Calc. for $C_6I_4(OC_2H_3O)_2$: I, 72.78; found: I, 73.11.

Properties.—It forms small white needles, which begin to decompose about 270° and melt at 285° (uncor.). It is slightly soluble in ethyl acetate; practically insoluble in cold alcohol, ether, acetone, chloroform, tetrachloride of carbon, glacial acetic acid, naphtha, benzene, nitrobenzene, or aniline, but soluble in each of these solvents, when hot, with the exception of alcohol and naphtha. Acids, or alkalies, seem to produce no immediate effect on it.

If iodoanil was heated for 10 or 15 minutes with acetic anhydride, the unaltered substance separated on cooling, but, if a few drops of strong sulfuric acid were added, the same length of heating produced a brown solution, which gave a precipitate with water, that after 4 crystallizations from benzene began to darken at 270° and melted at 284° (uncor.). It was therefore the tetraiodo-*p*-diacetoxybenzene.

Action of Chloride of Iodine on Quinone.—Twenty-five grams of chloride of iodine[1] were passed into 15 g. of quinone suspended in 200 cc. of tetrachloride of carbon, and the mixture gently warmed. After the reaction was complete, the precipitate of iodine was filtered out, the filtrate evaporated to dryness, and after removing the iodine by washing with aqueous potassium iodide the yellow residue crystallized from naphtha, until it showed the constant m. p. 161° (uncor.), which indicated that the substance was dichloroquinone, an inference confirmed by the following analyses:

Subs. 0.3284, 0.2167; AgCl, 0.5288, 0.3494.

Calc. for $C_6H_2Cl_2O_2$: Cl, 40.12; found: Cl, 39.81, 39.86.

CAMBRIDGE, MASS.

THE REACTION BETWEEN PHENYL-MAGNESIUM BROMIDE AND UNSATURATED COMPOUNDS THAT CONTAIN A NUMBER OF PHENYL GROUPS.

BY DOROTHY A. HAHN AND RUBY MURRAY.

Received April 24, 1914.

A comparison of the results obtained by treating highly phenylated compounds with the Grignard reagent, shows that phenyl groups, in both α and β positions, to carbonyl, effect a much greater hindrance to the reaction than the same number of groups in the α position. Thus, no reaction can be obtained by boiling tetraphenylpropenone[2]

$$(C_6H_5)_2C = C(C_6H_5)COC_6H_5,$$

with phenylmagnesium bromide, while benzpinacoline,

$$(C_6H_5)_3C.COC_6H_5,$$

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[1] Made according to Jackson and Bigelow, *Am. Chem. J.*, 46, 549 (1911).

[2] *Am. Chem. J.*, 38, 519 (1907).

reacts fairly readily with the same reagent. A similar resistance has been observed in diphenylpropionyl mesitylene,[1]

$$(C_6H_5)_2CH.CH_2COC_6H_2(CH_3)_3,$$

in which the inactivity of the carbonyl is due to diorthosubstitution.

In order to explain this difference, which is hardly in accord with the ordinary conceptions of steric hindrance, it is necessary to study the reaction with substances that contain other "negative" groups in the place of phenyl.

It is extremely difficult to determine the structure of the products that are obtained by applying the Grignard reagent to such complex substances, but the symmetrical dibenzoylstilbene,

$$C_6H_5COC(C_6H_5) = C(C_6H_5)COC_6H_5,$$

which has benzoyl in place of one of the phenyl groups of tetraphenylpropenone, offered some prospect of success. This was the principal substance used in the following investigation; but, for the sake of comparison, some experiments were made with the simpler dibenzoylcinnamene,

$$C_6H_5COCH = C(C_6H_5)COC_6H_5.$$

We have found that both of these substances react fairly readily with phenyl-magnesium bromide. Abenzoyl group, therefore, does not produce an effect equal to that of a phenyl group.

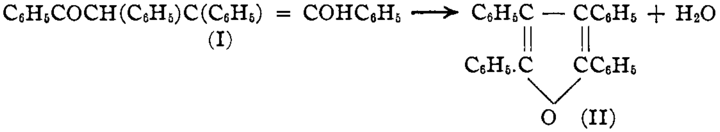
The reaction between dibenzoylcinnamene and phenyl-magnesium bromide gave only two products: dibenzoyldiphenyl ethane and lepidene. Both of these substances are plainly due to 1,4-addition.

$$C_6H_5COCH = C(C_6H_5)COC_6H_5 + C_6H_5MgBr =$$
$$C_6H_5COCH(C_6H_5)C(C_6H_5) = C(C_6H_5)OMgBr \longrightarrow$$
$$C_6H_5COCH(C_6H_5)C(C_6H_5) = C(C_6H_5)OH.$$

