Comparison of the earlier report[7] with this one shows only minor differences in lattice dimensions except for the $Fe_3Sn_2$ phase for which Ehret and Westgren were not able to find a satisfactory unit cell, in fact they had expressed the opinion that this "phase" might actually be a mixture of two. To test the latter point we prepared alloys richer, respectively, in iron and tin than the phase itself. Its diffraction pattern and lattice dimensions remained substantially unchanged in the new alloys, leading to the conclusion that it is a single phase.

When the results of the present analysis are compared with those for Co–Sn alloys[13] and Ni–Sn alloys,[14] the following points of similarity are noted: Each of the systems possesses one phase with nickel arsenide structure. The structures of CoSn and FeSn appear to be identical. Complex structures appear in each system when the atomic ratio is 3:2. The solubility of the transition element in tin is in each case negligibly small.

### Summary

A new phase diagram has been set up for the system iron–tin. It confirms the diagram sketched earlier by Ehret and Westgren and gives definite temperature intervals of stability for the several intermetallic phases.

Lattice constants are given for the five intermediate phases, namely, $Fe_2Sn$, $Fe_3Sn_2$, $\gamma$(NiAs structure), FeSn, and $FeSn_2$. Each of these phases possesses hexagonal symmetry.

NEW YORK, N. Y. RECEIVED DECEMBER 31, 1942

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[13] Nial, *Z. anorg. allgem. Chem.*, **238**, 287 (1938).

[14] Mikulas, *et al.*, *Trans. Am. Inst. Min. Met. Eng., Inst. of Metals Division*, (1936), p. 124.

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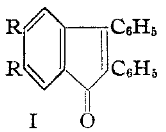
[CONTRIBUTION NO. 905 FROM THE KODAK RESEARCH LABORATORIES]

# Oxidoketones in the Indene Series

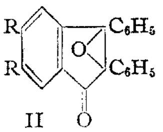
BY C. F. H. ALLEN AND J. W. GATES, JR.

Since the polyphenylindenones, the chemical behavior of which has been examined by us for some years,[1,2] are $\alpha,\beta$-unsaturated ketones, it would be expected that some reactions, characteristic of this linkage, would be found. However, owing to the high degree of substitution, any reactions subject to this sort of hindrance, such as halogen addition, would be suppressed. Up to now, only reduction has been observed to take place, resulting in an indanone.

Alkaline hydrogen peroxide forms oxidoketones with many $\alpha,\beta$-unsaturated ketones,[3,4] a reaction apparently unhindered by substitution, and applicable to cyclic compounds.[3] 2,3,5,6-Tetraphenylindenone I gives an oxidoketone II (R = $C_6H_5$) with this reagent. Like all members of this class of substances, it shows peroxidic properties, liberating iodine from potassium iodide in acetic acid.



I



II

When a cold solution of the oxidoketone in acetic acid is treated with dry hydrogen chloride in acetic acid, a white substance (III) is formed, that on warming in the same solvent with mineral acid is transformed into a lactone. The lactone is soluble in alkaline hydroxides, but not carbonates, and careful acidification gives an acid, which on warming alone or in solution, regenerates the lactone. Oxidation of both the acid and the lactone gives 4,5-diphenyl-2-benzoylbenzoic VI and benzoic acids. The structures are thus established as IV (R = $C_6H_5$) for the lactone and V (or its tautomer) for the acid.

The lactone IV (R = $C_6H_5$) acts normally with the Grignard reagent, addition of two equivalents giving rise to the ketones VII, VIII (R = $C_6H_5$); the expected tertiary alcohol could not be isolated when methylmagnesium iodide was used. Since the lactone is isomeric with the oxidoketone, rearrangement seems to have taken place. However, the isolation of an intermediary substance III (R = $C_6H_5$) enables one to establish the mechanism of the reaction.

