_6H_2(CH_3)_3 & (CH_3)_3C_6H_2CO\underset{\substack{|\\ OH}}{C}=CHCOC_6H_2(CH_3)_3 \arrow[l, "CH_2N_2"'] \arrow[d] \\
 & \text{Copper salt}
\end{tikzcd}$$

Reactions analogous to the formation of dibenzoyl-ethenol and dibenzoylmethoxy-ethylene from dibenzoyl-dibromo-ethane or dibenzoylacetylene (an intermediate) have been studied. In the former case one may cite the action of sulfuric acid on benzoylphenyl-acetylene[3] to give

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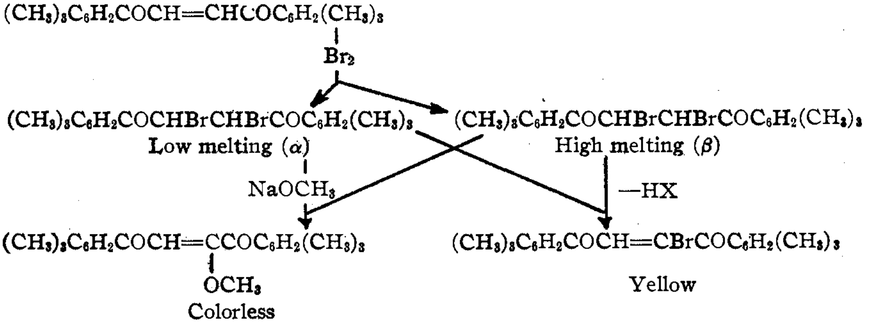
[3] Moureu and Delange, *Bull. soc. chim.*, [3] **25**, 302 (1901).

dibenzoylmethane, and in the latter the action of sodium ethylate on benzalacetophenone dibromide,[4] to give the ethyl ether of the enol of dibenzoyl-methane.[5]

Insofar as it has been studied di(2,4,6-trimethylbenzoyl)-ethenol behaves like oxalylacetone[6] and certain of its derivatives, which contain the same system of carbonyl groups in the 1,2,4 positions. Oxalylacetophenone,[7] a typical example, is known in but one modification and is presumably the enol, $C_6H_5COCH{=}C(OH)COOC_2H_5$, since it is acidic in character and readily forms a copper and a trimethylamine salt.[8] The enolic character of these substances has been confirmed by considerable evidence in other directions, including experiments on absorption of electric oscillations,[9] refractive index[10] and magnetic rotation.[11] One derivative of this type, the product of condensation of mesityl oxide and diethyl oxalate[12] by Claisen's method, has been prepared in two tautomeric modifications.

Dihalides of the Unsaturated 1,4-Diketones

In this research the dihalides of certain unsaturated 1,4-diketones were involved and a study of their preparations and certain of their properties has brought to light a number of new facts. In work previously reported[13] only one of the two possible stereo-isomeric dihalides has been obtained (except in the addition of chlorine to the *cis* and *trans* isomers of dibenzoyl-



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[4] Ruhemann and Watson, *J. Chem. Soc.*, **85**, 456 (1904). See also Pond, Maxwell and Norman, THIS JOURNAL, **21**, 955 (1899). Pond, York and Moore, *ibid.*, **23**, 789 (1901).

[5] Abell, *J. Chem. Soc.*, **101**, 989 (1912).

[6] Claisen and Stylos, *Ber.*, **20**, 2188 (1887). See also Schiff, *Ber.*, **31**, 1305 (1898).

[7] Beyer and Claisen, *Ber.*, **20**, 2178 (1887).

[8] Michael and Smith, *Ann.*, **363**, 55 (1908).

[9] Drude, *Ber.*, **30**, 955 (1897).

[10] Brühl, *J. prakt. Chem.*, **50**, 177, 203 (1894).

[11] Perkin, *J. Chem. Soc.*, **61**, 800 (1892).

[12] Claisen, *Ann.*, **291**, 39 (1896).

[13] Paal and Schulze, *Ber.*, **33**, 3800 (1900); **35**, 168 (1902). Oddy, THIS JOURNAL, **45**, 2156 (1923). See also Refs. 1 and 2.

ethylene to give in each case mainly a different dichloride).[1] The preparation of the dihalides from certain unsaturated 1,4-diketones was repeated. A second lower-melting, more soluble, diastereo-isomeric dihalide was found in practically every case, the relative yields of the stereo-isomers being dependent on experimental conditions.

