[CONTRIBUTION NO. 867 FROM THE KODAK RESEARCH LABORATORIES]

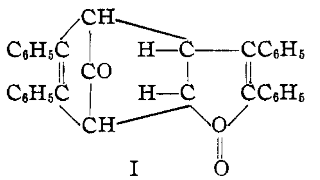
The Behavior of Certain Carbonyl Bridge Compounds with Alkaline Hydrogen Peroxide

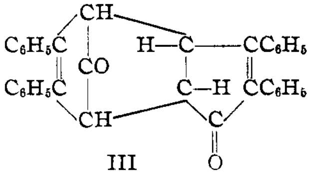
BY C. F. H. ALLEN AND J. W. GATES, JR.

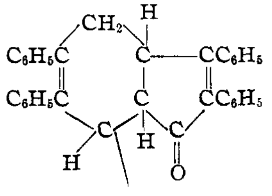
Some time ago[1] it was shown that when the bimolecular product I, that results from treatment of anhydroacetonebenzil with acidic dehydrating agents, was treated with chromium trioxide in acetic acid, poor and varying yields of an isomer were obtained. This new substance also lost carbon monoxide on heating, to give an indanone II having two phenyl groups on the same carbon atom. It was furthermore concluded that the isomerism was due to space relations. Since many new facts about the reactions of the bimolecular product are now available,[2] as a result of which the structure has been slightly modified,[2b] it was necessary to re-examine the "oxidation product" isomer III. During the course of this work degradation and synthesis established the correctness of the structure previously assigned to the indanone.

When the bimolecular product I is stirred at room temperature with a cold alkaline solution of hydrogen peroxide, a peroxide IV is formed; this contains four extra atoms of oxygen. It loses this oxygen almost explosively when heated, but seems stable at room temperature. Upon treatment with hydrogen bromide, bromine is liberated and the bimolecular product regenerated. It likewise liberates iodine from potassium iodide in acetic acid. When it is dissolved in acetic acid, oxygen is evolved and the "oxidation product" isomer III, previously secured with difficulty by means of chromic acid, was formed. These reactions are practically quantitative.

Both isomers I and III give the same derivatives; thus, with alkaline reagents the acid V results, phenylmagnesium bromide gives the same carbinol, and in the Grignard machine both show one active hydrogen and one addition. The only difference is in the results of pyrolysis: both lose carbon monoxide, but one gives the indanone II and the other its isomer VI, by way of two intermediate isomeric unsaturated ketones.[2] Since the same derivatives are obtained from both, the only difference being the result of pyrolysis, the difference between the isomers must be of a spatial nature. That is, the position of the hydrogens on the bond common to the two rings appears to be the significant factor, and, as concluded in the earlier paper,[1] the two substances are presumably geometrical isomers, as represented in I and III.


I


III


V

The above formulas differ from those previously assigned[1] only in the interchange of the angular phenyl group and one hydrogen atom at the other end of an allylic system. The fact that both give the same derivatives is explained on the basis of catalysis by acidic or basic substances present in all reactions. The only reaction carried out in the absence of a possible catalyst is the heating, and this leads quantitatively to a different product in each instance. The previous suggestion that the bimolecular product was a mixture has been abandoned,[2] but the reasons[1] for assigning it a *cis*-configuration I are retained.

The indanone II, in which the grouping —CH_2-CO— had been proved previously, has now been degraded to a lactone VII and to a hydrocarbon XI, both of which have been synthesized by reactions that leave no doubt as to their structures. The synthesis from the known keto acid VIII also establishes the position of the side chain.