The empirical formula of the intermediate differs from that of the oxidoketone by the addition of one molecule of water. It is well known that ethylene oxides are easily cleaved under acidic conditions, and that the products are open-

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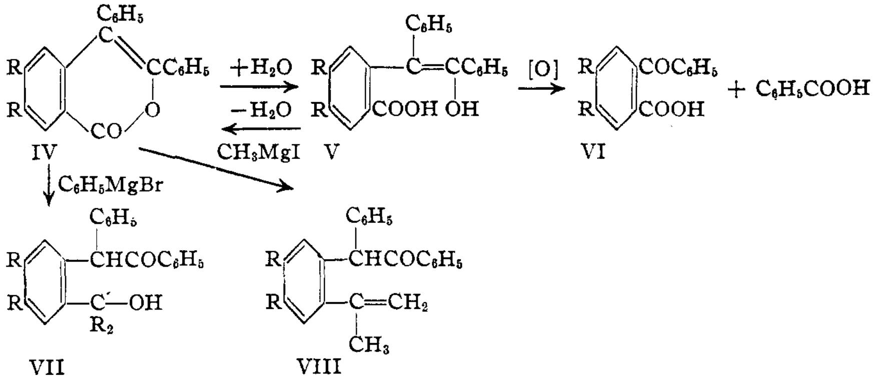
[1] Allen and Gates, THIS JOURNAL, **64**, 2120, 2123, 2127, 2439 (1942).

[2] Allen and VanAllan, *ibid.*, p. 1260 (this gives the earlier references).

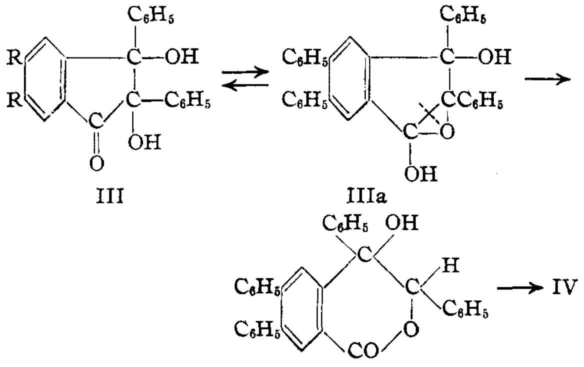
[3] Weitz and Scheffer, *Ber.*, **54**, 2327 (1921).

[4] Kohler, Richtmyer and Hester, THIS JOURNAL, **53**, 205 (1931).



chained and differ by the addition of HX. In this instance, the glycol III is the expected product; in agreement, it shows two active hydrogens and one addition in the Grignard machine. The glycol structure III is probably in equilibrium with the isomeric $\alpha$-oxanol structure IIIa; the latter accounts for the easy formation of the lactone IV. $\alpha$-Oxanols are aldol-like substances, a type easily and reversibly cleaved into their components. In this instance, the mechanism is an intramolecular cleavage; the hydroxylactone IX so formed, spontaneously loses a molecule of water to give the unsaturated lactone IV.

Similar series of reactions were carried through on 2,3-diphenyl-5,6-dimethylindenone (I, R = $CH_3$), 2,3-diphenyl-5,6-dibromoindenone (I, R = Br), and on the simple 2,3-diphenylindenone

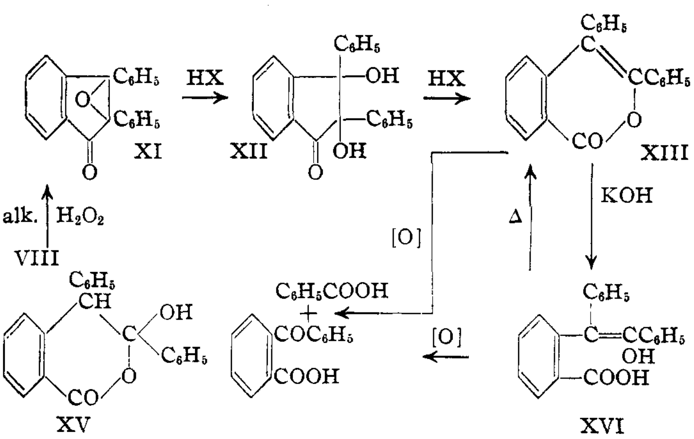


IX (not isolated)

X; the latter had been done in part by Weitzand Scheffer[5] but they did not give any proofs of structure; the products were all indicated with interrogation points. In our work it was found that the reactions were parallel in all respects, the oxidoketone XI giving a glycol XII and lactone XIII with mineral acids.

