[Contribution from the Chemical Laboratory of Harvard University]

THE ACTION OF ORGANIC MAGNESIUM COMPOUNDS ON ALPHA OXIDO KETONES AND ESTERS

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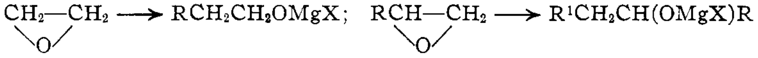
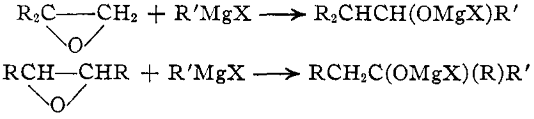
Oxido ketones and glycidic esters have two unsaturated groups in a relation which in other unsaturated compounds is known as conjugated. This relation, doubtless, is responsible for the ease with which they can be rearranged, but, owing to the nature of the reagents employed hitherto, little is known about the intermediates in these rearrangements. We have therefore undertaken an investigation of the behavior of representative oxido ketones and esters toward organic magnesium compounds, since these are capable of forming stable addition products with ethylene oxides as well as with ketones and esters.

From the work of Grignard[1] and a number of later investigators[2] it is known that organic magnesium compounds react much less readily with ethylene oxides than with ketones and esters. It is known also that the outcome of a reaction between an organic magnesium compound and an oxide depends almost entirely upon the number of hydrocarbon residues bounding the oxide ring. Thus the products which are obtained from ethylene oxide itself, and from its mono-alkyl and mono-aryl derivatives, indicate that the reagent opens the ring in the manner to be expected from other reactions of these oxides



$$\underset{\diagdown O \diagup}{CH_2{-}CH_2} \longrightarrow RCH_2CH_2OMgX;\quad \underset{\diagdown O \diagup}{RCH{-}CH_2} \longrightarrow R^1CH_2CH(OMgX)R$$

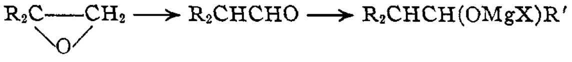
But no such simple reaction occurs in the case of disubstituted oxides



$$\underset{\diagdown O \diagup}{R_2C{-}CH_2} + R'MgX \longrightarrow R_2CHCH(OMgX)R'$$

$$\underset{\diagdown O \diagup}{RCH{-}CHR} + R'MgX \longrightarrow RCH_2C(OMgX)(R)R'$$

In order to account for these "abnormal" products it is customary to assume that the Grignard reagent first rearranges oxides of this type to the corresponding aldehydes or ketones and then combines with these rearrangement products in the usual manner



$$\underset{\diagdown O \diagup}{R_2C{-}CH_2} \longrightarrow R_2CHCHO \longrightarrow R_2CHCH(OMgX)R'$$

In agreement with what would be expected from an application of these facts to an oxido ketone in which the carbonyl group is not attached to

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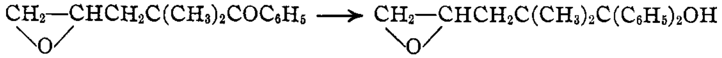
[1] Grignard, *Compt. rend.*, **136**, 1260 (1903).

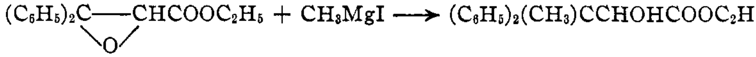
[2] See for example Fourneau and Tiffeneau, *Bull. soc. chim.*, [4] **33**, 741 (1905); *Compt. rend.*, **145**, 439 (1907); Hess, *Ber.*, **46**, 3117 (1913); Henry, *Compt. rend.*, **145**, 21, 406, 453 (1907).

the oxide ring, Haller and Ramart-Lucas[3] found that in a substance of this type the carbonyl group alone was attacked, despite the fact that a highly branched chain must have created a considerable hindrance to the reaction



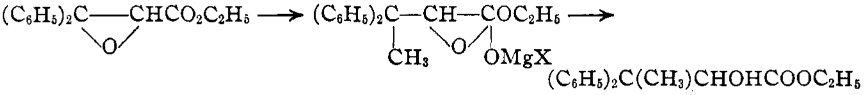
$$\underset{\diagdown O \diagup}{\mathrm{CH_2{-}CH}}\mathrm{CH_2C(CH_3)_2COC_6H_5} \longrightarrow \underset{\diagdown O \diagup}{\mathrm{CH_2{-}CH}}\mathrm{CH_2C(CH_3)_2C(C_6H_5)_2OH}$$

More interesting was a result reported by Bardon and Ramart[4] in the only case in which an organic magnesium compound has been allowed to react with a substance in which an oxido and a carbonyl group are adjoining

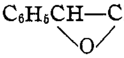


$$\underset{\diagdown O \diagup}{\mathrm{(C_6H_5)_2C{-}\!{-}CH}}\mathrm{COOC_2H_5} + \mathrm{CH_3MgI} \longrightarrow \mathrm{(C_6H_5)_2(CH_3)CCHOHCOOC_2H_5}$$

Here the carbonyl group reappeared intact, the ring was opened in a unique manner, and, since the authors obtained the same substance in boiling ether as in a freezing mixture, the primary product had to be a magnesium derivative of such a character as to prevent further reaction. A result like this could be explained only by 1,4-addition to the conjugated system



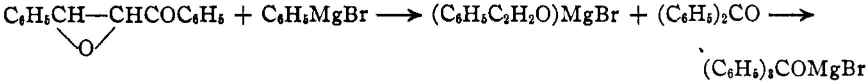
$$\underset{\diagdown O \diagup}{\mathrm{(C_6H_5)_2C{-}\!{-}CH}}\mathrm{CO_2C_2H_5} \longrightarrow \mathrm{(C_6H_5)_2}\underset{\mathrm{CH_3}}{\mathrm{C}}{-}\mathrm{CH}{-}\underset{\mathrm{OMgX}}{\mathrm{C}}\mathrm{OC_2H_5} \longrightarrow \mathrm{(C_6H_5)_2C(CH_3)CHOHCOOC_2H_5}$$

Our own experiments began with the oxide of benzal acetophenone,  $\underset{\diagdown O \diagup}{\mathrm{C_6H_5CH{-}CH}}\mathrm{COC_6H_5}$, a solid α-oxido ketone which can be obtained in a perfectly pure state and in any desired quantity. In view of the results reported by Bardon and Ramart, the behavior of this substance was surprising. It reacted very readily with two molecules of phenyl magnesium bromide and gave one molecule of triphenyl carbinol. It also reacted in a similar manner with ethyl magnesium bromide and gave phenyl diethyl carbinol. The reaction therefore results in cleavage, the hydrocarbon residues from the two molecules of the magnesium compound appear in the carbinol, and the cleavage is not due to an accumulation of phenyl groups.