The enolic compound formed, by decomposing the magnesium derivative with water, in part undergoes the usual rearrangement to the corresponding ketone, giving dibenzoyldiphenylethane (I),

$$C_6H_5COCH(C_6H_5)C(C_6H_5)HCOC_6H_5;$$

and in part undergoes dehydration, giving lepidene (II) or tetraphenylfurane.



$$C_6H_5COCH(C_6H_5)C(C_6H_5) = COHC_6H_5 \longrightarrow$$

(I) (II)

The reaction with dibenzoylstilbene gives two closely related substances of which the structure is somewhat uncertain. The empirical formula of the substances shows that both are formed by the interaction of one molecule of ketone and one molecule of Grignard's reagent. These two

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[1] *Am. Chem. J.*, 38, 519, 555 (1907).

substances give identical products both on reduction and on oxidation. The very close relation existing between them, and the nature of their reduction and oxidation products, indicate that they are due to 1,2-addition of phenyl-magnesium bromide to the carbonyl.

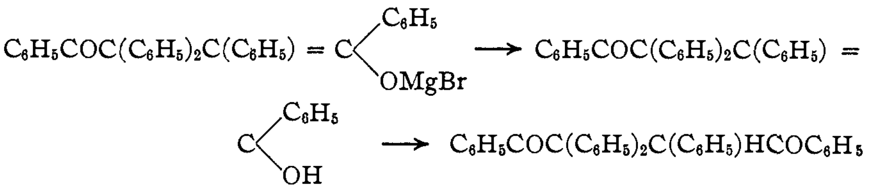
The two reactions possible between dibenzoylstilbene and phenyl-magnesium bromide are represented by the following equations:

I. (1,2-addition):

$$C_6H_5COC(C_6H_5) = C(C_6H_5)COC_6H_5 + C_6H_5MgBr =$$
$$C_6H_5COC(C_6H_5) = C(C_6H_5)C(C_6H_5)_2OMgBr \longrightarrow$$
$$C_6H_5COC(C_6H_5) = C(C_6H_5)COH(C_6H_4)_2$$

II. (1,4-addition):

$$C_6H_5COC(C_6H_5) = C(C_6H_5)COC_6H_5 + C_6H_5MgBr =$$



$$C_6H_5COC(C_6H_5)_2C(C_6H_5) = C\begin{matrix} \diagup C_6H_5 \\ \diagdown OMgBr \end{matrix} \longrightarrow C_6H_5COC(C_6H_5)_2C(C_6H_5) =$$
$$C\begin{matrix} \diagup C_6H_5 \\ \diagdown OH \end{matrix} \longrightarrow C_6H_5COC(C_6H_5)_2C(C_6H_5)HCOC_6H_5$$

Of these reactions, the first accounts for the existence of two substances of exactly the same chemical properties, by offering the possibility of geometrical isomerism. The two substances obtained by this reaction cannot represent 1,2- and 1,4-addition, respectively, since it is impossible for substances of the formula

$$(C_6H_5)_2COHC(C_6H_5) = C(C_6H_5)COC_6H_5$$

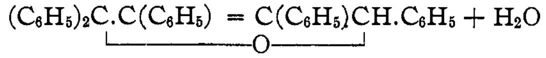
and

$$C_6H_5COC(C_6H_5)_2CHC_6H_5COC_6H_5,$$

to give the same reduction product by addition of two hydrogen atoms and subsequent loss of water.

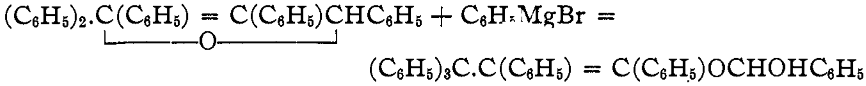
The two substances formed by the action of dibenzoylstilbene and phenyl-magnesium bromide melt at 208° and 157°, respectively. Both substances, on reduction, give a product melting at 185°. The analysis and molecular-weight determinations of this substance show that there has been no loss of phenyl groups during reduction. Assuming that the substances melting at 208° and 157° are geometrical isomers, and the result of 1,2-addition of phenyl-magnesium bromide to dibenzoylstilbene, the formation of their common reduction product may be represented by the following equations:

$$(C_6H_5)_2COHC(C_6H_5) = C(C_6H_5)COC_6H_5 + H_2 =$$
$$(C_6H_5)_2COHC(C_6H_5) = C(C_6H_5)CHOHOC_6H_5 \longrightarrow$$



