

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°.⁴ 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

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[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.

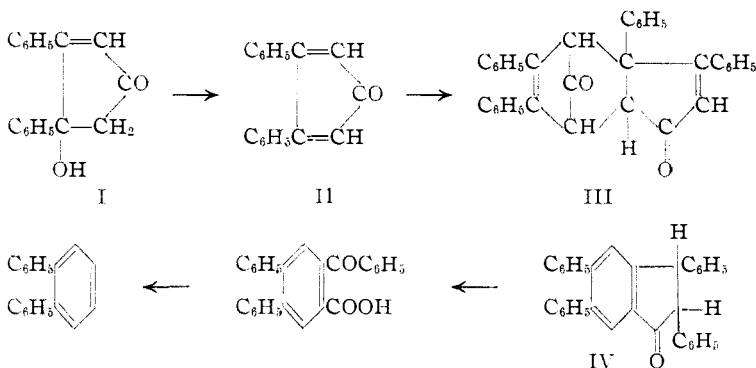
The two novel features were the presence of a phenyl group on a carbon atom common to two

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

(2) Dilthey, private communication.

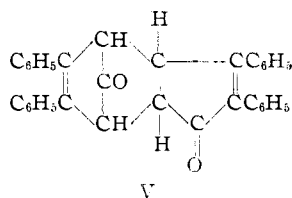
(3) Burton and Shoppee, *J. Chem. Soc.*, 201 (1934).

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



rings in III, and its apparent 1,3-shift to the position in which it is found in the indanone IV. No similar instances have been recorded in the literature. The formation of thiophenol, on sulfur fusion of the dienone formed after the decarbonylation of III, was interpreted in favor of the structure having the phenyl group on the bond common to the two rings, by analogy with the behavior under similar conditions of Ruzicka's alkyl decalins.⁵ Further work was accordingly undertaken, with the view of clearing up the uncertainty.

As a result⁶ isomeric indenones were discovered and the prevalence of allylic rearrangements in the series was noted. It was found that sulfur dehydrogenation (a high temperature reaction) gave varying amounts of thiophenol in instances where there was no reasonable doubt as to the absence of an angular phenyl group, so this argument lost its force. Furthermore, had the phenyl group been in this position, there should have been more isomers than were found experimentally. Finally, it has been possible⁶ to open one ring to form a monocarboxylic acid, which, on oxidation with permanganate, in alkaline solution, gave one of the dienones—all the reactions taking place below 100° under conditions too mild to bring about such a drastic change as a migration of a phenyl group. It has, thus, seemed necessary to abandon



(5) Ruzicka, *Helv. Chim. Acta*, **5**, 349 (1922).

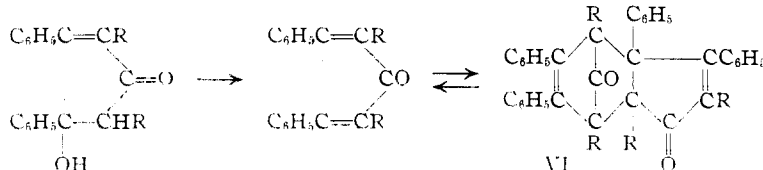
(6) Allen and Gates, *This Journal*, **64**, 2120 (1942).

both concepts, and to conclude that the phenyl group is in the position where it is found in the indanone, *alpha* to the carbonyl; the new structure is written in formula V.

It differs from the older one first proposed¹ only in an interchange of the angular phenyl group and one hydrogen atom. This was accounted for by assuming a 1,3-shift of a phenyl group. Such a re-

arrangement was, indeed, proposed in the first paper, but at a different point, namely, following the decarbonylation. The experimental conditions under which the bimolecular products are formed, favor such allylic rearrangements.

The mechanism of the reaction is, as previously outlined, a diene synthesis. Alternative interpretations have had to be excluded, because of the various experimental conditions under which the bimolecular product can be formed, and the fact that substituted anhydracetonebenzils can partake only if there is at least one hydrogen atom left to be removed as water with the hydroxyl group (this is, of course, essential to the production of the intermediate cyclopentadienone).

