[Contribution from the Chemical Laboratory of McGill University]

THE REACTIONS OF ANHYDRACETONEBENZIL WITH CERTAIN HALOGEN COMPOUNDS

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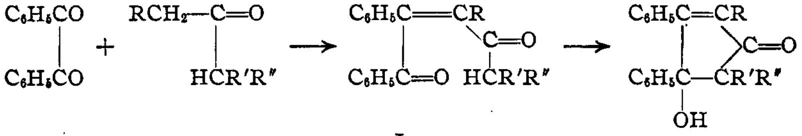
Received June 16, 1932 Published November 5, 1932

It has been shown by Japp and his co-workers[1] that benzil condenses with many aliphatic ketones; the primary product is an α,β-unsaturated ketone. If the latter still contains a hydrogen atom in the alpha position to the carbonyl group, it usually cannot be isolated but undergoes an intramolecular addition to form a cyclic ketone (I).

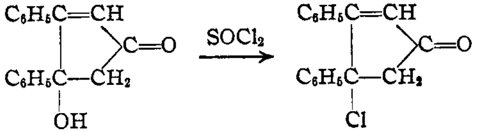


I

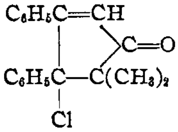
The ring compounds have been shown to be derivatives of cyclopentanone.

Gray[2] prepared the two isomeric benzal derivatives (XVI) of anhydracetonebenzil (II), both of which gave the same acetate when treated with acetic anhydride and sulfuric acid, and used this series of reactions as evidence for the presence of an OH group in the starting material. Because of the tendency for this substance (II) to lose water with the usual acylating and dehydrating agents, it does not form esters, although tertiary alcohols generally form halides rather than esters when treated with acid halides.

We have treated anhydracetonebenzil (II) and its dimethyl derivative (XX) (formula I, R′ and R″ = CH_3) with acetyl chloride and have obtained chlorides (III, IV). Since thionyl chloride acted in a similar manner to give the same substances it would seem conclusive evidence that there is a tertiary hydroxyl group as shown by the formula.



II III



IV

However, by the action of hydrogen chloride on anhydracetonebenzil, Japp prepared a chloride isomeric with ours, of which he was unable to determine the constitution, so it was necessary for us to account for the second chloride and determine the structures of both.

All the possible structures are represented by formulas III, V, VI, VII, VIII. Since the chlorides have a carbonyl group, the chlorofuran VII is

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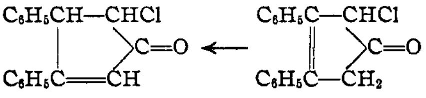
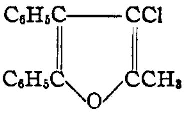
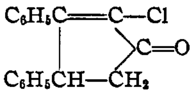
[1] Japp and co-workers, *J. Chem. Soc.*, (a) **47,** 11 (1885); (b) **51,** 420 (1887); (c) **57,** 662 (1890); (d) **71,** 1138 (1897); (e) **75,** 1017 (1899); (f) **79,** 1024 (1901); (g) **85,** 1473 (1904); (h) *Ber.*, **18,** 179 (1885); (i) **21,** 2933 (1888).

[2] Gray, *J. Chem. Soc.*, **95,** 2131 (1909).

excluded. Formula VI seems improbable, *a priori*, because, having hydrogen between two unsaturated linkages, the hydrogen could shift and, doubtless, would do so, resulting in V.

