THE GLASGOW AND WEST OF SCOTLAND
TECHNICAL COLLEGE,
GLASGOW.

November 1909.

I declare that the work contained in this thesis has been done entirely by myself.

This research in its original form was used as thesis for the Ph. D. degree of Leipzig University but it has been considerably extended since then.

I intend to investigate further some of the substances mentioned in this thesis. Some of these investigations have been already begun but are not as yet sufficiently advanced to be reported.

5416

STUDIES

on

SOME STEREOISOMERIC UNSATURATED SUBSTANCES.

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Presented as Thesis for D.Sc. Degree.

1910

Forsyth James Wilson, B.Sc., PH.D.,
Lecturer in Chemistry,
The Glasgow and West of Scotland Technical College.

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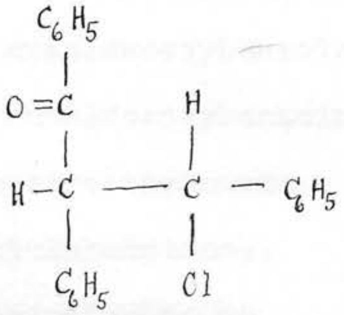
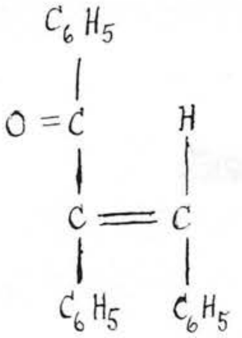
INTRODUCTION.

In 1901 Stobbe and Niedenzu[1] found that by eliminating hydrochloric acid from chlorobenzyldesoxybenzoin



two stereoisomeric benzaldesoxybenzoins



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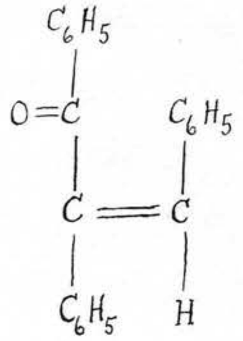

were produced. Of these the one modification is colourless, the other is yellow. By condensing benzaldehyde with desoxybenzoin by means of dry hydrochloric acid gas chlorobenzyldesoxybenzoin and the yellow benzaldesoxybenzoin were both produced. This yellow modification can be partly converted into its colourless stereoisomer by various reactions, such as by boiling its solution in presence of iodine, by exposing a solution of the substance in presence of iodine to sunlight, by the action of a little hydrochloric acid on the dissolved substance and by simply heating the substance. On the other hand, the colourless modification can be partly transformed into the yellow one by these same reactions.

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[1] Ber. 34, 3897.

I have prepared the following unsaturated ketones and investigated their transformations and stereoisomeric relationships:-

I. The piperonylidenedesoxybenzoins.
II. The o. nitrobenzaldesoxybenzoins.
III. The m. nitrobenzaldesoxybenzoins.
IV. The p. nitrobenzaldesoxybenzoins.
V. o. Methoxybenzalacetophenone.
VI. The piperonylideneacetones.
VII. Piperonylideneacetophenone.
VIII. Anisylideneacetone.
IX. Anisylideneacetophenone.

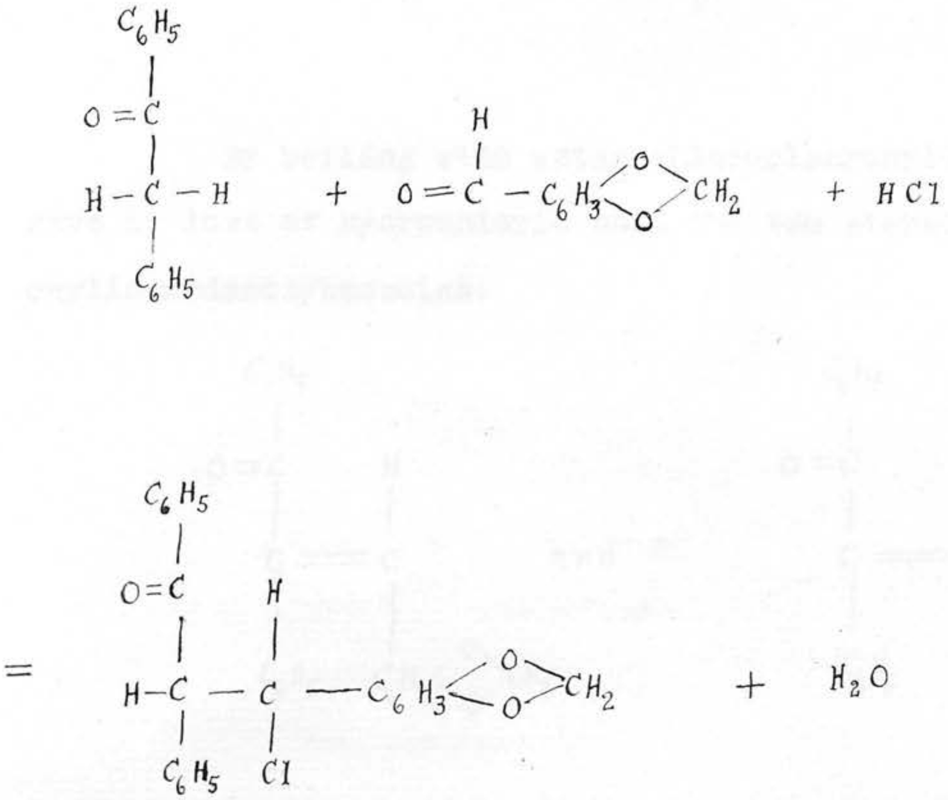
Theoretical Part.

I.

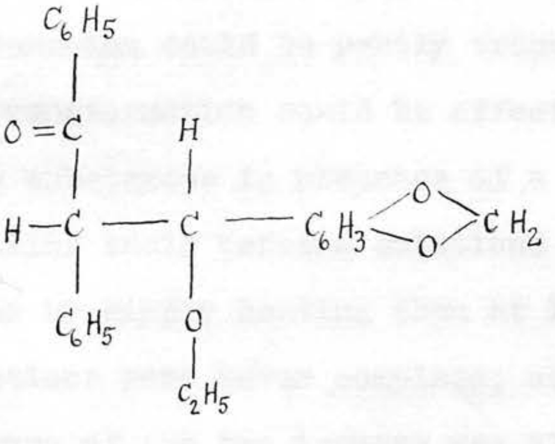
Condensation of Desoxybenzoin and piperonal.

The reaction was carried out in dry ethereal solution, dry hydrochloric acid gas being used as condensing agent. Klages and Tetzner[I.] had previously by this reaction obtained a body of the formula $C_{22}H_{15}O_2$ Cl (melting point, 203°-204°), the constitution of which is doubtful. This body is unattacked by soda solution or dilute caustic potash. Besides this body described by Klages and Tetzner, I found that chloropiperonyldesoxybenzoin was formed, apparently according to the equation:

[I.] Ber. 35, 3965.



The chloropiperonyldesoxybenzoin so obtained was boiled with ethyl alcohol in the hope of obtaining the two piperonylidenedesoxybenzoins.[I] It was found, however, that by this method a substitution of the chlorine atom by an ethoxy group[2] had taken place, and so ethoxypiperonyldesoxybenzoin

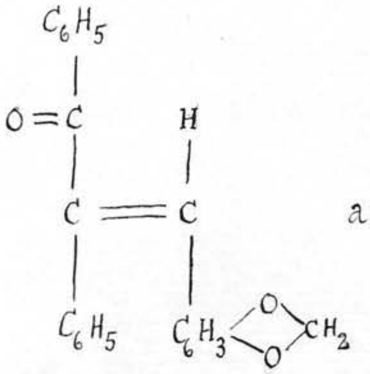


was formed. In the same way by using methyl alcohol methoxypiperonyldesoxybenzoin was obtained.

[I] Cf. Klages and Tetzner, Ber. 35, 3971: p. methoxychlorobenzyldesoxybenzoin gives with boiling alcohol the two p. methoxybenzaldesoxybenzoins.

[2] Cf. Pond and Schoffstall, Centralblatt 1900, II, 1014, who found that anisylideneacetophenonedibromide behaved similarly.

By boiling with water chloropiperonyldesoxybenzoin gave by loss of hydrochloric acid the two stereoisomeric piperonylidenedesoxybenzoins:



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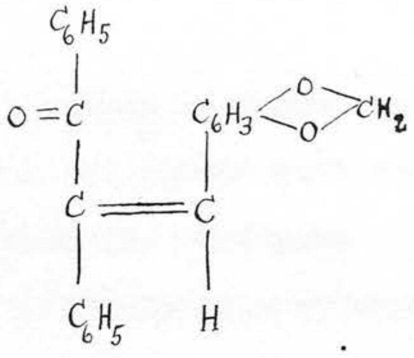


Of these the one consists of white prisms (m.p. 128°-129°), the other forms yellow prisms (m.p. 119°-120°). Both combine with bromine and decolourise alkaline permanganate solution, that is, they behave as unsaturated compounds. I have designated the white modification <u>Ketone A</u>, the yellow one <u>Ketone B</u>.

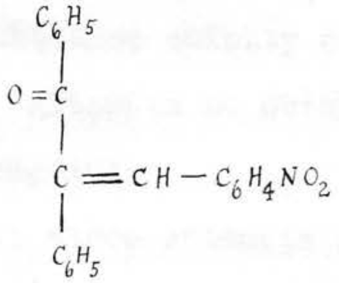
It was next shown that these two stereoisomeric piperonylidenedesoxybenzoins could be partly transformed into one another. The transformation could be effected by exposing the solutions of the substances in presence of a little iodine to sunlight, by boiling their benzene solutions in presence of a little iodine[I], or by simply heating them at 160° for four days. These transformations were never complete; at the end of these reactions a mixture of the two isomers was always obtained.

[I] The benzene solution contained 0·1 g of iodine per 100 g of benzene; in the sequel such a solution is simply referred to as "iodine-benzene solution."

II.

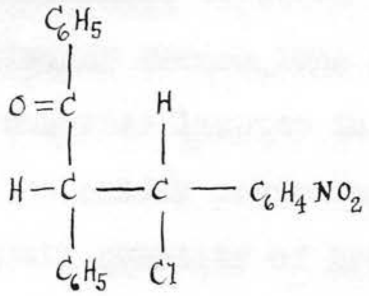
Condensation of o. nitrobenzaldehyde and desoxybenzoin.

By saturating a dry ethereal solution of these two substances with dry hydrochloric acid gas two bodies were obtained. Of these one was a yellow crystalline substance (m.p. 120°- 121°) which proved to be o. nitrobenzaldesoxybenzoin.



$$\begin{array}{l} C_6H_5 \\ \;| \\ O=C \\ \quad| \\ \quad C=CH-C_6H_4NO_2 \\ \quad| \\ \quad C_6H_5 \end{array}$$

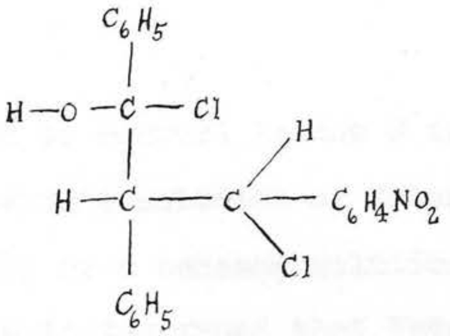
this body was named Ketone A. The other product of the reaction was chloro-o. nitrobenzyldesoxybenzoin, which formed white crystals melting at 132° - 133°. The formula of this substance is



$$\begin{array}{lll} & C_6H_5 & \\ & | & \\ & O=C & H \\ & | & | \\ H- & C\;- & C-C_6H_4NO_2 \\ & | & | \\ & C_6H_5 & Cl \end{array}$$

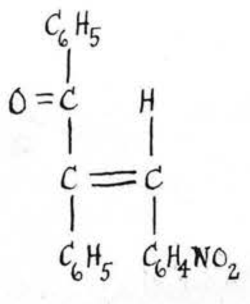
This chlorinated product was rather unstable; on standing it became yellow and evolved hydrochloric acid. For this reason it was difficult to recrystallise it without decomposition taking place. Once, when carrying out this condensation I obtained a product which was partly solid and partly oily. On working this up I obtained, besides Ketone A, white tablets of a body of the empirical formula $C_{21}H_{17}O_3NCl_2$ (m.p. 162° - 163°). Possibly/

Possibly this compound may possess the constitution



Solutions of this substance quickly decomposed with evolution of hydrochloric acid. Attempts to obtain this body in larger quantity were unsuccessful.