$$\underbrace{(C_6H_5)_2C.C(C_6H_5) = C(C_6H_5)CH}_{O}.C_6H_5 + H_2O$$

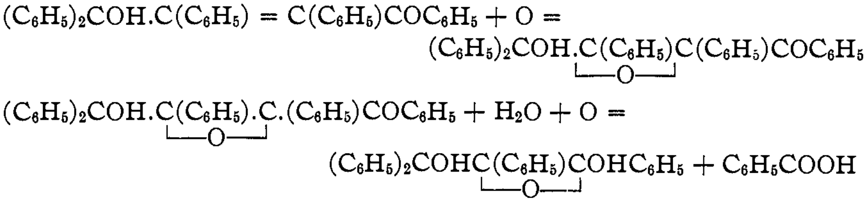
And if these equations correctly express the course of the reaction, it should be possible to open the ring by applying Grignard's reagent. It was found that the reduction product melting at 185° reacted readily with phenyl-magnesium bromide. The addition product was decomposed with ice and hydrochloric acid, and a crystalline substance melting at 232° was separated. Analysis showed it to be less rich in oxygen than the substance from which it was obtained. Its composition may be accounted for by supposing that the opening of the ring was attended by a loss of one molecule of water from two molecules of condensation product:



$$(C_6H_5)_2.\underbrace{C(C_6H_5) = C(C_6H_5)CH}_{O}C_6H_5 + C_6H_5MgBr = (C_6H_5)_3C.C(C_6H_5) = C(C_6H_5)OCHOHC_6H_5$$

$$2(C_6H_5)_3C.C(C_6H_5) = C(C_6H_5)CHOHC_6H_5 \longrightarrow [(C_6H_5)_3C.C(C_6H_5) = C(C_6H_5)CH(C_6H_5)]O + H_2O$$

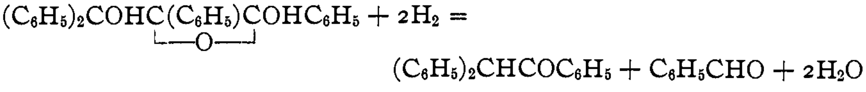
The two substances formed by the action of phenyl-magnesium bromide and dibenzoylstilbene give identical products when oxidized with chromic oxide dissolved in acetic acid. The process of oxidation does not always take the same course however, and it was found difficult to arrange the conditions so as to control it. In a series of experiments, the oxidation products showed that the original molecule had sometimes been completely broken down, and sometimes only partially broken down during oxidation. When the decomposition was complete the products were benzoic acid, benzil and benzophenone. Small quantities of a fourth substance were accumulated as the result of a series of oxidations. This substance melts at 143° and represents the incomplete breaking down of the original molecule by oxidation. Its constitution was arrived at by analysis and molecular-weight determinations and by a study of its reduction product. The substance was readily reduced, and its reduction product, melting at 135°, was identified as triphenylvinyl alcohol. The process of oxidation leading to the formation of the substance melting at 143° may be represented by the equations:



$$(C_6H_5)_2COH.C(C_6H_5) = C(C_6H_5)COC_6H_5 + O = (C_6H_5)_2COH.\underbrace{C(C_6H_5)C}_{O}(C_6H_5)COC_6H_5$$

$$(C_6H_5)_2COH.\underbrace{C(C_6H_5).C}_{O}.(C_6H_5)COC_6H_5 + H_2O + O = (C_6H_5)_2COH\underbrace{C(C_6H_5)C}_{O}OHC_6H_5 + C_6H_5COOH$$

The reduction of this substance to triphenylvinyl alcohol may be represented by the equation:



$$(C_6H_5)_2COH\underbrace{C(C_6H_5)C}_{O}OHC_6H_5 + 2H_2 = (C_6H_5)_2CHCOC_6H_5 + C_6H_5CHO + 2H_2O$$

Further confirmation of the assumption that the substances melting at 208° and 157° are geometrical isomers of the formula

$$(C_6H_5)_2COHC(C_6H_5) = C(C_6H_5)COC_6H_5,$$

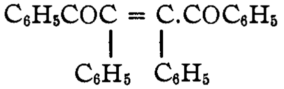
is to be found in their behavior toward acetic anhydride. When pure 208° or pure 157° is dissolved in acetic anhydride, an equilibrium mixture is obtained from which both substances crystallize.

In conclusion, it will be seen, by comparing the reactions of dibenzoylcinnamene and dibenzoylstilbene with phenylmagnesium bromide, that the introduction of a phenyl group in the β position to carbonyl, offers resistance to 1,4-addition. Thus, $C_6H_5COCH = C(C_6H_5)COC_6H_5$ shows 1,4-addition of phenylmagnesium bromide and

$$C_6H_5COC(C_6H_5) = C(C_6H_5)COC_6H_5,$$

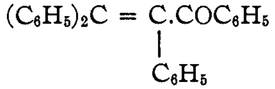
does not. This is in agreement with results obtained by Kohler,[1] where *α,β-triphenylpropenone*, $C_6H_5CH = C(C_6H_5)COC_6H_5$, *gave a yield of* 100% of a 1,4-addition product when treated with phenylmagnesium bromide, and tetraphenylpropenone, $(C_6H_5)_2C = C(C_6H_5)COC_6H_5$, gave no reaction when boiled with the same reagent.

