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°) $C_{43}H_{30}$: C, 94.5; H, 5.5. Found: (280°) C, 93.9; H, 5.6; (298°) C, 94.3; H, 5.5.

Cinnamalaniline[10] 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.

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[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]

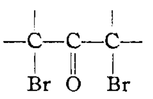
The Structures of Certain Highly Arylated Indenones and their Behavior with Bromine

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

Some time ago[1] 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.

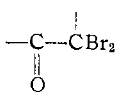
With one equivalent of bromine, the indanone I gives a monobromoketone, which, with an excess of the reagent, forms a dibromo compound; hydrogen bromide is evolved in both reactions. When the dibromo compound is treated with the Grignard reagent,[2] the monobromoketone is reformed, and a subsequent treatment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



$$-\underset{\mathrm{Br}}{\overset{|}{\underset{|}{\mathrm{C}}}}-\underset{\mathrm{O}}{\underset{\|}{\mathrm{C}}}-\underset{\mathrm{Br}}{\overset{|}{\underset{|}{\mathrm{C}}}}-$$

(a)



$$-\underset{\mathrm{O}}{\overset{|}{\underset{\|}{\mathrm{C}}}}-\mathrm{CBr}_2$$

(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

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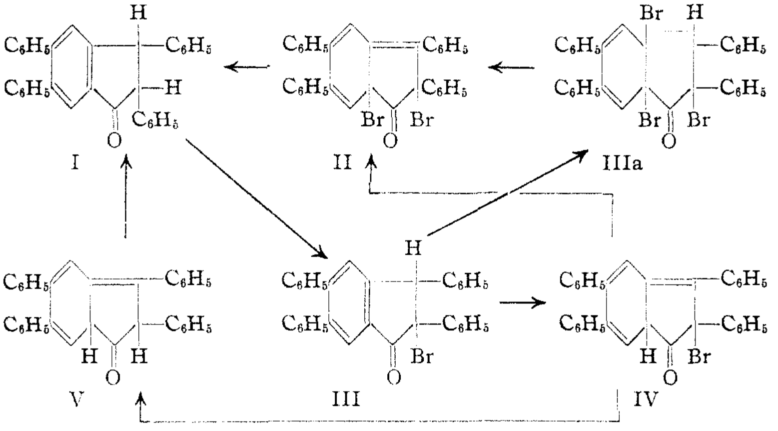
[1] Allen and Spanagel, THIS JOURNAL, **55**, 3773 (1933).

[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).

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

in question, consequently, it is best represented by Formula II.



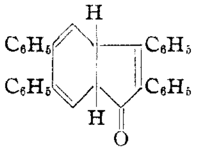
The formation of the dibromoketone II from the indanone I probably takes the following course; the hydrogen atom *alpha* to the carbonyl group is first replaced in the usual manner, giving a monobromoketone III. This can be considered to contain an allylic system, involving the double bond common to both rings, which is isomerized to IV under the influence of the hydrogen bromide present. The resulting ketone now contains a hydrogen atom *alpha* to the carbonyl group and is brominated in the usual way to form II.

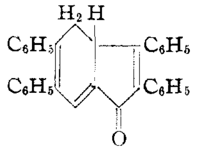
An alternative mechanism which avoids the rearrangement suggested is possible for the second step. If the monobromoketone had the structure III, a molecule of bromine could add to the double bond to give IIIa, which would then lose hydrogen bromide. Since this involves an aromatic double bond of the benzene ring, it seems less likely, although the *ortho*-phenyl groups may have a sufficient activating effect to permit of such an addition. Furthermore, the hydrogen atoms, not being *alpha* to a carbonyl group, will be much less active, and have less tendency to be eliminated as hydrogen bromide.

The position of the hydrogen atom in the monobromoketone is less certain. Since this substance was obtained by a reduction of the dibromide by the Grignard reagent, it would seem that it should have the structure IV; in confirmation, the monobromoketone, though secured from the indanone, is unaffected by hydrogen bromide, yet it brominates easily to give the dibromoketone II. Easy bromination is characteristic of only those ketones that have a hydrogen atom in the *alpha* position. Reduction of the dibromide with zinc and acetic acid also replaces the bromine by hydrogen; zinc in acetone or ethyl acetate has no effect—that is, in the dibromide the two bromine atoms are not on adjacent carbon atoms.