The diketone IX resulting from the action of

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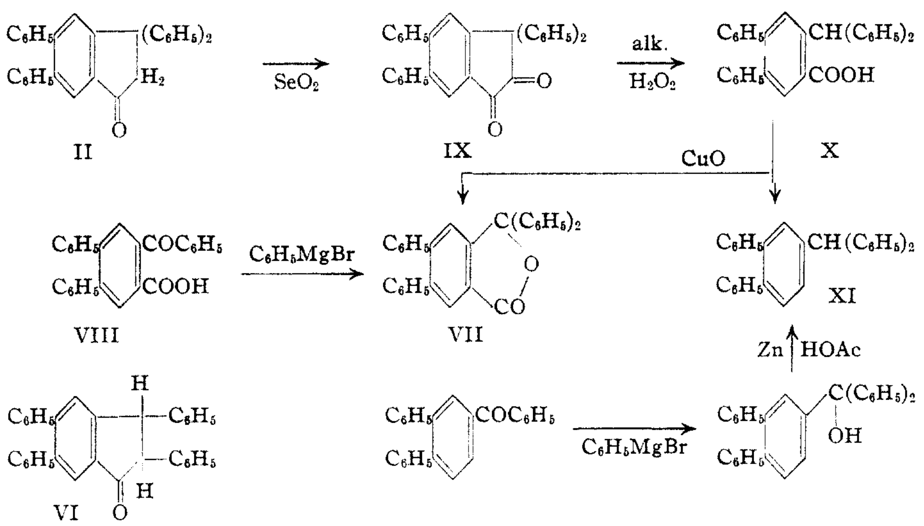
(1) Allen and Rudoff, *Can. J. Res.*, **B15**, 321 (1937).

(2) Allen and Gates, THIS JOURNAL, **64**, (a) 2120 (1942); (b) **64**, 2123 (1942).

selenium dioxide on the indanone is readily cleaved by alkaline hydrogen peroxide to the acid X. When the latter is treated under decarboxylating conditions with copper carbonate (or oxide), a portion loses the carboxyl group and gives the triphenylmethane derivative XI; this was synthesized, as shown in the outline, from 3,4-diphenylbenzophenone. The remainder of the product is the lactone VII, evidently formed by oxidation of the triphenylmethane hydrogen atom of X to hydroxyl, followed by closing of the lactone ring. The interrelation and lactone synthesis are shown in the chart.

Chart I

Degradation of the Indanone II; Synthesis of Two Products

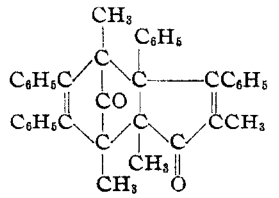


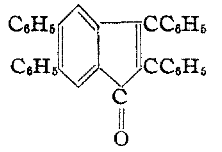
It is obvious that there has been a 1,2-shift of a phenyl group during the decarbonylation of the bimolecular product isomer III; this rearrangement must have been due to the heating. It has been shown previously that there was no rearrangement during the decarbonylation of the isomer I, by accomplishing the removal of the bridge carbonyl by the action of sodium methoxide at the boiling point of methanol[2a] and securing the same end-product in both reactions, the indanone VI; the phenyl groups are linked to the same carbon atoms in I and in VI.

The behavior of the indandione IX toward alkaline hydrogen peroxide is similar to that of the simpler 3,3-diphenylindandione-1,2, as described by Gagnon[3] but neither of these is in agreement with the results of Koelsch.[4] In the work described in this paper, all variations of experimental procedure always gave the same product, but the yields were much improved by the use of Gagnon's technique; the intermediate aroylformic acid was not isolated.

The indandione IX gives a quinoxaline with *o*-phenylenediamine, instead of the anil[1]; the last molecule of water is held very tenaciously. This observation may account for the disagreement reported on the quinoxaline of 3,3-diphenylindandione-1,2.[3,4] The diketone IX also gives a crystalline glycol XVIII with excess phenylmagnesium bromide.