In the next place attempts were made to convert Ketone A. into a stereoisomer. For this purpose an iodine-benzene solution of Ketone A was exposed for a considerable time to direct sunlight. On examining the solution it was found to contain chiefly unaltered substance, but also a small quantity of the stereoisomer, to which the name <u>Ketone B</u>. was given. This stereoisomer formed long yellow needles (m.p. 109° - 110°) and was somewhat lighter in colour than Ketone A. Ketone A. could also be partly converted into its stereoisomer by the action of a small quantity of hydrochloric acid gas on the benzene solution. Ketone A. was, however, quite unaffected by boiling with iodine-benzene solution or by heating it. These two substances (Ketones A and B) are stereoisomeric in the sense of the formulae



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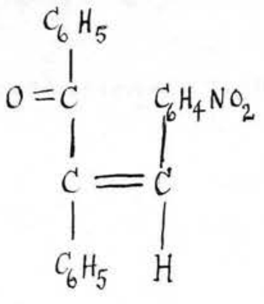
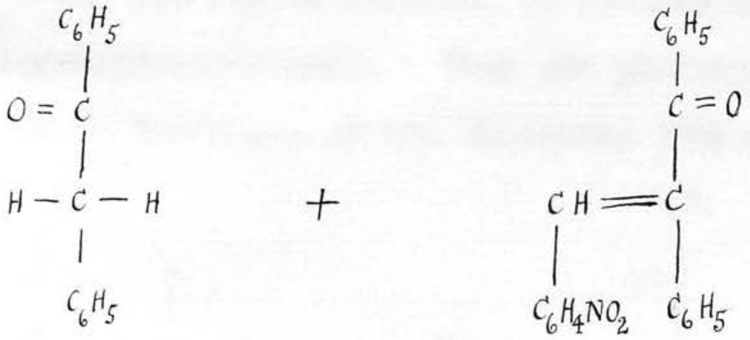


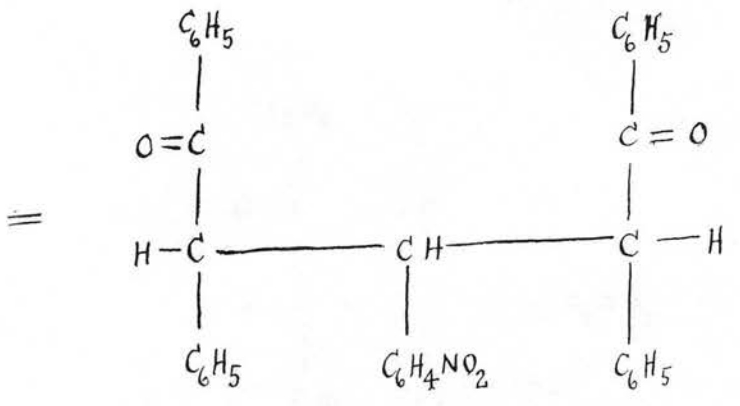
It was then attempted to convert Ketone B into Ketone A. By exposing an iodine-benzene solution of Ketone B to direct sunlight, or by acting on a benzene solution with a little hydrochloric acid gas it was found that Ketone B. could, to a large extent, be transformed into Ketone A. On boiling Ketone B. in iodine-benzene solution or by heating it no change took place.

The transformations of the two o. nitrobenzaldesoxybenzoins are therefore mutual and incomplete; probably a state of equilibrium between the two is reached.

To afford further proof as to the constitution of the two Ketones A and B, they were dissolved separately in absolute alcohol and treated with desoxybenzoin in presence of sodium ethylate. In both cases the same o. nitrobenzamarone (m.p. 237° - 238°) was formed according to the equation



(o.nitrobenzaldesoxybenzoin)

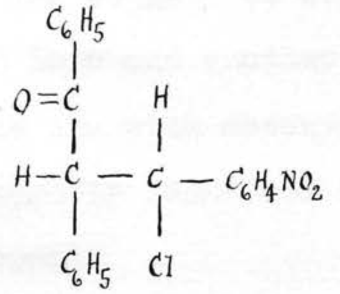


The two benzaldesoxybenzoins behave similarly towards desoxybenzoin[I], with both the same o. Nitrobenzamarone is produced.

III.

Condensation of m. nitrobenzaldehyde and desoxybenzoin.

By the action of dry hydrochloric acid gas on a dry ethereal solution of desoxybenzoin and m. nitrobenzaldehyde two substances containing chlorine were formed, their melting-points were 181°-182° and 192°-193°. Both these compounds possess the molecular formula $C_{21}H_{16}O_3NCl$ and may be regarded as hydrochlorides of m. nitrobenzaldesoxybenzoin. They are probably either isomeric in the sense of the following formulae



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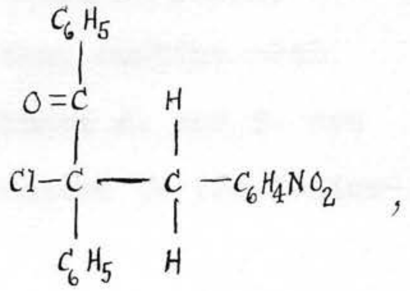
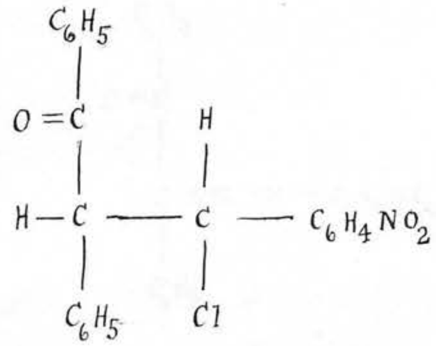


,

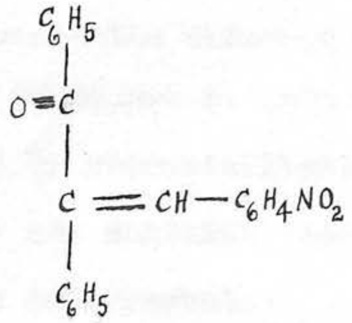
or stereoisomeric, since such a formula as

[I] Ber. 34, 3907.



contains two asymmetric carbon atoms.

It was found that hydrochloric acid could be removed from these two compounds by boiling with caustic potash; this reaction took place more readily with the body of melting-point 181°-182° than with the other. The chlorinated compound of melting-point 181°-182° yielded in this way two substances, one of these formed white crystals which melted at 85°·5 - 86°·5 and is hereafter referred to as <u>Ketone A</u>, the other formed yellow crystals of melting-ppint 86°·5 - 87°·5 and is in the sequel designated <u>Ketone B</u>. Ketone A. was the chief product of the reaction, Ketone B. was formed in smaller quantity. On the other hand, the chlorinated body of melting-point 192°-193° gave on boiling with caustic potash only Ketone A. These two substances, Ketones A. and B. had the same composition and the same molecular weight and could, as will be shown later, be partly converted into one another. Further, they combine with bromine and with desoxybenzoin. Ketones A. and B. are structurally identical and are represented by the following formula



$$C_6H_5-C(=O)-C(C_6H_5)=CH-C_6H_4NO_2$$

On recrystallising from various solvents Ketone B. was almost complete converted into a new body of melting-point $94^\circ.5$ - $95^\circ.5$; to this new body the name <u>Ketone C.</u> was given. Ketone C. has the same composition and the same molecular weight as Ketone B, it also united with bromine and with desoxybenzoin.

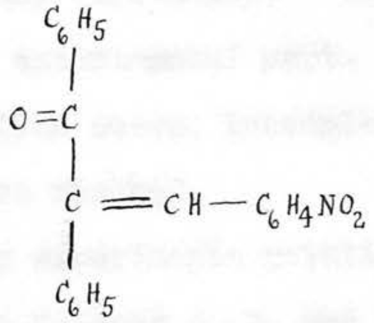
On recrystallisation, Ketone C. remains as a rule unchanged, but occasionally (apparently if the solution is concentrated) it gives a small quantity of Ketone B.

However, this conversion of Ketone B. into Ketone C. may not take place. A few years after the commencement of these experiments, I attempted, while working in another laboratory, to prepare Ketone C. by recrystallising a new specimen of Ketone B, but the attempt was completely unsuccessful, for Ketone B. was now completely unaffected by recrystallisation. I happened to have with me a small quantity of Ketone C. in a stoppered bottle. On "seeding" the solution of Ketone B. with a crystal of this old specimen of Ketone C. I found that Ketone C. crystallised out. Since then the preparation of Ketone C. from Ketone B. has offered no difficulties. It is now no longer necessary/

necessary to "seed" the solution with Ketone C. for the conversion of Ketone B. into Ketone C. can now be simply effected by recrystallisation. Apparently, this laboratory now contains "seeds" of Ketone C. which were previously not present.

The difference between Ketones B. and C. is apparently due to dimorphism. Mixtures of B. and C. in various proportions possessed the melting-point of Ketone C. (94°·5 - 95°·5), that is, under these conditions Ketone B is converted into Ketone C, the stable form.

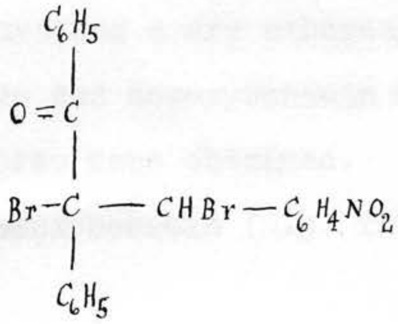
There exist, then, two structurally identical ketones of the formula



$$\begin{array}{l} \mathrm{C_6H_5} \\ \quad | \\ \mathrm{O=C} \\ \quad | \\ \mathrm{C=CH-C_6H_4NO_2} \\ | \\ \mathrm{C_6H_5} \end{array}$$

as is to be expected from theoretical considerations, and also a third ketone which is physically isomeric with one of them.

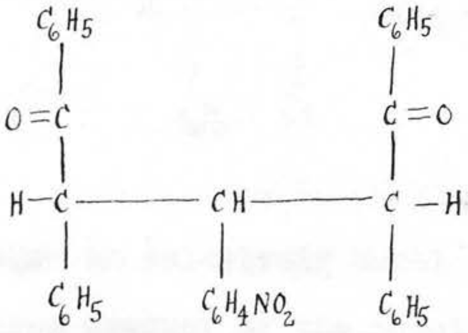
The action of bromine and of desoxybenzoin on these three ketones was also investigated. The ketones A, B, and C unite with bromine (two atoms) and give in each case the same dibromide



$$\begin{array}{l} \mathrm{C_6H_5} \\ \quad | \\ \mathrm{O=C} \\ \quad | \\ \mathrm{Br-C-CHBr-C_6H_4NO_2} \\ \quad | \\ \mathrm{C_6H_5} \end{array}$$

They/

They also combine with desoxybenzoin in alkaline solution and yield in each case the same m. nitrobenzamarone -



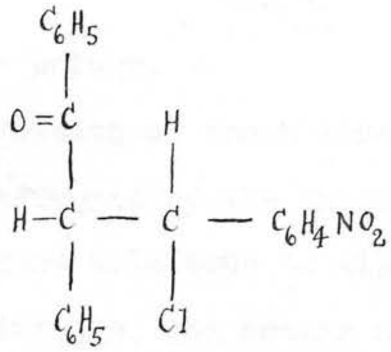
In addition, I have studied the mutual transformations of the three ketones. The methods were, as usual, exposure of the iodine-benzene solutions to light, boiling the iodine-benzene solutions, action of a small quantity of hydrochloric acid on the benzene solutions, and heating the dry substances. The results are given in detail in the experimental part. The transformations were, as in previous cases, incomplete, probably a state of equilibrium was reached.

Further experiments relating to the differences between the three Ketones A, B, and C are given in the experimental part.

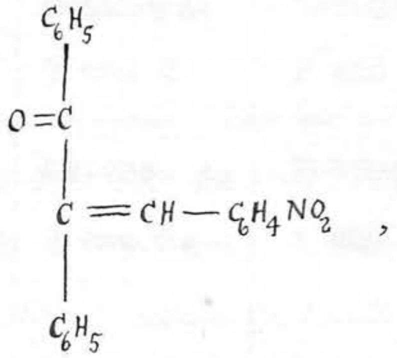
IV.

Condensation of p. nitrobenzaldehyde and desoxybenzoin.

On saturating a dry ethereal solution of p. nitrobenzaldehyde and desoxybenzoin with dry hydrochloric acid gas two bodies were obtained. The one was chloro - p. nitrobenzyldesoxybenzoin (m.p. 157° - 158°).



which was found in relatively small quantity, the other body, the chief product of the reaction, was a yellow compound melting at 164° - 165° which proved to be a p.-nitrobenzaldesoxybenzoin,



and was designated Ketone A. Occasionally a third body was obtained in very small quantity, it was also yellow, possessed the melting-point 148° - 149° and was regarded as a p.-nitrobenzalbesoxybenzoin. This third body is referred to as Ketone C.