The reactivity of the carbonyl in dibenzoylstilbene,



$$\begin{array}{c} C_6H_5COC = C.COC_6H_5 \\ \quad | \qquad | \\ C_6H_5 \quad C_6H_5 \end{array}$$

as compared with its complete inactivity in tetraphenylpropenone,



$$\begin{array}{c} (C_6H_5)_2C = C.COC_6H_5 \\ \qquad | \\ \qquad C_6H_5 \end{array}$$

is curious. It would seem as if the reactivity of the carbonyl group with phenylmagnesium bromide were more dependent upon other factors than upon the presence of a phenyl group in the α position.

Experimental.

The condensation of dibenzoylcinnamene with phenyl-magnesium bromine took place readily. The dibenzoylcinnamene was prepared as described by Jopp, Klingemann[2] and was added in finely powdered form to an ethereal solution of the magnesium compound. Fifteen parts by weight of ketone were used for every five parts of magnesium and every thirty-five parts of phenyl bromide. The ketone was added slowly, with constant shaking, and in small portions, which were allowed to dissolve completely before new portions were added. When all of the ketone had been added, the magnesium compound was decomposed at once by shaking with ice and hydrochloric acid, and the ethereal solution was then washed and dried over calcium chloride. The ethereal solution, on

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[1] *Am. Chem. J.*, 38, 515 (1907).

[2] *Trans. Chem. Soc.*, 57, 673.

evaporation, yielded a mixture of products which were separated by fractional crystallization from acetone. The mixture was found to consist of four substances, two of these representing the primary addition products of the reaction between dibenzoylcinnamene and phenylmagnesium bromide, and two representing secondary products resulting from the oxidation of the primary products.

Various modifications of this method of procedure were tried in attempts to minimize the amounts of secondary products. Glacial acetic acid was added at once to the dry ethereal solution, and most of the ether evaporated. The acetic acid, on cooling, precipitated a white crystalline mass, which, when filtered, dried, and weighed, was found to represent about 90% of solid product. The precipitate, however, consisted of a mixture which it was again necessary to separate by fractional crystallization. The only advantage of this method was that the separation of the mixture was in this case quicker and more complete.

In the separation of the mixtures obtained as the result of this condensation, the best method of procedure was to digest first with chloroform. Repeated extractions with small quantities of chloroform left a white insoluble residue which melted quite sharply and was found to be an almost pure substance. On crystallization from benzene this substance melted at 256°. The addition of a very small quantity of ether to the solution of substances in chloroform caused the separation of a second substance in almost pure state. The white crystalline precipitate was filtered and washed with ether, and, after crystallization from acetic acid, melted at 212–213°. The filtrate was then concentrated and hot alcohol was added. On cooling, glistening plates separated. These, after crystallization from acetic acid, melted at 175° and represented from 40–60% of the product of the condensation. A fourth substance was separated by concentrating the mother liquors. It was much more soluble than the other substances and was present in the mixtures only in very small quantities. After recrystallization from alcohol it melted at 157°.

An average yield of about 50% of the product melting at 175° was obtained directly and in almost pure condition, by adding glacial acetic acid to the magnesium addition product obtained in the reaction between dibenzoylcinnamene and phenylmagnesium bromide. The acid was added quite slowly to the ethereal solution of the magnesium compound, and the heat of the reaction was utilized to partially evaporate the ether. A substance separated on cooling which, after two recrystallizations from acetic acid, melted at 175°.

The substances melting at 175° and 256° were analyzed and were found to be lepidene and dibenzoyldiphenylethane, respectively. The identity of the lepidene was established by a study of its relationships and transformations, and by comparison with a specimen obtained by heating benzoin and hydrochloric acid saturated at 8°, in a sealed tube at 140°.[1] The identity of dibenzoyldiphenylethane was established by analysis, by comparison with a specimen obtained by the reduction of hydroxy lepidene with acetic acid and zinc, and by its behavior toward concentrated sulfuric and concentrated hydrochloric acids. The substance dissolved in concentrated sulfuric acid to give a green solution which gradually changed to brown. The solution, when decomposed with water and extracted with ether, gave lepidene.[2] These two substances represent the primary products of the reaction between dibenzoylcinnamene and phenylmagnesium bromide.

The substances melting at 212° and 157° were found to be dibenzoylstilbene and dihydroxylepidene, respectively. Their identity was established by comparison with specimens prepared by the oxidation of pure lepidene—with nitric acid[3] and by the oxidation of hydroxylepidene—with chromic oxide in acetic acid.[4] The condensation reaction between the first of these substances and phenyl magnesium bromide forms the main portion of the present paper.