As in the case of the tetraphenylated lactone IV, this lactone XIII was easily opened to the hydroxy acid XIV. Both lactone and acid gave only $o$-benzoylbenzoic and benzoic acids upon oxidation.

Respecting the glycol, Weitz and Scheffer write that their substance "cannot be the glycol, since it dissolves in alkali (not soda)," and that "probably it is a hydrate of an oxylactone," *i. e.*, a lactol, and "an oxylactone-like hydrate," of structure XV. This does not agree with our findings that in the Grignard machine it shows two active hydrogens and one addition. Lactols show one active hydrogen and two additions.[6] The lactol structure XV is thus excluded.



Although the glycol XII dissolves in alkali, it is not a simple solution, for, if warmed, it cannot be recovered upon acidification. Instead, a new, brilliant yellow substance is obtained. This new product is isomeric with the oxidoketone; it is not the known isomeric 1,2-diketone[7,8] as claimed by Weitz and Scheffer. They could not prepare a quinoxaline and suggested it was some sort of a dimeric diketone.

We have found that it is monomolecular and in the Grignard machine shows no active hydrogen, but one addition. Upon oxidation with chromium

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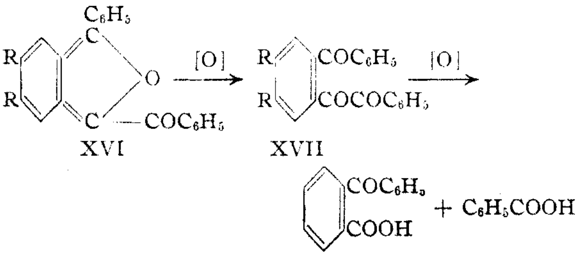
[5] Weitz and Scheffer, *Ber.*, **54**, 2344 (1921).

[6] Allen and Frame, *Can. J. Research*, **6**, 605 (1932); Allen, Normington and Wilson, *ibid.*, **11**, 382 (1934).

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

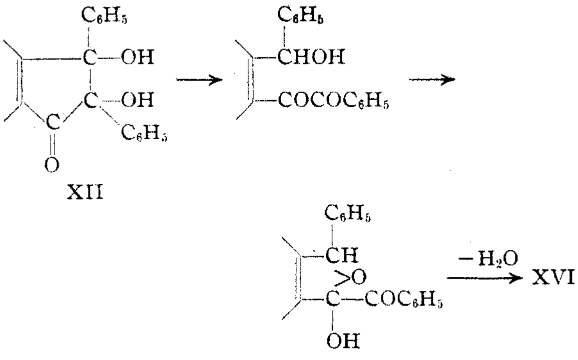
[8] Koelsch and Le Claire, *J. Org. Chem.*, **6**, 532 (1941).

trioxide, it gives benzoic and *o*-benzoylbenzoic acids, but, on cautious permanganate oxidation, it gives *o*-benzoylbenzil XVII (R = H). Thus, it cannot be greatly different from the oxidoketone in skeletal structure. A structure that is in agreement with these properties is that represented by the isobenzofuran XVI.

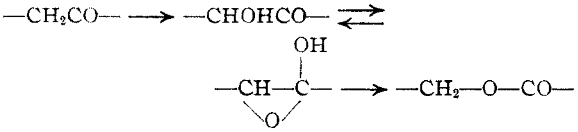

XVI XVII

As a substituted furan, XVI should give an unsaturated 1,4-diketone upon oxidation with nitric acid[9]; it does—the formation of XVII fulfills this requirement. The tetraphenylglycol III was destroyed by alkali, so that it was of no assistance in elucidating the nature of this yellow substance, but the dimethylated glycol, III (R = $CH_3$), also gives a yellow furan, which shows the same behavior.

The furan could be formed from the glycol by a retrograde aldol condensation to give a secondary alcohol, which then adds to an exposed carbonyl group; the hydroxy derivative then loses a molecule of water.