From a brief study of the chemical and physical characteristics of the dihalides it has been possible to divide them into two distinct classes. This has been shown in Table I where the dihalides have been listed, together with their melting points.

TABLE I

STEREO-ISOMERIC DIHALIDES OF THE UNSATURATED 1,4-DIKETONES

	Melting points of—	
	α-Isomer, °C.	β-Isomer, °C.
Dibenzoyl-dibromo-ethane	107–107.5	179[a,b]
Dibenzoyl-dichloro-ethane	86[a]	167[a,b]
Di(bromobenzoyl)-dibromo-ethane	138	208.5[b]
Di(bromobenzoyl)-dichloro-ethane	129–129.5	213.5[b]
Di(2,4,6-trimethylbenzoyl)-dibromo-ethane	161.5	207[a,b]
Di(2,4,6-trimethylbenzoyl)-dichloro-ethane	...	215[b]

[a] Melting points previously reported.
[b] With decomposition.

The dihalides of one group of diastereo-isomers listed in the table as alpha, possess markedly lower melting points (not decomposing at that temperature), and are much more soluble in all organic solvents than those of the other group (beta) which, on the contrary, have relatively high melting points, all decomposing at that temperature, and have markedly low solubilities in most organic solvents.

That these substances are diastereo-isomeric was shown by reduction of both isomers with zinc and acetic acid to the same saturated 1,4-diketone, and by conversion by means of sodium methylate into the same methoxy derivative. Conversion of one diastereo-isomer into the other has been effected in one case and indicated that the beta is the stable isomer under these conditions; when dibenzoyl-dibromo-ethane (alpha) was heated in alcohol, partial conversion to the high-melting (beta) isomer took place, together with partial decomposition and loss of hydrogen bromide and the formation of dibenzoyl-bromo-ethylene. It is improbable that the isomerization proceeds by the elimination and re-addition of hydrogen bromide because of the small amount of hydrogen bromide necessarily present.

It would be of great interest to determine which of these groups of diastereo-isomers corresponds to the meso and which to the racemic compounds, especially because of the possible bearing on the question of *cis* and *trans* addition. It is hoped that a way will be found to solve this problem in an investigation which is under way in this Laboratory.

Mechanism

The mechanism of the reactions involved in the synthesis of the 1,2,4-triketone and its enolic modification has been studied by the use of the more easily obtained phenyl derivatives. The mechanism of the general reaction (1) obviously involves as the first step the elimination of a molecule of halogen acid. From compounds of the type ArCOCHBrCHBr-COAr, the first molecule of hydrogen bromide is eliminated with extreme ease, mere heating with certain solvents in many cases being sufficient to bring about the reaction; both isomeric dichlorides and dibromides of dibenzoyl-ethylene gave the same chloro- and bromo-ethylene although the reactions were never complete under the conditions employed.[1] In the case of the mesityl derivatives, however, the two dibromides, when heated for several hours in alcohol, were converted nearly quantitatively into the same di(2,4,6-trimethylbenzoyl)-bromo-ethylene, which was intensely yellow, in contrast to the various known chloro- and bromo-ethylenic derivatives of dibenzoyl-ethylene, all of which are colorless.[1] Furthermore, it was found that the action on dibenzoyl-dibromo-ethane of sodium acetate (in acetone), and of trimethylamine yielded mixtures of products among which small amounts of dibenzoyl-bromo-ethylene were isolated.

The proof that the second step in the reaction (1) involved the elimination of the second molecule of the halogen acid was attended with difficulties in that most of the reagents under the conditions employed apparently reacted further with the assumed intermediate acetylenic-diketone. This was particularly true of alkaline reagents such as sodium acetate in alcohol, sodium alcoholates, ammonia,[1] etc. In this connection, methylamine was found to react like ammonia with dibenzoyl-dibromo-ethane, two molecules of hydrogen halide being eliminated with the subsequent addition of one molecule of methylamine to the intermediate dibenzoyl-acetylene. The substance obtained[14] is probably dibenzoyl-methylamino-ethylene, $C_6H_5COC(NHCH_3){=}CHCOC_6H_5$, or the isomeric methylimine, $C_6H_5COC({=}NCH_3)CH_2COC_6H_5$, analogs of which have been prepared in another series by the action of various substituted amines on benzoyl-phenyl-acetylene.[15]

Two methods were finally developed which gave moderate yields of dibenzoyl-acetylene, thereby showing conclusively by actual isolation under special conditions, that this substance was an intermediate.[16] Trimethyl-

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[14] Dibenzoyl-methylamino-ethylene is readily reduced to dibenzoyl-ethane, as also is dibenzoyl-amino-ethylene. This ease of elimination of the amino group during reduction is interesting and characteristic, then, of compounds of this type, and is equivalent to de-alkylation.