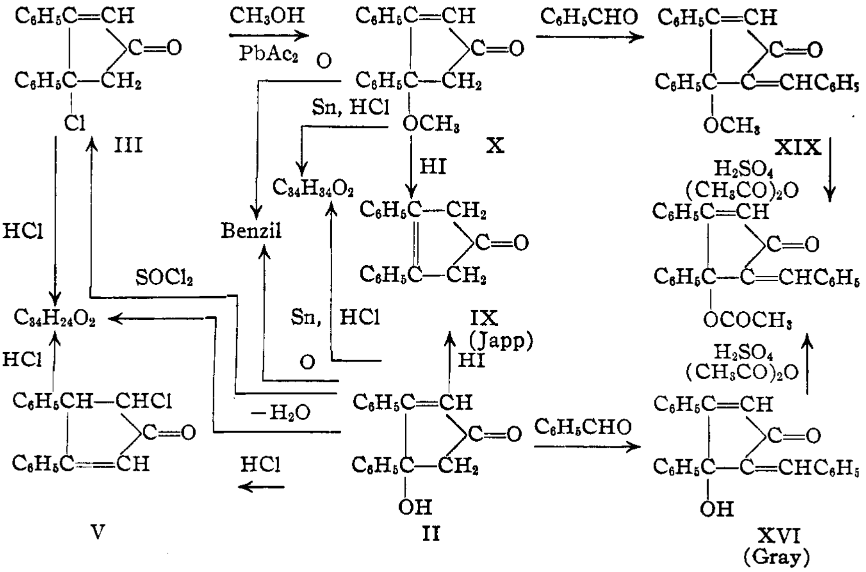

V VI


VII

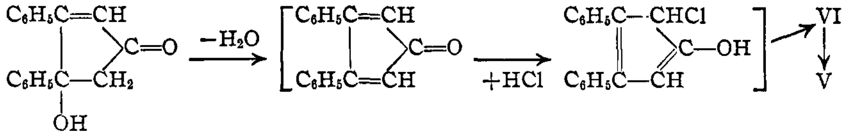

VIII

Our chloride formed a methyl ether when treated with potassium, lead or silver acetates in absolute methanol. This ether still contained the five-membered ring since it formed the same reduction products as anhydracetonebenzil (*e. g.*, hydrogen iodide gave a cyclopentenone (IX) and stannous chloride a bimolecular reduction product); oxidation gave benzil. It formed an oxime, and condensed with benzaldehyde to give a pair of geometrical isomers (XIX), showing that the CH_2 was still next to the carbonyl group. It gave a dibromosubstitution product with sodium hypobromite.

Both chlorides (Japp's and ours) on treatment with basic reagents lost hydrogen chloride and gave the same bimolecular product, $C_{34}H_{24}O_2$ (the structure of this will be taken up later; it is also formed from anhydracetonebenzil and dehydrating agents). Barring molecular rearrangements, only substances represented by formulas III and V could lose hydrogen chloride to give the same substance; accordingly our chloride is best represented by formula III and Japp's must be V. Additional evidence in favor of V for Japp's chloride is the non-formation of a benzal derivative. These reactions may be summarized by the flow sheet



Since alkaline reagents act alike on both chlorides and remove hydrogen chloride, a structure of a cyclopentadieneone (XII) can be written as possible for the primary product; in view of the ease with which cyclopentadiene polymerizes, it is not surprising that the ketone does. Now when anhydracetonebenzil is treated with hydrogen chloride without taking precautions, only the chlorine-free bimolecular product, $C_{34}H_{24}O_2$, is found; *i. e.*, the hydrogen chloride acts as a dehydrating agent. In view of this, Japp's chloride is probably formed by addition of hydrogen chloride to the ends of the conjugated system in the cyclopentadieneone (before it polymerizes), followed by the usual shift of enolic hydrogen on a double bond.



II XII

β,β-Dimethylanhydracetonebenzil (XX), which has no alpha hydrogen and cannot be dehydrated, did not give a chloride with hydrogen chloride. Also substance (III) gave a mixture of the bimolecular compound and Japp's isomer (V) when treated with hydrogen chloride. These reactions are in agreement with the proposed mechanism.

By the use of hydrogen bromide we have made a bromide that behaves like Japp's chloride in all respects, and loses hydrogen bromide with alkaline reagents to give the same bimolecular product; it is, therefore, represented by formula V (Br for Cl).

The only known cyclopentadieneone, which has been made by Dilthey,[3] is a tetraphenyl (two remaining H in XII replaced by C_6H_5); it does not polymerize, probably because of the hindrance of the additional phenyl groups.

In the absence of a solvent, phosphorus trichloride dehydrated anhydracetonebenzil and gave the bimolecular product, $C_{34}H_{24}O_2$; in dry benzene it formed the chloride (III). This same chloride was also obtained by the use of phosphoryl chloride and anhydrous aluminum chloride in benzene. Arsenic trichloride showed no action. Sulfur chloride reacted vigorously but gave intractable oils and gums.