Evidence as to the structure of the peroxide is not decisive. A homologous bimolecular product XII[5] that has no hydrogen in the positions *alpha* to the carbonyl group does not give a peroxide; neither does it show active hydrogen in the Grignard machine. Thus these two anomalous properties must be related in some way to the carbonyl bridge and adjacent hydrogen. The most obvious relation is that of an enol, and such has already been suggested[2b] to account for the active hydrogen. It is also well established that highly substituted enols are capable of forming peroxides.[6] These, however, have but two atoms of oxygen, whereas the bimolecular product peroxide has four.


XII


XIII

The isomer III does not form a peroxide; this suggests that the space relations also have an influence upon its formation.

During the preparation of the isomeric bimolecular product III by the action of chromic acid,[1]

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(3) Gagnon, Hudon, Cantin and Ganas, *Trans. Roy. Soc. Can.*, (III) **33**, 47 (1939).

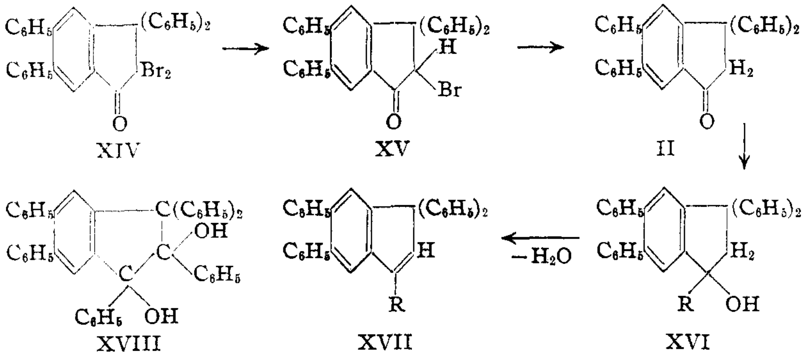
(4) Koelsch and LeClaire, *J. Org. Chem.*, **6**, 532 (1941).

(5) Allen and VanAllan, This Journal, **64**, 1260 (1942).

(6) Kohler and Mydans, *ibid.*, **54**, 4667 (1932).

substances of varying melting points resulted, all of which, upon analysis, were found to contain varying amounts of oxygen, and which gave no depression of melting point on admixture; upon heating, they all gave the indanone II practically quantitatively. This suggests that they were a single substance plus oxygen; the maximum value, plus four oxygen atoms, was only obtained by the use of alkaline hydrogen peroxide. A variety of products, which will be described in detail in a later paper, resulted when tetraphenylindenone, XIII, was treated with alkaline hydrogen peroxide. A true peroxide appears to be formed primarily, however.

The proof of the —CH_2CO— group in the rearranged indanone II previously proved in several ways has received confirmation in this paper through stepwise reduction of the dibromo substitution product XIV by means of the Grignard reagent. This is characteristic of α-haloketones[7]; one halogen is removed at a time, so the monobromoketone XV can be isolated as an intermediate during the process.



The indanone II gave carbinols XVI with Grignard reagents. On dehydration these gave hydrocarbons XVII. These are isomeric with other hydrocarbons[2] of which the structures are still in doubt, obtained from closely related carbinols; however, the non-identity shows that in the others there must be a different arrangement of phenyl groups around the indene ring.

Experimental

The Peroxide IV.—In a solution of 500 cc. of alcohol, 50 cc. of water and 8 g. of sodium hydroxide, was suspended 42 g. of bimolecular product I; to this was added 50 cc. of 16% hydrogen peroxide with vigorous stirring and the temperature kept below 30° for two hours. Then it was chilled externally by ice, filtered, rinsed with a little methanol, and air-dried. The yield was 40–42 g. It softens about 80°, gradually decomposing up to 200°.

Anal. Calcd. for $C_{34}H_{24}O_6$: C, 77.8; H, 4.5. Found: C, 77.3; H, 4.5.

The peroxide liberates the halogen from potassium iodide or hydrogen bromide in acetic acid, with regeneration of the bimolecular product, but if an acetic acid solution is heated to boiling, the solid dissolves with evolution of gas, and on cooling, the isomeric indenone III separates in rods which melt at 215°.

