

By the method of least squares, we find $b = 1.098$ and $c = 0.0993$. Hence

$$L_f = 4574 (b + 2cu) = 5022 - 9.08 \times 10^3(1/T - 1/T_0)$$

For the temperature $T_0 = 352.38$, we find $L_f = 5022$ cal.

B. Isodurene.—The data for the freezing points cover the range from 100 to 92% isodurene with a maximum depression of the freezing point of only four degrees. An analysis of the results leads to the conclusion that liquid isodurene has a higher heat capacity than solid isodurene, but the accuracy of the measurements is not sufficient to enable us to make a more exact statement. The molar latent heat of fusion of isodurene turns out to be about 2550 calories.

Summary and Conclusions

1. The freezing points of all of the polymethylbenzenes containing four or more methyl groups have been determined, using carefully purified materials.
2. A new method for making isodurene in quantity is given.
3. The freezing point diagram for the system durene-isodurene has been studied, and from these data the latent heats of fusion have been calculated.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF VIRGINIA]

1,6-ADDITION OF HYDROGEN TO UNSATURATED 1,4-DIKETONES

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RECEIVED MARCH 27, 1929

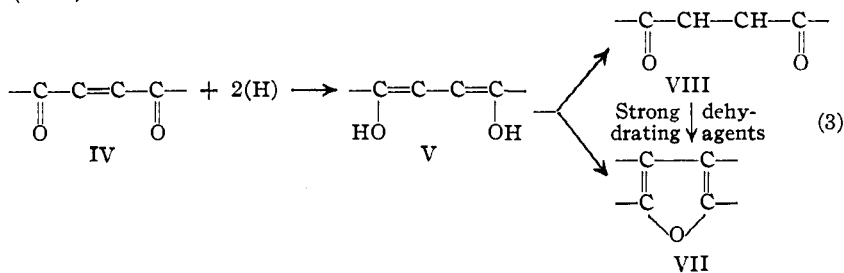
PUBLISHED OCTOBER 5, 1929

It is well known that conjugated systems of two or more multiple unions ending in oxygen are reduced with remarkable ease as compared with simple isolated ethylenic or carbonyl double linkages.¹ Typical examples are to be found in the conjugated systems of 1,2-diketones such as benzil, unsaturated 1,4-dicarbonyl and dinitro compounds such as fumaric and *o*-phthalic acids, unsaturated 1,4-diketones and ketonic acids, quinones, vat dyes and *o*-dinitrobenzenes; and doubly unsaturated 1,6-dicarbonyl and dinitro compounds such as muconic and *p*-phthalic acids and *p*-dinitrobenzene. The reductions of these compounds are generally interpreted as 1,4-, 1,6- or 1,8-addition of hydrogen to the terminal oxygen atoms to give dienols which, if the reductions are irreversible, immediately rearrange into stable forms or undergo some other secondary reaction such as the loss of water. Dibenzoyl ethylene (I), for example, is assumed to undergo the following changes in the course of reduction to dibenzoyl ethane (III).

¹ Thiele, *Ann.*, 306, 87 (1899); 308, 333 (1899).

Certain unsaturated 1,4-diketones behave in a peculiar manner toward reducing agents. Dibenzoyl-chloro-ethylene,⁷ $C_6H_5COCH=CClCOC_6H_5$, is reduced by titanous chloride to dibenzoyl-ethane, $C_6H_5COCH_2CH_2COC_6H_5$, but the reaction does not involve direct addition of hydrogen to the ethylenic double bond, as is shown by the fact that dibenzoyl-chloro-ethane, $C_6H_5COCH_2CHClCOC_6H_5$, is not reduced under these conditions and therefore is not an intermediate product. The chlorine must have been eliminated from some intermediate such as the dienol postulated by the theory of conjugate reduction.

It has been observed that the unsaturated 1,4-diketones, dibenzoyl-styrene,⁸ benzoyl-(trimethylacetyl)-styrene,⁹ and dibenzoylmethoxyethylene,⁷ are reduced under certain conditions to the corresponding triphenyl-, diphenyl-(*tert.*-butyl)- and diphenylmethoxyfurans; and that dibenzoylstilbene is reduced by zinc and acetic acid to a mixture of dibenzoyldiphenylethane and tetraphenylfuran.¹⁰ These isolated reactions have not been adequately studied. The formation of the furans, however, suggests that the mechanism of the reaction involves the formation, just as in Equation 1, of an intermediate dienol (V) which can undergo one or both of two possible transformations, dehydration to the furan (VII), and rearrangement into the stable saturated 1,4-diketone (VIII).



No evidence has been obtained in the experiments cited to show that the saturated 1,4-diketone (VIII) is not directly formed in the reduction, and that it would not itself be dehydrated to the furan under the experimental conditions. Dehydration to the furan is a characteristic reaction of saturated 1,4-diketones of this type, and is usually interpreted as enolization followed by the loss of water from the intermediate dienol¹¹ (second

⁷ Conant and Lutz, *THIS JOURNAL*, **47**, 883 (1925).

⁸ Japp and Klingemann, *J. Chem. Soc.*, **57**, 674 (1890); Japp and Burton, *ibid.*, **51**, 430 (1887).

⁹ Japp and Maitland, *ibid.*, **85**, 1496 (1904).