On boiling chloro-p. nitrobenzyldesoxybenzoin with caustic potash solution, one atom of hydrogen and one atom of chlorine were removed and the above mentioned Ketones A and C were produced.

By exposing a solution of Ketone A to sunlight and by other methods, a third p. nitrobenzal-desoxybenzoin (m.p. 133°·5 - 135°·5). was obtained - Ketone B. It also possessed/

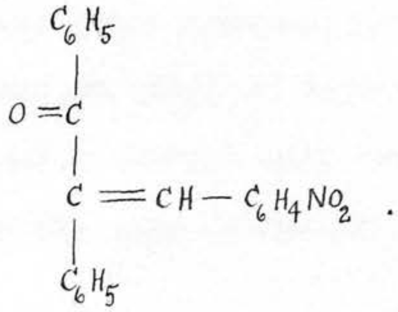
possessed a yellow colour.

The conversion of these three ketones into one another could be effected by the usual methods - exposure of the iodine-benzene solutions to light, boiling the iodine-benzene solutions, and acting on the benzene solutions with a little hydrochloric acid. The results are given in the following table:-

Method.	Ketone A. gave	Ketone B. gave	Ketone C. gave
Exposure to light.	Ketones A, B and C.	Ketones A, B and C.	Ketones A, B and C.
Boiling of the iodine-benzene solutions.	Ketones A, B and C.	Ketones A and B.	Ketones A, B and C.
Action of hydrochloric acid.	Ketones A and B.	Ketones A and B.	- -

Ketone C could be most conveniently prepared from Ketones A or B by means of one of the above mentioned methods of transformation. It was produced always in very small quantity, a fact which compelled me to limit considerably my investigations upon it.

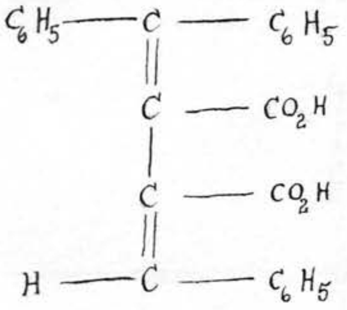
These transformations were, therefore, again mutual and incomplete. These three ketones A, B and C possess the same composition and the same molecular weight, and show a similar chemical behaviour. They must be regarded as three structurally identical forms of p. nitrobenzaldesoxybenzoin,



$$\begin{array}{l} \quad C_6H_5 \\ \quad\ | \\ O=C \\ \quad\ | \\ \quad C=CH-C_6H_4NO_2\ . \\ \quad\ | \\ \quad C_6H_5 \end{array}$$

As will be shown later, this cannot be a case of dimorphism. Therefore, three structurally identical p. nitrobenzaldesoxybenzoins exist, while according to theory only two are to be expected.

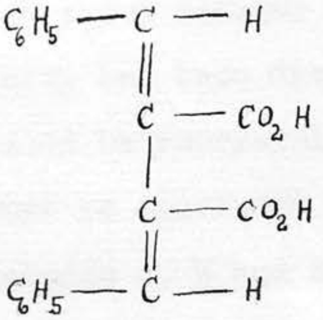
Similar exceptions to the theory are already known. For example, Stobbe and von Vigier[I.] found that the anhydride of benzaldiphenylitaconic acid



$$\begin{array}{rcl} C_6H_5- & C & -C_6H_5 \\ & \| & \\ & C & -CO_2H \\ & | & \\ & C & -CO_2H \\ & \| & \\ H- & C & -C_6H_5 \end{array}$$

occurs in three forms, while theoretically only two should be obtainable.

The same investigators, as well as Naoum[2.] discovered that four anhydrides of dibenzalsuccinic acid



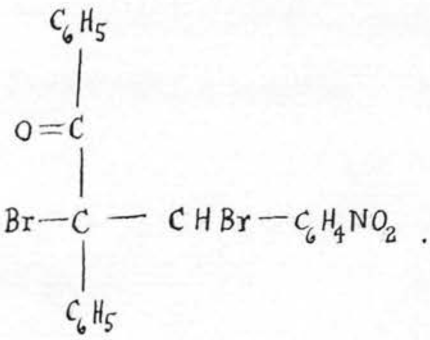
$$\begin{array}{rcl} C_6H_5- & C & -H \\ & \| & \\ & C & -CO_2H \\ & | & \\ & C & -CO_2H \\ & \| & \\ C_6H_5- & C & -H \end{array}$$

exist, whereas only three are to be expected.

[I.] von Vigier, Dissertation (Leipzig), 1904.

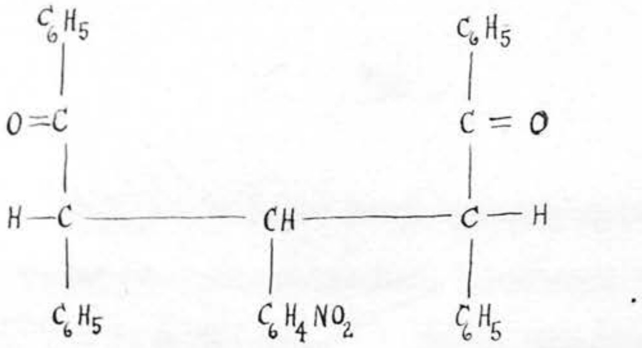
[2.] Naoum, Dissertation (Leipzig), 1898. Cf. also Centralblatt, 1900 II, 561.

In addition, I have studied the action of bromine on these three ketones and also their behaviour to desoxybenzoin in alkaline solution. These three ketones A, B and C combine with bromine only slowly and all three give the same dibromide



$$C_6H_5{-}CO{-}CBr(C_6H_5){-}CHBr{-}C_6H_4NO_2 .$$

In absolute alcoholic solution they unite with desoxybenzoin in presence of sodium ethylate and give in each case the same p.nitrobenzamarone



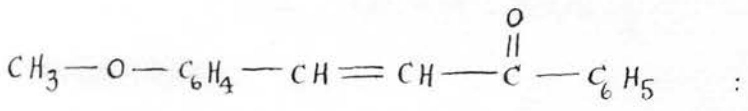
$$C_6H_5CO{-}CH(C_6H_5){-}CH(C_6H_4NO_2){-}CH(C_6H_5){-}COC_6H_5 .$$

Mixtures of two of the three ketones always showed a depression of the melting-point. "Seeding" experiments with supersaturated solutions and with the supercooled fused ketones gave in each case only that ketone which had been dissolved or melted. Also each ketone could be recrystallised without change. It can therefore be concluded that the differences between the ketones A, B and C cannot be due to dimorphism.

V.

Condensation of acetophenone and o. methoxybenzaldehyde.

These two substances can be easily condensed in alcoholic solution by the action of caustic soda: o. methoxybenzalacetophenone (m.p. 58° - 59°):



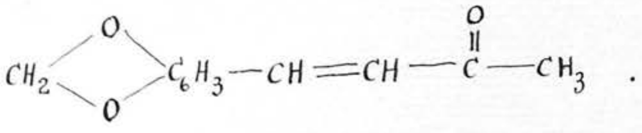
$$CH_3-O-C_6H_4-CH=CH-\overset{O}{\overset{\|}{C}}-C_6H_5 \quad :$$

is the product of the reaction.

Attempts were made to transform this compound into a stereoisomer according to the usual methods, but only resinous products could be obtained.

VI.

The yellow piperonylideneacetone[I.] (m.p. 107°) can be prepared by condensing piperonal with acetone by means of caustic soda. It is represented by the formula



For shortness, I refer to this body as Ketone A; it is almost insoluble in water. Its stereoisomer (Ketone B) is white, melts at 111°, is fairly soluble in hot water and can be prepared by boiling Ketone A with

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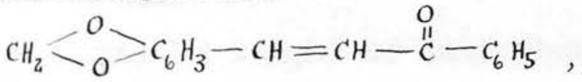
[I.] Ber. 24, 618.

water.

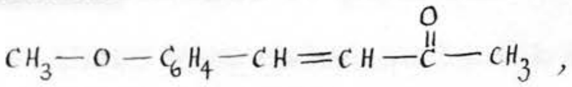
By exposing the solutions (containing iodine) to light, both substances can be partly converted into one another. On the other hand, boiling the solutions in presence of iodine or simply heating the substances does not cause the transformation to take place.

Piperonylideneacetophenone



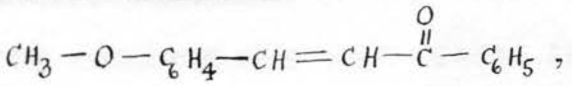
$$CH_2\langle{}^{O}_{O}\rangle C_6H_3-CH=CH-\overset{O}{\overset{\|}{C}}-C_6H_5\ ,$$

anisylideneacetone



$$CH_3-O-C_6H_4-CH=CH-\overset{O}{\overset{\|}{C}}-CH_3\ ,$$

and anisylideneacetophenone



$$CH_3-O-C_6H_4-CH=CH-\overset{O}{\overset{\|}{C}}-C_6H_5\ ,$$

are each known in only one modification, attempts to prepare stereoisomers were unsuccessful.

EXPERIMENTAL PART.

I.

Condensation of desoxybenzoin and piperonal by means of hydrochloric acid.

Preparation of Chloropiperonyldesoxybenzoin.

Two parts by weight of desoxybenzoin (1 mol.) and three parts by weight of piperonal (a little more than 2 mol. - these were found to be the most suitable proportions) were dissolved in dry ether (4 parts by weight). The solution was then cooled in ice, saturated with dry hydrochloric acid gas and allowed to stand over night. The yellowish mass which separated was filtered off, washed with water and then with benzene and recrystallised from benzene. The chloropiperonyldesoxybenzoin **so** obtained is a white crystalline powder melting at 167° - 168° with decomposition. This compound is easily soluble in hot benzene, but is difficultly soluble in alcohol, ether or acetone even on boiling.

The results of analysis were

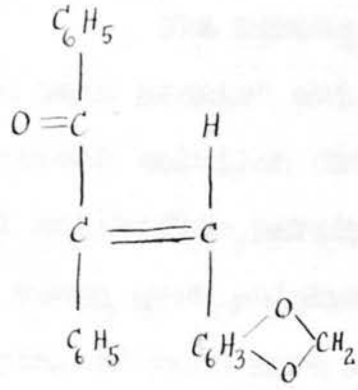
I. 0·1378 g. substance gave 0·3660 g. CO_2 and 0·0575 g. H_2O.
II. 0·1760 g. " " 0·0698 g. AgCl.

Calculated for $C_{22}H_{17}O_3Cl$.		Found. I.	II.
C	= 72·43%	72·44%	—
H	= 4·66%	4·64%	—
Cl	= 9·75%	—	9·81%

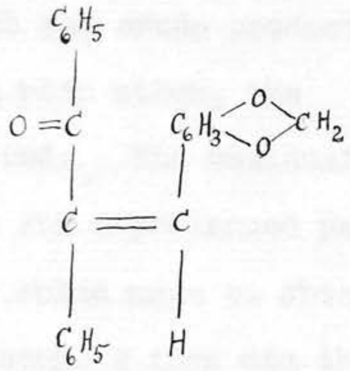
The mother-liquors from the reaction yielded yellow crystals of the body $C_{22}H_{15}O_2Cl$[1] described by Klages and Tetzner.

The yield of chloropiperonyldesoxybenzoin amounts usually to about half (occasionally more) of the desoxybenzoin employed. The yield is diminished by using less piperonal or by carrying out the reaction at higher temperatures.

Preparation of the two stereoisomeric piperonylidenedesoxybenzoins.



and



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Chloropiperonyldesoxybenzoin on boiling with water was gradually converted into a dark-coloured oil and the water acquired an acid reaction. The boiling was continued till a portion of the oil after washing with water no longer gave a chlorine reaction. After cooling, the liquid was extracted with ether, the ethereal solution dried over sodium sulphate and then evaporated in a current of dry air. A thick dark-coloured oil smelling strongly of piperonal was obtained; this solidified partly after long standing in vacuo over sulphuric acid. The mass was pressed out on a porous plate and the yellowish product

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[1] Ber. 35, 3965.

recrystallised from alcohol with addition of animal charcoal. In this way white and yellow prisms were obtained; the latter were somewhat more soluble in alcohol and ligroin than the former. These could not be well separated by recrystallisation; it was found better to separate them mechanically. These two bodies can be obtained in large crystals by allowing their ethereal solutions to evaporate. The white crystals (<u>Ketone A</u>) melted at 128° - 129°, the yellow ones (<u>Ketone B</u>) at 119° - 120°. Both compounds dissolve easily in benzene, boiling alcohol and ether, more difficultly in ligroin.