Anal. Calcd. for $C_{34}H_{24}O_2$: C, 87.9; H, 5.2. Found: C, 87.9; H, 5.1.

This melting point was not lowered on admixture with samples of widely varying melting points from chromic acid oxidation; these specimens melted with decomposition all the way up to 264° and contained fractional amounts of oxygen not corresponding with exactly one or two equivalents. Regardless of the melting point, each gave the same indanone II on decarbonylation and loss of oxygen.

The isomeric bimolecular product III no longer forms a peroxide; on heating at 260–270°, 3,3,5,6-tetraphenylindanone-1 II is formed practically quantitatively. It also gave the acid V with alcoholic potash, confirmed by conversion to its methyl ester, and the same phenyl carbinol[2b] with phenylmagnesium bromide and decomposition by iced ammonium chloride and corresponding hydrocarbon[2b] on dehydration above 300°.

The Quinoxaline of the Diketone IX.—This was obtained as previously described,[1] but recrystallized from benzene–ligroin. Before analysis it was dried at 100° *in vacuo* over phosphorus pentoxide for nineteen hours.

Anal. Calcd. for $C_{39}H_{26}N_2$: C, 89.7; H, 5.0. Found: C, 89.6; H, 5.2.

Cleavage of the Diketone IX.—To a suspension of 27 g. of the diketone[1] in 600 cc. of alcohol was added a solution of 12 g. of sodium hydroxide in 75 cc. of water; after cooling in ice and stirring for a half hour all had dissolved. Then 75 cc. of 16% hydrogen peroxide was added and after an additional two hours the solution was diluted with 600 cc. of water, filtered and the filtrate acidified with acetic acid. After extracting with chloroform and appropriate manipulation, 16 g. (61%) of the acid X, (4,5-diphenyl-2-benzhydrylbenzoic acid) m. p. 258–259°, was collected. The yield by this variation in procedure is much better than when sodium peroxide is used.[1] The acid dissolves in *dilute* alkali only.

Anal. Calcd. for $C_{32}H_{24}O_2$: C, 87.3; H, 5.5. Found: C, 87.5; H, 5.5.

The methyl ester, prepared in the usual manner, separates in rods from benzene–methanol; m. p. 165°.

Anal. Calcd. for $C_{33}H_{26}O_2$: C, 87.2; H, 5.7. Found: C, 87.5; H, 5.5.

The Lactone VII (3,4-Diphenyl-diphenylphthalide). (a) Synthesis.—This was accomplished by treatment of

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(7) Kohler and Tishler, THIS JOURNAL, **54**, 1594 (1932); **57**, 217 (1935).

TABLE I

PROPERTIES OF CARBINOLS AND HYDROCARBONS

Substance	M. p., °C.	Empirical formula	Analyses, % Calcd. C	Calcd. H	Found C	Found H
XVI, R = C_6H_5	233–234 d.[a]	$C_{39}H_{30}O$	91.1	5.8	91.0	5.9
XVII, R = CH_3	180[a]	$C_{34}H_{26}$	94.0	6.0	93.6	6.0
XVII, R = C_6H_5	227[a]	$C_{39}H_{28}$	94.4	5.6	94.1	5.6
XVII, R = α-$C_{10}H_7$	244[b]	$C_{43}H_{30}$	94.5	5.5	94.2	5.6
XVIII	159[c]	$C_{45}H_{34}O_2$	89.1	5.6	88.9	5.7

[a] Prisms. [b] Needles. [c] Tiny rods.

2-benzoyl-4,5-diphenylbenzoic acid VIII[8] with phenylmagnesium bromide, decomposing the complex with ammonium chloride, and recrystallizing from acetic acid. It forms rods; m. p. 180°.

Anal. Calcd. for $C_{32}H_{22}O_2$: C, 87.7; H, 5.0. Found: C, 87.7; H, 4.9.