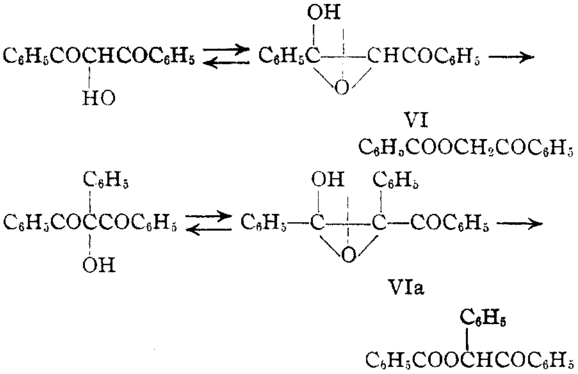

XII

It is our opinion that many reactions proceed through α-oxanols. For example, cyclic ketones are oxidized to lactones by Caro's acid.[10] The first step is perhaps the formation of an α-hydroxyketone, which is in equilibrium with its cyclic α-oxanol form. The latter is a sort of aldol, which reverses into its components (with cleavage of a carbon–carbon bond), the oxygen linkage remaining intact.


$$-\mathrm{CH_2CO}- \longrightarrow -\mathrm{CHOHCO}- \rightleftarrows -\mathrm{CH}-\overset{\mathrm{OH}}{\mathrm{C}}- \longrightarrow -\mathrm{CH_2}-\mathrm{O}-\mathrm{CO}-$$

This mechanism avoids the necessity of assuming any rearrangement; it uses only well-known types of reactions.

Two other instances, closely related to each other, are encountered in the behavior of dibenzoylcarbinol on distillation,[11] and of diphenyl triketone with the Grignard reagent.[12] Esters are formed in each case. These authors interpreted these results as rearrangements. Such an assumption is unnecessary if the possibility of oxanols as an intermediate step is admitted. The oxanols (VI, VIa) are aldol-like substances, and, as just described, can and probably do reverse in the same way.


VI VIa

Finally, 2-ethyl-3-phenylindenone XVIII has been treated with alkaline hydrogen peroxide[13] and the two products described, A, pale yellow, m. p. 45–46°, and B, orange yellow, m. p. 53–54°. Based on analogies with Weitz and Scheffer's work, and color reactions with concentrated sulfuric acid, the authors suggested that A was a diketone and B a lactone. Since Weitz and Scheffer's product is not a diketone, that argument fails to support such a structure for substance A. We have repeated this work and extended it sufficiently for comparison with the other substances described in this paper. While we likewise found two similarly-colored products, there was but one if the reaction was carried out for three and one half hours; furthermore, the melting points were different. One proved to be unchanged starting material—this is the yellow product that gives an emerald-green color with

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(9) Lutz and Stuart, This Journal, **59**, 2316 (1937).

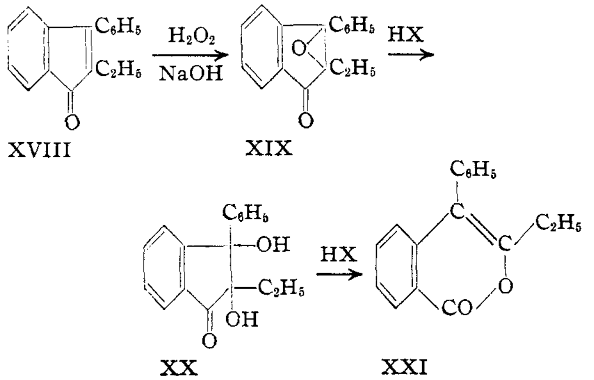
(10) Baeyer and Villiger, *Ber.*, **32**, 3625 (1897).

(11) Blatt, This Journal, **58**, 82 (1936).

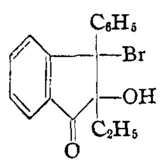
(12) Kohler and Erickson, *ibid.*, **53**, 2305 (1931).

(13) de Fazi and Pirrone, *Gazz. chim. ital.*, **60**, 277 (1930).