Sulfuryl chloride gave two products; one was formed by a simple substitution of one hydrogen in the alpha position, yielding a monochloroanhydracetonebenzil (XIII). The other was a bimolecular hexachloride, for which the most probable formula is represented by (XIV). Formula (XIII) is preferred to one having the chlorine on the doubly bound carbon by analogy with the dimethyl homolog (XX), which does not react at all

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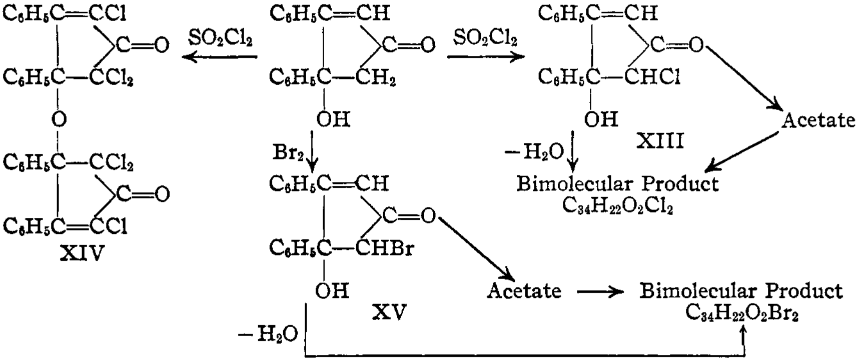
[3] Dilthey and Quint, *J. prakt. Chem.*, [2] **128,** 149(1930).

with sulfuryl chloride, and because the chlorine is active enough to be removed readily by alkaline reagents.

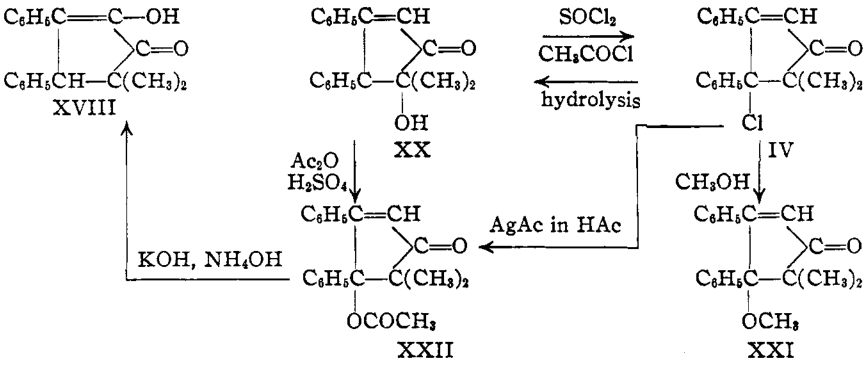


The monochloro ketone (XIII) was dehydrated under the same conditions as anhydracetonebenzil and formed a bimolecular product with essentially the same properties as $C_{34}H_{24}O_2$, but containing two chlorine atoms.

Japp brominated anhydracetonebenzil and obtained a monobromo substitution product for which he gave a melting point of 172° but wrote no formula. On trying to repeat his work, we also obtained a monobromo substitution product, but the melting point was 198°—we have been able to get but one and never any other melting point. Now if a formula (XV) is assigned to this substance, it is evident that two stereoisomers can exist—this may account for the variation. On dehydration this bromo ketone gave a bimolecular compound with the characteristic properties of $C_{34}H_{24}O_2$, but containing two bromine atoms. Therefore, by analogy, the structures of the bromo and chloro ketones and the bimolecular products are similar.

In the dimethyl series a few new relations have been established. With acetyl and thionyl chlorides, dimethylanhydracetonebenzil (XX) formed the chloride (IV). The latter regenerated the hydroxy compound with potassium hydroxide, and potassium or silver acetates in alcoholic solution, but with silver acetate in acetic acid gave the same acetate (XXII) that had been previously prepared by Gray[2] from the hydroxy compound, acetic anhydride, and sulfuric acid. The acetate, on hydrolysis with alcoholic potash, did not regenerate the hydroxy compound from which it was made, but the isomer (XVIII).[2] The latter was not affected by acetyl or thionyl chlorides. Neither of the hydroxyl compounds (XX, XVIII) was affected by concentrated sulfuric acid.