[15] Andrew, *Ann. chim. phys.*, **29**, 569 (1913). See also Ruhemann and Cunnington, *J. Chem. Soc.*, **75**, 954 (1899).

[16] It has already been shown that dibenzoyl-acetylene itself will react with the same reagents and under the same conditions as will dibenzoyl-dibromo-ethane to give de-

amine, itself unable to react with the product, reacted on heating with dibenzoyl-dibromo-ethane to give dibenzoyl-acetylene. The reaction with sodium acetate was successfully modified by using a small amount of the reagent (a fraction of one equivalent), with acetone and 5% of ethyl alcohol as the solvent and in the presence of an excess of solid sodium carbonate, insoluble in this solvent, which served to regenerate the sodium acetate by reacting with the acetic acid formed. The procedure gave promise of usefulness as a method of preparing dibenzoyl-acetylene.

We may then write the following general series of reactions: $\mathrm{ArCOCHBrCHBrCOAr} \longrightarrow \mathrm{ArCOCH{=}CBrCOAr} \longrightarrow \mathrm{ArCOC{\equiv}CCOAr} \longrightarrow \mathrm{ArCOC(OH){=}CHCOAr}$.

The third step in this general reaction has not been clearly explained. In the reactions involving the addition of the elements of alcohol or water to dibenzoyl-acetylene to give the methoxy-ethylene or the ethenol, one must assume first the addition of the alkaline reagent, sodium alcoholate or sodium acetate, with subsequent decomposition of the sodium derivative formed, by alcohol water or acetic acid (which is one of the products of the general reaction with sodium acetate). That alcohol and acetic acid do not add to dibenzoyl-acetylene, the active intermediate in these reactions, is shown by the fact that the latter substance can be heated with safety in alcohol and acetic acid as solvents, addition taking place only in the presence of the sodium derivatives.

In the formation of di(2,4,6-trimethylbenzoyl)-ethenol it was shown that the enolic modification was stable under the conditions of the reaction and that the keto form was unstable and was slowly converted on continued heating with sodium acetate into the enol, with no apparent reaction taking place in the reverse direction. It seems, therefore, since apparently the ketonic modification is first formed in the reaction, that a mechanism involving 1,4-addition of one molecule of sodium acetate to the acetylenic diketone followed by hydrolysis or alcoholysis, $\mathrm{ArCOC{\equiv}CCOAr} \longrightarrow \mathrm{(ArCOCH{=}C(OCOCH_3)COAr)} \longrightarrow \mathrm{ArCOCH{=}C(OH)COAr}$, cannot take place, because this reaction should be incapable of yielding the ketonic modification except as a final product of a tautomeric shift in a direction impossible under these conditions. The mechanism, then, probably involves the 1,4-addition of two molecules of sodium acetate followed by hydrolysis or alcoholysis and loss of water or alcohol, and the formation first of the unstable ketonic modification, which then undergoes a tautomeric change to yield the stable enol as the final product of the reaction. $\mathrm{ArCOC{\equiv}CCOAr} \longrightarrow \mathrm{(ArCOCH_2C(OCOCH_3)_2COAr)} \longrightarrow \mathrm{ArCOCOCH_2COAr} \longrightarrow \mathrm{ArCOC(OH){=}CHCOAr}$.

rivatives (amino, methoxy, hydroxy, etc.) of dibenzoyl-ethylene. See Ref. 1. However, the possibility, highly improbable as it is. that these reagents may act by direct replacement of the halogen atom in the system $\mathrm{ArCOCH{=}CBrCOAr}$, as well as by addition to the acetylenic 1,4-diketone, has not been absolutely disproved.

A further study is being made of the chemistry and tautomeric relationship of di(2,4,6-trimethylbenzoyl)-ethenol and its ketonic modification.