In addition to the carbinol, the reaction between the oxido ketone and magnesium compounds yielded only resins, which are evidently due to extensive polymerization. Since these resins were of no service it became necessary to resort to a less symmetrical oxido ketone in order to establish the point of cleavage. To this end the oxide of anisal acetophenone was prepared and added to excess of phenyl magnesium bromide in the same manner. It likewise gave triphenyl carbinol and a resin. It was evident, therefore, that the cleavage occurred between the carbinol group and the oxido ring, and it seemed likely that it took place during the early stages of the reaction

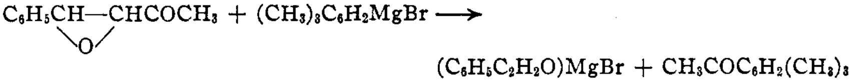
[3] Haller and Ramart-Lucas, *Compt. rend.*, **159**, 146 (1914).

[4] Bardon and Ramart, *ibid.*, **183**, 214 (1926).



$$\underbrace{C_6H_5CH-CH}_{O}COC_6H_5 + C_6H_5MgBr \longrightarrow (C_6H_5C_2H_2O)MgBr + (C_6H_5)_2CO \longrightarrow (C_6H_5)_3COMgBr$$

That one of the primary cleavage products is a ketone was definitely established by treating the oxide of benzal acetone with mesityl magnesium bromide, this combination having been selected because if any aceto mesitylene were formed it would survive, since organic magnesium compounds do not combine with mesitylenic ketones. In addition to the usual resin, this combination gave only aceto mesitylene



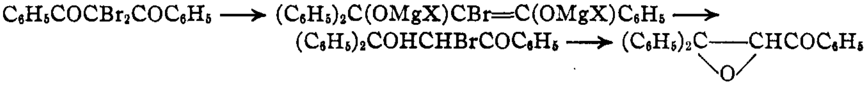
$$\underbrace{C_6H_5CH-CH}_{O}COCH_3 + (CH_3)_3C_6H_2MgBr \longrightarrow (C_6H_5C_2H_2O)MgBr + CH_3COC_6H_2(CH_3)_3$$

Having established both the stage and the place of this peculiar cleavage, it now became necessary to secure information on the second cleavage product. It seemed improbable that this could be accomplished without employing more highly substituted oxido ketones which might give magnesium derivatives less prone to polymerization. No such substances were known and none could be made by known methods of preparation. After many vain attempts we finally secured one in the following manner.

It has long been known that phenyl magnesium bromide removes bromine from α-bromo ketones and forms magnesium derivatives of the corresponding enols[5]

$$RCHBrCOC_6H_5 + 2C_6H_5MgBr \longrightarrow RCH{=}C(OMgBr)C_6H_5 + C_6H_5C_6H_5 + MgBr_2$$

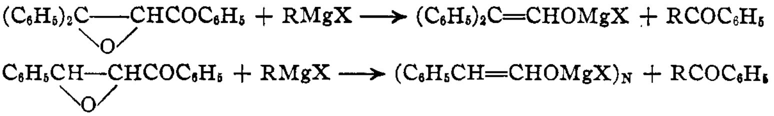
Applied to dibromo dibenzoyl methane, this process resulted in a bromohydrin that was readily converted into an α-oxido ketone of known structure



I II

$$C_6H_5COCBr_2COC_6H_5 \longrightarrow (C_6H_5)_2C(OMgX)CBr{=}C(OMgX)C_6H_5 \longrightarrow \underset{\text{I}}{(C_6H_5)_2COHCHBrCOC_6H_5} \longrightarrow \underset{\text{II}}{\underbrace{(C_6H_5)_2C-CH}_{O}COC_6H_5}$$

When this new oxido ketone was added to phenyl magnesium bromide it gave but two products, triphenyl carbinol and diphenyl acetaldehyde. From all that had gone before it was quite clear that the aldehyde represented the oxide group but we nevertheless repeated the operation with ethyl magnesium bromide and proved that in this case also the second product is diphenyl acetaldehyde. The action of organic magnesium compounds on α-oxido ketones can, therefore, be represented as follows



$$\underbrace{(C_6H_5)_2C-CH}_{O}COC_6H_5 + RMgX \longrightarrow (C_6H_5)_2C{=}CHOMgX + RCOC_6H_5$$

$$\underbrace{C_6H_5CH-CH}_{O}COC_6H_5 + RMgX \longrightarrow (C_6H_5CH{=}CHOMgX)_N + RCOC_6H_5$$

While these equations accurately represent one phase of the reaction, they leave the process almost as mysterious as before because they supply

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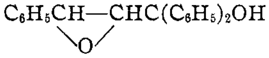
[5] Kohler and Johnstin, *Am. Chem. J.*, **33**, 39 (1905).

no adequate reason for the cleavage. These same α-oxido ketones react with substances which, in general, are much more destructive than organic magnesium compounds—ammonia, hydrazine, even alcoholic potassium hydroxide—and the entire molecule reappears in the product; there must therefore be some very special reason for this invariable cleavage by organic magnesium compounds. In a search for this reason the procedure was reversed; a single equivalent of phenyl magnesium bromide was added to an ethereal solution of the oxido ketone at −10° and the mixture was immediately decomposed with iced acid. The result was the oxido carbinol

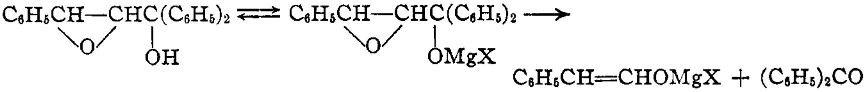


$$C_6H_5\underset{\diagdown O \diagup}{CH-CH}C(C_6H_5)_2OH$$

III

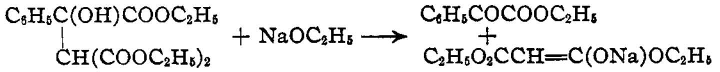
This oxido carbinol can be heated far above its melting point without causing any change and it is not decomposed by methyl alcoholic potassium hydroxide, but when it is added to phenyl magnesium bromide it is promptly cleaved, the final products as usual being triphenyl carbinol and resin. This cleavage is not due to the action of excess of reagent because the oxido carbinol can be made in any desired quantity by adding the oxido ketone to excess of reagent in the usual manner, provided only that the operation is carried out at a sufficiently low temperature and the mixture is decomposed immediately. Moreover, none of the oxido carbinol is obtained when the mixture resulting from the addition of a single equivalent of the reagent is allowed to remain at the ordinary temperature for some time before it is decomposed; it then yields the usual resin and—because no reagent is available for transforming it into triphenyl carbinol—benzophenone.