The chloride (IV) readily formed a methyl ether (XXI). These reactions are summarized in the following outline



Experimental

A. **Reactions with Anhydracetonebenzil, (II).** (a) **The Chloride (III).**—A mixture of 20 g. of anhydracetonebenzil[1e] and 40 cc. of acetyl chloride was stirred mechanically at room temperature until the solid had dissolved (eight hours). On spontaneous evaporation, 14 g. (65%) of a yellowish solid remained; after repeated crystallization from *n*-butyl ether it formed rods, m. p. 121°.

Anal. Calcd. for $C_{17}H_{13}OCl$: Cl, 13.2. Found: Cl, 13.4.

The chloride is sparingly soluble in petroleum ether and readily soluble in the other usual organic solvents. In alcoholic solution it reacted with the solvent and a bimolecular product, $C_{34}H_{24}O_2$, identical with the one described by Japp,[1b] separated. The latter substance was also formed by the action of heat or light on the chloride; it formed cubes from benzene, m. p. 199–200° with gas evolution.

This chloride was also prepared from anhydracetonebenzil and thionyl chloride, phosphorus trichloride, phosphoryl chloride and anhydrous aluminum chloride, in benzene solution by refluxing 1 g. of the ketone, 2 g. of the chloride, and 10 cc. of dry benzene for ten minutes, pouring into 100 cc. of water, separating the upper layer, washing and drying over calcium chloride. The solvent was evaporated from the filtered solution and the residue dissolved in ether; on slow spontaneous evaporation, 0.5 g. of the chloride crystallized. The yields were of this order except with the aluminum chloride, where a large amount of oily by-product resulted. In the absence of a solvent phosphorus trichloride acted only as a dehydrating agent to give the bimolecular product. Arsenic trichloride showed no action under any of the conditions tried. Sulfur chloride gave only unmanageable oils.

(b) **The Chloride (V) (Japp's).**—This was made as previously described[1b] as well as by the action of hydrogen chloride on the chloride (III). It melted at 128°.

Dry hydrogen chloride was bubbled through a solution of 0.5 g. of the chloride (III) in 10 cc. of ether until absorption ceased. The solvent was allowed to evaporate spontaneously after twelve hours; a residue composed of oil and two kinds of crystals was separated into the starting material and the bimolecular product, $C_{34}H_{24}O_2$. From the oil a few milligrams of the chloride (V) was isolated. All these substances were identified by means of mixed melting points.

The chloride was recovered unchanged after boiling with pyridine or either alcoholic or acetic acid solutions of silver and potassium acetate. Alcoholic potash, however, removed hydrogen chloride and the bimolecular product resulted. A mixture of 0.5 g. of the chloride, 1 cc. of 10% aqueous potassium hydroxide and 10 cc. of alcohol was refluxed for ten minutes, poured into water, and the precipitated solid filtered and recrystallized. The yield was practically quantitative. Its properties showed that it was the bimolecular product.

To prove the presence of a carbonyl group, the 2,4-dinitrophenylhydrazone was prepared. One gram of 2,4-dinitrophenylhydrazine was dissolved in 1 cc. of concentrated sulfuric acid and carefully diluted with 10 cc. of alcohol; this mixture was at once added to a solution of 1 g. of the chloride in 30 cc. of alcohol, and the whole warmed for five minutes. On cooling, a fine reddish solid separated and was filtered; it was purified by recrystallization from acetic acid, and formed red needles, m. p. 217°; yield, 0.9 g. or 54%. It is insoluble in all the common organic solvents

Anal. Calcd. for $C_{23}H_{17}N_4Cl$: N, 12.5. Found: N, 12.4.

(c) **The Bromide (V) (Br for Cl).**—Ten grams of anhydracetonebenzil was suspended in 25 cc. of chloroform, previously saturated with hydrogen bromide. After twenty-four hours the solvent was evaporated and the deeply colored residue taken up in alcohol and repeatedly crystallized. It yielded 6 g. (50%) of white, diamond-shaped prisms, m. p. 113°.