The dienone secured by reduction with the Grignard reagent, from its method of preparation and behavior on bromination, most probably is represented correctly by the structure V. In this, it will be noted that the hydrogen atom on the carbon atom common to the two rings is between three double bonds, and would be expected to be unusually likely to isomerize to a more stable system; by virtue of its aromatic structure, the most stable system is the indanone I. This dienone does form the indanone when warmed in solutions below its melting point; the change is very rapid in boiling acetic acid. For this reason, its reaction products, always formed in hot solutions, are identical with those of the indanone.

The dienone VI found earlier[1] was assigned its structure because it added maleic anhydride, gave some thiophenol when heated with sulfur, and was easily rearranged to the indanone I, showing it had the same skeletal structure. In view of the facile migration of hydrogen in this series, the production of thiophenol loses some of its significance—it is noticeable in all the sulfur melts. Its occurrence was interpreted[1] to indicate the presence of an angular phenyl group on the top carbon atom common to the two rings; this phenyl was then assumed to undergo a 1,3-shift in forming the indanone I. Such a shift was at that time without analogy, whereas 1,3-shifts of hydrogen in allylic systems are common. We are now[4] of the opinion that the phenyl group is already in the position where it is found in the indanone and that this dienone has the structure VI; this is in better accord with its chemical behavior.


VI


VII

Of these four isomers, the indanone I seems to be the most stable, for the three dienones are con-

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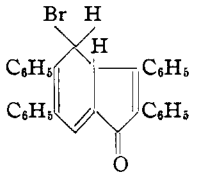
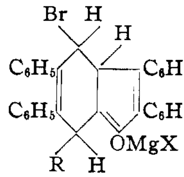
[4] Allen and Gates, This Journal, **64**, 2123 (1942).

verted to it by heating.[5] The indanone I is white, whereas the three isomers are various shades of yellow, and it does not add maleic anhydride. On heating with sulfur, hydrogen sulfide is evolved and a red indenone results; this substance has already been degraded stepwise[1] by unambiguous reactions to compounds of known structure.[6] The formula I seems in best accord with these properties. Although the dienone VII gave both 1,2- and 1,4-addition with phenylmagnesium bromide,[7] it was pointed out that this reagent was of no value in determining structures in this series, owing to the prevalance of allylic rearrangements.

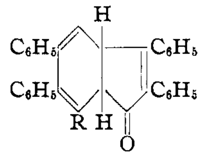
The isomeric dienones VI and VII give the same monobromoketone VIII upon bromination, with evolution of hydrogen bromide. This result would be expected in view of the known ease of the rearrangement of VI to VII.[7] Excess bromine dehydrogenates the monobromoketone. Examination of this ketone VIII in the Grignard machine[2] revealed little.[8] Both methylmagnesium iodide and phenylmagnesium bromide gave mixtures, from which were isolated bromine-free ketones, *different* from the original dienones. The 1,4-addition reaction, resulting in the formation of the ketones, which differ from the original by having an additional phenyl or methyl group, involves the carbonyl group. Thus, this group is not available for other purposes, and the elimination of the bromine must have been a side reaction. The following mechanism seems a plausible interpretation of the facts, and enables one to assign structure VIII to the bromoketone with a considerable degree of assurance. The magnesium enolate formed by the 1,4-addition of the Grignard reagent is shown in IX; upon acidification the enol XI ketonizes, but at some stage, there is a transannular elimination of hydrogen bromide, for the resulting ketone X contains no bromine. This probably occurs in the enol XI, for the requisite hydrogen atom in the 7-position is then activated by its position between the unsaturated linkages.[9,10]



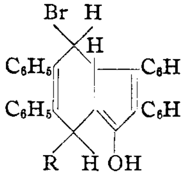
VIII



IX

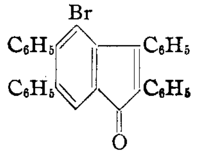


X

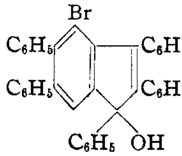


XI

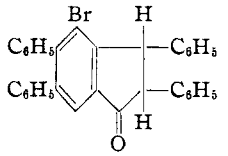
The aromatic ketone that results from the action of excess bromine upon the bromoketone VIII is probably 4-bromo-2,3,5,6-tetraphenylindenone XII. The bromine atom is inactive, phenylmagnesium bromide giving a carbinol XIII. The indenone is reduced to an indanone XIV by zinc and acetic acid, thus paralleling the behavior of the unbrominated indenone.