The porous plate, on which the crude product had been pressed out, was extracted with ether, the ethereal solution dried and evaporated. The residual oil solidified partly on being kept for a prolonged period in vacuo over sulphuric acid. The solid mass so obtained contained much more of the yellow Ketone B than did the part which had first solidified.

Analysis of Ketone A

0·1528 g substance gave 0·4505 g CO_2 and 0·0695 g H_2O.

Calculated for $C_{22}H_{16}O_3$.		Found.
C =	80·49%	80·41%
H =	4·88%	5·05%

Analysis of Ketone B

I. 0·1685 g substance gave 0·4965 g CO_2 and 0·0753 g H_2O.
II. 0·1710 g " " 0·5025 g CO_2 and 0·0755 g H_2O.

Calculated for $C_{22}H_{16}O_3$		Found. I.	II.
C =	80·49%	80·36%	80·14%
H =	4·88%	4·97%	4·90%.

Both ketones give with concentrated sulphuric acid/

acid dark red solutions which become dark brown on standing. Their chloroform solutions decolourise bromine readily, Ketone B somewhat more quickly than Ketone A. The two bodies are therefore unsaturated.

Transformation of the two piperonylidenedesoxybenzoins into one another.

I. Experiments with Ketone A.

1. A solution of this substance in iodine-benzene solution was exposed to sunlight for eight weeks (March and April). The solution was then decolourised with sodium thiosulphate and evaporated to dryness in a current of dry air. The residue consisted of a dark resinous mass from which a crystalline product could not be obtained. The following experiment gave a much better result: the iodine-benzoin solution of the ketone was exposed to sunlight for four days in summer, then treated with thiosulphate and evaporated in a current of dry air. The residue was recrystallised from alcohol with animal charcoal and yielded, besides unchanged substance, about 70% of Ketone B.

2. A solution of the ketone in iodine-benzoin solution was boiled for 12 hours, and, after cooling, shaken with a solution of sodium thiosulphate to remove the iodine. After evaporation the residue was recrystallised from alcohol and gave a mixture of the ketones A and B, the latter, however, in small quantity only.

3. Some of Ketone A. was heated for four days at 160° in a closed tube. The dark thick product was extracted with benzene, the benzene evaporated and the residue recrystallised/

recrystallised from alcohol. Chiefly Ketone A was obtained, a small quantity only of Ketone B was formed.

II. Experiments with Ketone B.

1. A solution of this compound in iodine-benzene solution was exposed to sunlight for four days in summer. The solution after treatment with thiosulphate and evaporation in a current of dry air gave a residue which, by crystallisation from alcohol, yielded a mixture of Ketones A and B; the amount of Ketone A was very small.

2. A solution of Ketone B in iodine-benzene solution was boiled for 12 hours, treated with thiosulphate and evaporated. The product after recrystallisation from alcohol was found to consist chiefly of Ketone B together with smaller quantities of Ketone A.

3. Some of Ketone B was heated at 160° for four days in a closed tube. After extracting with hot benzene, evaporation and recrystallisation from alcohol the product yielded a mixture of the two ketones A and B. The yield of Ketone A was fairly good.

In order to show that the difference between the two ketones was not caused by dimorphism, the melting-point of a mixture of equal quantities of the two was determined, it was found to be 102° - 106°. If the two substances were dimorphous, the mixture would possess the melting-point of the higher melting body, that is 128° - 129°.

Behaviour of chloropiperonyldesoxybenzoin towards methyl and ethyl alcohols.

In attempting to recrystallise chloropiperonyldesoxybenzoin from ethyl alcohol it was noticed that the melting/

Melting-point of the product so obtained was unsharp and lower than that of the original body.

In order to investigate the reaction further, chloropiperonyldesoxybenzoin was boiled with a quantity of ethyl alcohol insufficient to dissolve it completely. The substance gradually dissolved, the solution became yellowish brown in colour and acquired an acid reaction. After six hours' boiling, the solution on cooling deposited a crystalline product which was filtered off, washed with alcohol and recrystallised from alcohol. In this way white crystals melting at 114° - 115° were obtained; they contained no chlorine. If chloropiperonyldesoxybenzoin is boiled too long with ethyl alcohol only a resinous mass is obtained. These white crystals dissolve easily in most organic solvents, easily in hot alcohol, difficultly in ligroin; they separate unchanged from these solvents.

The compound, after drying in vacuo, was heated to its melting-point, no loss of weight occurred, so that it contained no alcohol of crystallisation.

Analysis

I. 0·1905g substance gave 0·5380g CO_2 and 0·1020g H_2O.

II. 0·1510g " " 0·4285g CO_2 and 0·0845g H_2O.

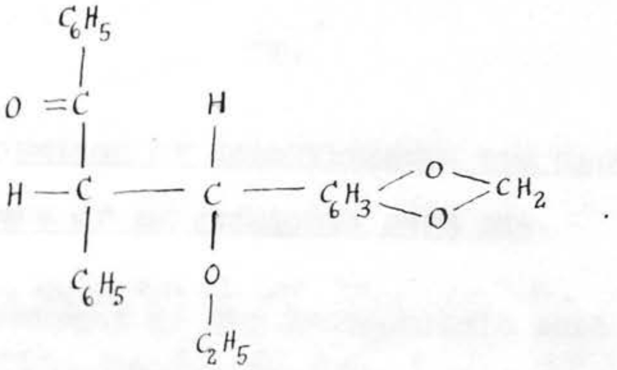
Calculated for $C_{24}H_{22}O_4$.		Found I.	Found II.
C	= 77·01%	77·02%	77·39%
H	= 5·88%	5·96%	6·22%

Molecular weight determination by boiling-point method, solvent chloroform:

Solvent.	Substance.	Elevation.	Molecular weight.	
g	g		Found.	Calculated for $C_{24}H_{22}O_4$
34·66	0·3345	0·098°	360	374
34·66	0·6325	0·187°	357	

An/

An acetic acid solution of the substance did not decolourise permanganate in the cold, neither did the body unite with bromine in chloroform solution. It was therefore regarded as saturated and considered to be ethoxypiperonyldesoxybenzoin



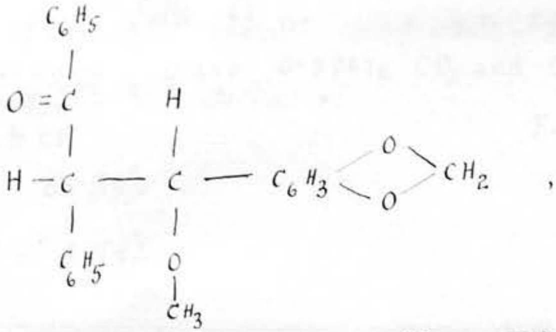
On boiling chloropiperonyldesoxybenzoin with methyl alcohol for a long time the substance dissolved, giving a yellowish red solution which reacted acid. Since no precipitate formed on cooling, water was added, when a red oil separated which solidified on rubbing. This was filtered off and recrystallised from methyl alcohol. In this way white crystals (m.p. 119° – 120°) wers obtained.

Analysis

0·1737 g substance gave 0·4860 g CO_2 and 0·0883 g H_2O.

Calculated for $C_{23}H_{20}O_4$		Found
C	= 76·66%	76·39%
H	= 5·55%	5·65%

This compound, methoxypiperonyldesoxybenzoin



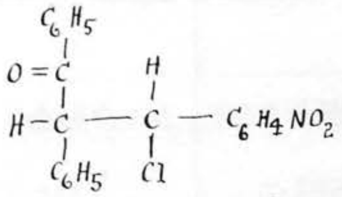
is easily soluble in benzene, ether and ligroin, very soluble/

soluble in hot methyl alcohol. It possesses a higher melting-point than the corresponding ethoxy derivative, a fact which has frequently been noticed in comparing homologous methoxy and ethoxy compounds.

II.

<u>Condensation of desoxybenzoin and o. nitrobenzaldehyde by means of hydrochloric acid gas.</u>

A current of dry hydrochloric acid gas was passed for six hours through a solution of 7 parts by weight of desoxybenzoin (1 mol.) and six parts by weight of o. nitrobenzaldehyde (1 mol.) in 36 parts by weight of dry ether, the solution being cooled in ice. The solution became deep yellow in colour and a mixture of white and yellow crystals separated. After standing in ice for three days, the solution was filtered and the crystalline precipitate[I.] washed with water and then with ether. Some of the white crystals were separated mechanically from the yellow ones and recrystallised from benzene. In this way small colourless tablet-like crystals were obtained, they melted at 132° - 133° and contained chlorine. According to the analysis they must be chloro-o. nitrobenzyldesoxybenzoin



$$\begin{array}{c} C_6H_5 \\ | \\ O=C \\ | \\ H-C \end{array} - \begin{array}{c} H \\ | \\ C \\ | \\ Cl \end{array} - C_6H_4NO_2$$

0·1493 g substance gave 0·3781 g CO_2 and 0·0615 g H_2O

Calculated for $C_{21}H_{16}O_3NCl$		Found.
C	= 68·95%	69·07%
H	= 4·38%	4·58%.

I. Referred to on page 28 as "Mixture X."

The substance is not very stable; on standing it becomes yellow and gives off hydrochloric acid. It dissolves with difficulty in ether, more readily in hot benzene: the solutions are very unstable, they are at first colourless but soon become yellow. For this reason it is not an easy matter to obtain the body in a pure state.

Some of the yellow crystals were then separated mechanically from the white ones, and recrystallised from alcohol or acetone. In this way clear yellow crystals melting at 120° - 121° were got, they contained no chlorine

Results of analysis:

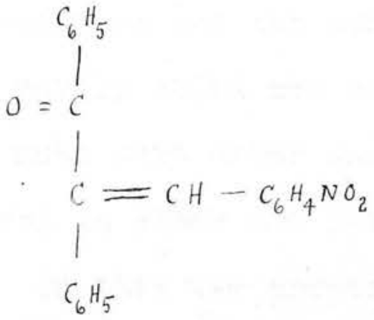
I. 0·2040 g substance gave 0·5730 g CO_2 and 0·0835 g H_2O.
II. 0·1860 g " " 7·1 c.c. N_2 at 23° and 749 m.m.
III. 0·1780 g " " 7·3 cc. N_2 at 21° and 749 m.m.

Calculated for $C_{21}H_{15}O_3N$		Found. I.	II	III.
C	= 76·59%	76·60%	—	—
H	= 4·56%	4·54%	—	—
N	= 4·25%	—	4·24%	4·59%

Molecular weight determination by freezing-point method: solvent, benzene, -

Solvent.	Substance.	Depression.	Molecular weight.	
g	g		Found.	Calculated for $C_{21}H_{15}O_3N$
13·60	0·2885	0·335°	316	329
13·60	0·4655	0·530°	323	

By this reaction o. nitrobenzaldesoxybenzoin (Ketone A, m.p. 120° - 121°).



$$\begin{array}{l} C_6H_5 \\ | \\ O = C \\ | \\ C = CH - C_6H_4NO_2 \\ | \\ C_6H_5 \end{array}$$

is produced, as well as the above mentioned chlorinated compound of melting-point 132° - 133°.

Ketone A. is easily soluble in benzene and chloroform and in hot acetone, more difficultly soluble in alcohol, ether and ligroin. By recrystallising from acetone the substance can be obtained in beautiful large crystals.

The ethereal mother-liquors from the reaction were evaporated in a current of dry air and gave a mixture of chloro-o. nitrobenzyldesoxybenzoin and Ketone A. This mixture together with the mixture which had separated from the ethereal solution during the reaction ("Mixture X") was boiled for several hours with a 20% solution of aniline in benzene in order to eliminate hydrochloric acid from the chloro-o. nitrobenzyldesoxybenzoin. After evaporating off the benzene the dark coloured residue was treated with hydrochloric acid to remove excess of aniline, washed with water and recrystallised from alcohol with addition of animal charcoal. In this way Ketone A only was obtained, a stereoisomer was not formed. Instead of aniline, dilute caustic potash can be used, but it is not so satisfactory.

The yields are very good; the amounts of Ketone A and of chloro-o. nitrobenzyldesoxybenzoin formed by the condensation are approximately equal.