Anal. Calcd. for $C_{17}H_{13}OBr$: Br, 25.6. Found: Br, 25.6.

Like the chloride, this bromide was not affected by the metal acetates, but with alcoholic potash gave the bimolecular product.

(d) **The Methyl Ether (X).**—In methyl alcohol in the presence of lead or silver acetates, the chloride (III) formed the corresponding methyl ether. The latter was also formed in small amounts when very dilute methyl alcoholic potassium acetate or hydroxide was used, but the principal product was the bimolecular compound; only the latter was obtained with more concentrated solutions.

A suspension of 10 g. of the chloride, 10 g. of lead acetate, and 60 cc. of methyl alcohol was refluxed for a half hour; the solid soon went into solution, and then lead chloride precipitated. The latter was removed by filtration and from the filtrate white hexagonal prisms separated in a yield of 7 g. (69%). These were recrystallized from methyl alcohol; m. p. 126°.

Anal. Calcd. for $C_{18}H_{16}O_2$: C, 81.7; H, 6.1; OCH_3, 11.7. Found: C, 81.2, 81.4; H, 6.2, 5.9; OCH_3, 12.0.

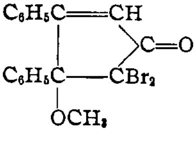
The methyl ether is insoluble in petroleum ether, sparingly soluble in ethyl ether, and readily soluble in the other usual organic solvents.

The oxime was prepared in the usual way and formed rods, m. p. 173°, after recrystallization from methyl alcohol.

Anal. Calcd. for $C_{18}H_{17}O_2N$: N, 5.0. Found: N, 5.0.

On reduction with red phosphorus and iodine[4] it formed the cyclopentenone (IX). It was not necessary to vacuum distil, as the solid separated on partial evaporation of the ether. It had a melting point of 110° which showed no depression when mixed with a sample prepared from anhydracetonebenzil. On reduction with tin and hydrochloric acid, it formed the same bimolecular reduction product, $C_{34}H_{34}O_2$, m. p. 187–8°, as anhydracetonebenzil.[1b]

The methyl ether is not attacked by potassium permanganate; in acetic acid hot chromic acid oxidizes it to benzil and benzoic acid. Sodium hypobromite oxidizes anhydracetonebenzil to desylacetic acid[1e] but attacks the methyl ether only very slowly and then introduces two atoms of bromine. The same dibromide was also formed by direct bromination. Since both the bromine atoms are removed by alcoholic potash it is unlikely that either is on the double bond, and the most probable formula is XXIII. Unfortunately, it was



XXIII

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[4] Ref. 1e, p. 131.

not possible to isolate any bromine-free hydrolysis products, complete decomposition having taken place.

A mixture of 5 g. of finely powdered methyl ether was mechanically stirred for two hours with a solution of 10 g. of bromine in an excess of 15% sodium hydroxide; no action was apparent. However, on close inspection the filtered solid seemed to be composed of two kinds of crystals; it was separated by means of methyl alcohol, 4 g. of the ether crystallizing first. On longer standing, 0.6 g. of needles formed—these melted at 175° and a mixture with the dibromo ether below also melted at 175°.

A chloroform solution containing an excess of bromine was added to a solution of 1 g. of the methyl ether in 10 cc. of chloroform and the mixture allowed to stand for two days at room temperature; hydrogen bromide was slowly evolved. The solvent and unused bromine were removed and the product crystallized from alcohol. It formed fine needles, m. p. 175°.

Anal. Calcd. for $C_{18}H_{14}O_2Br_2$: Br, 37.9; OCH_3, 7.4. Found: Br, 37.7; OCH_3, 7.4.

The Benzal Derivatives (XIX).—A solution of 30 cc. of absolute alcohol, 5 g. of the methyl ether, an equal weight of benzaldehyde, and the sodium ethylate from 0.5 g. of sodium and 10 cc. of alcohol was refluxed for ten minutes; the solid that separated was filtered and crystallized from alcohol; yield, 4.5 g. It formed rods, m. p. 160°. The reddish filtrate was poured into water to precipitate the isomeric form, which after several recrystallizations from alcohol or dilute acetone melted at 124°.