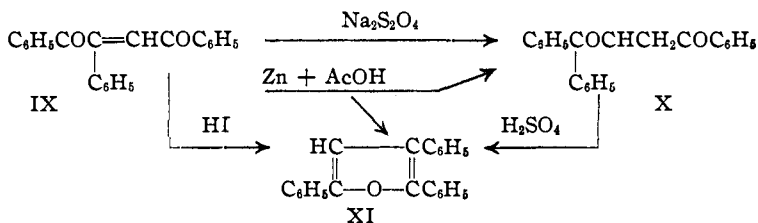
¹⁰ Zenin, *Z. Chem.*, **3**, 313 (1876); *Jahresber. Fort. Thier-Chem.*, 409 (1875); Dorn, *Ann.*, **153**, 358 (1870); Magnanini and Angeli, *Ber.*, **22**, 853 (1889).

¹¹ Smith, *Ann.*, **289**, 310 (1896); Knorr and Rabe, *Ber.*, **33**, 3801 (1900); Borsche and Fels, *ibid.*, **34**, 3877 (1906).

furans on any other hypothesis than that the dienol, already predicted by the theory, was actually formed as an intermediate product (Equation 3). Thus the theory of 1,6-addition of hydrogen to systems of this type seems to be strikingly confirmed.

Discussion of Results

Dibenzoylstyrene (IX) is reduced by zinc and acetic acid to a mixture of dibenzoylphenylethane (X) and triphenylfuran (XI), but under these conditions dibenzoylphenylethane, once formed, is stable and can be nearly quantitatively recovered unchanged in a test case. A much more powerful dehydrating agent (sulfuric acid) will convert it into the furan.¹²

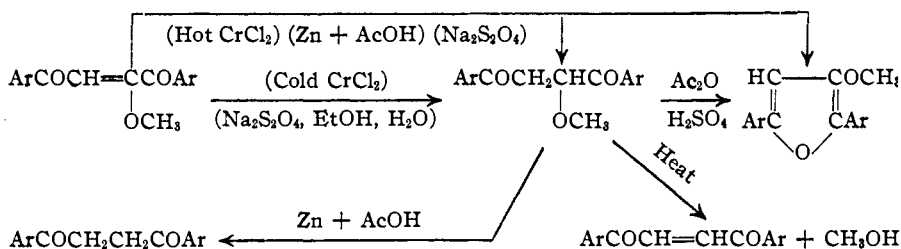


On varying conditions and temperature the relative yields of ethane and furan are greatly altered. Zinc added to a boiling acetic acid solution of dibenzoylstyrene gave the furan in the larger amount; heating a mixture to boiling (reduction nearly complete before actually boiling) gave a larger proportion of the ethane; heating a similar mixture diluted with alcohol, or heating in alcohol with sodium hydrosulfite, yielded only traces of the furan; heating with sodium hydrosulfite in an alcohol-water mixture gave a practically quantitative yield of ethane, no furan being isolated. Thus the yield of furan depends on conditions and solvent, the two extremes being boiling acetic acid, which favors dehydration, and the alcohol-water mixture, which does not. These results are consistent with Equation 3 and the obvious prediction of the theory, namely, that the relative yields of ethane and furan are determined by the velocities of the two competing reactions, ketonization and dehydration of the intermediate dienol, and that these reaction velocities, particularly that of dehydration, are in turn dependent on temperature and solvent.

The methoxy derivatives of dibenzoyl-, di-(chlorobenzoyl)- and di-(bromobenzoyl)-ethylenes, $\text{ArCOCH}=\text{C}(\text{OCH}_3)\text{COAr}$ ($\text{Ar}=\text{aryl}$), were reduced with zinc and acetic acid to the corresponding methoxy-ethanes. In many of the experiments the corresponding methoxy-ethanes, $\text{ArCOCH}_2\text{-CH}(\text{OCH}_3)\text{COAr}$, were also obtained in appreciable yields; in other cases, although probably formed in small amounts, they were not isolated in a crystalline form.¹⁸

¹² Smith, *J. Chem. Soc.*, **57**, 643 (1890).

¹⁸ The methoxy-ethanes of this series are low-melting solids which crystallize ex-



The methoxy-ethanes, prepared by other methods, were subjected to reducing conditions identical with those under which the unsaturated compounds were converted partly or largely into the corresponding furans. They were not always completely stable. Nevertheless, a variety of reducing conditions were found under which the unsaturated 1,4-diketones gave the furans, yet under which the corresponding methoxy-ethanes were not appreciably dehydrated. In a few cases traces of the furan were isolated, produced by the dehydrating action of the solvent, acetic acid, on the saturated 1,4-diketones; but the yields were in no case significant. In the tests upon dibenzoyl-methoxy-ethane no attempt was made to recover the unchanged material because of the experimental difficulty involved,¹³ but no appreciable conversion to the furan was observed (the furan is easily crystallized and significant amounts would have been found). In all of the other cases studied the bulk of the methoxy-ethanes was recovered unchanged and identified.

In many of the test experiments, particularly those carried out in acetic acid, small but definite amounts of the corresponding dibenzoylethanes, $\text{ArCOCH}_2\text{CH}_2\text{COAr}$, were produced by elimination of the methoxyl group. In one case a similar elimination of an aroxyl group was observed. The demethoxylated products were not obtained during reductions of the unsaturated 1,4-diketones where the furan was the sole or the main product. In qualitative tests it seemed that the methoxy-ethanes in the boiling solvents did not sufficiently decompose into the corresponding dibenzoylethylenes to account for the formation of the demethoxylated ethanes by reduction of this decomposition product. It would appear, then, that the methoxyl groups are directly reduced from the saturated methoxy 1,4-diketones.