Thus it has been established, step by step, that cleavage represents the spontaneous decomposition of a magnesium compound which is formed by the addition of one molecule of the reagent to the oxido ketone



$$C_6H_5\underset{\diagdown O \diagup}{CH-CH}\underset{\substack{| \\ OH}}{C}(C_6H_5)_2 \rightleftharpoons C_6H_5\underset{\diagdown O \diagup}{CH-CH}\underset{\substack{| \\ OMgX}}{C}(C_6H_5)_2 \longrightarrow C_6H_5CH{=}CHOMgX + (C_6H_5)_2CO$$

The magnesium derivative therefore decomposes at temperatures which are more than 100° below those at which the corresponding alcohol is perfectly stable. Some, no doubt, will attribute this great difference in the stability of the carbinol and its magnesium derivative to ionization; others, probably, will find an explanation in chelation. Fundamentally, the cleavage of the carbinol by the addition of an organic magnesium compound is the same as the reversal of an aldol condensation in the presence of alkali, for example[6]



$$\begin{array}{l} C_6H_5C(OH)COOC_2H_5 \\ | \\ CH(COOC_2H_5)_2 \end{array} + NaOC_2H_5 \longrightarrow \begin{array}{c} C_6H_5COCOOC_2H_5 \\ + \\ C_2H_5O_2CCH{=}C(ONa)OC_2H_5 \end{array}$$

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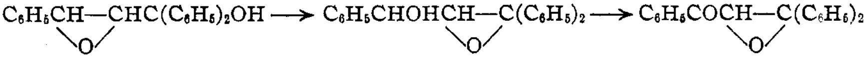
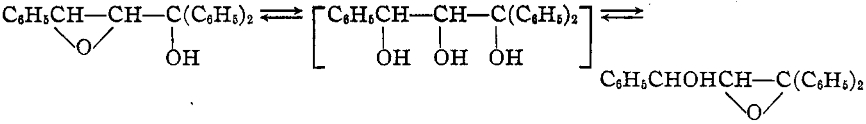
[6] Kohler and Corson, This Journal, **45**, 1975 (1923).

It therefore becomes necessary to consider why alkalies do not produce a corresponding effect on the oxido carbinol. The substance is, in fact, as sensitive to alkalies as it is to Grignard reagents, and alkalies transform it in a manner that is at least as interesting. Thus cold dilute methyl alcoholic potassium hydroxide gradually isomerizes it into an oxido alcohol which still contains an ethylene oxide ring

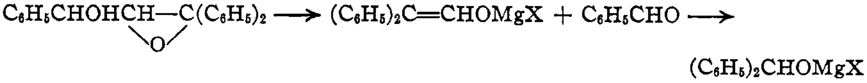

III IV II

This unexpected isomer gave no little trouble but in the end its structure was established with certainty by oxidation to the oxido ketone II. The process by which this new oxide is formed is probably reversible but it has not as yet been possible to establish this fact with certainty. Since methyl alcoholic alkalies are capable of adding water and methyl alcohol to ethylene oxides, it is conceivable that the rearrangement may occur by way of an open-chained compound



But in view of the fact that but one case is known in which it has been possible to convert a glycol into an ethylene oxide,[7] this mechanism seems exceedingly improbable. It is much more likely that the process is similar to that which is responsible for the rearrangement of substituted allyl alcohols, and that the oxide ring offers the same opportunity that is supplied by the double linkage in the alcohol. Whatever the route, the carbinol is rearranged instead of cleaved because, owing to its lack of acidity, it has little tendency to form a potassium compound corresponding to the magnesium derivative.

The product of this rearrangement—the oxido alcohol IV—is by far the most interesting substance that has appeared during the investigation. Like its isomer it can be heated far above its melting point without change, but, as would be expected from what has gone before, it is cleaved by phenyl magnesium bromide and the products in this case are diphenyl acetaldehyde and benzhydrol



The oxido alcohol is also very readily cleaved by dilute acids, a process which does not appear to be quite so inevitable as the foregoing, because it occurs under conditions which usually lead to the addition of methyl

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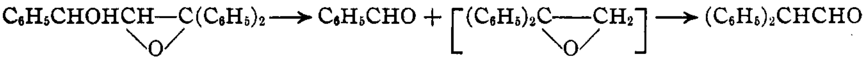
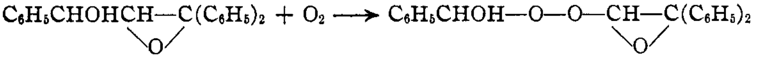
[7] Gardeur, *Bull. acad. roy. med. Belg.*, [3] **34**, 67 (1897).

alcohol to an ethylene oxide rather than to the rearrangement of the oxide to an aldehyde



$$C_6H_5CHOH\underbrace{CH{-}C}_{O}(C_6H_5)_2 \longrightarrow C_6H_5CHO + \left[(C_6H_5)_2\underbrace{C{-\!-}CH_2}_{O}\right] \longrightarrow (C_6H_5)_2CHCHO$$

Perhaps the most interesting property of the oxido alcohol is shown in its behavior toward free oxygen. Some preparations appear to undergo no change when they are kept in contact with air in diffused daylight, but others which have been obtained in essentially the same manner undergo autoxidation with sufficient rapidity to produce a perceptible rise in temperature. The process is accompanied by the formation of benzaldehyde and other degradation products, but the principal product is a peroxide which is formed by the insertion of two atoms of oxygen next to the oxide ring.

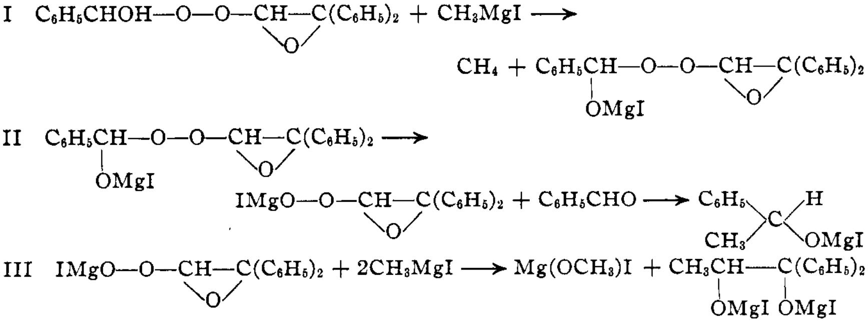


$$\underset{\text{IV}}{C_6H_5CHOH\underbrace{CH{-}C}_{O}(C_6H_5)_2} + O_2 \longrightarrow \underset{\text{V}}{C_6H_5CHOH{-}O{-}O{-}\underbrace{CH{-}C}_{O}(C_6H_5)_2}$$

The evidence for this strange formula is as follows. When the substance was heated, it decomposed briskly at the melting point and formed benzaldehyde, formic acid and benzophenone

$$C_6H_5CHOH{-}O{-}O{-}\underbrace{CH{-}C}_{O}(C_6H_5)_2 \longrightarrow C_6H_5CHO + HCOOH + (C_6H_5)_2CO$$