Anal. Calcd. for $C_{25}H_{20}O_2$: C, 85.2; H, 5.7; OCH_3, 8.8. Found: (160°) C, 85.5; H, 5.5; OCH_3, 8.8; (124°) C, 84.7; H, 5.6.

Both of these benzal derivatives on treatment with acetic anhydride and concd. sulfuric acid formed the known acetate (XVII), m. p. 175°, identical with the one prepared in the same manner from anhydracetonebenzil.[3]

Hydrogen chloride converted the methyl ether into a mixture of Japp's chloride (V), and the bimolecular compound, $C_{34}H_{24}O_2$; probably chloride (III) was a primary product, and then was altered as already described.

A solution of 1 g. of the ether in 20 cc. of alcohol was saturated with hydrogen chloride; the reddish solution was left at room temperature overnight and then poured into 150 cc. of water. The amorphous precipitate was filtered and taken up in alcohol; from the latter solution, 0.4 g. of the bimolecular compound separated first, and on spontaneous evaporation a few milligrams of Japp's chloride was isolated and identified by a mixed melting point.

(e) **Action of Sulfuryl Chloride; Preparation of Chlorides (XIII) and (XIV).**—From a mixture of 10 g. of anhydracetonebenzil, 30 cc. of benzene and 5 cc. of sulfuryl chloride that had stood overnight, 9 g. of a white solid separated; it crystallized from alcohol in fine white needles, m. p. 194°; the halogen could be removed quantitatively by alcoholic potash. On pouring the filtrate into water, an oil was precipitated—it soon became crystalline and after recrystallization from alcohol weighed 1.5 g. It formed flat rods, m. p. 129°.

Anal. Calcd. for $C_{17}H_{12}O_2Cl$ (194°): Cl, 12.5: for $C_{34}H_{20}O_3Cl_6$ (129°): Cl, 30.9; mol. wt., 688. Found: (194°) Cl, 12.6, 12.7 (129°) Cl, 30.8, 30.8; mol. wt., 546 (Rast's method).

(f) **Bromination.**—Anhydracetonebenzil was treated with bromine, following Japp's directions[1a] as exactly as possible. Our product, obtained in a yield of 6 g., also formed fine white needles from alcohol, but the melting point was 198° instead of the 172° he recorded.

Anal. Calcd. for $C_{17}H_{13}O_2Br$: Br, 24.3. Found: Br, 24.4.

The bromo compound gave an oil on treatment with alcoholic potash. With acetic anhydride and concd. sulfuric acid a mixture of an acetate and a bimolecular product containing two atoms of bromine was formed.

A suspension of 5 g. of the bromine compound (XV) in 15 cc. of acetic anhydride cleared up and became warm when a trace of sulfuric acid was introduced. On cooling, 1.5 g. of a solid separated and was filtered, and the filtrate decomposed by ice. An oily mixture resulted, from which 1.5 g. of an acetate and a small amount of the first solid separated. The acetate was purified by recrystallizing several times from alcohol, and formed needles, m. p. 148°.

Anal. Calcd. for $C_{19}H_{15}O_3Br$: Br, 21.6. Found: Br, 21.4.

The high melting solid was recrystallized from *n*-butyl ether; it formed prisms, m. p. 212°, with gas evolution.

Anal. Calcd. for $C_{34}H_{22}O_2Br_2$: Br, 25.7. Found: Br, 26.0.

It is practically insoluble in petroleum ether, ethyl ether, the alcohols, benzene, acetone, and glacial acetic acid, but moderately soluble in chloroform.

The chloride (XIII) on similar treatment with acetic anhydride and a trace of sulfuric acid also formed an acetate and a bimolecular product. The acetate separated as needles from alcohol, m. p. 159°, and the bimolecular product crystallized in very fine prisms from *n*-butyl ether, m. p. 217° with gas evolution.

Anal. Calcd. for $C_{19}H_{15}O_3Cl$ (159°): Cl, 10.9; for $C_{34}H_{22}O_2Cl_2$ (217°): Cl, 13.3. Found: (159°) Cl, 10.6, 10.8; (217°) Cl, 13.3.

