

that obtained by the alumina dehydration of carbinol (IV) a hydrocarbon was obtained instead. Ten ml. of solvent was slowly distilled from a solution of 500 mg. of the *i*-methyl ether (XII) in 100 ml. of xylene. To the remaining solution was added 8 g. of powdered activated alumina and the mixture was refluxed for three hours. The alumina was separated by filtration and washed with acetone. The acetone-xylene filtrates were concentrated *in vacuo* and the residue was dissolved in an acetone-methanol mixture from which there was obtained 320 mg. of crystalline material. Several crystallizations gave thick needles melting at 162.0–163.0°, $[\alpha]^{25D} - 18.5^\circ$ (51.3 mg. in 5 ml. of chloroform $\alpha_D - 0.19^\circ$, *l*, 1 dm.). The needles fluoresced in ultraviolet light.

Anal. Calcd. for $C_{36}H_{44}$: C, 90.70; H, 9.30. Found: C, 90.35; H, 9.33.

A solution of 48 mg. of the above hydrocarbon (XVII) in 15 ml. of glacial acetic acid was refluxed for four hours. The solvent was removed under reduced pressure and the colorless sirup crystallized from acetone-methanol to give 35 mg. of brilliant cubes, m. p. 165–166.5°. From the mother liquors a second crop of 8 mg. was obtained. There was no melting point depression when the substance was mixed with the acetoxy-diene (VII).

Summary

1. 6(α)-Methoxy-*i*-norcholonyldiphenylcarbinol (IV) was prepared by two different methods.
2. The dehydration product of the carbinol (IV) by treatment with activated alumina in boiling xylene was considerably different from compound (XII) where the unsaturated side chain (R_3') was prepared by conventional methods before introducing the *i*-methyl ether configuration. We have tentatively suggested that this may be due to the epimerization of the δ -methoxyl group.
3. In an attempt to epimerize the synthetic product (XII), by alumina in boiling xylene, an interesting hydrocarbon (XVII) was obtained.
4. Heating the hydrocarbon (XVII) in acetic acid caused the addition of acetic acid forming a normal acetate. A mechanism for this reaction has been proposed.
5. Several intermediates and conversion products have been described.

EVANSTON, ILLINOIS

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[COMMUNICATION NO. 854 FROM THE KODAK RESEARCH LABORATORIES]

The Action of Alkaline Reagents on the Bimolecular Product Formed by the Action of Acidic Dehydrating Agents on Anhydracetonebenzil

BY C. F. H. ALLEN AND J. W. GATES, JR.

The bimolecular product I that results from the action of acidic dehydrating agents on anhydracetonebenzil is a very reactive substance, having many points of attack for reagents. In this paper are described the results secured by the use of alkaline reagents.

It had previously been observed¹ that Japp's chloride was converted to the bimolecular product by a short (ten-minute) treatment with alcoholic potash, whereas a longer time resulted in a viscous product.² It has now been found that this material, also obtainable directly from the bimolecular product itself, will crystallize in time, or at once, if seeded, and that it is mainly a carboxylic acid. The use of sodium methylate or ethylate gives the corresponding methyl and ethyl esters in a few minutes; the ethyl ester has been hydrolyzed to the acid, and the latter re-esterified by diazomethane and also converted to an anilide.