A quantitative analysis with methyl magnesium iodide in isoamyl ether showed that the substance reacted with slightly more than four moles of the reagent and liberated one mole of gas, indicating the presence of one hydroxyl group. When this reaction was repeated in ordinary ether the products were methyl diphenyl glycol—proving the presence of the oxide ring—and methyl phenyl carbinol



$$\begin{aligned}
&\text{I}\quad C_6H_5CHOH{-}O{-}O{-}\underbrace{CH{-}C}_{O}(C_6H_5)_2 + CH_3MgI \longrightarrow \\
&\qquad\qquad CH_4 + C_6H_5\underset{\displaystyle OMgI}{\underset{|}{C}}H{-}O{-}O{-}\underbrace{CH{-}C}_{O}(C_6H_5)_2 \\
&\text{II}\quad C_6H_5\underset{\displaystyle OMgI}{\underset{|}{C}}H{-}O{-}O{-}\underbrace{CH{-}C}_{O}(C_6H_5)_2 \longrightarrow \\
&\qquad\qquad IMgO{-}O{-}\underbrace{CH{-}C}_{O}(C_6H_5)_2 + C_6H_5CHO \longrightarrow \begin{matrix}C_6H_5 & & H\\ & C & \\ CH_3 & & OMgI\end{matrix} \\
&\text{III}\quad IMgO{-}O{-}\underbrace{CH{-}C}_{O}(C_6H_5)_2 + 2CH_3MgI \longrightarrow Mg(OCH_3)I + CH_3\underset{\displaystyle OMgI}{\underset{|}{CH}}{-\!-}\underset{\displaystyle OMgI}{\underset{|}{C}}(C_6H_5)_2
\end{aligned}$$

These transformations show that the peroxide belongs to a class which heretofore has been obtained only from free radicals or substances which are readily dissociated into free radicals. The problems suggested by its formation are still under investigation but it is clear already that these oxido carbinols and oxido alcohols constitute a remarkable group of substances.

Nothing in the foregoing account suggests the kind of conjugation of the oxido and carbonyl groups that it is necessary to assume in order to explain the results which Bardon and Ramart obtained with diphenyl glycidic ester. We prepared this ester and treated it with phenyl magnesium bromide. Rather to our surprise we found that it was not cleaved. Depending only on the conditions under which the reaction was carried out, it yielded in succession the hydroxy ester VII, the hydroxy ketone VIII and the glycol IX—substances which are manifestly derived from the keto ester VI which is isomeric with the glycidic ester

$$\underset{\text{VI}}{(C_6H_5)_2CHCOCOOC_2H_5} \longrightarrow \underset{\text{VII}}{(C_6H_5)_2CHC(C_6H_5)OHCOOC_2H_5} \longrightarrow$$

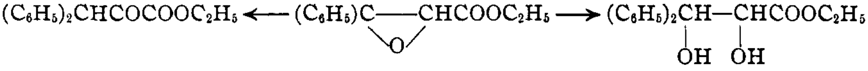
$$\underset{\text{VIII}}{(C_6H_5)_2CHC(C_6H_5)OHCOC_6H_5} \longrightarrow \underset{\text{IX}}{(C_6H_5)_2CHC(C_6H_5)OHC(C_6H_5)_2OH}$$

The great rapidity with which the first reaction occurs even in a freezing mixture led to the suspicion that the supposed glycidic ester of Pointet,[8] and of Bardon and Ramart,[4] was in reality the ketonic ester. This proved to be the case because the substance does not combine with water, but readily forms a phenyl hydrazone at the ordinary temperature and is oxidized to diphenyl acetic acid by alkaline hydrogen peroxide

$$(C_6H_5)_2CHC(=NNHC_6H_5)COOC_2H_5 \longleftarrow (C_6H_5)_2CHCOCOOC_2H_5 \longrightarrow$$

$$(C_6H_5)_2CHCOOH + CO_2 + C_2H_5OH$$

The ester had been prepared by condensing benzophenone with chloro-ethyl acetate both by the method of Pointet and by that of Claisen.[9] The primary product of this condensation is the desired glycidic ester, but this cannot be separated from the unchanged benzophenone. When the mixture is distilled under diminished pressure the glycidic ester is rearranged to the ketonic ester,[10] and when it is distilled with steam the glycidic ester combines with water and forms a glycolic ester



$$\underset{\text{VI}}{(C_6H_5)_2CHCOCOOC_2H_5} \longleftarrow (C_6H_5)C\underset{\diagdown O \diagup}{\text{——}}CHCOOC_2H_5 \longrightarrow \underset{\text{X}}{(C_6H_5)_2\underset{\substack{| \\ OH}}{CH}-\underset{\substack{| \\ OH}}{CH}COOC_2H_5}$$

VI X

When the crude condensation product—a mixture of the glycidic ester, benzophenone and chloro-ethyl acetate—was added to excess of phenyl magnesium bromide, the product contained diphenylacetaldehyde, showing both that the ester is cleaved in the manner to be expected and also that the products described by Bardon and Ramart are derived from the ketonic ester

$$(C_6H_5)_2CHCOCOOC_2H_5 \longrightarrow (C_6H_5)_2CHC(OH)CH_3COOC_2H_5 \longrightarrow$$

$$(C_6H_5)_2C(OH)CH_3COOH$$

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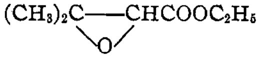
[8] Pointet, *Compt. rend.*, **148,** 418 (1909).

[9] Claisen, *Ber.*, **38,** 693 (1905).

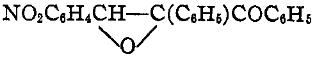
[10] Troell, *ibid.*, **61,** 2498 (1928), likewise concluded that distillation converts the glycidic into the ketonic ester but could not induce the latter to crystallize.

Two other substances were treated with phenyl magnesium bromide—an aliphatic glycidic ester and an oxido ketone with a phenyl group in the α-position



$(CH_3)_2C\underset{O}{\text{——}}CHCOOC_2H_5$

XI



$NO_2C_6H_4CH\underset{O}{\text{—}}C(C_6H_5)COC_6H_5$

XII

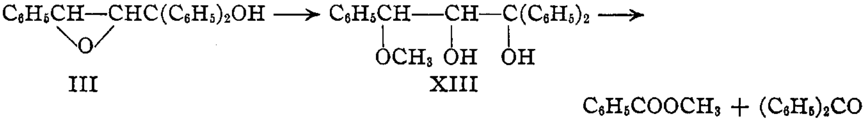
Both gave triphenyl carbinol. There is, therefore, no evidence that any oxido compounds can form 1,4-addition products with organic magnesium compounds.

Experimental Part

I. Experiments with α-Oxido Ketones

Four oxido ketones were treated with organic magnesium compounds for the various reasons specified in the introductory section, but only the reaction between the oxide of benzalacetophenone and phenyl magnesium bromide was studied with care. The structure of the primary product of this reaction was established in the following manner.