The structures of the various products are shown by the transformations indicated above. The methoxy-ethanes in every case decompose on heating into the corresponding dibenzoylethylene and methyl alcohol, ceedingly slowly, particularly when they are obtained as oils and in a crude state. These properties explain why dibenzoylmethoxy-ethane was not obtained crystalline in an earlier investigation (ref. 7). In general these oils will stand for weeks before solidifying. Once well started crystallization occurs in from a few hours to several days or a week.

a reaction analogous to the easy elimination of water from β -hydroxy acids, and parallel with the decomposition of α -methoxy- β -(5-bromo-2,4-methoxybenzoyl)-propionic acid and its ester.¹⁴ Two of the methoxyethanes are dehydrated by means of acetic anhydride and sulfuric acid to the corresponding furans. Dibenzoyl-methoxy-ethane does not yield the furan but undergoes some transformation not yet understood.

On the basis of the theory of conjugate reduction the factor governing whether or not reduction will occur is the potential of the reducing agent,³ but the relative yields of furan and ethane should be independent of the nature and potential of the reducing agent,¹⁵ except for specific catalysis of either of the two competing reactions, ketonization and dehydration. It is difficult to predict the extent of this possible catalytic effect, but it is probably concerned mainly with the hydrogen-ion concentration rather than with any specific effect of the reducing agent itself. However, I think it may be said that if the nature of the solvent and the temperature are not greatly altered (even if the hydrogen-ion concentration varies somewhat) different reducing agents should give results of the same order. Thus if sodium hydrosulfite reduced an ethylene to the furan, then in the same solvent and at the same temperature reduction by means of chromous chloride, and even by zinc and acetic acid (assuming its reducing action to depend on potential), ought to give comparable yields of the furan.

Experiments in boiling 95% ethyl alcohol on two methoxyethylenes show that chromous chloride, sodium hydrosulfite and zinc and acetic acid give in each case considerable and comparable yields of the furan. With chromous chloride the yield of furan was rather low, but as a certain amount of water was present in the reagent the discrepancy in relative yields is not significant. The experiments are thus in qualitative agreement with prediction and are consistent with the view that the second step in Equation 3 is independent of the nature of the reducing agent,¹⁵ but is dependent on the nature of the solvent and its effectiveness in promoting dehydration. I hope to investigate this problem further.

The aroxy-dibenzoylethylenes, $C_6H_5COCH=C(OAr)COC_6H_5$, are easily reduced but usually only to the corresponding dibenzoyl-aroxy-ethanes. Reduction by zinc in boiling acetic acid and acetic anhydride, however, gives simultaneously the aroxy-ethanes and the furans; under these conditions the aroxy-ethanes are perfectly stable. Dibenzoyl-phenoxy-ethane decomposes into dibenzoylethylene and phenol on heating and can be readily converted by acetic anhydride and sulfuric acid into the furan.

¹⁴ Rice, *THIS JOURNAL*, 50, 229 (1928).

¹⁵ I refer to the ordinary reducing agents as distinct from "hydrogenating" agents such as platinum and hydrogen, the action of which certainly cannot be expressed in terms of reduction potential [Conant and Cutter, *ibid.*, 44, 2651 (1922)]. Investigation of the catalytic hydrogenation of the unsaturated 1,4-diketones is now under way in this Laboratory.

intermediate both in reduction of unsaturated 1,4-diketones and in dehydration of saturated 1,4-diketones) can either rearrange or pass into the furan by the loss of water. Furthermore, these results can be explained reasonably only by assuming the intermediate formation of this dienol in the process of reduction. Therefore, although the dienol has not been and probably cannot be isolated and studied directly, the evidence so far accumulated points clearly toward its existence momentarily as the primary intermediate reduction product, and thus affords confirmation of the theory of 1,6- or conjugate addition of hydrogen to the unsaturated 1,4-diketones and related substances.

Certain of the preliminary experiments on dibenzoylstyrene were carried out by Mr. William B. Brown at New York University, as a part of Senior Research under the Department of Chemistry.

Experimental Part

Preparation of Methoxy Unsaturated 1,4-Diketones.—The methoxy unsaturated 1,4-diketones were prepared by methods outlined in earlier investigations.^{7,17} The following preparation of the di-(chlorobenzoyl)-methoxy-ethylene (new) illustrates the general procedure employed.

dl-1,2-Di-(4-chlorobenzoyl)-1,2-dibromo-ethane, $C_{10}H_8Cl_2COCHBrCHBrCO-C_6H_4Cl$.—Seventy g. of di-(chlorobenzoyl)-ethylene (*trans*) was dissolved in hot chloroform and treated with a chloroform solution of 37 g. of bromine. The temperature was maintained at about 60° by the heat of reaction. On cooling 49 g. of nearly pure *meso*-dibromide⁷ separated, and on evaporation of the solvent 49.5 g. of nearly pure *dl*-isomer was obtained. The total yield of dibromides was 92%. The *dl*-isomer (new) was recrystallized from alcohol and was more soluble than the *meso*; m. p. 124.5°.

Anal. Calcd. for $C_{18}H_{10}O_2Cl_2Br_2$: Cl, Br, 49.53. Found: Cl, Br, 49.78.

When bromine was added to 50 g. of the ethylene in glacial acetic acid, 55 g. of the *meso*-dibromide crystallized from the mixture and 18 g. of the *dl*-isomer was isolated from the filtrate (total yield, 95%).