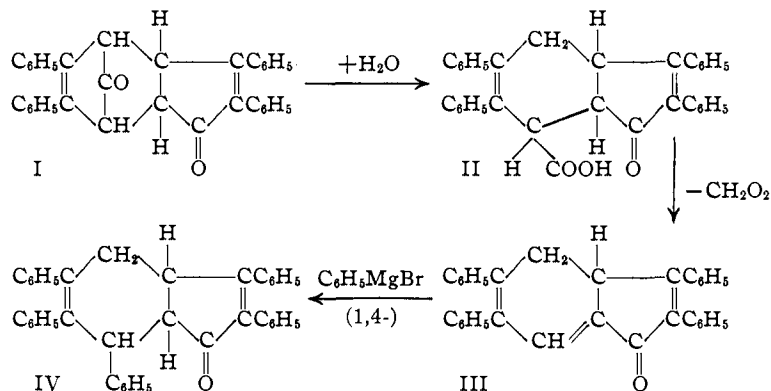
Analyses show that the only change is the addition of one molecule of water (or alcohol, depending upon the reagent); hence the carboxyl group must comprise one of the two carbonyl groups present originally. Since the acid does not lose carbon monoxide when heated, it is the carbonyl bridge that has been cleaved. The bimolecular product and the esters are not attacked by permanganate in acetone, perhaps because of their insolubility, but the sodium salt of the acid is easily oxidized. During the reaction the carboxyl group disappears, and a dienone is formed; this new dienone is an isomer of the one (V) previously obtained by heating the bimolecular product, when the carbonyl bridge is lost as carbon monoxide.¹ Analyses show that the loss, in the case of the acid, is CH_2O_2 .

The new dienone is an α,β -unsaturated ketone (III), for it gives both 1,4- and 1,2-addition with the Grignard reagent; this establishes the location of one double bond. Although there is, to be sure, another α,β -unsaturated system involving the

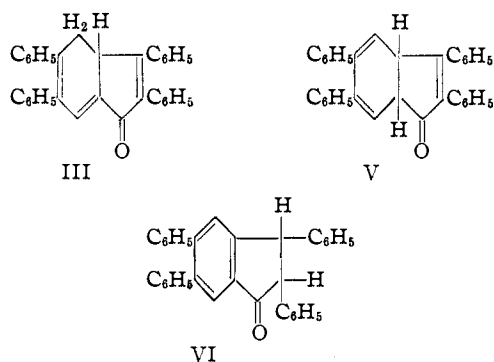
(1) Allen and Spanagel, *THIS JOURNAL*, **55**, 3773 (1933).

(2) Allen and Rudoff, *Can. J. Res.*, **B15**, 327 (1937).

indene ring, the possibility of 1,4-addition of the Grignard reagent to this is excluded by the observation that other indenones containing the same system give only carbinols, formed by 1,2-addition. Taken in conjunction with the disappearance of the carbonyl bridge by alkali, the structure of the acid II follows. The oxidation results are accounted for by a retrograde Michael reaction, in which formic acid (CH_2O_2) is split off, and destroyed by the permanganate.



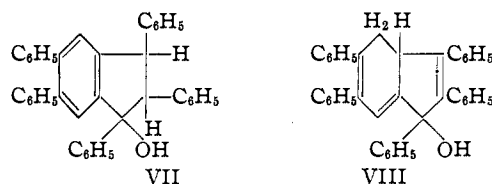
The new dienone III, in contrast to the isomer previously described,² does not add maleic anhydride, but, like it, is isomerized by heating to the known indanone VI. The only difference is in the position of the extra hydrogen atoms and double bonds; that is, these are allylic systems, in which rearrangements occur with the greatest of ease; the most stable form is that of the indanone VI, owing to its aromatic structure. The mobility of



the systems makes it almost impossible to state positively which structure goes with which substance, but the available evidence seems to be in best agreement with the structures as assigned.

Even as gentle a reagent as phenylmagnesium bromide is not useful. For example, the carbinol VIII, formed by 1,2-addition and mentioned above, is isomeric with one (VII) easily obtained

from the indanone VI, whereas the dienone V



forms a glasslike product with phenylmagnesium bromide.³ All give the same hydrocarbon on removal of water, that is, there must have been a rearrangement in two of the dehydrations. These reactions will form the subject of a later paper.

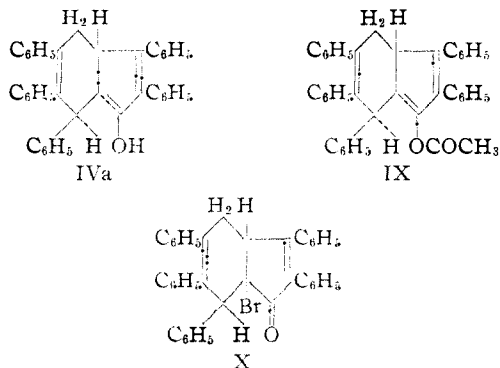
When attempts were made to repeat the earlier preparation of the dienone (V), the results were erratic; sometimes it was readily isolated after decarbonylation of the bimolecular product, but at others, under what appeared to be identical conditions, only the rearrangement product, the indanone VI, could be obtained.