XII



XIII



XIV

Experimental

2,3,5,6-Tetraphenyl-2,7a-dibromo-2,7a-dihydroindenone-1 II.—This compound was obtained by bromination of the indanone I in the usual manner, using two equivalents of bromine and acetic acid as the solvent. It was also formed by a further bromination of the monobromoketone IV. The latter was secured by a similar procedure, but using one equivalent of bromine and chloroform as a solvent. The properties of these substances are given in Table I.

Both bromoketones were unaffected by hydrogen bromide in acetic acid, and did not add maleic anhydride. The dibromoketone was reduced to the monobromoketone

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(5) Examination of the formulas of the isomeric ketones reveals that all the indenones have hydrogen atoms activated by adjacence to two or more double bonds, which are part of an allylic system. They would, therefore, be expected to rearrange to the more stable indanone I system.

(6) Allen, Bell, Bell and VanAllan, THIS JOURNAL, **62**, 656 (1940).

(7) Allen and Gates, *ibid.*, **64**, 2120 (1942).

(8) It should be emphasized that abnormal results from the Grignard machine have little significance, other than to indicate that several reactions are taking place simultaneously. It is always necessary to isolate and determine the nature of the reaction products before drawing useful conclusions. If there is no immediate evolution of gas, it indicates the absence of an active hydrogen atom.

(9) In one fortuitous instance, with methylmagnesium iodide, a bromoketone was isolated; immediate analysis showed 85% of the calculated amount of bromine, all of which was lost on recrystallization.

(10) A direct replacement of bromine in VIII by double decomposition with the Grignard reagent is an admitted possibility, and reaction products of this type may be present in the residual oils which comprise about one-half the reaction product.

TABLE I

PROPERTIES OF NEW SUBSTANCES

Substance	Yield, %	M. p., °C.	Empirical formula	Analyses, %					
				Calcd.			Found		
				C	H	Br	C	H	Br
II	75	270d.[a,d]	$C_{33}H_{22}OBr_2$			26.9			26.5
III	84	241d.[b,e]	$C_{33}H_{23}OBr$			15.5			15.2
V	50	125[a,e]	$C_{33}H_{24}O$	90.8	5.5		90.7	5.4	
VIII	84	196[a,f]	$C_{33}H_{23}OBr$	76.9	4.5	15.5	76.8	4.4	15.3
X, R = CH_3	33	170[a,e]	$C_{34}H_{26}O$	90.9	5.6		90.9	5.6	
X, R = C_6H_5	27	246[a,e]	$C_{39}H_{28}O$	91.4	5.5		90.9	5.4	
Xa	10	217[a,e]	$C_{34}H_{26}O$	90.9	5.6		89.5	6.0	
XII	90	235[c,f]	$C_{33}H_{21}OBr$	77.2	4.1	15.6	77.2	4.0	15.4
XIII	52	249[b,e]	$C_{39}H_{27}OBr$			13.5			13.2
XIV	57	175[a,f]	$C_{33}H_{23}OBr$			15.5			15.0
XV	69	240[a,e]	$C_{45}H_{34}O$	91.5	5.8		91.3	5.8	
XVI	50	194[c,e]	$C_{39}H_{27}Br$	81.4	4.7	13.9	81.6	4.8	13.8
XVII	20	229d.[b,e]	$C_{78}H_{57}O_2Br$	84.7[g]	5.2	7.2	85.2	4.9	6.8, 6.5
XVIII	80	239[a,e]	$C_{34}H_{25}OBr$	77.3	4.5		77.1	4.6	

[a] Prisms. [b] Needles. [c] Rods. [d] From xylene. [e] From benzene–petroleum ether. [f] From benzene–alcohol. [g] Calcd. mol. wt. 1105; found, mol. wt. (in benzene) 522, 519. The explanation of this discrepancy is unknown.

by reduction with potassium iodide in acetic acid, alcoholic potash, and the Grignard reagent, and to the parent indanone with zinc and acetic acid, by the customary procedures.