An analysis of the substance with methyl magnesium iodide in the machine[11] showed that it contains one hydroxyl group and one other reactive group. In the presence of a little hydrochloric acid the substance combines with methyl alcohol to form a methyl ether which has two hydroxyl groups, but no other group capable of reacting with methyl magnesium iodide; the substance is, therefore, an oxide. The methyl ether formed by addition of methyl alcohol is oxidized by chromic acid to methyl benzoate and benzophenone



$$\underset{\text{III}}{C_6H_5CH\underset{O}{\text{—}}CHC(C_6H_5)_2OH} \longrightarrow \underset{\text{XIII}}{C_6H_5\underset{OCH_3}{CH}\text{—}\underset{OH}{CH}\text{—}\underset{OH}{C}(C_6H_5)_2} \longrightarrow C_6H_5COOCH_3 + (C_6H_5)_2CO$$

Moreover, the dihydroxy ether was synthesized by a method recently described by Kohler and Addinall.[12] For this purpose benzalacetophenone dibromide was treated with sodium alcoholate and thus converted into an acetal which was readily hydrolyzed to the corresponding ketone. And when this ketone was treated with phenyl magnesium bromide it gave the same dihydroxy ether that had been obtained from the oxido carbinol

$$C_6H_5CHBrCHBrCOC_6H_5 \longrightarrow \underset{\text{XIV}}{C_6H_5CH(OCH_3)CHOHC(OCH_3)_2C_6H_5} \longrightarrow$$

$$\underset{\text{XV}}{C_6H_5CH(OCH_3)CHOHCOC_6H_5} \longrightarrow \underset{\text{XIII}}{C_6H_5CH(OCH_3)CHOHC(C_6H_5)_2OH}$$

Three of the oxido ketones were prepared by the excellent method of Weitz and Scheffer,[13] but for the preparation of benzalacetophenone oxide,

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[11] Kohler and Richtmyer, THIS JOURNAL, 52, 3736 (1930).

[12] Kohler and Addinall, *ibid.*, 52, 3728 (1930).

[13] Weitz and Scheffer, *Ber.*, 54, 2329 (1921).

which was needed in large quantities, the method was modified in the interest of economy and convenience. The procedure is as follows.

Eighty grams of sodium peroxide powder is slowly poured into 650 cc. of cracked ice and water contained in a flask immersed in a good freezing mixture and provided with an efficient motor stirrer; 142 cc. of concentrated (12 normal) hydrochloric acid is then allowed to drop in slowly, stirring vigorously and keeping the temperature below 5° throughout, if necessary by adding a little more cracked ice from time to time. At the end, 50 cc. of alcohol is added.

In the meantime 104 g. (0.5 mole) of benzalacetophenone is dissolved in 2 liters of alcohol and brought to 35° in a beaker supplied with an effective motor stirrer. The cold peroxide solution is at once filtered through glass wool and run into the benzalacetophenone solution with vigorous stirring, in a continuous rapid stream; the addition should be completed within two minutes. Seed is added at intervals until, near the end, the oxide crystallizes rapidly. The yellow color of benzalacetophenone then fades, and the solution becomes practically colorless. The vessel is immersed in a freezing mixture, and stirred slowly until the temperature reaches zero, when the oxide is at once filtered and washed well with cold 60% alcohol; 95 g. of white crystalline oxide, of m. p. 85–90°, is obtained, a yield of 85%. The filtrate contains about 5 or 10 g. more, which is hardly worth recovering. The oxide is easily purified by dissolving in cold acetone, filtering, evaporating to a small volume and adding petroleum ether. The product crystallizes in snow-white flakes, melting at 89–90°. When treated with methyl magnesium iodide in the "machine" it liberates only a negligible amount of gas but consumes two moles of reagent.

Reaction with Ethyl Magnesium Bromide.—To an ethereal solution containing five equivalents of ethyl magnesium bromide was added 35 g. of powdered oxide; stirring was continued at room temperature for forty minutes. The reaction mixture was decomposed with ice and concentrated hydrochloric acid, and the ethereal solution washed, dried and evaporated. Steam distillation left a yellow gummy residue, but the distillate consisted of a colorless oil which was identified by its physical constants and an analysis as diethyl phenyl carbinol. There was obtained 17 g. (66%) of liquid boiling at 110–112° at 20 mm., with n_D^{20} 1.5172. Klages[14] records a boiling point of 107–109° at 14 mm., and n_D^{12} 1.5166.

Anal. Calcd. for $C_{11}H_{16}O$: C, 80.5; H, 9.8. Found: C, 80.1; H, 9.6.

Reaction with Phenyl Magnesium Bromide.—When solid benzalacetophenone oxide is added to a solution containing five equivalents of phenyl Grignard reagent at room temperature, heat is evolved, and the solution passes through a characteristic purple stage which we have come to associate with the formation of triphenyl carbinol in reactions of this type. At the end the solution becomes greenish, and a thick, dark-colored gum adheres to the walls of the flask. The solution, upon decomposition with ice and acid, yields large amounts of triphenyl carbinol, while the gum produces mainly a thick yellow sirup which gives no test for phenyl acetaldehyde and has resisted all attempts at depolymerization. The yield of triphenyl carbinol is about 70%.

Preparation of the Oxido Carbinol, III.—A Grignard reagent was prepared from 8 g. of magnesium (0.33 mole) and 47 g. (0.30 mole) of bromobenzene in 600 cc. of ether. The filtered solution, in a 3-necked flask equipped with thermometer and mechanical stirrer, was chilled in a freezing mixture so that its temperature was always below −10°. Finely powdered oxide (34 g. = 0.15 mole) was added in the course of thirty minutes, and the mixture stirred for another fifteen minutes. The flask then contained a clear, pale green liquid, and a gum which contained solid unchanged oxide as well as products

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[14] Klages, *Ber.*, **36**, 3692 (1903).

resulting from the action of more than one equivalent of Grignard reagent on the oxide. The liquid was decanted at once into a mixture of ice and concentrated hydrochloric acid; the ethereal layer was washed with several portions of water, dried over calcium chloride, and evaporated to a small volume. Upon dilution with petroleum ether it deposited 22 g. of practically pure product.

If prepared by the inverse method, the procedure was as follows. Into a solution of 15 g. of oxide in 800 cc. of dry ether kept at −10° was allowed to dribble one equivalent of phenyl magnesium bromide during the course of an hour. A yellowish white solid appeared. After another hour's stirring in the freezing mixture the contents of the flask were poured on iced acid and the ethereal layer treated as before. There was obtained 9 g. of pure product, besides some unchanged oxide and a rather unstable halogen compound which was not further investigated.

When a similar solution was allowed to stand at room temperature overnight instead of being decomposed immediately upon removal from the freezing mixture, no primary product could be isolated. Some yellowish white magnesium derivative was filtered and decomposed separately; it yielded the unstable halogen compound, melting at about 100° with vigorous decomposition. The filtrate, after being decomposed, was subjected to steam distillation. Much benzophenone was obtained, and the gummy polymer remained in the flask. From this and other observations we may conclude that cleavage of the primary magnesium derivative is not due to excess of Grignard reagent.