Experimental Part

Halogen Addition Compounds with Unsaturated 1,4-Diketones.—In every case the dihalides were prepared by adding the calculated amount of halogen slowly to a solution or suspension of the unsaturated 1,4-diketone in a suitable solvent, acetic acid or chloroform. The two stereo-isomeric dihalides were separated by differences of solubilities; usually, the high-melting (beta) isomer crystallized out of the reaction mixture on cooling and the low-melting isomer was isolated from the mother liquors. The results of several experiments are given in Table II.

TABLE II

HALOGEN ADDITION COMPOUNDS WITH UNSATURATED 1,4-DIKETONES

	Solubility	Yield, %	M. p., °C.[a]	Analyses		
				Calcd., %		Found, %
$C_6H_5COCHBr$[b]	α S. CH_3COOH	14	107–107.5	Br	40.4	40.4
$C_6H_5COCHBr$	β Ins. CH_3COOH	82	179 decomp.	See Ref. 13		
$C_6H_5COCHCl$[b]	α S. CH_3COOH	31	86	See Ref. 1		
$C_6H_5COCHCl$	β Ins. CH_3COOH	49	167 decomp.	See Ref. 1		
$BrC_6H_4COCHBr$[c]	α S. $CHCl_3$	45	138	Br	57.74	57.87
$BrC_6H_4COCHBr$	β Ins. $CHCl_3$	55	208.5 decomp.	Br	57.74	58.00
$BrC_6H_4COCHCl$[c]	α S. $CHCl_3$	41	129–129.5	Ag	0.2268 g.	0.2293 g.
$BrC_6H_4COCHCl$	β Sl. s. $CHCl_3$	59	215.5 decomp.	Halides	0.2067 g.	0.2063 g.
$(CH_3)_3C_6H_2COCHBr$	α Sl. s. CH_3COOH, S. C_2H_5Br	6.4[b] 50[c]	161.5	Br	33.3	33.1
$(CH_3)_3C_6H_2COCHBr$	β Ins. CH_3COOH, C_2H_5Br	93[b] 50[c]	207 decomp.	See Ref. 1		
$(CH_3)_3C_6H_2COCHCl$ $(CH_3)_3C_6H_2COCHCl$	β Ins. C_2H_5OH, CH_3COOH Sl. S. $CHCl_3$		215 decomp.	Cl	18.2	18.6

[a] Melting points newly determined in this research are corrected for exposed mercury column.

[b] Addition of halogen carried out in CH_3COOH as solvent.

[c] In $CHCl_3$ as solvent.

[d] Addition of chlorine was slow and accompanied by chlorination. Only a small yield of one dichloride (corresponding to the beta isomer) was obtained.

The dihalides of each group (except those previously prepared) were reduced by means of zinc and acetic acid to the same dibenzoyl-ethane (or corresponding aryl derivative), and were converted by means of sodium methylate in the usual manner[1] into dibenzoyl-methoxy-ethylene (or the corresponding derivative).

Conversion of the Low-melting to the High-melting Isomer.—A sample of pure, low-melting (alpha) dibenzoyl-dibromo-ethane was heated in 95% alcohol under a return condenser for 20 hours, and on subsequent addition of water and fractional crystallization of the residue from alcohol, a mixture of products was obtained, consisting largely of unchanged material together with approximately a 10–20% yield of dibenzoyl-bromo-ethylene, 10–20% of high-melting (beta) dibenzoyl-dibromo-ethane and some residual oily mixtures.

Di(bromobenzoyl)-methoxy-ethylene, $BrC_6H_4COC(OCH_3){=}CHCOC_6H_4Br$.—Both stereo-isomers of di(bromobenzoyl)-dibromo-ethane were treated in the usual manner with solutions of two equivalents of sodium methylate in absolute methyl alcohol. In each case samples of the same methoxy derivative of di(bromobenzoyl)-ethylene were obtained in excellent yields. The product was purified by recrystallization from alcohol and was colorless; m. p., 155°.

Anal. Calcd. for $C_{17}H_{12}O_3Br_2$: Br, 37.7. Found: 37.9.