The bimolecular chloride was the only product if acetic acid was substituted for the anhydride. It was also formed in all attempts to hydrolyze the acetate, even when using ammonia at room temperature.

The bimolecular chloride and bromide exhibit the same peculiar properties as Japp's bimolecular compound, $C_{34}H_{24}O_2$; their structures will be considered in a later paper.

(g) **Reactions with β,β-Dimethylanhydracetonebenzil (XX).**—This was prepared by a method essentially like Japp's.[1f] The requisite methyl *i*-propyl ketone and *i*-butyraldehyde were obtained by oxidation of methyl-*i*-propylcarbinol and *i*-butyl alcohol, respectively; the carbinol was made by the action of methylmagnesium iodide on *i*-butyraldehyde. The latter was prepared by the general directions for propionaldehyde,[5] keeping the water in the reflux condenser at 65°; the yield was 50%.

The methyl-*i*-propylcarbinol was made through the Grignard reaction as follows. In the usual type of apparatus were placed 150 cc. of dry ether and 53 g. of magnesium turnings, and a mixture of 355 g. of methyl iodide and 150 cc. of dry ether added, with stirring, at such a rate as to keep the solution refluxing vigorously, followed by thirty minutes' heating on the water-bath. The mixture was then chilled to −5°, and, with stirring, 159 g. of *i*-butyraldehyde in 150 cc. of dry ether slowly admitted; the whole was then heated on the water-bath for two hours. The contents of the flask were decomposed by pouring upon 1 kg. of cracked ice and the basic magnesium salt was dissolved by the addition of 500 cc. of 15% sulfuric acid. The upper layer was separated, the aqueous solution extracted with three 150-cc. portions of ether, the combined ethereal solutions washed with sodium carbonate and water, and dried over anhydrous sodium sulfate. The solvent was removed and the residue fractionated; 94 g. (60%) of carbinol, b. p. 109–111°, was obtained.

The methyl *i*-propyl ketone was then prepared by oxidation of this carbinol as follows. In a 1-liter three-necked flask, fitted with a good fractionating column, stirrer and dropping funnel, was placed 73 g. of the above carbinol, the flask was immersed in a water-bath, the temperature of which was 60°, and, while stirring vigorously, a mixture of 82 g. of potassium dichromate, 60 cc. of concd. sulfuric acid and 500 cc. of water was

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[5] "Organic Syntheses," Vol. XII.

slowly admitted through the dropping funnel. When addition had been completed, the contents of the flask were distilled as long as oily drops appeared in the condenser. The distillate, composed of two layers, was saturated with solid potassium carbonate, the ketone separated and dried with potassium carbonate. On fractionating, 39 g. (55%) of a product was secured, b. p. 90–94°. Potassium permanganate was unsatisfactory as an oxidizing agent. Diethyl ketone was similarly prepared from the commercial diethylcarbinol, at 65°, and methyl *n*-propyl ketone from methyl-*n*-propylcarbinol at 60° in yields of 73 and 70%, respectively.

Neither dimethylanhydracetonebenzil (XX) nor its isomer (XVIII) was affected by dissolving in concd. sulfuric acid; they were precipitated unchanged when the colored solutions were poured upon ice. The former gave deep green solutions with mineral acids, but we were unable to isolate a perchlorate. The latter was not affected by thionyl chloride.

The Chloride (IV).—A mixture of 3 g. of dimethylanhydracetonebenzil and 10 cc. of thionyl chloride was refluxed for a half hour, poured into water and filtered. The solid was then dissolved in ether, the solution dried with calcium chloride and decanted, and a small amount of petroleum ether added; on spontaneous evaporation a solid separated. The latter formed fine needles when recrystallized from *n*-butyl ether, m. p. 133°. It is very soluble in the usual solvents except petroleum ether, and the only one suitable for crystallizing was the one used.

Anal. Calcd. for $C_{19}H_{17}OCl$: C, 76.4; H, 5.7. Found: C, 76.9; H, 5.7.

Hydrolysis.—On refluxing 0.1 g. with a very dilute solution of potassium hydroxide in alcohol for ten minutes, a white solid separated; this was filtered and found to be the hydroxyl compound by mixed melting point and solubilities. Potassium and silver acetates in alcohol led to the same result.