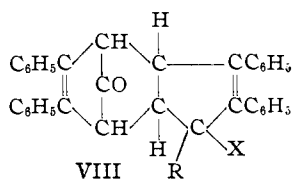
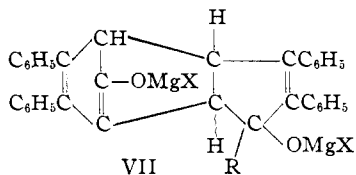


Now, when in the bimolecular product, R = H, it will exchange (an allylic rearrangement) with the angular phenyl group, giving a substance of type V, but if both R's = CH₃, there will be no further change—in fact, it has been shown that this type, VI, dissociates into its components in most reactions.⁷ Any open-chain structure for the bimolecular product is also excluded because such a structure would be impossible with the dimethyl homolog (both R's = CH₃).

The behavior of the bimolecular product with the Grignard reagent is unusual; in the Grignard machine it shows one active hydrogen and one addition. Previous work⁶ has shown that in indenones the carbonyl group always gives carbinols, and that a carbonyl bridge does likewise in the absence of adjacent *alpha* hydrogen atoms.⁷ Since the product is always a monocarbinol, that

(7) Allen and VanAllen, *ibid.*, **64**, 1260 (1942).

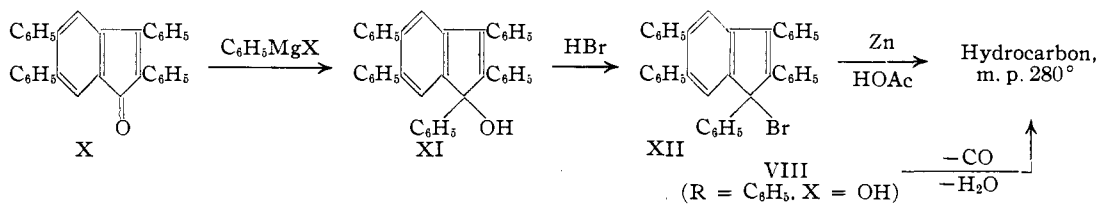
loses carbon monoxide on heating, it is the keto group on the indene ring that has been attacked, *i. e.*, the one addition has occurred here. But, since no exposed carbonyl group could persist unchanged, the carbonyl bridge must have been protected in some way from the action of the excess reagent. The obvious explanation is that it



forms an enolate, VII, thus a α -counting for the one active hydrogen observed; acidification then regenerates the original carbonyl group. Carbinols, VIII (X = OH), have been prepared in which R = CH₃, C₆H₅, α -C₁₀H₇. All carbinols lost carbon monoxide and water, when heated, and gave hydrocarbons. The carbinols were studied in more detail; in the Grignard machine they showed two active hydrogens (one due to enolate and one to carbinol). The hydroxyl was replaced by halogens on treatment with acid halides; they gave isomeric acetates with acetic anhydride and acetyl chloride. The acetates (VIII: R = CH₃, X = OCOCH₃) showed one active hydrogen and two additions in the Grignard machine, and regenerated the carbinol, as would be expected.

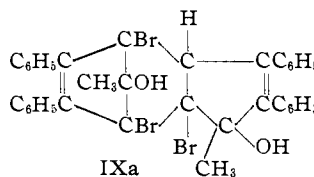
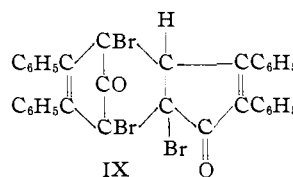
The bimolecular product was previously reported¹ to give two stereoisomeric dioximes. Both of these have now been hydrolyzed, with production of the bimolecular product; this excludes the possibility that the starting material was a mixture.