(b) **From the Acid X.**—An intimate mixture of 15 g. of the acid and 2 g. of copper carbonate was heated at 260–265° for a half hour, and the cooled melt extracted with hot benzene; it was filtered from metallic copper and diluted with ligroin. The lactone was deposited in a yield of 20%. From the filtrate 3,4-diphenylbenzhydrylbenzene XI crystallized in a 30% yield. It forms needles and rods from acetic acid, m. p. 143°.

Anal. Calcd. for $C_{31}H_{24}$: C, 93.9; H, 6.1. Found: C, 93.9; H, 6.0.

The hydrocarbon XI was also synthesized from 3,4-diphenylbenzophenone and phenylmagnesium bromide; the oily carbinol was reduced by zinc and acetic acid.

The lactone is unaffected by bromine, acetyl chloride and chromic acid. It is reduced to the acid X by zinc and acetic acid.

2-Bromo-3,3,5,6-tetraphenylindenone, XV, was obtained when the dibromoketone XIV[1] was treated with excess phenylmagnesium bromide in the usual manner. It separates in needles from benzene, m. p. 240°. The yield was 60%. Repetition of the treatment on this bromoketone gave the indanone II.

Anal. Calcd. for $C_{33}H_{23}OBr$: C, 76.9; H, 4.5; Br, 15.5. Found: C, 76.7; H, 4.4; Br, 15.4.

The carbinols, XVI, were secured by the usual procedure, decomposing the organometallic complex with ammonium chloride. The corresponding hydrocarbons XVII were produced by refluxing 4 g. of the carbinols in 50 cc. of 2% sulfuric acid in acetic acid for a half hour. Their properties are collected in Table I.

The glycol, 1,2,3,3,5,6-hexaphenylindandiol-1,2,XVIII, was prepared from the diketone IX and an excess of phenylmagnesium bromide in butyl ether for six hours at 100°.

Summary

The bimolecular product, formed by the action of acidic dehydrating agents on anhydracetonebenzil, forms a peroxide, upon treatment with alkaline hydrogen peroxide. This substance loses its oxygen and gives an isomer in acetic acid solution. The isomer affords a previously described indanone on decarbonylation.

The indanone has been degraded to known products, the syntheses of two of which are described. It has also been converted into a carbinol and hydrocarbon isomeric with some closely related substances.

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[8] Allen, A. C. Bell, A. Bell and VanAllan, THIS JOURNAL, **62**, 656 (1940).

[CONTRIBUTION FROM THE NICHOLS CHEMISTRY LABORATORY OF NEW YORK UNIVERSITY]

Deamination of 5-Amino-8-nitroisoquinoline[1]

BY BERTRAM KEILIN AND W. E. CASS[2]

In an attempt to prepare 8-nitroisoquinoline, 5-acetylaminoisoquinoline[3] was nitrated and the resulting acetylaminonitroisoquinoline hydrolyzed to an aminonitroisoquinoline. When the aminonitroisoquinoline was diazotized in hydrochloric acid solution and treated with hypophosphorous acid,[4] there was obtained 8-chloroisoquinoline, identified by analysis and by comparison with a known sample of 8-chloroisoquinoline.[5]

In the preceding diazotization-deamination, the nitro group was displaced by chlorine, nitrous acid being evolved. This displacement of the nitro group possibly occurred during diazotization,

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[1] Constructed, in part, from the B.A. research paper of Bertram Keilin, New York University, University College, 1942.

[2] Present address: Research Laboratory, General Electric Company, Schenectady, New York.

[3] Craig and Cass, THIS JOURNAL, **64**, 783 (1942).

[4] Adams and Kornblum, *ibid.*, **63**, 188 (1941).

[5] Pomeranz, *Monatsh.*, **18**, 1 (1897), prepared, but did not analyze, 8-chloroisoquinoline by ring closure of *o*-chlorobenzalaminoacetal.