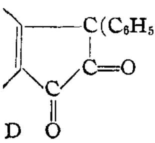
concentrated sulfuric acid. The other is pale yellow and is the epoxide, m. p. 58–59°; this is the substance that gives a yellow-green color with sulfuric acid.

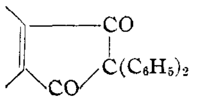

XVIII XIX XX XXI

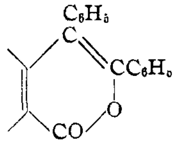
The epoxide XIX exhibits the same behavior as those described in the earlier portion of the paper, acidic reagents forming the glycol XX and lactone XXI; the latter is white, gives only a pale yellow color with concentrated sulfuric acid, and has a melting point of 100°, which definitely excludes it from being the product B claimed above. With cold hydrogen bromide this epoxide gives a bromohydrin. Since the bromine atom is not removed by methylmagnesium iodide, it cannot be in the *alpha* position; this evidence supports the structure XXII given to the bromohydrin.

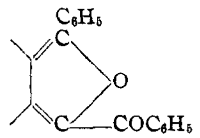

XXII

When the oxidoketone II in glacial acetic acid solution is boiled for a long time, or for a short time in the presence of a little mineral acid, a bright red substance is formed. This new product is isomeric with the oxidoketone. It is not acidic. In the Grignard machine, it shows two additions, but no active hydrogen. Upon oxidation, it gives 4,5-diphenylbenzoylbenzoic and benzoic acids. With zinc dust in acetic acid solution, it forms the lactone IV; this is not a reduction, for zinc acetate produces the same result. These facts show that the sidechain cannot be greatly different and that the points of attachment must be the same. All the ordinary type structures (D-G) have to be excluded (only partial formulas are used for brevity).


D

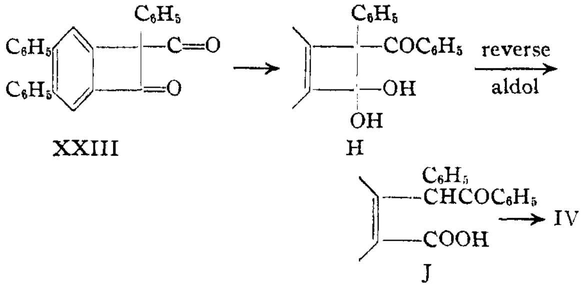

E


F


G

The 1,2-diketone D and lactone F are known and different; both D and E would require two molecular rearrangements, one for the formation, and one for the degradation. The furan type G is excluded because it would add only one molecule of Grignard reagent, because it would not be expected to give the lactone without shift of a phenyl group, and because the examples already described in this paper do not resemble the red substance.

A structure that appears to be in best accord with all the properties except color is that of a hitherto unknown benzocyclobutanone XXIII. Its oxidation products would be those found. It would add two moles of Grignard reagent. The lactone could be formed by an $\alpha,\gamma$-type rearrangement, or by the addition and elimination of water mechanism (XXIII-J). The zinc acetate isomerization could be visualized as a zinc atom coördinating with the carbonyl groups prior to the breaking of the single bond. However, the same isomerization takes place very slowly in the presence of potassium acetate. Attempts to form an oxime with hydroxylamine hydrochloride result in the same isomerization.


XXIII H J

The observation that one of the oxygen atoms in oxidoketones and oxidoesters is peroxidic,[14,15] might be taken to indicate some unusual sort of linkage involving the carbonyl group. That this group is free has been established by us by the rapid formation of a 2,4-dinitrophenylhydrazone of benzalacetophenone oxide; in fact, it has been known for some time that the carbonyl group of oxido ketones is unusually active, easily taking part in aldol condensations,[14] and forming oxanols with phenylmagnesium bromide.[4]

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(14) Bodforss, *Ber.*, **49**, 2795 (1916).

(15) Darzens, *Compt. rend.*, **150**, 1245 (1910).