These results correspond with those previously reported on other dihalides of dibenzoylethylene;¹⁷ nearly equal yields of the two isomers were obtained using chloroform as the solvent at elevated temperature, but the product was largely *meso* when acetic acid was used. That the configurations are as I have assumed is evident by analogy to the mode of preparation and properties of the dihalides of dibenzoylethylene the configurations of which are known.¹⁸

1,2-Di-(4-chlorobenzoyl)-methoxy-ethylene, $C_{10}H_8Cl_2COCH=C(OCH_3)COC_6H_4Cl$.—Di-(chlorobenzoyl)-dibromo-ethane was treated in the usual way⁷ with two equivalents of sodium methylate. The colorless product was recrystallized from alcohol; m. p. 130°; soluble in hot alcohol and in cold chloroform, benzene and acetone; insoluble in cold alcohol and petroleum ether.

Anal. Calcd. for $C_{17}H_{12}O_3Cl_2$: Cl, 21.23. Found: Cl, 21.30.

Preparation of Dibenzoyl-aroxy-ethylenes

Dibenzoylphenoxy-ethylene.—The method of preparation formerly used⁷ involved the action of sodium phenolate in ether on dibenzoyldibromo-ethane. The procedure

¹⁷ Lutz, *THIS JOURNAL*, **43**, 2905 (1926).

¹⁸ Lutz, *ibid.*, **49**, 1106 (1927).

was altered. The sodium was first dissolved in absolute ethyl alcohol, treated with an excess of phenol and added to a suspension of dibenzoyldibromo-ethane in absolute ethyl alcohol. The method gave fair results and was rapid. Using *m*-cresol a mixture of two stereoisomers was obtained, analogous to the two di-(2,4,6-trimethylbenzoyl)-methoxy-ethylenes.¹⁷ One new compound was prepared by this method, dibenzoyl-(3-methoxyphenoxy)-ethylene.

In a typical experiment 20 g. of phenol was added to a solution of 5 g. of sodium in 200 cc. of absolute ethyl alcohol. This solution was added to a suspension of 40 g. of dibenzoyldibromo-ethane in 160 cc. of absolute alcohol. The mixture was boiled for a few minutes and diluted with water. The gummy precipitate was crystallized from alcohol and gave 21 g. of nearly pure dibenzoylphenoxy-ethylene (63%).

A 62% yield of dibenzoyl-(4-methylphenoxy)-ethylene was obtained by this method using *p*-cresol instead of phenol.

1,2-Dibenzoyl-(3-methoxyphenoxy)-ethylene, $C_6H_5COCH=C(OC_6H_4OCH_3\text{-}m)COC_6H_5$.—By the above method, using resorcinol monomethyl ether instead of phenol, a small yield (about 10%) of colorless crystals was separated from an oil and recrystallized from alcohol; m. p. 110°.

Anal. Calcd. for $C_{23}H_{18}O_4$: C, 77.08; H, 5.06. Found: C, 76.79; H, 4.93.

1,2-Dibenzoyl-(3-methylphenoxy)-ethylene (Low-Melting Isomer), $C_6H_5COCH=C(OC_6H_4CH_3\text{-}m)COC_6H_5$.—*m*-Cresol was substituted for phenol in the above reaction. The product obtained was partially separated by fractional crystallization from alcohol into the known dibenzoyl-(3-methylphenoxy)-ethylene (m. p. 103°),⁷ and a stereoisomer. The latter, purified by repeated recrystallization from alcohol, was obtained as nearly colorless needles which melted at 95° to a pale yellow liquid. When crystallized slowly the high-melting isomer (103°) gave bunches of flat, thin, long, radiating, colorless needles. The low-melting isomer (95°) gave long thick prisms which had a very pale yellowish luster. The latter probably corresponds in configuration to the yellow isomer of di-(2,4,6-trimethylbenzoyl)-methoxyethylene.

Anal. Calcd. for $C_{23}H_{18}O_3$: C, 80.69; H, 5.30. Found: C, 80.70; H, 5.32.

Reduction of both isomers by means of (a) chromous chloride, (b) zinc and acetic acid and (c) sodium hydrosulfite gave nearly quantitative yields of the known dibenzoyl-(3-methylphenoxy)-ethane.⁷ Zinc and acetic acid reductions failed to give appreciable amounts of a furan; in one case, however, a trace of dibenzoyl-ethane was isolated.

Preparation of Reduction Products

1,2-Dibenzoylmethoxy-ethane, $C_6H_5COCH_2CH(OCH_3)COC_6H_5$.—A mixture of 2 g. of dibenzoylmethoxy-ethylene, 5 g. of sodium hydrosulfite, 20 cc. of alcohol and 12 cc. of water, was boiled for forty minutes and diluted with water. The precipitated oil was dissolved in methyl alcohol and cooled; 0.04 g. of diphenylmethoxyfuran separated. The filtrate was diluted with water and the precipitated oil was separated and allowed to stand for several weeks. It finally crystallized and 1.5 g. of crude product (m. p. 41–43°) was obtained. It was quite soluble in most organic solvents but was insoluble in petroleum ether. The product tends to precipitate as an oil which crystallizes exceedingly slowly. Recrystallization was accomplished by dissolving the substance in ethyl bromide, cooling and diluting the solution with petroleum ether until very slightly turbid. The mixture was then seeded and allowed to stand in an ice-bath for four to six hours, during which time more petroleum ether was added. Colorless crystals formed slowly and after two such operations melted at 48.5–49°.