This difficulty was traced finally to small amounts of sulfuric acid in the bimolecular product (the latter was always formed in the presence of that acid). The mineral acid was thereafter eliminated by adding potassium acetate to the solution from which crystallization took place.

This result influenced us to examine the effect of acid alone upon the dienone V; it was found that mineral acids brought about an isomerization to a different dienone—which proved to be identical with III, described above. Both these, on heating, gave the indanone VI. This is an additional instance of the mobility of the allylic systems present in this series.

The 1,4-addition product IV probably exists largely in the enolic modification IVa, for it evolves 0.7 equivalent of methane when treated with methylmagnesium iodide, and gives an enol acetate IX with acetyl chloride. The latter consumes two equivalents of methylmagnesium iodide, and regenerates the enol; this is the usual behavior of an enol acetate. It is readily brominated, forming a monobromo ketone X, which is unaffected by acetyl chloride. The bromine is in the α position, since it is removed by methylmagnesium iodide, with regeneration of the starting material.

(3) The absence of mineral acid was ensured by decomposition of the complex with ammonium chloride; otherwise, dehydration occurs and the carbinol cannot be isolated.



Experimental

I. The Acid, 3a,4,7,7a-Tetrahydro-2,3,5,6-tetraphenyl-7-carboxyindanone-1 (II) and Related Substances.—The bimolecular product I, 3a,4,7,7a-tetrahydro-2,3,5,6-tetraphenyl-4,7-methanoinden-1,8-dione, was prepared in the usual way,¹ but the benzene solution was refluxed for half an hour, after the addition of anhydrous sodium or potassium acetate, filtered hot and diluted with twice the volume of alcohol or petroleum ether. The average yield of several preparations was 90%.

The acid II was secured as follows. To an alcoholic solution of potassium hydroxide (23 g. in 300 cc.) was added 46.4 g. of the bimolecular product, and the mixture refluxed for four hours; at the end of this time all the solid had dissolved. The solution was poured into 2 l. of water, 70 cc. of concentrated hydrochloric acid added, and the mixture extracted with three 100-cc. portions of chloroform. After drying the extract, distilling two-thirds of the solvent, and diluting with an equal volume of benzene and two volumes of petroleum ether, the acid separates in a yield of 38 g. (79%). After purification from benzene-ligroin, it forms prisms which melt at 275–276°. It is practically insoluble in absolute ethanol.

Anal. Calcd. for $\text{C}_{33}\text{H}_{26}\text{O}_3$: C, 84.7; H, 5.4. Found: C, 84.3; H, 5.3.

The methyl ester, prepared by use of sodium methylate, separated when the solution was chilled after three hours; the yield was 76%, and it forms prisms that melt at 193°. It also resulted when the acid was esterified by diazomethane.

Anal. Calcd. for $\text{C}_{35}\text{H}_{28}\text{O}_3$: C, 84.6; H, 5.4. Found: C, 84.3; H, 5.7.

The ethyl ester was secured in a similar manner but only ten minutes of refluxing was required. Some acid was formed during the manipulation; this was removed by triturating the oil with absolute ethanol. The ethyl ester crystallizes in prisms from alcohol-petroleum ether; m. p. 159–160°.

Anal. Calcd. for $\text{C}_{36}\text{H}_{30}\text{O}_3$: C, 84.7; H, 5.9. Found: C, 84.9; H, 5.9.

The anilide was prepared from the acid chloride in the usual manner; it forms prisms from benzene-petroleum ether; m. p. 269°.

Anal. Calcd. for $\text{C}_{40}\text{H}_{31}\text{O}_2\text{N}$: N, 2.5. Found: N, 2.5.