TABLE I

PROPERTIES OF NEW SUBSTANCES

| No. | Substance | M. p., °C. | Empirical formula | Analyses Calcd., % C | H | Found, % C | H |
|---|---|---|---|---|---|---|---|
| I, R = $CH_3$ | An indenone | 229 | $C_{23}H_{18}O$ | 89.0 | 5.8 | 89.3 | 5.6 |
| I, R = Br | An indenone | 196 | $C_{21}H_{12}OBr_2$ | 57.3 | 2.7 | 58.0 | 2.9 |
|  | Benzal-4,5-dibromophthalide | 244 | $C_{15}H_8O_2Br_2$ | 47.4 | 2.1 | 47.2 | 2.3 |
|  | Benzal-4,5-dimethylphthalide | 166 | $C_{17}H_{14}O_2$ | 81.6 | 5.6 | 81.3 | 5.8 |
| II, R = $CH_3$ | An epoxide | 197 | $C_{23}H_{18}O_2$ | 84.7 | 5.5 | 84.6 | 5.4 |
| II, R = Br | An epoxide | 178 | $C_{21}H_{12}O_2Br_2$ | 55.3 | 2.6 | 55.6 | 2.8 |
| II, R = $C_6H_5$ | An epoxide | 200 | $C_{33}H_{22}O_2$ | 88.0 | 4.9 | 88.4 | 4.8 |
| XIX | An epoxide | 59 | $C_{17}H_{14}O_2$ | 81.6 | 5.6 | 81.9 | 5.8 |
| III, R = $C_6H_5$ | A glycol | 215 | $C_{33}H_{24}O_3$ | 84.6 | 5.1 | 83.9 | 5.3 |
| III, R = $CH_3$ | A glycol | 145 | $C_{23}H_{20}O_3$ | 80.2 | 5.8 | 80.8 | 6.2 |
| XX | A glycol | 122 | $C_{17}H_{16}O_3$ | 76.1 | 6.0 | 76.3 | 5.9 |
| XVI, R = $CH_3$ | Isobenzofuran | 132 | $C_{23}H_{18}O_2$ | 84.7 | 5.5 | 84.4 | 5.5 |
| V, R = $C_6H_5$ | A ketoacid | 244 | $C_{33}H_{24}O_3$ | 84.6 | 5.1 | 84.6 | 5.1 |
| IV, R = $C_6H_5$ | A lactone | 230 | $C_{33}H_{22}O_2$ | 88.0 | 4.9 | 87.9 | 4.8 |
| IV, R = $CH_3$ | A lactone | 208 | $C_{23}H_{18}O_2$ | 84.7 | 5.5 | 84.6 | 5.8 |
| IV, R = Br | A lactone | 229 | $C_{21}H_{12}O_2Br_2$ | 55.3 | 2.6 | 56.0 | 2.7 |
| XXI | A lactone | 101 | $C_{17}H_{14}O_2$ | 81.6 | 5.6 | 81.7 | 5.8 |
| XXII | Bromohydrin | 129 | $C_{17}H_{15}O_2Br$ | 61.6 | 4.5 | 61.4 | 4.4 |
| VIII |  | 256 | $C_{35}H_{28}O$ | 90.5 | 6.0 | 90.5 | 6.2 |
| VII |  | 186 | $C_{45}H_{34}O$ | 89.1 | 5.6 | 89.1 | 5.5 |

## Experimental

The substituted indenones were all prepared by procedures previously described.[16,17] The properties of the new ones are given in Table I.

The required 4,5-dimethylphthalic anhydride was secured in a 50% yield by a sulfur dehydrogenation of the maleic anhydride addition product with 2,3-dimethylbutadiene.[18] We are indebted to Dr. C. V. Wilson for the 4,5-dibromophthalic anhydride.