Anal. Calcd. for $C_{17}H_{16}O_3$: C, 77.25; H, 6.11. Found: C, 76.64; H, 6.08.

In a second experiment the time of heating was cut down to ten minutes; 1 g.

of furan was obtained from 10 g. of the ethylene. Since long heating does not appreciably affect the yield of furan, it follows that dibenzoylmethoxy-ethane, once formed, is stable and not appreciably dehydrated to the furan under these conditions.

Acetic anhydride and concd. sulfuric acid failed to dehydrate the ethane to the furan, but gave instead oils and a colorless solid which will be investigated further.

Decomposition of Dibenzoylmethoxy-ethane.—One-tenth gram of dibenzoylmethoxyethane was heated to 210–215° for twenty minutes. The molten mass turned yellow and decomposed with the evolution of a droplet of methyl alcohol which was collected and identified by conversion into the methyl ester of 3,5-dinitrobenzoic acid. The residue was crystallized from alcohol and gave 0.45 g. of dibenzoylethylene (identified by mixed melting point).

A small sample of dibenzoylmethoxy-ethane was boiled for a few minutes in an acetic acid–anhydride mixture. The solution remained colorless and no evidence of decomposition was observed.

2,5-Di-(4-chlorophenyl)-methoxyfuran, $\text{ClC}_6\text{H}_4\text{C}=\text{CH}-\text{C}(\text{OCH}_3)=\text{C}(\text{C}_6\text{H}_4\text{Cl})\text{O}$.—A mixture of 14 cc. of glacial acetic acid, 1 cc. of acetic anhydride, 6 g. of zinc dust and 2 g. of di-(chlorobenzoyl)-methoxy-ethylene was brought to a boil, filtered and poured into water. The product was crystallized from alcohol; yield, 1.1 g.; m. p. 114°.

Anal. Calcd. for $\text{C}_{17}\text{H}_{12}\text{O}_3\text{Cl}_2$: Cl, 22.14. Found: Cl, 22.22.

1,2-Di-(4-chlorobenzoyl)methoxy-ethane, $\text{ClC}_6\text{H}_4\text{COCH}_2\text{CH}(\text{OCH}_3)\text{COC}_6\text{H}_4\text{Cl}$.—A mixture of 6 g. of di-(chlorobenzoyl)-methoxy-ethylene, 25 g. of sodium hydrosulfite, 120 cc. of alcohol and 30 cc. of water was boiled under a reflux condenser for twenty minutes, cooled and diluted with water. The resulting oil, after standing for several weeks, was induced to crystallize. It was purified by dissolving in enough warm methyl alcohol to prevent immediate precipitation as an oil on cooling to room temperature. It was then seeded and allowed to stand for one to two days to crystallize. The yield of nearly pure material (m. p. 58–59°) was 5.7 g. It was soluble in hot ligroin, petroleum ether and alcohol but insoluble cold, and soluble in cold acetic acid, benzene, chloroform and ether. It formed colorless granular crystals, m. p. 61.5°.

Anal. Calcd. for $\text{C}_{17}\text{H}_{14}\text{O}_3\text{Cl}_2$: C, 61.45; H, 4.25; Cl, 21.35. Found: C, 61.47; H, 4.14; Cl, 21.04.

A small sample was converted by the action of acetic anhydride containing a trace of sulfuric acid into di-(chlorophenyl)-methoxy-furan, which was identified by mixed melting points. The yield was low.

Decomposition of Di-(chlorobenzoyl)-methoxy-ethane.—Two-tenth gram of di-(chlorobenzoyl)-methoxy-ethane was heated for ten minutes at 200° in a suitable apparatus. Decomposition took place. A droplet of distillate was obtained and identified as methyl alcohol by conversion into the methyl ester of 3,5-dinitrobenzoic acid. The dark orange residue was crystallized from acetone and gave 0.05 g. of yellow crystals which were identified by mixed melting points as di-(chlorobenzoyl)-ethylene.

In a qualitative experiment a sample of di-(chlorobenzoyl)-methoxyethane dissolved in an acetic acid–anhydride mixture to give a colorless solution which remained colorless on boiling. Failure to develop a yellow color indicated that no decomposition into dibenzoylethylene occurred.

2,5-Di-(4-bromophenyl)-methoxy-furan, $\text{BrC}_6\text{H}_4\text{C}=\text{CH}-\text{C}(\text{OCH}_3)=\text{C}(\text{C}_6\text{H}_4\text{Br})\text{O}$.—A mixture of 1 g. of di-(bromobenzoyl)-methoxy-ethylene, 2 g. of zinc dust and 15 cc. of glacial acetic acid was brought to a boil, filtered and diluted with water. The product (0.82 g.) was recrystallized several times from alcohol and obtained as a mat of colorless needles melting at 113°.

Anal. Calcd. for $C_{17}H_{12}O_2Br_2$: C, 50.01; H, 2.97; Br, 39.17. Found: C, 49.83; H, 3.01; Br, 39.45.

1,2-Di-(4-bromobenzoyl)-methoxy-ethane, $BrC_6H_4COCH_2CH(OCH_3)COC_6H_4Br$.—A mixture of 6 g. of di-(bromobenzoyl)-methoxy-ethylene, 120 cc. of alcohol, 30 cc. of water and 25 g. of sodium hydrosulfite was boiled for twenty minutes. On dilution with water an oil was obtained which was induced to crystallize after standing for several weeks. It was purified by dissolving in warm methyl alcohol, cooling, seeding and allowing to stand for twenty-four hours; yield, 4.5 g. The recrystallized product was colorless, melted at 72° and was soluble in benzene, acetone, ether and hot alcohol, and slightly soluble in cold alcohol.