Dibenzoylstilbene was prepared in quantity by oxidizing pure lepidene, dissolved in acetic acid, with a mixture of nitric and acetic acids or with a solution of chromic oxide in acetic acid. Since the separation, of pure lepidene was a somewhat tedious process, and since dibenzoyl stilbene was obtained along with lepidene as a result of the reaction between dibenzoylcinnamene and phenylmagnesium bromide, the attempt was made to prepare dibenzoylstilbene directly from the condensation product without separating the lepidene. In general, two methods of procedure were followed: In the first case the dry ethereal solution, containing lepidene, dibenzoyldiphenylethane, and hydroxylepidene, was treated with a mixture of nitric acid and acetic acid. During the oxidation the greater part of the ether was evaporated, and on cooling, quite pure hydroxylepidene separated. The yield varied from 40–60% of theoretical, but the melting point of the product remained at 205–206°, even after repeated crystallizations and although analysis for carbon and hydrogen showed the substance to be pure. Rather better results were obtained in the second case, where the oxidation was effected by means of bromine. This was added directly to the ethereal solution of the magnesium addition product formed by the action of dibenzoylcinnamene and phenylmagnesium bromide. One molecule of bromine was calculated for every molecule of dibenzoylcinnamene. A slight excess of the calculated quantity of bromine was always used; but it was found, as the re-

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[1] *Z. Chem.*, 1867, 313.

[2] *Ber.*, 22, 855 (1889).

[3] *Z. Chem.*, 1867, 314.

[4] *Z. Ibid.*, 1871, 483.

sult of a series of experiments, that any considerable excess of bromine was harmful to the reaction, since it led to the formation of secondary products which interfered with the separation of hydroxylepidene. In one case, where a large quantity of bromine was used, a yield of 60% of dibromolepidene was obtained.

A convenient method of procedure was as follows: The bromine was added slowly and with constant shaking, and the temperature was not allowed to rise. After it had been added the mixture was decomposed at once by shaking with ice and hydrochloric acid, when an immediate separation of dibenzoylstilbene took place. The thick oily ethereal soluture was decanted and washed. After it had been separated from water as completely as possible, the mass was filtered under pressure, the process of filtration being facilitated by the addition of small quantities of cold acetic acid to the oily mass. The precipitate was finally washed repeatedly with small quantities of acetic acid. The substance, after one crystallization from acetic acid, melted at 212°–213°, and the results of analysis for carbon and hydrogen showed it to be pure dibenzoylstilbene. The yield was 60–80% of theoretical, and this method was the one finally employed for the preparation of the dibenzoylstilbene used in the following experiments:

The reaction between dibenzoylstilbene and phenylmagnesium bromide took place readily in the cold. The hydroxylepidene used in the condensations was prepared by all of the four methods described, and the results of the reactions were found to be the same in the case of all specimens. The method of procedure was as follows: 15 g. of finely powdered dibenzoylstilbene were added slowly to an ethereal solution containing 5 g. of magnesium and 35 g. of phenyl bromide. After the addition of the ketone the mixture was decomposed at once by shaking with ice and hydrochloric acid. The ethereal solution was separated, washed, and dried over calcium chloride. Usually the separation of a white crystalline solid took place at once, but sometimes the separation of the substance was very slow and very incomplete. The substance was filtered and washed with ether, and, after several recrystallizations from glacial acetic acid, melted at 208°. In a series of about twenty experiments the yield varied from 75–85° of pure product. From the ethereal filtrate from this substance a second product crystallized. This was much more soluble than the first and its separation was much slower. It was purified by repeated crystallizations from acetone, from which it separated in large rhombic crystals melting at 157°. These two substances represent the sole products of the reaction between dibenzoylstilbene and phenylmagnesium bromide.

An attempt was made to facilitate the separation of the substance melting at 208° by adding acetic acid to the dry ethereal solution obtained as a result of the condensation. In the process the ether was distilled off and the temperature was allowed to rise to 100°. It was hoped that on cooling most of the substance melting at 208° would separate out from the solution. Crystals began to separate from the mixture almost immediately, but the separation was very slow and was complete only after several days. The crystalline product was filtered and washed with acetic acid. It was found to consist of an almost pure substance, which after several crystallizations, melted at 157°, and was identical with the substance mentioned in the preceding experiment. In a series of experiments, the yield of pure substance melting at 157° varied from 70–90%. The mother liquids yielded small quantities of the substance melting at 208°, and all of the material used in the successive condensations was quantitatively accounted for.

In order to ascertain whether the substance melting at 208° was unstable in the presence of acid, 20 g. of pure substance were added to 200 cc. alcohol, and the alcohol was then saturated with dry hydrogen chloride gas. Although the substance melting at 208° is almost insoluble in alcohol, it slowly dissolved in the alcoholic solution of hydrogen chloride, the dry gas being passed into the mixture until the solution of the substance melting at 208° was complete. The separation of a crystalline solid from the alcoholic solution began immediately on cooling, but the crystals formed slowly and the process was complete only after several days. The crystalline precipitate was filtered and washed and was found to consist of an almost pure substance. After recrystallizing several times from ether, and then from chloroform-alcohol mixtures, this substance melted at 157°. The yield varied from 80 to 90%. The mother liquors slowly yielded the substances melting at 157° and 208° and all of the material was finally accounted for quantitatively. By modifying the experiment, and by adding a small quantity of alcohol to the dry ethereal solution obtained by condensing dibenzoylstilbene and phenylmagnesium bromine, and then saturating the mixture with dry hydrogen chloride, it was found possible to obtain directly yields of from 80 to 90% of the substance melting at 157°.