Once/

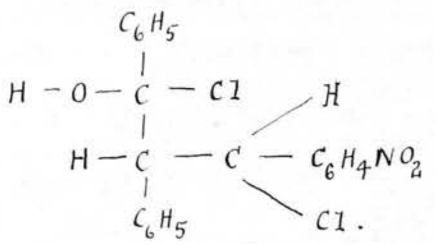
Once in carrying out the condensation a product was obtained which was partly solid and partly oily. The oil solidified for the most part after short standing: both these solids were dissolved in ether and the solution allowed to partly evaporate. In this way crystals of Ketone A were obtained and also yellowish white tablets which contained chlorine. These tablets were recrystallised several times from cold ether and melted at 162° - 163°. This substance was very unstable; on boiling with benzene it underwent decomposition with evolution of hydrochloric acid.

Chlorine estimation:

0·1840 g substance gave 0·1295 g AgCl

Calculated for $C_{21}H_{16}O_3NCl$	Calculated for $C_{21}H_{17}O_3NCl_2$	Found
Cl = 9·71%	Cl = 17·66%	17·48%

The substance then contains one atom of hydrogen and one atom of chlorine more than chloro-o. nitrobenzyldesoxybenzoin and may have the formula



As the quantity of this compound was very small, further investigation with it could not be made.

Transformations of Ketone A.

Preparation of the stereoisomeric Ketone B.

1. A solution of Ketone A in iodine-benzene solution was exposed to sunlight for three months during summer. The solution was then shaken with a solution of sodium thiosulphate, and/

and the benzene evaporated in a current of dry air. The semi-solid residue solidified for the most part after standing in vacuo over sulphuric acid. It was then pressed out on a porous plate and recrystallised from alcohol (animal charcoal). The solution deposited, besides unaltered substance, long thin yellow prisms which melted at 109° - 110°. This body, named <u>Ketone B</u>, is somewhat more soluble in alcohol than Ketone A and the two bodies can be fairly well separated in this way; however, the separation is usually better carried out mechanically. Yield of Ketone B, about 10% of Ketone A.

Results of analysis

I. 0·1590 g substance, 0·4440 g CO_2 and 0·0703 g H_2O obtained.
II. 0·1810 g " gave 6·7 c.c. N at 17° and 758 m.m.

Calculated for $C_{21}H_{15}O_3N$	Found. I.	II.
C = 76·59%	76·16%	–
H = 4·56%	4·91%	–
N = 4·25%	–	4·28%

Molecular weight determination by freezing-point method; solvent, benzene -

Solvent	Substance.	Depression.	Molecular weight.	
g	g		Found.	Calculated for $C_{21}H_{15}O_3N$
9·21	0·1402	0·255°	298	329
9·21	0·2587	0·445°	315	

Ketone B dissolves easily in benzene and chloroform, more difficultly in alcohol and ether, easily in hot acetone. Both Ketones A and B give with concentrated sulphuric acid deep yellow solutions which on dilution with water become almost colourless.

2. A solution of Ketone A in iodine-benzene solution was boiled for 12 hours. After treatment with thiosulphate and evaporation/

evaporation the residue gave, on recrystallisation from alcohol, unaltered substance only. Even on boiling a solution of Ketone A in iodine-benzene solution for a week no change took place.

3. Dry hydrochloric acid gas was led for a few minutes through a benzene solution of Ketone A. After standing for ten days the solution was evaporated in a current of dry air and the residue recrystallised from alcohol. Besides unaltered substance Ketone B was obtained (yield about 10%).

4. Ketone A, after heating at 160° in a closed tube for three days, yielded a dark coloured mass which, after recrystallisation from alcohol (animal charcoal) proved to be unaltered substance. Longer heating led merely to the formation of a resinous mass.

5g. Ketone A and 10 g. naphthalene were heated together in a closed tube for 5 hours at 200°. The dark coloured product was extracted with benzene, the benzene evaporated and the residue steam-distilled to remove the naphthalene. It was then repeatedly recrystallised from alcohol (animal charcoal) and gave chiefly unaltered substance; in addition a very small quantity of white needles (m.p. 213° - 214°) was obtained; they dissolve more easily in alcohol than Ketone A.

10g. Ketone A and 10g naphthalene were heated together in a closed tube for 4 days at 200°. After extraction with hot benzene, evaporation and treatment with steam a brown very resinous product was obtained. This was dissolved in benzene and the solution "layered" with ligroin. In this/

this way a small quantity of solid matter was obtained; this after recrystallisation from alcohol proved to be the white body of m.p. 213° – 214° mentioned above (white needles). From the mother liquors no crystalline substance could be obtained. The amount of this body (only about 0·2g) was too small to permit of further investigation: possibly it was a decomposition product of Ketone A.

Transformations of Ketone B.

1. A solution of this body in iodine-benzene solution was exposed to sunlight for 5 days in summer. The solution was then treated with thiosulphate, the benzene evaporated in a current of dry air and the residue recrystallised from alcohol; in this way approximately equal quantities of the Ketones A and B were got.

2. A solution of Ketone B in iodine-benzene solution was boiled for 24 hours, then shaken with thiosulphate and evaporated. The residue on recrystallisation from alcohol proved to consist of unaltered substance: as in the case of Ketone A this method had not caused any change.

3. A current of dry hydrochloric acid gas was passed for a few minutes through a benzene solution of Ketone B and the solution was allowed to stand for a week. It was then evaporated in a current of dry air and the residue recrystallised from alcohol. It was found that approximately equal quantities of the two Ketones A and B had been formed.

4. A mixture of one part by weight of Ketone B and three parts by weight of naphthalene was heated first for five hours, then for four days in a closed tube at

200°

200°. After extraction with hot benzene the solution was evaporated, the residue treated with steam and then recrystallised from alcohol: merely unaltered substance was obtained.

Addition of desoxybenzoin to the Ketones A and B.

Ketone A. 1g. substance and 0·6g. desoxybenzen were dissolved in absolute alcohol, about 20 drops of a concentrated solution of sodium ethylate added and the mixture allowed to stand overnight. Since apparently no reaction had set in, the solution was boiled for four hours, neutralised with acetic acid and concentrated. Crystals (0·2g) were deposited, these after recrystallisation from benzene melted at 237° - 238°. The substance proved to be completely identical with the o. nitrobenzamarone described below: a mixture of the two preparations melted at 237° - 238°.

Ketone B. An absolute-alcoholic solution of 1g of Ketone B and 0·6g desoxybenzoin was treated with about 20 drops of a concentrated sodium ethylate solution, boiled for a quarter of an hour and allowed to stand. After a few days a precipitate (0·2g) formed, this was recrystallised from benzene and melted at 237° - 238°. This compound was identical with the one obtained in a similar manner from Ketone A: a mixture of the two melted at 237° - 238°.

Preparation of o. nitrobenzamarone .

Since this body was unknown, its preparation was carried out: this was accomplished by a method similar to that used in preparing benzamarone itself.[I.]

[I.] Ber. 21, 2935, also Ber. 26. 437.

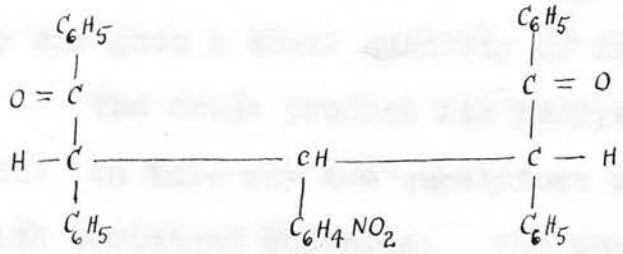
6·9g. desoxybenzoin and 2·7g. o. nitrobenzaldehyde were dissolved in absolute alcohol and a solution of 2g. caustic potash in absolute alcohol added. A precipitate soon formed, after the elapse of one day this was filtered off, washed with alcohol and then with water and dried: it weighed 5·7g. It was recrystallised several times from benzene and then melted at 237° - 238°.

Nitrogen estimation:

I. 0·3847 g substance gave 9·2 cc. N at 13° and 735 m.m.
II. 0·4298 g " " 10·0 cc. N at 13° and 749 m.m.

Calculated for $C_{35}H_{27}O_4N$	Found. I.	II.
N = 2·66%.	2·78%	2·76%.

The substance was therefore the expected o. nitrobenzamarone.



it forms yellowish felted crystals which dissolve with difficulty in cold alcohol, benzene or acetone, more easily in hot acetic acid.

The product obtained from desoxybenzoin and the two Ketones A and B agrees in its properties with this o. nitrobenzamarone.

III.

Condensation of desoxybenzoin and m. nitrobenzaldehyde by means of hydrochloric acid.

6 Parts by weight of m. nitrobenzaldehyde and 7 parts by weight of desoxybenzoin were dissolved in 41 parts by weight of dry ether, the solution cooled in ice and a current of dry hydrochloric acid gas passed through it for about 5 hours: a white precipitate soon formed. After three days' standing in ice this precipitate, which had increased considerably, was filtered off, washed with water and dried on a porous plate. The yield of crude product amounted to about 85% of the theory. The mother-liquors on evaporation in a current of dry air gave a small quantity of impure product.

The crude product was recrystallised from benzene: in this way two substances were obtained, both of which contained chlorine. The one melted at 181° - 182° and formed white felted asbestos-like masses, in quantity it amounted to about 70% of the crude product. The other body melted at 192° - 193°, was white in colour and formed small rounded crystals, it constituted about 30% of the crude product. Both substances are easily soluble in hot benzene, more difficultly in alcohol, they can be recrystallised unchanged from these solvents; the body of melting-point 192° - 193° is the more difficultly soluble. A mixture of equal quantities of the two compounds melted at 166° - 172°.

According to analysis and molecular weight estimations both compounds possess the formula $C_{21}H_{16}O_3NCl$

I. Body of m.p. 181° - 182°.

Analysis:

I. 0·1865 g substance gave 0·4728 g CO_2 and 0·0729 g H_2O.
II. 0·2040 g " " 6·4 cc N at 18° and 764 m.m.
III. 0·1625 g " " 0·0625 g AgCl.
IV. 0·1910 g " " 0·0740 g AgCl.

Calculated for $C_{21}H_{16}O_3NCl$	Found. I.	II.	III.	IV.
C = 68·95%	69·14%	—	—	—
H = 4·38%	4·34%	—	—	—
N = 3·83%	—	3·72%	—	—
Cl = 9·71%	—	—	9·45%	9·58%

Molecular weight estimation (boiling-point method: solvent, chloroform):

Solvent	Substance.	Elevation.	Molecular weight.	
g	g		Found.	Calculated for $C_{21}H_{16}O_3NCl$.
21·65	0·2710	0·130°	352	365·5
21·65	0·4420	0·220°	339	

II. Body of melting-point 192° - 193°.

Analysis:

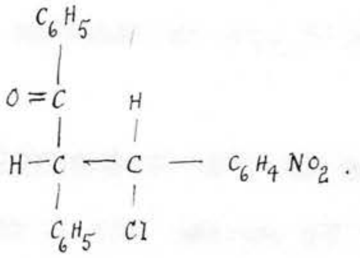
I. 0·1705 g substance gave 0·4328 g CO_2 and 0·0712 g H_2O
II. 0·2225 g " " 6·9 cc N at 13° and 765 m.m.
III. 0·1965 g " " 6·2 cc N at 20° and 763 m.m.
IV. 0·2295 g " " 0·0860 g AgCl.
V. 0·2242 g " " 0·0845 g AgCl.

Calculated for $C_{21}H_{16}O_3NCl$	Found. I.	II.	III	IV.	V.
C = 68·95%	69·23%	—	—	—	—
H = 4·38%	4·64%	—	—	—	—
N = 3·83%	—	3·72%	3·72%	—	—
Cl = 9·71%	—	—	—	9·27%	9·32%

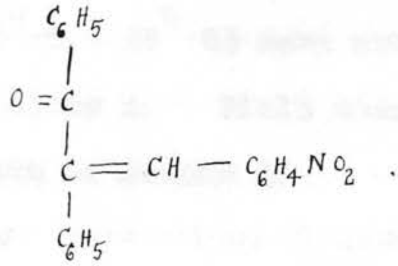
Moleuclar weight estimation (boiling-point method; solvent, chloroform):

Solvent.	Substance.	Elevation.	Molecular weight.	
g	g		Found.	Calculated for $C_{21}H_{16}O_3NCl$.
21·1	0·2090	0·115°	315	365·5.
21·1	0·3400	0·180°	321.	

As already mentioned, the substances are possibly the stereoisomeric chloro-m. nitrobenzyldesoxybenzoins



Preparation of the three m. nitrobenzaldesoxybenzoins.