Anal. Calcd. for $C_{17}H_{14}O_3Br_2$: C, 47.91; H, 3.32. Found: C, 47.93; H, 3.37.

Decomposition of Di-(bromobenzoyl)-methoxy-ethane.—Fifteen hundredths of a gram of di-(bromobenzoyl)-methoxy-ethane was heated to 210 – 220° for ten minutes. Decomposition took place and a droplet of methyl alcohol distilled and was identified as the methyl ester of 3,5-dinitrobenzoic acid. The yellow residue was dissolved in hot chloroform and 0.05 g. of yellow crystals was obtained and identified as di-(bromobenzoyl)-ethylene.

1,2-Dibenzoylphenoxy-ethane, $C_6H_5COCH_2CH(OC_6H_5)COC_6H_5$.—Reductions of 0.5 g. of dibenzoylphenoxy-ethylene by (a) chromous chloride and (b) sodium hydrosulfite gave, respectively, 0.47 g. and 0.49 g. of nearly pure dibenzoylphenoxy-ethane. The product was purified for analysis by recrystallizations from alcohol (m. p. 120°). Reduction of 1.65 g. of dibenzoylphenoxy-ethylene with zinc and acetic acid gave 0.9 g. of the ethane.

Anal. Calcd. for $C_{22}H_{18}O_3$: C, 79.99; H, 5.49. Found: C, 80.10; H, 5.77.

2,5-Diphenyl-3-phenoxyfuran, $C_6H_5C=CH-C(OC_6H_5)=C(C_6H_5)O$.—One gram of dibenzoylphenoxy-ethane was treated with acetic anhydride containing a drop of concd. sulfuric acid. Immediate reaction occurred accompanied by color formation. The mixture was decomposed in water and the product (0.9 g.) recrystallized several times from alcohol; m. p. 91° .

Anal. Calcd. for $C_{22}H_{16}O_2$: C, 84.57; H, 5.17. Found: C, 84.74; H, 5.12.

Decomposition of Dibenzoylphenoxy-ethane.—A sample of dibenzoylphenoxy-ethane was heated to 270° . A droplet of phenol distilled and was identified by its odor and conversion into tribromophenol. A good yield of dibenzoyl-ethylene was obtained by recrystallizing the dark colored residue.

1,2-Dibenzoyl-(4-methylphenoxy)-ethane, $C_6H_5COCH_2CH(OC_6H_4CH_3)COC_6H_5$.—Dibenzoyl-(4-methylphenoxy)-ethylene was reduced by (a) sodium hydrosulfite and (b) zinc and acetic acid, to give in each case nearly theoretical yields of dibenzoyl-(4-methylphenoxy)-ethane, which was obtained after repeated crystallization from alcohol as colorless crystals melting at 108.5° .

Anal. Calcd. for $C_{23}H_{20}O_3$: C, 80.18; H, 5.85. Found: C, 80.28; H, 5.84.

2,5-Diphenyl-3-(4-methylphenoxy)-furan, $C_6H_5C=CHC(OC_6H_4CH_3-p)=C(C_6H_5)O$.—One gram of dibenzoyl-(4-methylphenoxy)-ethane was dissolved in acetic anhydride containing a trace of concd. sulfuric acid. The mixture was decomposed with water and the product crystallized from alcohol; yield, 0.7 g.; m. p. (pure) 113° .

Anal. Calcd. for $C_{23}H_{18}O_2$: C, 84.60; H, 5.56. Found: C, 84.18; H, 5.59.

A Study of the Formation of Furans During Reduction of Unsaturated 1,4-Diketones

Methods of Reduction and Isolation of Products.—Three reducing

agents, sodium hydrosulfite, chromous chloride and zinc and acetic acid were used under different conditions in this research.