Thus it was found possible in the condensation of dibenzoylstilbene and phenylmagnesium bromide, so to modify the procedure as to obtain an average yield of 80% of either of the two products of this reaction. A study of the transformations of these two substances showed that they were very closely related.

γ-Benzoyltetraphenylpropenol, $C_6H_5CO.C(C_6H_5) = C(C_6H_5)COH(C_6H_5)_2$.—This substance, melting at 208°, was one of the products resulting from the reaction between dibenzoylstilbene and phenylmagnesium bromide. The substance separated from the ethereal solution in almost pure condition. It was purified by several rapid recrystallizations from glacial acetic acid

0.1073 g. and 0.1167 g. of subs. gave 0.3443 and 0.3737 g. CO_2 and 0.0536 and 0.0582 g. H_2O.

Calc. for $C_{34}H_{26}O_2$: C, 87.55; H, 5.58; found: 87.51 and 87.32; 5.55 and 5.54.

γ-Benzoyltetraphenylpropenol is difficultly soluble in ether, almost insoluble in alcohol, soluble in hot acetic acid and difficultly soluble in cold acetic acid, soluble in acetone and very soluble in chloroform. When left in contact with alcohol for a long time it slowly dissolves. In solution in acetic acid and acetic anhydride it is slowly changed into a substance having the same empirical formula and melting at 157°. When crystallized from acetone or from chloroform-alcohol mixtures it slowly took up water and passed over into a hydrate. This process was slow and was complete only after a great number of recrystallizations from these solvents. It was followed by repeated analyses of the substance during the process of recrystallization. It was found that the percentage of carbon in the substance decreased until a limit was reached, corresponding to the addition of one molecule of water to one molecule of substance. At intermediate stages mixtures of the hydrate and of the anhydrous substance crystallized out together.

0.1769 and 0.1825 g. subs. gave 0.5491 and 0.5661 g. CO_2, and 0.0950 and 0.0984 g. H_2O.

Calc. for $C_{34}H_{26}O_2.H_2O$: C, 84.3; H, 5.8; found: 84.6, 84.5 and 6.0, 5.9.

The hydrate crystallized from acetone in very large transparent plates or prisms that melted at 203–206°. Its solubility and appearance was the same as that of the anhydrous form. It was, however, very unstable and lost water at ordinary temperatures, the clear transparent crystal becoming opaque and coated with a white powder. When heated at 130° it rapidly lost in weight, but the loss in weight never corresponded to the loss of one molecule of water. In the hope of obtaining quantitative results showing the loss of one molecule of water the hydrate was dissolved in acetic anhydride. The substance separated from this solvent on cooling and was recrystallized once from the same solvent and analyzed.

0.1462 g. subs. gave 0.4658 g. CO_2 and 0.0708 g. H_2O.

Calc. for $C_{34}H_{26}O_2$: C, 87.55; H, 5.58; found: 86.88 and 5.38.

It was observed that the melting point of the product crystallizing from acetic anhydride had been lowered to 190–192°. This was interpreted as due to the formation of a small quantity of the low melting isomer; and such was probably the case, since, after extracting several times with small quantities of anhydrous ether and recrystallizing from glacial acetic acid, the melting point of the product was raised to 204–206° and the percentage of carbon and hydrogen remained unchanged.

The molecular weight of the anhydrous form of γ-benzoyltetraphenylpropenol was determined by the freezing-point method. Solvent benzene:

Calc. for $C_{34}H_{26}O$: M, 466; found: 415, 419, 428, 420.

γ-Benzoyltetraphenylpropenol, $C_6H_5COC(C_6H_5) = C(C_6H_5)COH(C_6H_5)_2$, melting at 157°, was formed together with its geometrical isomer when dibenzoylstilbene reacted with phenylmagnesium bromide. It may be prepared by starting with the pure substance melting at 208° and dissolving it in alcohol that has been saturated with hydrogen chloride gas. The substance was purified by crystallization, first from ether and then from acetone.

0.2021 and 0.1598 g. subs. gave 0.6490 and 0.5124 g. CO_2 and 0.1086 and 0.0862 g. H_2O.

Calc. for $C_{34}H_{26}O_2$: C, 87.55; H, 5.58; found: 87.5, 87.4 and 5.9, 5.9.

Molecular-weight determination by the freezing-point method. Solvent benzene, K = 5000.