The chlorinated compound of m.p. 181° - 182° gave after several hours' boiling with 40% caustic potash solution a dark coloured oil which contained no chlorine. After cooling the gummy mass was filtered off, washed with water, and dissolved in ethyl acetate. On cooling this solution in ice and salt white solid masses separated, this was filtered off, washed with a little alcohol and recrystallised from a large quantity of alcohol. If the treatment with ethyl acetate is omitted and it is attempted to recrystallise the product directly from alcohol or other solvents/

solvents, merely an oil is obtained: further, it is advisable to recrystallise from dilute solutions and to "seed" the solutions to prevent the formation of oil. In this way long white needles melting at $85^{\circ}\cdot5$ - $86^{\circ}\cdot5$ (Ketone A) were obtained, also a small quantity of light-yellow crystals (thick prisms) melting at $86^{\circ}\cdot5$ - $87^{\circ}\cdot5$ (Ketone B). For the most part these two substances had to be separated mechanically: to obtain well-formed crystals alcohol is the best solvent to use. The total yield of the two substances was about 40% of the theoretical.

The chlorinated body of m.p. 192° - 193° is fairly resistant towards the action of boiling caustic potash solution. Even after several hours' boiling with 50% caustic potash, it still contained some chlorine. The reaction product was filtered off, washed with water and recrystallised from a large quantity of alcohol. White needles (m.p. $85^{\circ}\cdot5$ - $86^{\circ}\cdot5$) were obtained, these were identical with Ketone A. Yield about 60% of the theory.

Analysis of Ketone A:

I. 0·1397 g substance gave 0·3907 g CO_2 and 0·0630 g H_2O.
II. 0·1910 g " " 7·3 cc. N at 15° and 740 m.m.
III. 0·1792 g " " 7·0 cc N at 16° and 740 m.m.

Calculated for $C_{21}H_{15}O_3N$	Found. I	II.	III.
C = 76·59%	76·28%	—	—
H = 4·56%	5·01%	—	—
N = 4·25%	—	4·35%	4·43%

Molecular weight determination of Ketone A by freezing-point method (solvent, benzene):

Solvent.	Substance	Depression.	Molecular weight.	
g	g		Found.	Calculated for $C_{21}H_{15}O_3N$
9·57	0·1003	0·165°	336	329
9·57	0·1795	0·290°	343	

Analysis of Ketone B:

I. 0·1307 g substance gave 0·3663 g CO_2 and 0·0585 g H_2O

II 0·2150 g " " 8·2 cc. N at 19·5° and 760 m.m.

III. 0·2175 g " " 8·8 cc. N at 24° and 758 m.m.

Calculated for $C_{21}H_{15}O_3N$	Found. I.	II.	III.
C = 76·59%	76·43%	—	—
H = 4·56%	5·00%	—	—
N = 4·25%	—	4·38%	4·51%

Molecular weight determination of Ketone B by freezing-point method (solvent, benzene):

Solvent.	Substance.	Depression.	Molecular weight.	
g	g		Found.	Calculated for $C_{21}H_{15}O_3N$
8·57	0·1225	0·240°	315	329
8·57	0·2245	0·410°	338	

Ketones A and B are easily soluble in benzene, acetone, methyl and ethyl acetates, carbon disulphide and hot alcohol, less easily soluble in ether and acetic acid, difficultly soluble in ligroin.

On recrystallisation from alcohol or other solvents, such as benzine or ligroin, the yellow Ketone B (m.p. 36°·5 - 37°·5) is converted almost completely into a white body melting at 94°·5 - 95°·5 (Ketone C). If this Ketone C is recrystallised (from alcohol or ether) it is as a rule unaltered but occasionally (if the solution is concentrated) it yields a small quantity of Ketone B. In presence of Ketone A Ketone B is much more stable and can be recrystallised with but little change. As already mentioned in the theoretical part (p.10) the conversion of Ketone B into Ketone C does not necessarily take place by this method.

Analysis of Ketone C:

I. 0·2092 g substance gave 0·5848 g CO_2 and 0·0918 g H_2O.

II. 0·2255 g " " 8·9 cc. N at 26° and 758 m.m.

Calculated for $C_{21}H_{15}O_3N$		Found. I.	Found. II.
C	= 76·59%	76·23%	–
H	= 4·56%	4·87%	–
N	= 4·25%	–	4·37

Molecular weight determination of Ketone C by freezing-point method (solvent, benzene):

Solvent	Substance.	Depression.	Molecular weight.	
g	g		Found.	Calculated for $C_{21}H_{15}O_3N$
15·70	0·2685	0·270°	335	329
15·70	0·4305	0·420°	346	

Ketone C dissolves easily in benzene, chloroform and hot alcohol, with difficulty in ether and ligroin.

Melting-points of mixtures of the three Ketones A, B and C.

Equal weights of Ketone A (m.p. 85°·5 – 86°·5) and of Ketone B (m.p. 86°·5 – 87°·5) melted at 76° – 83°.

Equal weights of Ketone A (m.p. 85°·5 – 86°.5) and of Ketone C (m.p. 94°.5 – 95°.5) melted at 71° – 76°:

Mixtures of Ketones B and C in different proportions were prepared and the melting-points of these mixtures were determined (m.p. of Ketone B is 86°.5 – 87°.5, m.p. of Ketone C is 94°.5–95°.5):

2.5 parts by weight of B + 0.5 part by weight of C sintered at 87°.5 and melted at 94°.5 – 95°.5.

1 part by weight of B + 1 part by weight of C melted at 94°.5–95°.5 without sintering.

1.2 parts by weight of B + 4 parts by weight of C melted at 94°.5 – 95°.5 without sintering.

This would indicate that the difference between Ketones B and C is due to dimorphism, C being the stable form.

On the other hand, the difference between Ketones A and B and A and C respectively cannot be due to this cause, as the melting-points were depressed by the admixture. Further, the previously mentioned fact (p. 10) that the transformation of Ketone B into Ketone C can be prevented by excluding Ketone C altogether from the neighbourhood lends support to this view regarding the difference between them. Ketone A is quite unaffected by recrystallisation or by "seeding" its solution with either Ketone B or Ketone C. neither do Ketones B or C give A on "seeding" their solutions with A.

Transformations of the three Ketones A, B and C into one another.

1. Each Ketone in iodine-benzene solution was during summer exposed to sunlight for 11 days. After shaking with thiosulphate and removing the benzene in a current of dry air the residue was recrystallised from alcohol.

2. Each Ketone was boiled for 12 hours with iodine-benzene solution, the solution treated with thiosulphate, then evaporated and the product recrystallised from alcohol.

3. A current of dry hydrochloric acid gas was passed for a few minutes through a benzene solution of each ketone. The solution, after standing for a week, was evaporated in a current of dry air and the residue recrystallised from alcohol.

4. Each Ketone was heated in a closed tube and the product recrystallised from alcohol.

The results of these methods are given in the following table:

Method.	Ketone A.	Ketone B.	Ketone C.
1. Exposure to light.	Ketones A and B, C in small amount.	Ketones A, B and C.	Ketone C, A & B in small amount.
2. Boiling of Solution.	Ketones A, B and C.	Ketones A & B in approx. equal amounts, a small quantity of C.	Ketone C, A and B in small quantity
3. Action of HCl.	Ketones A, B & C (C not found on one occasion)	Ketone B, A in small amount, occasionally also C.	Ketones A & B, occasionally C as well.
4. Heating:			
24 hours at 140°.	Ketones A, B & C.	Ketones B & C (A not formed)	Ketone C, no change.
24 hours at 160°.	Ketones A, B & C.	Ketones B & C (A in small quantity.	Ketone C, traces of A & B.

Addition of desoxybenzoin to the three Ketones A, B and C.

With Ketone A. A solution of 1g. substance and 0·6g. desoxybenzoin in absolute alcohol was treated with about 20 drops of a concentrated sodium ethylate solution and allowed to stand overnight. The precipitate which formed was filtered off, washed with water and recrystallised from acetic acid. White crystals of the already known m. nitrobenzamarone (m.p. 220° - 221°) were obtained. Yield, 1.3g.

With Ketone B. About 20 drops of a concentrated sodium ethylate/

ethylate solution were added to a solution of 1g. Ketone B and 0.6g. desoxybenzoin in absolute alcohol. Since on standing no reaction appeared to take place, the mixture was boiled for six hours, precipitated with water and the product recrystallised from acetic acid. 0.2g. of m. nitrobenzamarone was obtained.

With Ketone C. The reaction was carried out as with Ketone B, except that the mixture was boiled for two hours only. 1g. Ketone C gave 0.8g. m. nitrobenzamarone.

In order to compare the products of these reactions with m. nitrobenzamarone itself, this body was prepared by Klingemann's[I.] method. The products mentioned above proved to be identical with the m. nitrobenzamarone so prepared: this was confirmed by the mixture-melting-point method, whereby always the melting-point of the m. nitrobenzamarone was observed.

Addition of Bromine to the three Ketones A, B and C.

These reactions, which proceeded slowly, were carried out in chloroform solution. The ketone was dissolved in chloroform, the calculated quantity of bromine (dissolved in chloroform) added, and the mixture allowed to stand in a stoppered bottle. The solution was allowed to stand until the colour due to the bromine did not become paler; this required several days. The chloroform was then removed by means of a current of dry air and the residue recrystallised from a mixture of benzene and petroleum ether. In this way each ketone yielded colourless glancing prisms containing bromine, they dissolved easily in benzene, but were insoluble in petroleum ether. These crystals did not possess a sharp

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melting-point but decomposed vigorously on heating. In order to see whether the products got from the three ketones were identical or not, they were heated in the same melting-point bath and the decomposition-points observed, they decomposed at almost the same temperature (159° - 161°). In addition, the decomposition-points of mixtures of any two of the three products were the same as the decomposition-points of the products themselves if the heating was carried out in the same melting-point bath. For these reasons, the products derived from the three ketones were regarded as identical.

In the case of Ketone A the yield was almost theoretical.

Bromine estimation:

I. 0·2230 g substance gave 0·1702 g AgBr

II. 0·2247 g " " 0·1704 g AgBr.

Calculated for $C_{21}H_{15}O_3NBr_2$	Found.	
	I.	II.
Br = 32·73%	32·48%	32·27%

With Ketone B the yield amounted to about 40% of the theory.

Bromine estimation:

0·1988 g substance gave 0·1515 g AgBr

Calculated for $C_{21}H_{15}O_3NBr_2$	Found.
Br = 32·73%	32·43%

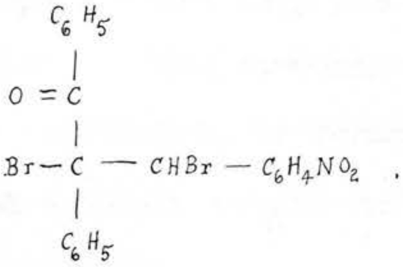
With Ketone C the addition of bromine took place rather more slowly, a small quantity of iodine was added to hasten the reaction. Yield, about 50% of the theoretical.

Bromine estimation:

0·1935 g substance gave 0·1470 g AgBr.

Calculated for $C_{21}H_{15}O_3NBr_2$	Found.
$Br = 32{\cdot}73\%$	$32{\cdot}33\%$

The three m. nitrobenzaldesoxybenzoins, therefore, unite with bromine and give the same dibromide



$$\begin{array}{l} \quad\;\; C_6H_5 \\ \qquad | \\ O = C \\ \qquad | \\ Br - C - CHBr - C_6H_4NO_2 \\ \qquad | \\ \quad\;\; C_6H_5 \end{array} .$$

IV.

Condensation of desoxybenzoin and p. nitrobenzaldehyde by means of hydrochloric acid gas.

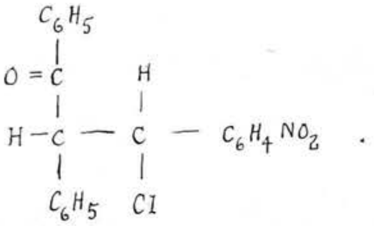
7 Parts by weight of desoxybenzoin and 6 parts by weight of p. nitrobenzaldehyde were suspended in 80 parts by weight of dry ether (p. nitrobenzaldehyde dissolves only slightly in ether)[I], the mixture cooled in ice and dry hydrochloric acid gas passed through it for five hours. After standing in ice for eleven days, during which time a large quantity of crystals had separated, the ether was evaporated in a current of dry air and the solid residue fractionally recrystallised from alcohol. In this way, a small quantity of white crystals were obtained, these were purified by recrystallisation from a mixture of benzene and petroleum ether and then melted at 157° - 158°, they contained chlorine.