2,3,5,6-Tetraphenyl-2,7a-dihydroindenone-1 V.—To a 0.1 mole of phenylmagnesium bromide in 100 cc. of ether was added 6 g. of the monobromoketone III. After it had been stirred for an hour, the mixture was decomposed by ammonium chloride, and the organic material crystallized from benzene–petroleum ether; the yield was 3 g. Heated in the ordinary way, in a capillary tube, it melts at 95°, then solidifies and remelts at 164–166°; if the tube and sample are plunged into a heated bath, the melting point is found to be 125°. By repeated recrystallizations, it isomerizes, most rapidly in acetic acid, to the indanone II, m. p. 176°.

2,3,5,6-Tetraphenyl-3a,4-dihydro-4-bromoindenone-1 VIII resulted when either indenone VI or VII in chloroform solution was brominated in the usual way. It crystallized from benzene–alcohol in lemon-yellow prisms, m. p. 196°d. It does not add maleic anhydride and is unaffected by hydrogen bromide. In the Grignard machine it shows 0.5 active hydrogen and 1.5 addition. Upon treatment with bromine in chloroform, hydrogen bromide is evolved, and an orange indenone (2,3,5,6-tetraphenyl-4-bromoindenone-1 XII, m. p. 234–235°) is isolated from the residue by evaporating to dryness on a water-bath.

This last substance is reduced by zinc and acetic acid (without removal of the bromine) to an indenone XIV in exactly the same way as the unbrominated analog, 2,3,5,6-tetraphenylindenone[1] gave the indanone I, m. p. 176°. It gave a phenyl carbinol XIII with phenylmagnesium bromide.

Reaction Products from the Bromoindenone VIII.—(a) Phenylmagnesium bromide gave a complex mixture, from which the ketone X, (R = C_6H_5) and a bimolecular product were isolated in this order. In the Grignard machine the ketone consumed one equivalent of reagent and evolved a half equivalent of gas (possibly indicating 50% enolization). When treated with phenylmagnesium bromide it gave a new carbinol, 1,2,3,5,6,7-hexaphenyl-3a,7a-dihydroindenol-1 XV, which did not dehydrate with a 2% solution of sulfuric acid in acetic acid.

The ketone behaved in a puzzling manner with hydrogen bromide, the oxygen being lost and a bromine atom introduced. Possibly the acid is added to the carbonyl group and then water is split off. The product XVI is a bromohydrocarbon.

The bimolecular product XVII was assumed to be such because of the bromine analyses; the minimum molecular weight, if one bromine atom is present, is 1100–1200. The substance was secured from two different preparations, and was unchanged on recrystallization from two different solvents. It consumed 2.7 equivalents of reagent (on the basis of this molecular weight), showing two active hydrogens. Upon acidification, about half the starting material was recovered from the black oil. It was not investigated further.

(b) Methylmagnesium iodide likewise gave a complex mixture, from which was isolated the ketone, 2,3,5,6-tetraphenyl-7-methyl-3a,7a-dihydroindenone-1 (X, R = CH_3). In the Grignard machine it consumed one equivalent of reagent and evolved 0.3 equivalent of gas. It was unaffected by hydrogen bromide and did not add maleic anhydride. It readily substituted with bromine; the α-bromoketone, 2,3,5,6-tetraphenyl-7-methyl-3a,7a-dihydro-7a-bromoindenone-1 XVIII, was reduced back to the starting material by methylmagnesium iodide. In one instance a very small amount of an isomeric ketone Xa was obtained.

Summary

The behavior of several closely related isomeric polyphenylated indenones with bromine has been determined. Structures have been assigned the various substances, in accord with the experimental evidence obtained from a series of reactions. The occurrence of allylic rearrangements has again been noted.

ROCHESTER, N. Y. RECEIVED MAY 29, 1942