Calc. for $C_{34}H_{26}O_2$: M, 466; found: 447, 448, 440.

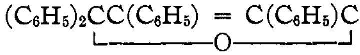
Molecular-weight determination by the boiling-point method. Solvent benzene, K = 2160.

Calc. for $C_{34}H_{26}O_2$: M, 466; found: 378, 433, 433.

The substance melting at 157° was readily soluble in ether, acetic acid, hot alcohol and acetone. It easily separated from the isomeric form melting at 208° by extraction with ether, and then recrystallized from acetone or from chloroform-alcohol mixtures. It separated from acetone in the form of large plates or prisms, resembling very closely the crystalline form of its geometrical isomer.

When boiled with acetic anhydride the substance melting at 157° was slowly changed into the high melting form. Eleven grams of substance were boiled with acetic anhydride in a flask connected with a return condenser for 24 hours. After evaporating off most of the anhydride a mixture was obtained from which 0.35 g. of pure 203–206° was finally separated.

Reduction of γ-Benzoyltetraphenylpropenol.—The substances melting at 208° and 157° were attacked by reducing agents. With stannous chloride and hydrochloric acid, and with hydrogen iodide and red phosphorus, each gave a reduction product melting at 185°.

Pentaphenylbutenyl Oxide,  $(C_6H_5)_2\underbrace{CC(C_6H_5) = C(C_6H_5)CH}_{O}C_6H_5$.—In general, the same method of procedure was followed in the reduction of γ-benzoyltetraphenylpropenol; but the high melting form was much less reactive than the low melting form, and the time required for any given reaction was therefore greater. In reducing with stannous chloride, the substance was dissolved in alcohol or in a mixture of chloroform and alcohol, the calculated quantities of stannous chloride and hydrochloric acid added, and the mixture heated on a water bath for several days. When the high melting form was used, it was necessary to heat the mixture for ten days or more in order to insure a complete reaction. During the heating, fresh quantities of hydrochloric acid were added at intervals. At the close of the reaction the mixture was poured into water and the oil extracted with ether. On evaporation of the ether, a substance crystallized out which, after several recrystallizations from alcohol, melted at 185°. The reaction was never quantitative, 5 g. of substance yielding 0.5 g. of this reduction product; and, in the case of both the high and the low melting forms, the greater part of the original substance used for the reaction was recovered unchanged. In reducing with hydrogen iodide the usual procedure was followed. The substance was heated with hydrogen iodide and red phosphorus in a sealed tube at 160° for 24 hrs., and at the end of that time the contents of the tube were extracted with ether, and the ether washed and dried. On evaporation of the ether, a substance crystallized out, and, after recrystallization from alcohol, melted sharply at 185°. Two specimens of this reduction product prepared respectively, from the high melting and the low melting forms of γ-benzoyltetraphenylpropenol were analyzed after their identity had been established.

0.1631 g. subs. (from 208°) gave 0.5395 g. CO_2 and 0.0844 g. H_2O.

0.1503 g. subs. (from 157°) gave 0.4962 g. CO_2 and 0.0788 g. H_2O.

Calc. for $C_{34}H_{26}O$: C, 90.6; H, 5.7; found: 90.2, 90.0 and 5.7, 5.8.

The molecular weight was determined (*a*) by the boiling-point method. Solvent chloroform, K = 3590.

Calc. for $C_{34}H_{26}O$: M, 450; found: 534, 506, 491, 480, 493, 494.

(*b*) By the freezing-point method, solvent benzene, K = 4900.

Calc. for $C_{34}H_{26}O$: M, 450; found: 502, 430, 421.

Pentabutenyl oxide is difficultly soluble in cold alcohol and ether and readily soluble in chloroform and in hot alcohol. It crystallizes from hot alcohol in the form of large plates that grow in characteristic roset-like groups. The substance reacts with phenylmagnesium bromide to give a crystalline addition product.

Hexaphenylbutenyl Ether $[(C_6H_5)_3CC(C_6H_5) = C(C_6H_5)CH(C_6H_5)]O$, was prepared by adding pentaphenylbutenyl oxide, in the form of a fine powder, to an ethereal solution of phenylmagnesium bromide. There was no apparent reaction in the cold, but solution took place quickly after the mixture had been warmed for a moment on the water bath. The magnesium addition product was decomposed at once by shaking with ice and hydrochloric acid. The separation of a white crystalline solid took place immediately. It was filtered and crystallized several times from chloroform-alcohol mixtures from which it separated in the form of large transparent plates or prisms melting at 232°.

0.1389 and 0.1063 g. subs. gave 0.4719 and 0.3603 g. CO_2 and 0.0737 and 0.0566 g. H_2O.

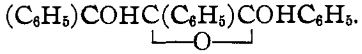
Calc. for $C_{80}H_{62}O$: C, 92.4; H, 5.9; found: 92.6, 92.4 and 5.9, 5.9.