α-Phenyl-β-(diphenyl-hydroxy-methyl) Ethylene Oxide, III.—The product obtained by the above procedures is very soluble in ether, moderately soluble in methyl alcohol, and difficultly soluble in petroleum ether. From a mixture of ether and petroleum ether it separates in clusters of large needles which melt at 129–130°. With methyl magnesium iodide it liberated 1.0 mole of gas and consumed 2.1 moles of reagent.

Anal. Calcd. for $C_{21}H_{18}O_2$: C, 83.4; H, 6.0. Found: C, 83.7; H, 5.9.

With excess phenyl magnesium bromide at −10° for one hour, most of the substance was recovered unchanged; at room temperature, however, triphenyl carbinol was the only product which could be isolated. A sample maintained for one hour at 150° showed no evidence of decomposition, and the melting point was unaffected. The compound was not attacked by acetic anhydride, even on warming and allowing the solvent to evaporate over caustic alkali in a vacuum desiccator. Concentrated ammonium hydroxide alone, or in methyl alcohol, was also without effect.

Addition of Methyl Alcohol: α,α,γ-Triphenyl-α,β-dihydroxy-γ-methoxy Propane, XIII.—A solution of 5 g. of the primary product III in 70 cc. of absolute methyl alcohol containing 10 drops of concentrated hydrochloric acid was boiled for one hour. Dilution with water precipitated an oil which smelled strongly of benzaldehyde, but which deposited a mass of crystals when petroleum ether was added. The solid was filtered and washed with petroleum ether. The petroleum ether solution was concentrated and distilled with steam; the first fractions contained benzaldehyde, the latter fractions diphenylacetaldehyde, which was identified through its semicarbazone melting at 158–160° by comparison with a specimen at hand.

The solid can be obtained in much better yield by shaking at room temperature, thereby avoiding the destructive cleavage to benzaldehyde and diphenylacetaldehyde. The product is moderately soluble in acetone and ether, sparingly soluble in petroleum ether; it crystallizes from ether in clusters of prisms which melt at 154–155°. With methyl magnesium iodide it evolved 2.0 moles of gas and consumed 2.1 moles of reagent. Oxidized with chromic acid in glacial acetic acid it yielded methyl benzoate and benzophenone, identified by the odor and mixed melting point, respectively

Anal. Calcd. for $C_{22}H_{22}O_3$: C, 79.0; H, 6.6. Found: C, 78.3; H, 6.9.

Independent Synthesis of the Dihydroxy Ether: The Dimethyl Acetal of α-Hydroxy-β-methoxy-β-phenyl Propiophenone, XIV.—To a solution of 22 g. of sodium in 500 cc. of dry methyl alcohol which was cooled in a freezing mixture was added 170 g. of pure solid benzalacetophenone dibromide. The mixture was allowed to remain in the freezing mixture for five hours, then kept at nearly 0° in a refrigerator for three days. By this time all of the solid dibromide had disappeared but the very pale yellow solution was still slightly alkaline.

The solution was allowed to evaporate in an open dish. It left a residue composed of sodium bromide and colorless needles of an organic compound imbedded in a large quantity of pale yellow oil. This residue was dissolved in ether and water. The ethereal layer was thoroughly washed with water, dried over sodium sulfate, concentrated, and inoculated with the needles previously obtained. It gradually deposited 24 g. of the solid acetal, and 5 g. more was obtained by diluting the oily filtrate with low-boiling petroleum ether, and cooling it in a freezing mixture. The solid was thoroughly washed with petroleum ether and then recrystallized from dry methyl alcohol, from which it separates in stubby prisms with a brilliant luster. The melting point is 122°. It is readily soluble in ether and acetone, moderately soluble in methyl alcohol, sparingly soluble in petroleum ether.

Anal. Calcd. for $C_{18}H_{22}O_4$: C, 71.5; H, 7.3. Found: C, 71.2; H, 7.4.

Hydrolysis, Followed by Reaction with Phenyl Magnesium Bromide.—The acetal group is readily hydrolyzed to the corresponding ketone by dilute acid. Thus, 9 g. of acetal was shaken with 200 cc. of dry methyl alcohol containing 3 cc. of concentrated hydrochloric acid. After ten minutes the solution was diluted with water and extracted with ether. The ethereal solution was thoroughly washed with water, dried over calcium chloride to remove the last traces of water and alcohol, and evaporated to about 100 cc.

Since a preliminary experiment had failed to produce a crystalline ketone, the ethereal solution itself was added to an excess of phenyl magnesium bromide. A white precipitate formed and redissolved. The mixture was boiled gently for fifteen minutes and then poured into ice and hydrochloric acid. The ethereal layer deposited 8 g. of the dihydroxy ether—a quantitative yield.

Isomerization of the Oxido Carbinol: α,α-Diphenyl-β-(hydroxy-benzyl) Ethylene Oxide, IV.—A solution of 0.8 g. of potassium hydroxide in 2 cc. of water was added to a solution of 20 g. of the oxido carbinol in 400 cc. of methyl alcohol. The mixture was shaken for two days, during which all of the carbinol dissolved. One-fourth of the solution was then gradually diluted with ice water while the walls of the vessel were rubbed with a glass rod. It precipitated the new oxide in small prisms, hexagonal in outline, along with some unchanged oxido carbinol. Whether the latter was due to incomplete reaction or whether it indicates that the process is reversible has not yet been established. The yield of pure isomer from one-fourth of the solution was at least 3 g.

The new compound is very soluble in alcohol and in ether, sparingly soluble in petroleum ether. After two recrystallizations from ether-petroleum ether, the melting point was constant at 103°. The substance was recovered unchanged after being heated to 150°. In the machine it liberated 0.9 mole of gas and consumed 2.1 moles of reagent.

Anal. Calcd. for $C_{21}H_{18}O_2$: C, 83.4; H, 6.0. Found: C, 83.3; H, 6.2.

Oxidation to Benzoyl Diphenyl Ethylene Oxide II.—A portion of the isomer was added to a warm solution of one equivalent of chromic acid in glacial acetic acid. As the mixture became green instantly, it was poured at once into water. The ethereal extract, after being washed with water and sodium carbonate, and dried over calcium chloride, was concentrated to a small volume. Crystals of the ketonic oxide, II, separated, and were identified by a mixed melting point with this substance, which is to be described later.

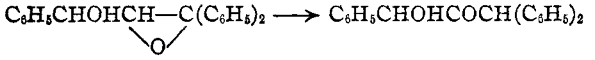
Reaction with Phenyl Magnesium Bromide.—The product from 2 g. of the oxido alcohol, after treating with an excess of phenyl Grignard reagent, was a yellowish mobile oil which showed no tendency to solidify. A fractional distillation with steam enabled us to separate first a diphenyl fraction; then an intermediate fraction containing diphenylacetaldehyde, which was identified as the semicarbazone; and finally benzhydrol, which crystallized in the aqueous distillate in fine needles, and was identified by a mixed melting point.