[I] Instead of ether, alcohol and chloroform, in which p. nitrobenzaldehyde is more soluble, were tried, but it was found that ether gave the best results.

The chief product of the reaction was a yellow body (short prisms) which after recrystallisation from alcohol melted at 164° - 165° and contained no chlorine. The separation of these two substances is a tedious operation and is best accomplished by using alcohol as solvent, in this way well-formed crystals are obtained.

Sometimes a third body was obtained, but only in very small quantity. This compound was recrystallised from a large quantity of alcohol, it formed very long pointed prisms possessing a yellow colour and melting at 148° - 149°. It contained no chlorine.

The chlorinated body of m.p. 157° - 158° proved to be chloro-p. nitrobenzyldesoxybenzoin:



$$\begin{array}{ccccl} & C_6H_5 & & & \\ & | & & & \\ O= & C & & H & \\ & | & & | & \\ H- & C & - & C & - C_6H_4NO_2 \; . \\ & | & & | & \\ & C_6H_5 & & Cl & \end{array}$$

Analysis of this body:

I. 0·2025g substance gave 7·0cc. N at 17° and 754 mm.

II. 0·1528 g " " 0·0607g AgCl.

Calculated for $C_{21}H_{16}O_3NCl$	Found I.	Found II.
N = 3·83%	3·97%	–
Cl = 9·71%	–	9·82%

Chloro-p. nitrobenzyldesoxybenzoin forms very fine colourless prisms which are easily soluble in hot benzene, more difficultly soluble in alcohol and insoluble in petroleum ether. The yield of this body amounted to about only 6% of the theoretical.

The yellow body of m.p. 164° - 165° gave the following results on analysis:-

I. 0·1240 g substance gave 0·3488 g CO_2 and 0·0540 g H_2O.

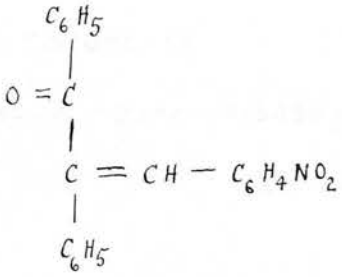
II. 0·2285 g " " 8·2 cc. N at 14° and 774 m.m.

Calculated for $C_{21}H_{15}O_3N$	Found. I.	Found. II.
C = 76·59%	76·71%	—
H = 4·56%	4·84%	—
N = 4·25%	—	4·30%

Molecular weight determination by boiling-point method (solvent, chloroform):

Solvent.	Substance.	Elevation.	Molecular weight	
g	g		Found.	Calculated for $C_{21}H_{15}O_3N$
20·55	0·5350 g	0·297°	321	329
20·55	0·7005	0·392°	318	

This compound was therefore a p.-nitrobenzaldesoxybenzoin



$$\begin{array}{l} C_6H_5 \\ | \\ O=C \\ | \\ C=CH-C_6H_4NO_2 \\ | \\ C_6H_5 \end{array}$$

and is for shortness designated Ketone A. It dissolves with difficulty in boiling alcohol, more easily in benzene, acetone, chloroform and acetic acid, but is insoluble in petroleum ether. The yield of this body amounted to about 80% of the theory.

The third body, melting at 148° - 149°, gave the following results on analysis:

I. 0·1787 g substance gave 0·5000 g CO_2 and 0·0780 g H_2O.

II. 0·2007 g " " 7·9 cc. N at 25° and 757 m.m.

Calculated for $C_{21}H_{15}O_3N$	Found. I	Found. II.
C = 76·59%	76·31%	—
H = 4·56%	4·85%	—
N = 4·25%	—	4·36%

Molecular weight determination by boiling-point method (solvent, chloroform):

Solvent.	Substance.	Elevation.	Molecular weight.	
g	g		Found.	Calculated for $C_{21}H_{15}O_3N$
22·05	0·3875	0·197°	326	329
22·05	0·5345	0·277°	320	

It was also regarded as a p.-nitrobenzaldesoxybenzoin (Ketone C) This body dissolves with difficulty in alcohol and acetic acid, more easily in benzene, chloroform and methyl acetate; it can be conveniently recrystallised from a mixture of alcohol and benzene. By recrystallisation from alcohol magnificient long pointed prisms can be obtained.

It was found that a third p. nitrobenzaldesoxybenzoin- Ketone B - could be obtained from Ketone A (see p.49).

Analysis of Ketone B:

1. 0·2157 g substance gave 0·6049 g CO_2 and 0·0862 g H_2O

II. 0·2180 g " " 8·3 cc N at 21°·5 and 752 m.m.

Calculated for $C_{21}H_{15}O_3N$	Found. I.	II.
C = 76·59%	76·44%	—
H = 4·56%	4·45%	—
N = 4·25%	—	4·28%

Molecular weight determination (solvent, chloroform) by boiling-point method:

Solvent.	Substance.	Elevation.	Molecular weight.	
g	g		Found	Calculated for $C_{21}H_{15}O_3N$.
21·41	0·2300	0·120°	327	329
21·41	0·4045	0·216°	320	

Ketone B forms long yellow prisms melting at $133^{\circ}.5$ - $135^{\circ}.5$ and is much more soluble in alcohol than either Ketone A or Ketone C, the difference of solubility in other liquids is less pronounced/

pronounced.

Action of caustic potash on chloro-p. nitrobenzyldesoxybenzoin.

This compound was boiled for 4 hours with 50% caustic potash solution, the crude product filtered off, washed with water and then recrystallised from alcohol (animal charcoal). In this way Ketones A and C only were obtained; the yield was poor.

Transformation of the three Ketones A, B, and C into one another.

I. Experiments with Ketone A.

1. A solution of 1g. of the substance in iodine-benzene solution was exposed to sunlight for four months in summer. After working up the solution in the usual way and recrystallising the product from alcohol there was obtained 0.7g of Ketone B, 0.2g unaltered substance and 0.05g of Ketone C.

2. 40g of Ketone A was boiled for 12 hours with iodine-benzene solution and the solution then subjected to the usual treatment. On recrystallising the product from alcohol it gave 14g of Ketone B and 0.8g of Ketone C, the remainder consistred of unaltered substance.

3. A benzene solution of 1.2g Ketone A was treated with dry hydrochloric acid gas for a few minutes, the solution, after standing for a week, was evaporated in a current of dry air. Thw product on recrystallisation from alcohol gave unaltered substance and 0.4g Ketone B.

II. Experiments with Ketone B.

1. 1g of this body in iodine-benzene solution was exposed to sunlight for four months in summer. After working up the solution/

solution as usual the product after recrystallisation from alcohol was found to consist of 0.75g unalatered substance, 0.1g Ketone A and about 0.03g of Ketone C.

2. 2g of Ketone B was boiled for 12 hours with iodine-benzene solution and the solution then worked up in the usual manner. 0.7g of Ketone B was obtained, the rest consisted of unaltered substance.

3. A benzene solution of 1.5g of Ketone B was treated with dry hydrochloric acid gas for a few minutes and the solution, after standing for a week was worked up in the usual way. The product contained, besides unaltered substance, 0.7g of Ketone A.

III. Experiments with Ketone C.

1. A solution of the substance in iodine-benzene solution was, during summer, exposed to sunlight for a week, then worked up by the usual methods. Approximately equal quantities of Ketones A and C were isolated, also a small quantity of Ketone B.

2. 1g of the compound was boiled for 12 hours with iodine-benzene solution. After the usual treatment the product yielded chiefly unaltered substance, but smaller quantities of the other Ketones A and B were also found.

Melting-points of mixtures of the three Ketones A, B and C.

The mixtures consisted of equal weights of each of two ketones. The results were:

Ketone A (m.p. $164^\circ - 165^\circ$) + Ketone B (m.p. $133^\circ.5-135^\circ.5$) melted at $135^\circ - 150^\circ$.

Ketone A (m.p. $164^\circ - 165^\circ$) + Ketone C (m.p. $148^\circ - 149^\circ$) melted at $136^\circ - 142^\circ$.

Ketone B (m.p. $133^\circ.5-135^\circ.5$) + Ketone C m.p. $148^\circ - 149^\circ$) melted at $135^\circ - 138^\circ$.

Apparently/

Apparently, then, the difference between the three bodies cannot be due to dimorphism.

"Seeding experiments with supersaturated solutions of the three ketones and with the fused substances.

Hot saturated solutions of each ketone in a mixture of alcohol and benzene were prepared and three portions of each cooled supersaturated solution were "seeded" separately with a crystal of one of the three ketones. The results were as follows:-

I. Supersaturated sol. of Ketone A "seeded" with A gave A only.
" " " " " " " B " A only.
" " " " " " " C " A only.
II. Supersaturated sol. of Ketone B "seeded" with A gave B only.
" " " " " " " B " B only.
" " " " " " " C " B only.
III. Supersaturated sol. of Ketone C "seeded" with A gave C only.
" " " " " " " B " C only.
" " " " " " " C " C only.

Each ketone was then melted, allowed to cool, and three parts of each supercooled still liquid substance were "seeded" separately with a crystal of one of the three ketones. The identity of the product (on solidification) with one of the three ketones A, B or C was established by means of the melting-point. The results were:

I. Ketone A "seeded" with A gave A only.
" " " " B " A only.
" " " " C " A only.
II. Ketone B "seeded" with A gave B only.
" " " " B " B only.
" " " " C " B only.

III/

III. Ketone C "seeded" with A gave C only.
" " " " B " C only.
" " " " C " C only.

In these experiments the three ketones A, B and C are indifferent towards each other. The differences between them cannot, therefore, be due to dimorphism.

Addition of desoxybenzoin to the three Ketones A, B and C.

With Ketone A. In this case the reaction took place only with difficulty and the yield was poor. 1g of Ketone A and 0.6g desoxybenzoin were dissolved in the necessary quantity of boiling absolute alcohol, 20 drops of a concentrated sodium ethylate solution added, and the mixture boiled for six hours. On cooling, a precipitate formed, this was filtered off, the filtrate neutralised with acetic acid and concentrated. The united crystalline fractions were recrystallised from alcohol. In this way, there were obtained fine white needles (o.2g) melting at 236° - 237° which proved to be p. nitrobenzamarone (see below) and also 0.5g of unaltered Ketone A, the only other substances obtained were of a resinous nature. The yield of p. nitrobenzamarone amounted therefore to only 12% of the theory.

With Ketone B, the reaction was more satisfactory. A cold absolute-alcoholic solution of 1g of Ketone B and 0.6g desoxybenzoin was treated with a concentrated sodium ethylate solution (20 drops) and the mixture allowed to stand for two days. The precipitate which formed was filtered off, the filtrate was again trated with the same quantity of sodium ethylate and allowed to stand further. A precipitate again formed, this was filtered off, the filtrate neutralised with acetic/

acetic acid and then concentrated. The united crystalline fractions were recrystallised from alcohol. The products were: 0.55g of white crystals (m.p. 236° - 237°, p. nitrobenzamarone), 0.1g of Ketone A and 0.05g of Ketone C; a partial transformation of Ketone B into Ketones A and C had therefore taken place. Yield of p. nitrobenzamarone, about 33% of the theoretical.

With Ketone C, the reaction proceeded very easily, and the yield was excellent. A cold absolute alcoholic solution of 0.5g Ketone C and 0.3g desoxybenzoin was treated with 20 drops of a concentrated sodium ethylate solution and allowed to stand. A precipitate (0.7g) separated; this on recrystallisation from alcohol proved to be p. nitrobenzamarone (m.p. 236° - 237°) only. Yield, about 88% of the theory.

As p. nitrobenzamarone has not previously been obtained, it was prepared in the same way as benzamarone itself:

39 Parts by weight of desoxybenzoin and 13 parts by weight of p. nitrobenzaldehyde were dissolved in the necessary quantity of absolute alcohol, a solution of 1 part by weight of caustic potash in absolute alcohol was then added. After standing for a day, the precipitate which had formed was filtered off, washed with alcohol, then with water, dried and recrystallised from benzene. Fine white needles (m.p. 236° - 237°) were obtained. Yield, about 95% of the theory.

Nitrogen estimation:

I. 0·4588g substance gave 11·4 cc. N at 20° and 769 m.m.

II. 0·4025g " " 9·8 cc. N at 16° and 755 m.m.

Calculated for $C_{35}H_{27}O_4N$	Found. I.	II
N = 2·66%	2·88%	2·88%.

p/

p. Nitrobenzamarone dissolves with difficulty in cold benzene, acetone or alcohol, more easily in hot benzene, but not very easily in hot acetone or alcohol.