The bimolecular product was brominated to



form a tribromoketone IX, gave a monochloroketone with phosphorus pentachloride, did not condense with aromatic aldehydes, and was destroyed by concentrated sulfuric acid. The tribromoketone is the result of complete replacement of all the available hydrogen atoms in the α positions to both carbonyl groups. Its formation

excludes any of the open-chained isomeric structures that might be written, confirming the conclusion already mentioned above, concerning the formation of bimolecular products from substituted anhydracetonebenzils. In the Grignard machine it consumes two moles of reagent without evolution of gas. The product is a di-carbinol IXa, for it evolves two equivalents of gas when treated with excess methylmagnesium iodide. These reactions afford confirmation of the assumption previously made in regard to the bimolecular product, that the production of gas is connected with the presence of an enolizable hydrogen; in the tribromoketone there is no α hydrogen, and the two carbonyl groups behave normally, giving two additions.



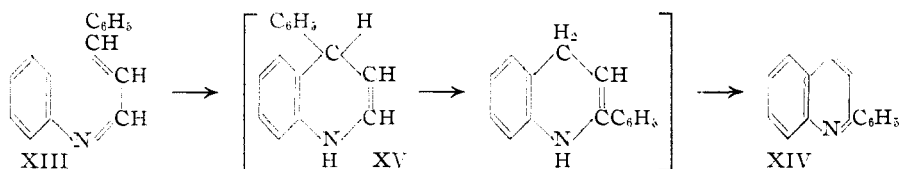
The monochloroketone is isomeric with one described as a result of chlorination of 3,4-diphenylcyclopenten-3-one-1.⁸

It was mentioned earlier that hydrocarbons were formed by loss of water during decarbonylation. From the phenyl carbinol (VIII: R = C₆H₅, X = OH) the hydrocarbon obtained was identical with one secured from 2,3,5,6-tetra-phenylindenone X by the following sequence of reactions

It is obvious from inspection of the formulas that in one instance there has been a rearrangement. The substance in question is also isomeric with a closely related hydrocarbon described previously⁹; a discussion of these and other related compounds will be considered separately.

(8) Burton and Shoppee, *J. Chem. Soc.*, 265 (1934).

One other instance, best explained as a 1,3-shift of a phenyl group, has been found in the literature. When cinnamalaniline XIII is heated in acid solution, it forms 2-phenylquinoline XIV.⁹ It must be assumed *either* that a 1,3-shift of a phenyl group is involved, *or* that the anil is hydrolyzed in part to its components, the aniline so formed then adding to a molecule of unchanged anil, with subsequent ring closure and dehydrogenation. In considering the first alternative, it should be noted that *before* dehydrogenation the substance XV has an allylic system, in which rearrangements are facile and common.



The explanation involving a 1,3-shift of a phenyl group seems preferable in this case, for Peine showed that cinnamalaniline showed a remarkable stability to acids, there being but a very slight hydrolysis to the components. It is much simpler than the necessary series of consecutive reactions required by the second alternative. We have found that cinnamalaniline is monomolecular, thus excluding interpretations involving polymeric forms.

Experimental

The bimolecular compound V and its two dioximes were prepared as reported previously.¹ Both dioximes (m. p. 176 and 229°) were hydrolyzed by refluxing a suspension of 4 g. of the dioxime in 100 cc. of alcohol containing 25 cc. of concentrated hydrochloric acid for twenty-four hours; after cooling, the precipitate was filtered. The yield was 2.5 g.; the melting point, 202–204°, was not lowered when mixed with the pure bimolecular product.

Bromination: 3a,4,7,7a-Tetrahydro-2,3,5,6-tetraphenyl-4,7,7a-tribromo-4,7-methanoinden-1,8-dione, IX; a mixture of 100 cc. of glacial acetic acid and 5 g. each of bromine and the bimolecular product was heated on the steam-bath for seventy-two hours; after the usual manipulative procedures, 1.5 g. of tribromoketone was obtained. It crystallizes from benzene–ligroin in prisms, m. p. 229–230°.

Anal. Calcd. for C₃₄H₂₁O₂Br₃: Br, 34.2. Found: Br, 33.6.

2,3,5,6-Tetraphenyl-1,8-dimethyl-4,7,7a-tribromo-1,8-dihydroxy-3a,4,7,7a-tetrahydro-4,7-methanoindene, IXa, was formed when the diketone IX reacted with methylmagnesium iodide. It crystallizes from benzene–ligroin in rods, m. p. 278°.