Reaction with Methyl Magnesium Iodide (Inverse).—A solution of 3 g. of the freshly recrystallized alcohol in absolute ether was cooled in ice and treated with 1.25 equivalents of methyl magnesium iodide. The mixture, which contained a yellow precipitate in a pale red solution, was boiled for twenty minutes and then decomposed with iced acid. The ethereal layer was washed with thiosulfate and water, evaporated, and fractionally distilled with steam. In the first fraction benzaldehyde was identified by its odor and by conversion into the phenyl hydrazone. In the last fraction diphenyl acetaldehyde was identified by means of its semicarbazone melting at 160–161°.

The residue left in the distilling flask was dissolved in ether. The dried ethereal solution deposited 0.7 g. of a sparingly soluble solid which crystallized from acetone–petroleum ether in needles melting at 128°.

Anal. Calcd. for $C_{21}H_{18}O_2$: C, 83.4; H, 60. Found: C, 83.4; H, 6.1.

According to the analysis this is still another isomer of oxido carbinol. In the "machine" it reacted with 2.2 moles of reagent and liberated 1.8 moles of gas, and it was recovered unchanged. Since it was neither affected by hydrochloric acid in methyl alcohol nor cleaved by methyl magnesium iodide, it is presumably an α-hydroxy ketone formed during the steam distillation from unchanged oxido alcohol



$$C_6H_5CHOH\underbrace{CH—C}_{O}(C_6H_5)_2 \longrightarrow C_6H_5CHOHCOCH(C_6H_5)_2$$

Autoxidation: The Peroxide, V.—A batch of 8.2 g. of the oxido alcohol freshly recrystallized from ether and petroleum ether was placed in a small glass dish covered with a watch glass. In the course of three hours, it developed a perceptible temperature and a strong odor of benzaldehyde. It was left to itself for five days and then well washed with ether. The residue—5.1 g.—was recrystallized from acetone. It separated in fine needles, sparingly soluble in alcohol, ether and acetone. It melts at about 160° with brisk decomposition.

Anal. Calcd. for $C_{21}H_{18}O_4$: C, 75.5; H, 5.4. Found: C, 75.3; H, 5.6.

In the machine, 1 mole of the substance consumed 4.2 moles of reagent and liberated 1 mole of gas.

Thermal Decomposition.—One and one-half grams of the peroxide was distributed in eight boats placed end to end in a combustion tube. As each boat was heated at one point until the peroxide melted, decomposition started and spread through the boat. The decomposition products were collected in ether. From the ethereal solution water extracted formic acid, which was identified by its reducing action on mercuric oxide.[15] The ethereal solution was fractionally distilled with steam; the first fraction contained benzaldehyde—identified as its phenyl hydrazone—the later fractions benzophenone, which was identified by its melting point before and after mixing with a sample.

Reaction with Methyl Magnesium Iodide.—To a solution of methyl magnesium iodide containing 1 g. of magnesium was added 1.8 g. of the peroxide in the form of a finely ground solid. The solid dissolved with evolution of gas and precipitated a gum which disappeared after prolonged stirring. The clear colorless solution was then de-

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[15] Mulliken, "Identification of Pure Organic Compounds," 1914, p. 83.

composed with iced acid, the ether extract washed with thiosulfate and water, dried and concentrated. It deposited a solid which after recrystallization from ether–petroleum ether melted at 94–95°.

Anal. Calcd. for $C_{15}H_{16}O_2$: C, 79.0; H, 7.0. Found: C, 78.8; H, 7.1.

In the machine one mole of the substance reacted with two moles of methyl magnesium iodide, liberated two moles of gas, and was recovered after addition of water.

The composition, crystalline form and melting point indicated that the substance was diphenyl methyl glycol. This glycol was therefore synthesized by treating ethyl lactate with excess of phenyl magnesium bromide. A comparison of the two products proved their identity.

The mother liquors from the glycol, on evaporation, left an oil. From the amount of reagent consumed it was to be expected that this oil contained methyl phenyl carbinol. It was therefore oxidized with a slight excess of chromic acid in glacial acetic acid. The oxidation product, isolated in the usual manner, was acetophenone. It was identified by condensing it with *m*-nitro benzaldehyde and comparing the condensation product with a sample of *m*-nitro benzalacetophenone.

Preparation of Benzoyl Diphenyl Ethylene Oxide: α-Bromo-β,β-diphenyl-β-hydroxy Propiophenone, I.—To an ice-cold Grignard reagent prepared from 24 g. of magnesium and 140 g. of bromo benzene was added 85 g. of dibromo dibenzoylmethane. Considerable heat was evolved and a transient yellow color appeared with each addition of solid. After fifteen minutes' stirring at the ordinary temperature the mixture was poured into iced acid, and the precipitated bromohydrin filtered and washed with ether, in which it is sparingly soluble. For analysis a small sample was purified by recrystallization from chloroform and petroleum ether, from which it separated in colorless, rectangular plates. It melts, with effervescence, at about 180°.

Anal. Calcd. for $C_{21}H_{17}O_2Br$: C, 66.2; H, 4.5. Found: C, 66.3; H, 4.4.

Benzoyl Diphenyl Ethylene Oxide, II.—A methyl alcoholic solution of sodium methylate was added to a suspension of the bromohydrin until the solution was slightly alkaline and the yellow color permanent; the suspended material now consisted of the oxido ketone and sodium bromide. The mixture was acidified with a little acetic acid, the product collected on a filter, washed with methyl alcohol and water, and recrystallized from acetone. It separated in clusters of short acicular prisms and melted at 124–125°. It is sparingly soluble in cold ether, alcohol and acetone. The yield was very nearly quantitative.

Anal. Calcd. for $C_{21}H_{16}O_2$: C, 84.0; H, 5.3. Found: C, 84.2; H, 5.6.

With methyl magnesium iodide the oxide consumed two moles of reagent and liberated only a negligible quantity of gas.

Reaction with Phenyl Magnesium Bromide.—Heat was evolved and a reddish-purple color developed when 2 g. of oxide was added to excess phenyl Grignard reagent at room temperature. The color soon faded to a light green, and after fifteen minutes the solution was decomposed with ice and acid. The ethereal solution, after being washed with water and dried over sodium sulfate, was concentrated, whereupon it deposited 0.8 g. of triphenyl carbinol. The residue was distilled with steam; from the middle fractions, treated with semicarbazide hydrochloride and sodium acetate in alcohol, was obtained the semicarbazone of diphenyl acetaldehyde, melting at 158–160°. Mixed with a known sample it melted at 158–161°.

Reaction with Ethyl Magnesium Iodide.—The oxide was treated in the same way with an excess of ethyl Grignard reagent. The ethereal solution, after concentration, was distilled with steam, and diphenyl acetaldehyde identified in the second half of the distillate.

Reaction with Other Oxido Ketones.—The experiments with the oxides of benzalacetone, anisalacetophenone, and α-phenyl-*p*-nitrobenzalacetophenone need not be described in detail because, as explained in the introduction, they were performed for special reasons and the general procedure was the same as that which has been described under the oxide of benzalacetophenone.