Di(2,4,6 - trimethylbenzoyl) - bromo - ethylene, $(CH_3)_3C_6H_2COCH{=}CBrCOC_6H_2(CH_3)_3$.—Four g. of di(2,4,6-trimethylbenzoyl)-dibromo-ethane was heated for 24 hours under a return condenser in an excess of 95% ethyl alcohol. The solution became yellow within a few minutes and the suspended dibromide dissolved slowly. When the liquid was cooled and diluted with water a crystalline solid of intense yellow color separated in a crude yield of 3.2 g. The substance was quite soluble in most organic solvents including chloroform and hot alcohol, and was recrystallized from small amounts of alcohol, and also from ligroin and petroleum ether; m. p., 110°. The same substance was obtained from the low-melting dibromide in nearly quantitative yield.

Anal. Calcd. for $C_{22}H_{23}O_2Br$: Br, 20.0. Found: 19.9.

Attempts were made to add bromine to this compound in chloroform, both at ordinary temperature and at 100° in a sealed tube, but considerable amounts of hydrogen bromide were evolved and oils were obtained, the material consisting mainly of a mixture of bromination products.

Di(bromobenzoyl)-ethenol, $BrC_6H_4COC(OH){=}CHCOC_6H_4Br$.—One g. of di(bromobenzoyl)-dibromo-ethane (beta) was heated with an alcoholic solution of 1 g. of sodium acetate until complete solution of the dibromide took place with the formation of a deep orange colored solution. On cooling and adding water acidified with hydrochloric acid, a yellow precipitate was obtained which was extremely soluble in most organic solvents, alcohol, chloroform, benzene and ether, but was sparingly soluble in petroleum ether and ligroin. The yield was 0.7 g. It was recrystallized from a concentrated alcoholic solution and was obtained as orange-colored crystals; m. p., 101.5–102.5°.

Anal. Calcd. for $C_{16}H_{10}O_3Br_2$: Br, 38.9. Found: 39.0, 39.1.

The substance was very sensitive to chemical reagents and formed resinous materials when heated with many solvents. When an ethereal solution of the substance was shaken with an aqueous solution of copper acetate a small yield of a brilliant green copper salt was obtained which was moderately soluble in ether. When treated with an ether solution of diazomethane immediate evolution of nitrogen took place.

Di(2,4,6-trimethylbenzoyl)-ethanone, $(CH_3)_3C_6H_2COCOCH_2COC_6H_2(CH_3)_3$.—Two and five-tenths g. of di(2,4,6-trimethylbenzoyl)-dibromo-ethane (beta) was heated for one and a half hours under a return condenser with 10 g. of sodium acetate and 75 cc. of absolute ethyl alcohol. Water was then added and the mixture was extracted with ether. An oil was obtained on evaporation which was taken up with ligroin and from which a yellow solid crystallized. The yield of nearly pure material was 0.95 g. The substance on repeated recrystallization from ligroin melted at 145–145.5°. The alpha isomeric dibromide was used in a similar experiment with the same results.

Anal. Calcd. for $C_{22}H_{24}O_3$: C, 76.4; H, 7.0. Found: C, 76.2, 76.4; H, 7.2, 7.1.

This substance in chloroform solution failed to react with bromine. On shaking an ethereal solution in which it was only sparingly soluble with an aqueous copper acetate solution, no formation of a copper salt nor change in color of the ethereal layer was observed. The substance on reduction with zinc and acetic acid yielded a colorless, oily material.

The ligroin filtrate from the crude precipitate of the triketone on evaporation yielded an oil of intense yellow color, which was taken up with ether, in which it was quite soluble, and the solution was shaken with an aqueous solution of copper acetate. An olive-colored, crystalline precipitate of the copper salt formed within a short time and showed that a considerable amount of the enolic modification was formed during the reaction.

Di(2,4,6-trimethylbenzoyl)-ethenol, $(CH_3)_3C_6H_2COC(OH)=CHCOC_6H_2(CH_3)_3$.—Five g. of di(2,4,6-trimethylbenzoyl)-dibromo-ethane was heated in alcohol for eight to ten hours with a large excess (20 g.) of sodium acetate, both stereo-isomers of the dibromide being used in several experiments with identical results. The mixture was treated with water, extracted with ether and the solution allowed to evaporate spontaneously. Nearly quantitative yields of crude yellow crystals were obtained which were very soluble in all organic solvents. The substance was recrystallized from small amounts of alcohol; m. p., 103.5–104.5°. A solution of the substance in chloroform decolorized a dilute solution of bromine instantly.

Anal. Calcd. for $C_{22}H_{24}O_3$: C, 76.4; H, 7.0. Found: C, 76.5; H, 7.2.