The p. Nitrobenzamarone so prepared agreed completely in its properties with the p. nitrobenzamarone obtained from the three ketone A, B and C. A mixture of the p. nitrobenzamarone so prepared with the p. nitrobenzamarone got from Ketone A possessed the melting-point 236° - 237°, this was also the case with the products got from the ketones B and C.

Action of bromine on the Ketones A, B and C.

Each ketone was dissolved in carbon tetrachloride, the calculated quantity of bromine (dissolved in carbon tetrachloride) added and the solution allowed to stand for 9-10 days. Since in each case the action proceeded very slowly, a small quantity of iodine was added. After removing the solvent in a current of dry air, the residue was recrystallised from a mixture of benzen and petroleum ether. In this way each ketone yielded colourless blunt prisms which on heating melted with strong decomposition. The melting-point varied somewhat according to the method of heating: the three products from the three ketones all melted at 156° - 157° if the melting-points were all determined in the same (previously warmed) melting-point bath. Further, the melting-points of mixtures of any two of these three products were the same as the melting-points of the products themselves provided the melting-points were determined in the same (previously warmed) melting-point bath. The/

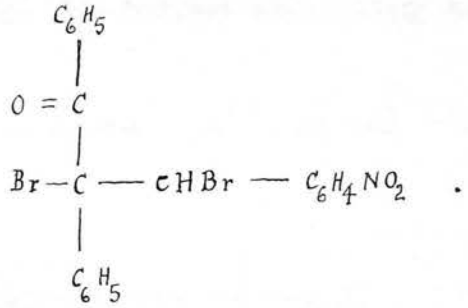
The three products, each of which contained bromine, were therefore regarded as identical.

Analysis:

I. 0·1348 g substance gave 0·1030 g AgBr.
II. 0·3200 g " " 7·9 cc. N at 17° and 751 mm.

Calculated for $C_{21}H_{15}O_3NBr_2$	Found. I.	II.
Br = 32·73%	32·51%	–
N = 2·87%	–	2·89%

Therefore the substance was p. nitrobenzaldesoxybenzoin-dibromide



$$\begin{array}{c} C_6H_5 \\ | \\ O = C \\ | \\ Br - C - CHBr - C_6H_4NO_2 \\ | \\ C_6H_5 \end{array} .$$

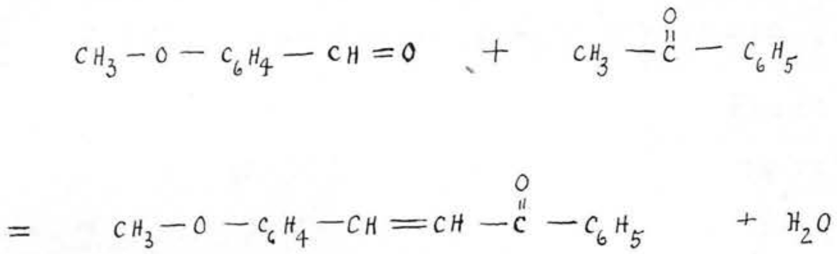
It does not dissolve in petroleum ether, but is easily soluble in benzene.

The yield from Ketone A amounted to about 70% of the theory, the amount of dibromide got from Ketone B was almost quantitative, while Ketone C gave about 50% of the theoretical amount of dibromide.

V.

Condensation of acetophenone and o. methoxybenzaldehyde by means of caustic soda.

To a solution of 15g of o. methoxybenzaldehyde and 13.3g of acetophenone in 70g of alcohol 20g of a 10% aqueous solution of caustic soda were added. The mixture immediately acquired a greenish yellow colour and an oil soon separated. After standing for 16 hours the oil was solidified by rubbing, filtered off, washed with water and recrystallised from ligroin. The substance, o. methoxybenzalacetophenone, is formed according to the equation



$$CH_3-O-C_6H_4-CH=O \quad + \quad CH_3-\overset{O}{\overset{\|}{C}}-C_6H_5$$

$$= \quad CH_3-O-C_6H_4-CH=CH-\overset{O}{\overset{\|}{C}}-C_6H_5 \quad + \quad H_2O$$

It forms yellowish-white felted needles (m.p. 58° - 59°) which are easily soluble in benzene, alcohol and ether, more difficulty soluble in ligroin. By precipitating the alcoholic mother-liquors from the reaction with water further quantities of the substance can be obtained; the yield amounted to 80-90% of the theory.

Analysis:

0·1205g substance gave 0·3558g CO_2 and 0·0687g H_2O.

Calculated for $C_{16}H_{14}O_2$.	Found.
C = 80·67%	80·52%
H = 5·88%	6·33%

The substance reduces permanganate at once and gives an orange coloured solution with concentrated sulphuric acid/

acid.

Attempts to obtain a stereoisomeric o. methoxybenzalacetophenone.

1. 13g of the substance in 30g of iodine-benzene solution was exposed to sunlight for 5 weeks in March and April. After working up the solution as usual the product was recrystallised from a mixture of ether and ligroin. Much unaltered substance was obtained, the mother-liquors on evaporation yielded a brown transparent resin (4g) which could not be crystallised. It was dried in vacuo over sulphuric acid and analysed:

1. 0·2605g substance gave 0·7522g CO_2 and 0·1445g H_2O.

Calculated for $C_{16}H_{14}O_2$	Found.
C = 80·67%	78·75%
H = 5·88%	6·16%

It could not therefore be determined whether a stereoisomer was present in this resin or not.

2. A solution of o. methoxybenzalacetophenone in iodine-benzene solution was boiled for 12 hours, then worked up as usual and the product recrystallised from a mixture of ether and ligroin. Unaltered substance was obtained, together with a small quantity of a brown resin. This resin, which could not be crystallised, was not investigated further.

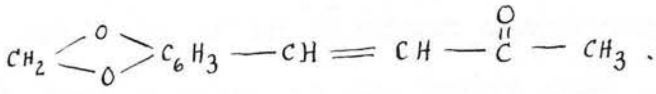
3. The substance was heated for three days in a closed tube at 120°, the product then recrystallised from a mixture of ether and ligroin. The only product obtained was unaltered substance.

The attempts to prepare a stereoisomer of o.methoxybenzalacetophenone (m.p. 58° - 59°) were accordingly unsuccessful/

unsuccessful.

VI.

Transformations of the two stereoisomeric piperonylideneacetones.



$CH_2<\overset{O}{\underset{O}{}}>C_6H_3-CH=CH-\overset{O}{\overset{\|}{C}}-CH_3$.

The two stereoisomers are known, the one possesses a strong yellow colour and melts at 107° (<u>Ketone A</u>), the other is white and melts at 111° (<u>Ketone B</u>). They were prepared by Haber's method.[I.]

I. Experiments with Ketone A.

1. 4g of the substance in iodine-benzene solution were exposed to sunlight for 5 weeks. After the usual procedure, the product being recrystallised from alcohol (animal charcoal), 0.7g of Ketone B was obtained; the remainder consisted of unaltered substance.

2. 4g substance in iodine-benzene solution was boiled for 12 hours, the solution subjected to the usual treatment and the residue recrystallised from alcohol (animal charcoal). Only unaltered substance was got.

3. 1·5g of Ketone A was heated in a closed tube for four days, first at 140°, then at 160°. Only unaltered substance could be isolated from the product.

4. Some of the powdered substance was placed between two glass plates and exposed to sunlight. In an hour or two the substance had become pronouncedly paler in colour, probably owing to the formation of some of the white stereoisomer. The substance is therefore fairly sensitive to light and is best

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I. Ber. 24, 618.

kept in the dark.

II. Experiments with Ketone B.

1. 1.2g of this ketone was dissolved in a 0.1% chloroform solution of iodine and exposed to sunlight for a week. After working up the solution as in previous cases and recrystallising the product from alcohol it was found that almost the whole of Ketone B had been converted into the yellow stereoisomer Ketone A; only a small quantity of substance remained unaltered. If, instead of a chloroform solution, a benzene solution of Ketone B was exposed to light, resinous products only were obtained.

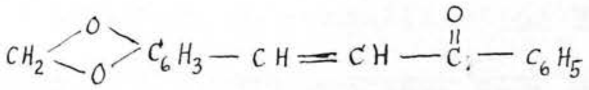
2. 0.8g of Ketone B was boiled for 12 hours with a 0.1% chloroform solution of iodine. After proceeding as usual, unaltered substance only was obtained.

3. Some of the substance was heated at 160° for 4 days in a closed tube. On recrystallisation from alcohol it was found that no change had taken place.

VII.

Attempt to convert piperonylideneacetophenone into a stereoisomer.

This body



$CH_2\langle O_2 \rangle C_6H_3-CH=CH-\overset{O}{\overset{\|}{C}}-C_6H_5$

was prepared by condensing piperonal and acetophenone[1] in alcoholic solution by means of caustic soda. It melts at 122°, a stereoisomer is unknown.

10g of the compound in iodine-benzene solution was

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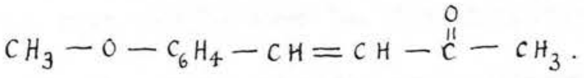
[1] Ber. 29, 1892.

exposed to sunlight for 5 weeks. After removing the iodine with thiosulphate the solution was evaporated almost to dryness and then "seeded" with a crystal of the substance. It solidified almost completely, the mass after filtration was recrystallised from alcohol and gave unchanged substance only. The benzene mother-liquors on evaporation yielded a resin (4g) which was dissolved in ether, ligroin was then added to the solution. On standing, crystals gradually separated, these after recrystallisation from alcohol proved to consist of unchanged substance only. The ether-ligroin mother-liquors yielded resinous products only.

The attempt to prepare a stereoisomer in this way was accordingly unsuccessful.

VIII.

Attempts to prepare a stereoisomer of anisylideneacetone.



$$CH_3 - O - C_6H_4 - CH = CH - \overset{O}{\overset{\|}{C}} - CH_3.$$

This substance can be obtained by condensing anisaldehyde with acetone[I.], it melts at 74°. A stereoisomer has not yet been prepared.

1. 8.5g substance in iodine-benzene solution was exposed to sunlight for 5 weeks. The solution after the usual treatment gave a product which on recrystallisation from methyl alcohol yielded unchanged substance together with a small quantity of a resin.

2. 3g of the compound was boiled for 12 hours with iodine-benzene solution. After treating the solution in the usual way the product was recrystallised from methyl alcohol.

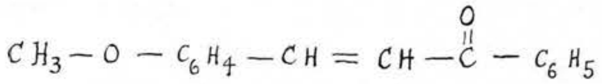
[I.] Ber. 25,3536: Baeyer & Villiger. Ber. 35, 1191.

Chiefly unaltered substance was obtained, a small quantity of a resin was also got.

IX.

Attempts to transform anisylideneacetophenone into a stereoisomer.

Anisylideneacetophenone (m.p. 75° - 76°)



$$CH_3-O-C_6H_4-CH=CH-\overset{\overset{O}{\parallel}}{C}-C_6H_5$$

is already known[I], a stereoisomer has not yet been prepared.

1. 15g of the substance in 30g iodine-benzene solution was exposed to sunlight for 5 weeks. After working up the solution in the usual way a red coloured product was obtained, This was repeatedly extracted with ligroin which dissolved out the unaltered anisylideneacetophenone. The undissolved residue was deep red in colour and melted very unsharply. It was amorphous and could not be crystallised, it dissolved in alcohol and ether, more easily in benzene and acetone, with difficulty in ligroin. This red substance (2g) was dissolved in benzene and the solution carefully "layered" with ligroin. On standing, yellow flakes separated, these were still amorphous and obviously impure.

It was next attempted to prepare the semicarbazone of this amorphous body in the hope of obtaining a crystalline product. The reaction was carried out in the usual way, alcohol being used as solvent. Crystals soon separated, after ten days standing these were filtered off and recrystallised from water: it then was found that these crystals consisted merely of hydrazodicarbonamide, a decomposition product of semicarbazide. The filtrate from the reaction -

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[I] Private communication.

product on concentration or precipitation with water gave resinous products only.

A shorter exposure to light gave no better results.

2. Anisylideneacetophenone was boiled for 12 hours with iodine-benzene solution. The solution was worked up in the usual manner, the product was recrystallised from alcohol, and gave chiefly unaltered substance besides a small quantity of a red coloured resin.

3. 2g of the substance was heated at 120^0 for three days in a closed tube. Since on cooling no change appeared to have taken place, the heating was continued for a day and a half longer at 160^0. After recrystallisation from alcohol unaltered substance only was obtained.

It was therefore not found possible to prepare a stereoisomer by these methods.