TABLE II
ACTION OF REDUCING AGENTS ON UNSATURATED 1,4-DIKETONES

Red. agent	Subs., g.	Solvent and conditions	Red. prods. and yields, %	Prods. from action of red. agents on corresponding satd 1,4-diketones, %
Dibenzoylphenylethylene				
Zn + AcOH	1.0	4 g. Zn + 15 cc. AcOH, Δ^a	Ethane, 44; furan, 29	Recov. ^b 93
	0.5	In 50 cc. Δ AcOH, add 1 g. Zn	Ethane, 34; furan, 52	Recov. 95
	5.0	75 cc. 95% EtOH, 25 cc. AcOH, Δ 1 h.	Ethane, 64; furan, 5.6
Na ₂ S ₂ O ₄	6	95% EtOH, Δ 1 h.	{ Mainly ethane; furan, 2
	0.5	75 cc. 63% EtOH, Δ 0.5 h.	Ethane, 90
Dibenzoylmethoxyethylene				
Zn + AcOH	2.0	Zn + AcOH, Δ	Furan, 75	Ethane, ^d 2, + oil ^{e,f}
	0.5	0.5 cc. AcOH, 25 cc. 95% EtOH, Δ 1 h.	Furan, 82 + oil ^e
Na ₂ S ₂ O ₄	2.0	20 cc. 75% EtOH, Δ 25 min.	Furan, 80 + oil ^e	Oil ^e
	2.0	32 cc. 60% EtOH, Δ 40 min.	{ Methoxyethane, 75; furan, 2
CrCl ₂ (EtOH)	2.0	In 95% EtOH, add CrCl ₂	Furan, 23%, + oil ^e	Ethane ^d (tr.) + oil ^e
	6.0	In 80 cc. cold 50% EtOH, add CrCl ₂ , then Δ	{ Methoxyethane, 40; ethane, ^d 5
Di-(4-chlorobenzoyl)-methoxy-ethylene				
Zn + AcOH	2.0	14 cc. AcOH, 1 cc. Ac ₂ O, Δ	Furan, 55	{ Recov. 40; ethane, ^d 10; furan, 4
	2.0	In 50 cc. AcOH at 70°, add Zn	{ Furan, 31; methoxyethane, 43; mixture, 10	{ Recov. 77; ethane 13; furan, 1.5
Na ₂ S ₂ O ₄	6.0	150 cc. 76% EtOH, Δ 20 min.	Methoxyethane, 95	Recov.
	2.0	100 cc. 95% EtOH, Δ 1 h.	Furan, 53
Di-(4-bromobenzoyl)-methoxy-ethylene				
Zn + AcOH	1.0	5 cc. AcOH, Δ	Furan, 82	{ Recov. 25; ethane ^{d,o} 20; furan, 16
		AcOH, EtOH (equal vol.), Δ	Largely furan	{ Recov. 61; ethane, ^d 6
	2.0	In AcOH at 70°, add Zn	{ Furan, 54; methoxyethane, 25
Na ₂ S ₂ O ₄	6.0	150 cc. 76% EtOH, Δ 20 min.	Methoxyethane, 75	Recov. 96
	3.0	150 cc. 95% EtOH, Δ 1 h.	{ Recov. 34; furan, 26; methoxyethane, 73	Recov. 95
CrCl ₂ (EtOH)		Cold 95% EtOH	{ Methoxyethane, furan (trace)
	2.0	In 50 cc. 95% EtOH, add CrCl ₂	{ Methoxyethane, 53; furan, 43
Dibenzoylphenoxyethylene				
Zn + AcOH	3.0	75 cc. AcOH, 25 cc. Ac ₂ O, Δ , add Zn	{ Phenoxyethane, ^h 60; furan, 37	Recov. 94
Dibenzoyl-(4-methylphenoxy)-ethylene				
Zn + AcOH	2.0	85 cc. AcOH, 25 cc. Ac ₂ O, Δ , add Zn	{ Aroxyethane, ⁱ 43; furan, 24	Recov. 91

^a The symbol " Δ " indicates heating the solution to boiling or heating at the boiling point (unless another temperature is specified).

^b "Recov." = starting material recovered unchanged.

^c When the amount of reducing agent is not specified a considerable excess was used. Reagents were added in the order named.

^d "Ethane" refers to the saturated 1,4-diketones from which the methoxyl or aroxy group has been eliminated.

^e The dibenzoylmethoxyethanes were often obtained as oils and in these cases no attempt was made to crystallize them. When dissolved in methyl alcohol and cooled, no crystalline products were isolated (other than those specified). Even small amounts of the furans crystallized from mixtures under these conditions. These residual oils are therefore assumed to consist largely of dibenzoylmethoxyethane.

^f If the furan is not mentioned it was not found among the products.

^g A sample of this ethane was prepared by reduction of the *dl*- and *meso*-di-(bromobenzoyl)-dibromo-ethanes by means of zinc and acetic acid, both isomers yielding the same di-(bromobenzoyl)-ethane (known), Hale and Thorpe, THIS JOURNAL, 35, 272 (1913).

^h The crude diphenylphenoxyfuran was freed from the last traces of the less soluble dibenzoylmethoxyethane by dissolving in hot alcohol and allowing to cool quietly to room temperature. The furan separated first and was filtered off rapidly; the ethane, remaining up to this point in supersaturated solution, immediately crystallized from the filtrate.

ⁱ The separation of the 4-methylphenoxy derivatives was facilitated by the following procedure. A hot alcohol solution of the mixture was allowed to cool quietly to room temperature and was seeded with the ethane. Bunches of radiating hair-like needles spread rapidly through the solution, and were quickly filtered off. The furan, remaining up to this point in supersaturated solution, rapidly crystallized from the filtrate and was obtained nearly pure.

The reductions with sodium hydrosulfite were carried out in alcohol as the solvent, but varying amounts of water were added in order to increase the solubility of the reducing agent and to decrease the dehydrating action of the solvent. The procedure was the same in every case. The substance being reduced was placed in a mixture of alcohol and water, sodium hydrosulfite was added and the mixture was boiled under a reflux condenser. The products were isolated by diluting the mixture with water, allowing the gummy precipitate to settle out (usually overnight) and then fractionally crystallizing the residue in order to isolate the components; products in every case were identified finally by mixed melting points with known materials. The yields in Table II refer to nearly pure products actually separated out, and which melted within a few degrees of the theoretical.

Reductions with zinc and acetic acid were carried out by heating a mixture of the substance and the reducing agent under the conditions selected, followed by rapid suction filtration while hot to remove the zinc. The filtrate was diluted with water and allowed to stand (usually overnight) until the gummy precipitate settled. The residue was separated by fractional crystallization (usually from alcohol) into its components, which were identified in every case by mixed melting point methods.