II. The Dienone III, 3a,4-Dihydro-2,3,5,6-tetraphenylindan-1-one.—Twenty-four grams of the acid was dis-

solved in 2 l. of 3% potassium carbonate, and, while stirring at 85–95°, 350–370 cc. of 6% aqueous potassium permanganate was added dropwise; a yellow precipitate was formed. The cooled suspension was extracted with three 150-cc. portions of chloroform, the solvent removed, and the residue recrystallized from xylene or acetic acid. It forms lemon-yellow prisms that melt at 239–240°. The yield was 12 g. (56%).

Anal. Calcd. for $\text{C}_{33}\text{H}_{24}\text{O}$: C, 90.8; H, 5.5. Found: C, 90.7; H, 5.5.

The isomeric dienone V, reported previously as being obtained by a carefully controlled pyrolysis, resulted in a 70–75% yield by heating the purified bimolecular product for only five to six minutes at 220–225°. When 10 g. of this dienone (m. p. 167°) was suspended in 50 cc. of glacial acetic acid and treated with 5 cc. of 32% hydrogen bromide in acetic acid, the solution became dark red; after warming for half an hour on the steam-bath, the dienone III crystallized quantitatively. A dilute solution of sulfuric acid in acetic acid brought about the isomerization equally well.

The new dienone does not add maleic anhydride. In the Grignard machine it shows one addition without evolution of gas. It isomerized to the indanone VI by heating for half an hour at 300°.

1,2,3,5,6-Pentaphenylindanol-1, VII, was obtained by the action of phenylmagnesium bromide upon the indanone VI in ether in the usual way, decomposing the complex with ammonium chloride. It crystallizes in prisms from benzene-petroleum ether; m. p. 228–229° with dec.

Anal. Calcd. for $\text{C}_{39}\text{H}_{30}\text{O}$: C, 91.0; H, 5.8. Found: C, 90.5; H, 5.7.

This carbinol gave the hydrocarbon, m. p. 222°, described below, when treated with an acetic acid solution of sulfuric acid. The dienone V gave a glasslike carbinol, which formed the same hydrocarbon upon dehydration.

III. The Grignard Reaction.—To a solution of phenylmagnesium bromide (4.8 g. of magnesium, 31.5 g. of bromobenzene, 200 cc. of ether) at room temperature was added a suspension of 25 g. of the dienone III in 50 cc. of ether. After stirring for one hour, the mixture was decomposed by ammonium chloride, and the oily product worked up by an appropriate manipulation; it was found advantageous to inoculate the dried and concentrated solution with some of the carbinol VIII from a previous preparation, and remove it first. The second product was the ketone IV. When the Grignard mixture was decomposed by mineral acid, the hydrocarbon was obtained instead of the carbinol, being isolated after the ketone.

The carbinol, 3a,4-dihydro-1,2,3,5,6-pentaphenylindan-1-ol (VIII) was obtained in a yield of 25%; it separates from benzene-ligroin in needles, m. p. 233°.

Anal. Calcd. for $\text{C}_{38}\text{H}_{30}\text{O}$: C, 91.0; H, 5.8. Found: C, 91.0; H, 6.0.

The hydrocarbon crystallizes in bunches of prisms from benzene-ligroin; m. p. 222°.

Anal. Calcd. for $\text{C}_{39}\text{H}_{28}$: C, 94.4; H, 5.7. Found: C, 94.1; H, 5.6.

This hydrocarbon does not add maleic anhydride, nor is it affected by hydrogen bromide in acetic acid.

The ketone, 3a,4,7,7a-tetrahydro-2,3,5,6,7-pentaphenyl-

inden-1-one (IV, IVa), forms prisms on crystallization from benzene-petroleum ether. The melting point is usually 178-179°, but occasionally a low-melting form is obtained: this melts at 145-146°, but on admixture with the higher melting form, the observed melting point is 178-179°. The yield was 60%.

Anal. Calcd. for $C_{30}H_{30}O$: C, 91.1; H, 5.9. Found: C, 90.9; H, 6.1.

This ketone does not react with maleic anhydride nor form an oxime. In the Grignard machine it evolves 0.67 mole of methane, indicating that it is enolized to a considerable extent. An acetate is secured in a 70% yield by refluxing an acetyl chloride solution for half an hour; it separates from benzene-ligroin in prisms that melt at 115°.