(9) Peine, *Ber.*, **17**, 2117 (1884).

Anal. Calcd. for C₃₆H₂₃O₂Br₃: C, 58.9; H, 4.0; Br, 32.7. Found: C, 59.2; H, 3.7; Br, 33.0.

It evolved two equivalents of methane in the Grignard machine, consuming 2.7 moles of reagent. Upon acidification, most of the starting material was recovered unchanged.

Chlorination: The monochloroketone was secured by refluxing for one-half hour a benzene solution of 4.6 g. of the bimolecular product and 6.2 g. of phosphorus pentachloride. It separates in prisms from benzene, m. p. 215°.

Anal. Calcd. for C₃₅H₂₃O₂Cl: Cl, 7.1. Found: Cl, 6.6.

The Grignard reaction products (carbinols, VIII) were prepared in the usual manner with yields of 75–85%.

There was nothing new in the experimental procedures employed when they were treated with acetyl chloride, acetic anhydride and a trace of sulfuric acid, thionyl chloride, hydrogen bromide in glacial acetic acid or phosphorus pentachloride. The properties of the various compounds are given in Table I.

TABLE I

PROPERTIES OF SUBSTANCES RELATED TO THE CARBINOLS

Formula R	VIII X	Yield, %	M. p., °C.	Analyses, %			
				Calcd. C	H	Found C	H
CH ₃	OH	80 ^a	262	87.5 ^e	5.8	87.6	5.8
CH ₃	OCOCH ₃	75 ^{b,f}	202	85.1 ^h	5.7	85.3	5.8
CH ₃	OCOCH ₃	75 ^{b,g}	180	85.1 ^h	5.7	84.9	5.9
CH ₃	Cl ⁱ	50 ^d	219	(Cl 7.1)		(Cl 7.3)	
CH ₃	Br ⁱ	60 ^b	191	(Br 14.7)		(Br 14.3)	
C ₆ H ₅	OH	81 ^a	226	88.6 ^e	5.5	88.6	5.5
C ₆ H ₅	OCOCH ₃	30 ^g	235	86.3 ^h	5.5	86.6	5.6
C ₆ H ₅	Cl	50 ^{b,k}	216	(Cl 6.3)		(Cl 6.4)	
α-C ₁₀ H ₇	OH	80 ^a	295	89.2 ^e	5.4	89.1	5.5
α-C ₁₀ H ₇	Br ⁱ	85 ^b	233	(Br 12.2)		(Br 12.2)	

^a Prisms, from xylene. ^b Prisms, from benzene–petroleum ether. ^c Rods, from benzene–petroleum ether. ^d Needles, from benzene–petroleum ether. ^e Two active hydrogens, no addition in Grignard machine. ^f Action of acetyl chloride. ^g Action of acetic anhydride and one drop of concentrated sulfuric acid. ^h One active hydrogen, two additions in Grignard machine and recover carbinol. ⁱ Action of phosphorus pentachloride. ^j Action of 32% hydrogen bromide in acetic acid. ^k Action of thionyl chloride.

2,3,5,6-Tetraphenylindenone X was obtained in a 20% yield from the indenone, m. p. 167°,¹ or in a 70% yield from its isomer, m. p. 240°,⁶ by heating at 220–280° for fifteen minutes with sulfur; there is a strong odor of thiophenol in each instance.

1,2,3,5,6-Pentaphenylindenol-1, XI, was obtained in a yield of 87% from 2,3,5,6-tetraphenylindenone and phenylmagnesium bromide in the usual manner. It separates from benzene–petroleum ether in prisms, m. p. 220°.

Anal. Calcd. for C₃₈H₂₈O: C, 91.4; H, 5.5. Found: C, 91.2; H, 5.5.

1,2,3,5,6-Pentaphenyl-1-bromoindene, XII, resulted on warming an acetic acid solution of hydrogen bromide (30–32%) with one-fourth its weight of the above carbinol for one hour; it was then cooled and diluted with an equal volume of acetic acid; the yield was 89%. It forms prisms, m. p. 203°.

Anal. Calcd. for $C_{39}H_{27}Br$: Br, 13.9. Found: Br, 13.6.