COPPER SALT.—An ethereal solution of this substance, when shaken with an aqueous solution of copper acetate, became dark green and in a short time deposited fine, scaly crystals with the ultimate discharge of color in the ether layer. The copper salt was olive or slate-colored and was obtained in nearly quantitative yield. It was sparingly soluble in all solvents.

Anal. Calcd. for $C_{44}H_{46}O_6Cu$: C, 72.0; H, 6.3. Found: C, 72.0; H, 6.8.

The ketonic modification was treated with sodium acetate under the conditions employed in the preparation of the enol and complete conversion took place into the enolic modification. A sample of the enol was heated with absolute ethyl alcohol, a small amount of acetic acid and a trace of sodium acetate, conditions which, when applied to di(2,4,6-trimethylbenzoyl)-dibromo-ethane, permitted the formation and isolation of the ketonic modification. The enol was recovered as the copper salt and no evidence of ketonization was noted.

Di(2,4,6-trimethylbenzoyl)-methoxy-ethylene (yellow isomer), $(CH_3)_3C_6H_2COC(OCH_3)=CHCOC_6H_2(CH_3)_3$.—One and two-tenths g. of di(2,4,6-trimethylbenzoyl)-ethenol was treated with an ethereal solution of an excess of diazomethane, and immediate evolution of nitrogen was observed. On evaporation of the ether a yellow solid was obtained which was recrystallized from alcohol; m. p., 107.5–108°; yield, 0.98 g.

Anal. Calcd. for $C_{23}H_{26}O_3$: C, 78.8; H, 7.5. Found: C, 78.54; H, 7.5.

The preparation of di(2,4,6-trimethylbenzoyl)-methoxy-ethylene (colorless isomer) by the action of sodium methylate and di(2,4,6-trimethylbenzoyl)-dibromo-ethane[1] was repeated. The main product obtained by recrystallization of the crude material from alcohol was colorless and melted at 120°. The filtrate was yellow and the remaining organic material was precipitated by diluting with water, and melted at 85–95°. It was fractionally recrystallized from ligroin. Considerable amounts of yellowish solid were obtained which on purification proved to be mainly the colorless modification. The final filtrate from the fractional crystallization was intense yellow. It was allowed to evaporate spontaneously and a mixture of colorless crystals was obtained together with a small number of short, thick, intensely yellow crystals which were picked out by hand and studied separately. The yellow substance was the more soluble and was difficult to separate from the predominating colorless isomer. It was roughly estimated that the yield of the yellow isomer was 1%. The crystals thus isolated melted at 106–107°. The mixed melting point with the previously prepared methoxy derivative from di(2,4,6-trimethylbenzoyl)-ethenol and diazomethane was 106.5–107°.

Preparation of Dibenzoyl-acetylene

Many variations of reagents, solvents, and conditions were tried in an attempt to eliminate two molecules of hydrogen bromide from dibenzoyl-dibromo-ethane and to stop the reaction at that point. The best conditions found made it possible to prepare dibenzoyl-acetylene from dibenzoyl-dibromo-ethane in moderate yields.

Fifty g. of the dibromide was treated with 0.5 g. of sodium acetate and 40 g. of sodium carbonate in 600 cc. of acetone and 40 cc. of absolute ethyl alcohol. The sodium acetate was slightly soluble and was present in insufficient concentration to react at all rapidly with the acetylenic diketone, but it was sufficiently reactive to eliminate hydrogen bromide from the dibromide. The sodium carbonate was insoluble in the solvent and served to regenerate the sodium acetate by reacting with the acetic acid liberated. The mixture was heated under a reflux condenser for two hours, then filtered to remove sodium carbonate and sodium bromide, diluted with a small amount of water, and allowed to crystallize; 12.5 g. of dibenzoyl-dibromo-ethane crystallized and was recovered. More water was added and a crude sample of dibenzoyl-acetylene crystallized slowly and on recrystallization gave 9.5 g. of pure material. Further addition of water gave 1.0 g. of dibenzoyl-bromo-ethylene and a residual oil. The yield of dibenzoyl-acetylene calculated from the dibromide actually used up in the reaction was 44%.