The Acetate (XXII).—A mixture of 0.2 g. of the chloride and 0.3 g. of silver acetate in 10 cc. of glacial acetic acid was refluxed for ten minutes, cooled and filtered into 100 cc. of water. The precipitated acetate was removed and crystallized from alcohol; it melted at 137° and a mixture with a sample of the acetate prepared by Gray's method likewise melted at 137°. On hydrolysis as described by Gray, it formed the hydroxy ketone (XVIII).

The Ether (XXI).—A mixture of 1 g. of the chloride and an equal weight of silver acetate in 15 cc. of absolute methyl alcohol was refluxed a quarter hour, filtered hot and water added slowly to precipitate the ether. It crystallized from dilute methyl alcohol in clusters of prisms, m. p. 144°; the yield was 0.6 g. It was very soluble in alcohol, acetic acid, benzene and acetone, but separated from the first two on dilution with water.

Anal. Calcd. for $C_{20}H_{20}O_2$: OCH_3, 10.6. Found: OCH_3, 10.7.

This work has been assisted by a grant from the Cyrus M. Warren Fund of the American Academy of Arts and Sciences.

Summary

1. By the action of thionyl, acetyl, phosphoryl, and anhydrous aluminum chlorides on anhydracetonebenzil, a tertiary chloride that resembled triphenylchloromethane in several respects was prepared. This reaction furnished direct proof of the presence of a tertiary hydroxyl group in anhydracetonebenzil.

2. The structure of an isomeric chloride formerly prepared by Japp has been established, and a mechanism proposed to account for its formation.

3. Sulfuryl chloride acted principally as a chlorinating agent.
4. Some new relations were determined in the dimethyl series.

MONTREAL, CANADA

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF HARVARD UNIVERSITY]

CONDENSATIONS AND RING CLOSURES IN THE NAPHTHALENE SERIES. III.[1] *PERI*-SUCCINOYLACENAPHTHENE

BY LOUIS F. FIESER AND (IN PART) MARY A. PETERS

RECEIVED JUNE 16, 1932 PUBLISHED NOVEMBER 5, 1932

Having found that the condensation of β-naphthol with phthalic anhydride leads to the production of a compound of an unusual structural type,[1a] it has become a matter of interest to study the reaction of various other naphthalene derivatives with this and other anhydrides. It has been our immediate concern to investigate more fully certain condensations which fall within the field specified, but which have been described only in the patent literature. These condensations are between succinic or maleic anhydride and various substitution products of naphthalene. In a series of patents originating with the I. G. Farbenindustrie,[2] it is claimed that cyclic compounds of novel structure may be obtained either by heating the components in molten sodium aluminum chloride or by applying this method of condensation to the intermediate products resulting from the Friedel and Crafts reaction of the anhydride with the hydrocarbon.

After some trial of these reactions it was decided that the case most favorable for detailed study was that of the condensation of succinic anhydride with acenaphthene. As specified in the patents, these components interact smoothly at 0° in nitrobenzene solution in the presence of aluminum chloride.[3] The keto acid melting at 208° is not, however, the sole reaction product, but is accompanied by an isomer melting at 181°. The separation of the isomers is easily accomplished and it was further found that the relative proportions of the two acids is somewhat dependent upon the reaction temperature. Thus the yields at 0° were 78 and 15% for the higher and the lower melting isomers, respectively, while at −15° the yields were 87 and 5%. The structures were established by oxidation. The higher melting acid is β-(3-acenaphthoyl)-propionic acid, I, for it yields 1,4,5-naphthalenetricarboxylic acid on controlled permanganate oxidation. No acid of the naphthalene series could be obtained from the

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[1] (a) First paper, Fieser, THIS JOURNAL, 53, 3546 (1931); (b) second paper, Fieser and Peters, THIS JOURNAL, 54, 3742 (1932).

[2] (a) I. G. Farbenindustrie, French Patent 636,065 (1928); (b) Swiss Patent 131,959 (1929); (c) H. Gruene, U. S. Patent 1,759,111 (1930).

[3] The reaction is also described by F. Mayer, German Patent 376,635 (1923).