The method of preparation of the epoxides is fairly general, but the actual details may have to be determined in each instance, for some are more sensitive to the reagent than others, and the reaction may proceed beyond the desired point; low temperatures are sometimes essential. A typical reaction is illustrated by the preparation of 2,3,5,6-tetraphenylindenone epoxide (II, R = $C_6H_5$). A suspension of 22 g. of the indenone in 500 cc. of alcohol, containing 4 g. of sodium hydroxide in 30 cc. of water, was warmed to 60–70°, stirred vigorously, and 30 cc. of 15% hydrogen peroxide was added dropwise. After two hours and cooling, the epoxide separated and was filtered. The yield was 20 g. Benzene–alcohol was the solvent used for crystallization. The purified oxide (15 g.) melts at 199–200°. All the epoxides liberate iodine from an acetic acid solution of potassium iodide when warmed. They are unstable in light, turning deep yellow or pink; they become red at the melting point. Two of the indenones, 4,7-dimethyl-2,3,5,6-tetraphenyl and 2,3,4,7-tetraphenyl, failed to form peroxides, being recovered unchanged.

The glycol (III, R = $C_6H_5$) was secured by suspending 4 g. of the epoxide (II, R = $C_6H_5$) in 80 cc. of cold acetic acid, and then adding 40 cc. of a saturated solution of hydrogen chloride in acetic acid. After standing one-half hour, with occasional shaking, it was diluted by adding 50 cc. of water, dropwise and with stirring. The glycol that separated was filtered and recrystallized from dioxane–ligroin. The yield was 2.5 g. In the Grignard machine, it showed two active hydrogens and one addition. 2,3-Diphenyl-2,3-dihydroxyindanone (III, R = H) exhibits a similar behavior; this substance is called a "hydrate" by Weitz and Scheffer.[5] The glycol III (R = Br) has m. p. 166°.

Except for III (R = $C_6H_5$) which was destroyed by hot alkali, the other glycols (III, R = H or $CH_3$) gave yellow isobenzofurans with this reagent, by the procedure previously described.[5] 2-Phenyl-5-benzoyl-3,4-isobenzofuran (XVI, R = H) is monomolecular, does not form a quinoxaline, and is not cleaved by alkaline hydrogen peroxide (hence not a 1,2-diketone).

*Anal.* Calcd. for $C_{21}H_{14}O_2$: mol. wt., 298. Found: mol. wt. 300.

This is the "gelber Körper" of Weitz and Scheffer.[5] In the Grignard machine, it shows no active hydrogen and one addition. Oxidation by permanganate or nitric acid[8] gave the known benzil (XVII, R = H),[19] whereas chromic acid degraded it to benzoic and *o*-benzoylbenzoic acids. The *o*-benzoylbenzil (XVII, R = H) was identified by comparison with a specimen prepared as directed in the literature. The melting point, 94–95°, was not depressed on admixture.

The lactones IV were obtained by heating for ten minutes acetic acid solutions of the glycol or epoxide containing mineral acid; even in acetic acid alone (with the exception of 2,3,5,6-tetraphenylindenone epoxide, as described below), they were formed very slowly (six hours).[20] The lactones also resulted when the keto acids were heated above their melting points or in hot acetic acid solutions.

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[16] Allen and Gates, THIS JOURNAL, **65**, 419 (1943).

[17] de Fazi, *Gazz. chim. ital.*, **45**, 143 (1915).

[18] Diels and Alder, *Ann.*, **470**, 102 (1929).

[19] Ivanov and Dalef, *Ann. univ. Sofia, II, Faculté phys. math.*, Livre 2, **33**, 305 (1937) [*Chem. Abs.*, **32**, 3371 (1938)].

[20] This point was left in doubt by Weitz and Scheffer; ref. 3, p. 2343.

The keto acids V could be secured by dissolving the lactones in sodium hydroxide, and acidifying, care being taken to keep the temperature low.

Upon chromic acid oxidation, the lactones gave benzoic and an *o*-benzoylbenzoic acid; the same products resulted if the lactone was first dissolved in sodium hydroxide, and then oxidized with permanganate.

When treated in the Grignard machine, the lactone showed no active hydrogen but two additions as expected. The product, worked up in the usual way, gave the ketone VIII ($R = C_6H_5$), the carbinol group having been dehydrated. With phenylmagnesium bromide, a carbinol VII ($R = C_6H_5$) was secured without any difficulty.