Dibenzoyl-methylamino-ethylene, $C_6H_5COC(NHCH_3){=}CHCOC_6H_5$.—Five g. of dibenzoyl-dibromo-ethane (beta) was treated with an excess of methylamine in alcohol and the mixture was warmed slightly until all of the solid dibromide had dissolved. On the addition of water, extraction with ether and partial evaporation of the solvent, a solid was obtained which was recrystallized from alcohol. Pale yellow scales were obtained melting at 164°. The yield was 1.0 g., and considerable oil was obtained as a by-product. Qualitative tests for nitrogen were positive. It was sparingly soluble in cold alcohol and ether.

Anal. Calcd. for $C_{15}H_{15}O_2N$: C, 77.0; H, 5.7. Found: C, 77.0; H, 5.8.

The substance was easily reduced by means of zinc and acetic acid to dibenzoyl-ethane.

Action of Dimethylamine on Dibenzoyl-dibromo-ethane.—In an experiment similar to that described above, dimethylamine (from a commercial grade of the hydrochloride) was used to eliminate hydrogen bromide from dibenzoyl-dibromo-ethane. Two products were obtained, one of which crystallized from an ether solution of the mixture. It melted at 164° and was identified as dibenzoyl-methylamino-ethylene, being produced apparently from methylamine as an impurity in the dimethylamine. The second product was separated by its greater solubility in ether. It crystallized in beautiful yellow needles upon the addition of petroleum ether; m. p., 96.5°. Qualitative tests for nitrogen were positive. The substance was reduced with ease to dibenzoyl-ethane by means of zinc and acetic acid.

Anal. Calcd. for $C_{19}H_{22}O_2N_2$: C, 73.5; H, 7.15. Found: C, 73.5, 73.5; H, 4.46, 7.1.

A further investigation is being made of these amino derivatives.

Action of Trimethylamine on Dibenzoyl-dibromo-ethane.—A sample of dibenzoyl-dibromo-ethane was heated in an alcoholic solution of trimethylamine. On decomposition with water and fractional crystallization of the mixture of products from alcohol, the following substances were isolated: unchanged dibenzoyl-dibromo-ethane, dibenzoyl-bromo-ethylene, dibenzoyl-acetylene, dibenzoyl-methylamino-ethylene (from methylamine as an impurity in the trimethylamine) and a small amount of an unidentified colorless substance melting above 230° which contained both nitrogen and halogen. The yield of dibenzoyl-acetylene, calculated from dibromide used up, was approximately 25%, and the yield of methylamino derivative 45%.

Summary

1. Two tautomeric modifications of a 1,2,4-triketone can be prepared from di(2,4,6-trimethylbenzoyl)-dibromo-ethane by the action of sodium acetate, the ketonic modification, di(2,4,6-trimethylbenzoyl)-ethanone, which is unstable when heated with sodium acetate, and the enol, di(2,4,6-trimethylbenzoyl)-ethenol.

2. Diazomethane reacts with the enolic modification to yield a yellow methyl ether which is stereo-isomeric with colorless di(2,4,6-trimethylbenzoyl)-methoxy-ethylene. The yellow isomer is formed in small amounts in the preparation of the colorless isomer from di(2,4,6-trimethylbenzoyl)-dibromo-ethane and sodium methylate.

3. Di(bromobenzoyl)-ethenol can be prepared by the action of sodium acetate on di(bromobenzoyl)-dibromo-ethane.

4. Two stereo-isomeric dibromides can be obtained by the addition of bromine to *trans*-di(2,4,6-trimethylbenzoyl)-ethylene, the relative yields varying considerably with conditions. Both isomers are reduced to the same ethane and react with sodium methylate to give the same di(2,4,6-trimethylbenzoyl)-methoxy-ethylene.

5. Two stereo-isomeric dichlorides and two dibromides of di(bromobenzoyl)-ethylene and a second isomeric dibromide of dibenzoyl-ethylene have been prepared by the action of halogens on the unsaturated 1,4-diketones.

6. Dibenzoyl-acetylene has been prepared in moderate yields from dibenzoyl-dibromo-ethane by the action of sodium acetate, and of trimethylamine.

7. Methylamine reacts with dibenzoyl-dibromo-ethane to give dibenzoyl-methylamino-ethylene.

8. Dibenzoyl-bromo-ethylene and -acetylene are shown to be intermediates in the formation of dibenzoyl-ethenol from dibenzoyl-dibromo-ethane. The mechanism of the reaction as applied to the mesityl derivatives is discussed.

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