Oxidation of γ-Benzoyltetraphenylpropenol.—Both substances formed by the action of phenylmagnesium bromide and dibenzoylstilbene gave the same products when oxidized with chromic oxide in acetic acid. The low melting form was very readily oxidized and reduced chromic oxide as rapidly as it was added, while the high melting form was reduced very slowly and its oxidation was complete only after prolonged heating. The method of procedure in the case of the substance melting at 157° was to dissolve the substance in acetic acid and to add to its hot solution a solution of chromic oxide in the same solvent. The reagent was added rapidly with constant shaking, until a permanent brown color remained for a moment or two. The solution was then poured immediately upon ice, when a solid precipitate usually separated. This was filtered and the filtrate was repeatedly extracted with ether. The ethereal solution was extracted several times with a solution of sodium carbonate to remove acids, washed, and dried over calcium chloride. The aqueous solution containing sodium carbonate gave a heavy white precipitate when acidified with hydrochloric acid, and the precipitate, after several crystallizations, was identified as benzoic acid. The ethereal solution, on evaporation, yielded a mixture of three substances, two of which were identified as benzil and benzophenone, while the third was found to be a new substance. The precipitate which separated when the oxidizing mixture was poured upon ice, consisted almost entirely of this third substance, and it was most easily isolated at this point. The quantities of this substance obtained in successive experiments varied greatly—10 g. portions of the substance melting at 157° yielding from a few tenths of a gram to as much as 3 g. We were not able to determine the conditions most favorable for the formation of this substance, but the rapidity with which the oxidation was carried through seemed to be a determining factor. The substance, after several crystallizations from alcohol, melted sharply at 143°.

In the case of the high melting form of γ-benzoyltetraphenylpropenol, the method of procedure was the same except that the chromic oxide was reduced so slowly that it was impossible to follow the course of the reaction by the change in color. Even after boiling with chromic oxide for fifteen minutes, the greater part of the original substance was recovered unchanged. The unchanged portion of the substance melting at 208° was, because of its insolubility in most solvents, readily separated from the oxidation products. These were found, as in the case of the substance melting at 157°, to consist of benzoic acid, benzil, benzophenone and a third neutral substance melting at 143°. This last substance was isolated only in very small quantities from the oxidation products of the high melting isomer, and was found only when oxidation was incomplete and where part of the original substance was recovered unchanged. The oxidation of the isomer melting at 208° was complete after boiling the substance for several hours with chromic oxide in solution in acetic acid;

but the only products of oxidation in this case were benzoic acid, benzil and benzophenone.

As shown in the introduction, the product (m. p. 143°) obtained by oxidizing both the high and low melting forms of γ-benzoyltetraphenylpropenol has the formula represented by



$$(C_6H_5)COHC(C_6H_5)COHC_6H_5.$$

It was purified by several crystallizations from hot alcohol, from which it separated in well-defined plates having the characteristic habit of growing in roset-like groups.

0.1620 and 0.1088 g. subs. gave 0.4875 and 0.3264 g. CO_2 and 0.0763 and 0.0468 g. H_2O.

Calc. for $C_{27}H_{22}O_3$: C, 82.2; H, 5.5; found: 81.9, 81.8 and 5.2, 5.2.

The molecular weight was determined (*a*) by the boiling-point method, solvent chloroform, K = 3590.

Calc. for $C_{27}H_{22}O_3$: M, 394; found: 369, 372, 365, 365, 362, 366.

(*b*) by the freezing-point method, solvent benzene, K = 4900.

Calc. for $C_{27}H_{22}O_3$: M, 394; found: 334, 326, 363, 362, 366, 365.

The substance is quite soluble in all organic solvents. It dissolved in concentrated nitric acid and concentrated sulfuric acids to give a brilliant red solution. Oxidized in acetic acid with chromic oxide, it gave benzophenone and benzoic acid.

The substance was not acted upon by metallic sodium and alcohol, but when dissolved in acetic acid it was slowly acted upon by zinc and hydrochloric acid. The product of the reaction was a substance melting at 135°. The same reduction product was obtained when the substance in solution in alcohol was reduced by the action of stannous chloride and hydrochloric acid. The method of procedure in this case was to dissolve the substance in alcohol, add the calculated stannous chloride and hydrochloric acid, and heat on the water bath for 6 hrs. A crystalline product separated on cooling and this was filtered. The addition of water to the filtrate caused more of this substance to crystallize and this was again filtered. The filtrate had a strong odor of benzaldehyde. The reduction product, separating in this way, was found to be almost pure, and after one or two crystallizations from alcohol melted sharply at 135°. The analysis and molecular-weight determinations of this substance showed that it corresponded to the formula $C_{20}H_{16}O$; and it was identified as triphenylvinyl alcohol by comparison with a specimen of that substance prepared by heating trichloroacetyl chloride with benzene in the presence of aluminium chloride.

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