The hydrocarbon, m. p. 280°, was isolated, after refluxing a mixture of 4 g. of the bromoindene, 10 g. of zinc dust, and 50 cc. of acetic acid for three hours, by pouring into 200 cc. of water. The hydrocarbon crystallized on chilling the chloroform extract of the aqueous mixture. It separates in prisms.

The same hydrocarbon was formed by heating the phenyl carbinol (m. p. 226°) of the bimolecular product at 290–310° for one hour; steam and carbon monoxide were evolved. The residue was crystallized from chlorobenzene.

The α -naphthyl homolog was prepared in a similar manner; it forms tiny prisms, m. p. 298°.

Anal. Calcd. for (280°) $C_{39}H_{28}$: C, 94.4; H, 5.7; for (298°) $C_{48}H_{30}$: C, 94.5; H, 5.5. Found: (280°) C, 93.9; H, 5.6; (298°) C, 94.3; H, 5.5.

Cinnamalaniline¹⁰ is monomolecular in boiling alcohol, the calculated value being 187, whereas 194 was found.

Acknowledgment.—We are greatly indebted to Dr. Bell of this Laboratory for the many quantitative examinations, in the Grignard machine, of the substances described in this and related papers.

Summary

A new structure, differing only in the position of a phenyl group and a hydrogen atom, has been proposed for the bimolecular product resulting from the action of acidic dehydrating agents upon anhydracetonebenzil. The new structure is in better accord with the chemical behavior of the substance.

The nature of the Grignard reaction products and related substances is described. A tribromo substitution product has been obtained.

(10) Doebner and Miller, *Ber.*, **16**, 1665 (1883). We are indebted to Mr. VanAllan for the preparation of this substance.

ROCHESTER, N. Y.

RECEIVED MAY 26, 1942

[COMMUNICATION NO. 856 FROM THE KODAK RESEARCH LABORATORIES]

The Structures of Certain Highly Arylated Indenones and their Behavior with Bromine

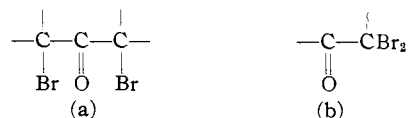
By C. F. H. ALLEN AND J. W. GATES, JR.

Some time ago¹ it was shown that decarbonylation of the bimolecular product that resulted from the dehydration of anhydracetonebenzil gave a dienone that was rearranged by gentle heating to an isomeric indanone I. On account of the peculiar features of this rearrangement, it was considered desirable to examine the behavior of these substances with other reagents. The action of bromine upon these and closely related substances is described in this paper, and the pertinent structures are discussed. Owing to the reactivity of the system and to the many possible structures, it usually takes a sequence of reactions to enable one to draw significant conclusions.

With one equivalent of bromine, the indanone I gives a monobromoketone, which, with an excess of the reagent, forms a dibromo compound; hydrogen bromide is evolved in both reactions. When the dibromo compound is treated with the Grignard reagent,² the monobromoketone is

formed, and a subsequent treatment of this with more Grignard reagent removes the remaining bromine atom and furnishes a fourth, isomeric dienone. The new indenone is very sensitive to heat reverting to its isomer I below its melting point. For this reason, its reactions appear to be those of the indanone, *e. g.*, both give the same dibromo substitution product, and the same phenyl carbinol. Neither of the bromoketones appears to add maleic anhydride.

The replacement of the bromine atoms, stepwise, by the Grignard reagent with the formation of a ketone, shows that they must be in positions *alpha* to the carbonyl group,³ *i. e.*, either (a) or (b)



Dibromoketones of type (b), having both bromine atoms on the same carbon atom, however, are very easily hydrolyzed to α -diketones; this property is not exhibited by the dibromoketone

(3) Kohler and Tishler, *ibid.*, **54**, 1594 (1932).

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

(2) It is of interest to note that in the Grignard machine [Kohler and Richtmyer, *ibid.*, **52**, 3736 (1930)] α -bromoketones show no immediate evolution of gas and use up one mole of reagent (usually interpreted as addition).