Chromous chloride reductions were carried out in alcohol as the solvent. The reagent was prepared by treating 50 g. of chromic chloride with 350 cc. of alcohol, 50 g. of zinc and 100 cc. of concd. hydrochloric acid. It was preserved under an atmosphere of hydrogen in a suitable apparatus.

Reductions were carried out in closed vessels protected by an atmosphere of carbon dioxide. In a few experiments the reducing agent was introduced through the side arm of the reaction flask into a rapidly boiling solution of the substance to be reduced, the chromous chloride being protected from the air by the vapor of the solvent. The products were isolated by diluting with water, fractionally crystallizing the gummy precipitate from some solvent (usually methyl or ethyl alcohol) and identifying the products in the usual way by means of mixed melting points.

The Action of Reducing Agents on Saturated 1,4-Diketones.—Samples of the saturated 1,4-diketones were tested with the reducing agents under conditions identical with those under which the reductions of the unsaturated 1,4-diketones were carried out. Although smaller amounts of materials were used, the same proportions were maintained. In these experiments the oxidized form of the reducing agent was added in order to make sure that conditions were identical with those actually involved during a reduction. Thus sodium bisulfite was added in tests with sodium hydrosulfite as the reducing agent, zinc acetate in zinc and acetic acid reductions and chromic chloride (by rapid oxidation of the chromous chloride through contact with the air) in tests with chromous chloride. The products were isolated and identified in the usual way.

The results of reductions of the six unsaturated 1,4-diketones and the effects of the reducing agents on the saturated 1,4-diketones are given in Table II.

Reduction of 1-Benzoyl-2-trimethylacetylstyrene.—Benzoyltrimethylacetylstyrene was reduced nearly quantitatively under various conditions with zinc, acetic acid and acetic anhydride to the known benzoyl-(trimethylacetyl)-phenylethane (desylpinacoline).¹⁹ This product was found to be unstable when heated with hydriodic acid (sp. gr. 1.96).

Elimination of Methoxyl and Aroxy Groups by Reduction.—In a number of experiments small amounts of unsubstituted saturated 1,4-

TABLE III^a

THE ELIMINATION OF METHOXYL AND AROXYL GROUPS FROM SUBSTITUTED SATURATED 1,4-DIKETONES BY THE ACTION OF REDUCING AGENTS

Substituted ethane	Reducing agent	Yield of ethane, %
Dibenzoylmethoxy-	(a) CrCl ₂ , 50% EtOH, cold, then Δ	5
	(b) 95% EtOH, Zn + AcOH, Δ	2
	(c) Add CrCl ₂ to Δ95% EtOH	Trace
Di-(chlorobenzoyl)-methoxy-	Zn + AcOH, (a) boil, (b) Δ at 70°	10-13
Di-(bromobenzoyl)-methoxy-	Zn + AcOH, Δ to boiling	20
	Zn + AcOH + EtOH, boiled	8-10
Dibenzoyl-(3-methylphenoxy)-	Zn + AcOH, Δ to boiling	Trace

^a Data drawn from Table II.

¹⁹ Boon, *J. Chem. Soc.*, 97, 1258 (1910).

diketones were obtained, resulting from the elimination of the methoxyl or aroxyl group through the action of the reducing agents. The loss of methoxyl or aroxyl occurs only in experiments in which the methoxy- or aroxyethanes, $\text{ArCOCH}_2\text{CH}(\text{OCH}_3)\text{COAr}$, are the starting materials or are the principal products in the reactions concerned. Apparently these substances do not decompose (splitting out alcohol or phenol) under the most drastic conditions involved during a reduction, namely, boiling in an acetic acid-anhydride mixture. The reaction, therefore, must involve direct reduction. In Table III are listed the methoxy- and aroxyethanes reduced in this manner.

Summary

1. A variety of reducing conditions are described under which six different substituted unsaturated 1,4-diketones are converted into the corresponding furans, and under which conditions the corresponding saturated 1,4-diketones are stable.

2. The bearing of these facts on the theory of 1,6-addition of hydrogen to unsaturated 1,4-dicarbonyl compounds is discussed and the conclusion is drawn that the dienol postulated by the theory is actually formed as the primary intermediate in reduction and accounts for the formation of the furans.

3. The diaryl-methoxy- and aroxy-substituted 1,4-diketones are easily dehydrated to the corresponding furans and decompose on heating into the corresponding dibenzoyl ethylene and alcohol or phenol.

4. The methoxyl groups in certain cases are eliminated by reduction from the methoxy-saturated 1,4-diketones.

5. New aroxy- and methoxydibenzoyl ethylenes are described.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF MOUNT HOLYOKE COLLEGE]

ISOMERS OF 2-PENTENE. I. PENTENE-2 FROM 3-BROMOPENTANE AND FROM 3-PENTANOL¹

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RECEIVED MARCH 29, 1929

PUBLISHED OCTOBER 5, 1929

The present study is one of a series involved in an investigation of the preparation and properties of the isomeric 2-pentenenes.² Wurtz³ was the first to report the preparation of 2-pentene and the reaction of this with

¹ Presented in abstract before the Organic Division, at the Swampscott Meeting of the American Chemical Society, September, 1928.

² The work originated in the request of Professor Morris Kharasch (September, 1926) that Professor Carr make, in this Laboratory, absorption spectra measurements of a 2-pentene obtained from 3-bromopentane and of an isomeric form of this 2-pentene which Professor Kharasch had obtained by heating 2-pentene in xylene.

³ Wurtz, *Ann.*, **125**, 114 (1863).