Anal. Calcd. for $C_{41}H_{32}O_2$: C, 88.5; H, 5.8. Found: C, 88.1; H, 6.0.

When treated quantitatively with methylmagnesium iodide, the acetate consumes two equivalents of reagent without evolution of gas; upon acidification the ketone IV is obtained.

The bromoketone, 3a,4,7,7a-tetrahydro-7a-bromo-2,3,5,6,7-pentaphenylinden-1-one (X) was secured by bromination in chloroform in the usual manner; it crystallized from chloroform-alcohol solution in pale yellow rods; m. p. 218-219°. It separated from benzene solutions in pointed rods with solvent of crystallization; the solid softened at about 144°, finally melting at 234°.

Anal. Calcd. for (A) $C_{30}H_{29}OBr$: Br, 13.5; for (B) $C_{30}H_{29}OBr \cdot C_6H_6$: C, 80.5; H, 5.2; Br, 11.9. Found: (A) Br, 13.8, 13.2; (B) C, 80.4, 80.2; H, 5.1, 5.1; Br, 11.9, 12.0.

In the Grignard machine both forms consume one mole

(4) Drs. Jelley and Titus of these Laboratories report that examination of these substances failed to show any significant differences of readily determinable optical properties.

of reagent without evolution of gas, and regenerate the parent ketone IV.

The bromine is not removed by pyridine or potassium acetate (*e. g.*, there is no adjacent hydrogen atom in the *alpha* position to the carbonyl group) but alcoholic potash gave an intractable black oil. It is unaffected by hydrogen bromide, by acetyl chloride, or by excess bromine.

Summary

The bimolecular product, resulting from the action of acidic dehydrating agents upon anhydracetonebenzil, is transformed into a carboxylic acid by the action of alkaline reagents. The carbonyl bridge disappears in the process, being converted into the carboxyl group.

The acid is decarboxylated and dehydrogenated to give a new dienone, isomeric with one previously known.

The new dienone is also obtained by the action of mineral acids on the one described earlier, and both are isomerized to the same known indanone by acids or heat.

The new dienone gives products with phenylmagnesium bromide formed by both 1,2- and 1,4-addition. The 1,4-addition product is an easily enolizable ketone.

The 1,2-addition product is a carbinol, isomeric with one obtained from the closely related indanone. Both are dehydrated to the same hydrocarbon, which is also formed from the isomeric dienone.

ROCHESTER, NEW YORK

RECEIVED MAY 5, 1942

[COMMUNICATION NO. 855 FROM THE KODAK RESEARCH LABORATORIES]

The Structure of the Bimolecular Product Formed by the Action of Acidic Dehydrating Agents on Anhydracetonebenzil

By C. F. H. ALLEN AND J. W. GATES, JR.

Several years ago¹ from an examination of the substance obtained by degrading the bimolecular product, formed by the action of acidic dehydrating agents upon anhydracetonebenzil I, a structure, III, which seemed in best accord with the available evidence, was suggested for this substance and a mechanism proposed to account for its formation. Others interested in this field^{2,3} appear to have accepted these conclusions. The salient features were the dehydration of anhydracetonebenzil to diphenylcyclopentadienone II, which

then underwent a diene synthesis with itself, forming the bimolecular product III. The latter lost carbon monoxide on heating, to give an indanone that was rearranged to an isomeric indanone IV, which was then degraded, stepwise, by unambiguous reactions to *o*-terphenyl. Later on⁴ several of the intermediate degradation products were synthesized, so that the position of the various groups around the benzene ring was established. Only the pertinent formulas are given below.

The two novel features were the presence of a phenyl group on a carbon atom common to two

(1) Allen and Spanagel. *THIS JOURNAL*, **55**, 3773 (1933).

(2) Dilthey, private communication.

(3) Burton and Shoppee. *J. Chem. Soc.*, 201 (1934).

(4) Allen, Bell, Bell and VanAlban. *THIS JOURNAL*, **62**, 656 (1940).