The bromohydrin XXII resulted when the epoxide from 2-ethyl-3-phenylindenone was allowed to stand at 10–15° for one-half hour with five times its weight of 30–32% hydrogen bromide in acetic acid. The yield was 80%. It gave an oily carbinol with methylmagnesium iodide that still retained the halogen.

**2-Phenyl-2-benzoyl-(*Bz*-4,5-diphenyl)-cyclobutenone-1, XXIII.**—Five grams of the epoxide from 2,3,5,6-tetraphenylindenone was added to 40 cc. of 15% hydrogen bromide in acetic acid, the whole mixture boiled for ten minutes, cooled, and crystallization initiated by scratching the side of the flask. The red ketone that separated was filtered and recrystallized from benzene–ligroin. The yield was 4 g. The ketone crystallizes in brick-red prisms, often diamond-shaped, m. p. 219–220°.

*Anal.* Calcd. for $C_{33}H_{22}O_2$: C, 88.0; H, 4.9. Found: C, 88.4; H, 4.9.

The same substance was formed when a 25% solution of sulfuric acid in acetic acid was used, and even by six hours of refluxing in acetic acid alone.

In the Grignard machine, the red ketone shows no active hydrogen and two additions. With the Grignard reagent, it gave the same product (VIII) as the lactone. Upon chromic acid oxidation, it gave benzoic and 4,5-diphenyl-2-benzoylbenzoic acids.

When 1.5 g. of the red ketone was added to 50 cc. of alcohol containing 2 g. of potassium hydroxide, refluxed for three hours, poured into water, and acidified cold, the acid V ($R = C_6H_5$) resulted. Attempts to reduce the red ketone by zinc dust and acetic acid gave the lactone—this apparent anomaly was traced to the zinc acetate formed. In acetic acid solution, in less than five minutes, zinc acetate caused the red color to disappear; the lactone separated on cooling. The same change is brought about by potassium acetate in eight hours, and by hydroxylamine hydrochloride in two hours.

The 2,4-dinitrophenylhydrazone of benzalacetophenone oxide was prepared in the usual manner; it separated from methanol in orange needles, m. p. 205°.

*Anal.* Calcd. for $C_{21}H_{16}O_5N_4$: C, 62.6; H, 4.0. Found: C, 62.4; H, 4.0.

## Summary

A number of oxidoketones have been prepared in the indene series; the reaction appears to be fairly general.

With mineral acid, most of them give isomeric glycols in the cold, and lactones when heated; the glycols are isomerized to the same lactones by warm mineral acids.

The epoxides from 2,3-diphenyl- and 2-ethyl-3-phenylindenones give bromohydrins with cold hydrogen bromide in acetic acid.

The epoxide from 2,3,5,6-tetraphenylindenone gives an isomer for which a benzcyclobutenone structure has been proposed.

The glycols are isomerized by alkaline reagents to isobenzofurans.

A mechanism has been proposed to account for certain reactions previously termed rearrangements.

The carbonyl group is still present in oxidoketones.

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# NOTES

## Conversion of 2,7-Dibromofluorene to 2,7-Dibromophenanthrene

BY WELDON G. BROWN AND BEN A. BLUESTEIN

We have previously reported[1] a synthesis of phenanthrene, starting from fluorene, in which the ring enlargement is accomplished by a Wagner rearrangement of 9-fluorenylcarbinol. A similar series of reactions, resulting in the conversion of 2,7-dibromofluorene into 2,7-dibromophenanthrene, has been carried through which it seems desirable to record as the work has been discontinued.

### Experimental

**2,7-Dibromo-9-formylfluorene.**—Potassium ethoxide was formed from 3.9 g. (0.1 mole) of potassium and 4.6 g. (0.1 mole) of absolute alcohol in 250 cc. of dry ether. To this mixture was added 33 g. (0.1 mole) of 2,7-dibromofluorene resulting, after a few minutes refluxing, in a dark brown solution. The slow addition of 7.4 g. (0.1 mole) of ethyl formate caused the solution to become first green,

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(1) Brown and Bluestein, THIS JOURNAL, **62**, 3256 (1940).