II. Experiments with Glycidic and Glyoxylic Esters

At first we prepared glycidic esters by the very convenient method of Claisen,[9] but found that the products contained considerable quantities of acid amides, which complicated still further the problem of isolating pure substances. We therefore turned to the method of Darzens.[16] For the preparation of diphenyl glycidic ester the procedure was as follows.

Into a well-cooled mixture of 182 g. of benzophenone and 122.5 g. of chloro-ethyl acetate, 68 g. of finely divided dry sodium ethylate was introduced at such a rate that the temperature could be kept below 5°. The mixture was allowed to remain at room temperature for twelve hours, then heated to 100° for six hours. After acidification with acetic acid it was diluted with water, which dissolved the salts and precipitated the oily ester. This was extracted with ether, the ethereal solution washed and dried. A small portion of the ethereal solution, evaporated at this stage, left a residue of 4.8 g. of an oil which when distilled with steam yielded 3.9 g. of diphenyl glycolic ester, showing that about 75% of the ketone had been converted into the glycidic ester.

The rest of the ethereal solution was fractionally distilled under a pressure of 3–10 mm. The fraction boiling at 190° was again examined by distillation with steam. It contained some benzophenone, which appeared in the distillate, but no sparingly soluble glycolic ester could be found in the residue. Distillation therefore destroys the oxido ester.

Reaction with Phenyl Magnesium Bromide.—Since it was impossible to isolate the pure oxido ester, an ethereal solution of the crude ester was added to a large excess of phenyl magnesium bromide in the customary manner. The product was manipulated in the usual manner and the residue left after removing triphenyl carbinol was distilled with steam. The first fractions contained diphenyl, the later fractions diphenyl acetaldehyde, which was identified as its semicarbazone. The α-oxido ester, therefore, does not give products of the type described by Bardon and Ramart but is cleaved like the oxido ketones.

Diphenyl Glyoxylic Ester, VI.—Since the oil obtained by distilling the crude glycidic ester failed to solidify in a freezing mixture, a small quantity of it was hydrolyzed by the method of Pointet.[8] The resulting sodium salt was converted into the silver salt, and from the silver salt the ester was regenerated by boiling it for three hours with ethyl iodide. The ester obtained in this manner was a solid. Large quantities of this same solid ester were then obtained by diluting the remainder of the oily distillate with ether and petroleum ether, cooling the solution in a freezing mixture and inoculating it with the solid. After repeated recrystallization from ether and petroleum ether the ester melted at 37°, and this melting point remained constant during five consecutive crystallizations. Pointet reported a melting point of 47°, but either this is a typographical error or else as Troell suggests Pointet's solid was benzophenone.

Anal. Calcd. for $C_{17}H_{16}O_3$: C, 76.1; H, 6.0. Found: C, 76.2; H, 6.2.

The ester crystallizes in prisms which are readily soluble in alcohol and in ether, moderately soluble in petroleum ether. With methyl iodide it evolved 0.3 mole of gas,

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[16] Darzens, *Compt. rend.*, **139**, 1214 (1904); **141**, 766 (1905).

indicating a tendency toward enolization similar to that of phenyl benzhydryl ketone. In order to prove that the substance is in reality a glyoxylic ester, it was turned into a phenyl hydrazone and oxidized with alkaline hydrogen peroxide.

Phenylhydrazone.—A solution of the ester in alcohol containing phenyl hydrazine hydrochloride deposited the phenyl hydrazone at the ordinary temperature within half an hour. The hydrazone is moderately soluble in ethyl alcohol, from which it separates in yellow prisms melting at 99–100°.

Anal. Calcd. for $C_{23}H_{22}O_2N_2$: C, 77.1; H, 6.1. Found: C, 77.4; H, 6.3.

Oxidation.—To a solution of 1 g. of ester and 3 cc. of 20% hydrogen peroxide in 25 cc. of ethyl alcohol, dilute aqueous sodium hydroxide was added drop by drop during the course of an hour until somewhat more than one equivalent had been added. After another hour the solution was diluted with water and extracted with ether to remove any unchanged ester. The alkaline solution was acidified and extracted with ether; the latter was washed with water, dried with calcium chloride and evaporated. The residue, crystallized from ether–petroleum ether, melted at 145–146°; diphenyl acetic acid melts at 146° (Pointet).

Saponification: Phenylhydrazone of Diphenyl Glyoxylic Acid.—As a control for the above oxidation, 1 g. of ester was treated in the same way in the absence of hydrogen peroxide and another acid melting at 110–115° obtained. This is diphenyl glyoxylic acid, of melting point 116° (Pointet), and not diphenyl glycidic ester as Pointet believed. It readily forms an alkali-soluble phenyl hydrazone which crystallizes from hot methyl alcohol in yellow needles and melts with decomposition at about 210° (when heated slowly) or at about 245° (instantaneously on a block).[17]

Anal. Calcd. for $C_{21}H_{18}O_2N_2$: C, 76.4; H, 5.4. Found: C, 76.4; H, 5.1.

The Methyl Ester: $(C_6H_5)_2CHCOCOOCH_3$.—The methyl ester was prepared in the hope that the methyl ester of phenyl glycidic acid—formed by condensing benzophenone with methyl chloro-acetate—might be obtained as a solid. All attempts to induce the crude condensation product to solidify were unsuccessful and distillation rearranged the glycidic into the glyoxylic ester. In order to get the latter to crystallize it likewise was necessary to secure a small quantity of solid for inoculation by methylating the acid through the silver salt. The ester boils at 175° under 5 mm., crystallizes from methyl alcohol in prisms, and melts at 75°.

Anal. Calcd. for $C_{16}H_{14}O_3$: C, 75.6; H, 5.5. Found: C, 75.8; H, 5.7.

Reaction with Phenyl Magnesium Bromide.—The reaction between the ethyl ester of diphenyl glyoxylic acid and phenyl magnesium bromide was investigated by Bardon and Ramart,[4] who thought, however, that they were dealing with the glycidic ester. They reported an ester alcohol melting at 130° and another product melting at 203–205° but identified neither of these substances.

Ethyl α,β,β-Triphenyl-α-hydroxy Propionate, VII.—An ethereal solution of 10 g. of the glyoxylic ester was added to an excess of phenyl magnesium bromide in an ice-bath, and the mixture was immediately poured into iced acid. The ethereal layer yielded 8 g. of a solid product and a small quantity of oil. A better yield (10 g.) of the same product was obtained by operating in an inverse manner. The hydroxy ester is moderately soluble in ether, from which it separates in nodules of minute needles melting at 118–120°.

Anal. Calcd. for $C_{23}H_{22}O_3$: C, 79.7; H, 6.4; OC_2H_5, 13.0. Found: C, 79.5; H, 6.4; OC_2H_5, 13.7.

α,β,β-Triphenyl-α-hydroxy Propiophenone, VIII, and $\alpha,\alpha,\beta,\gamma,\gamma$-Pentaphenyl-$\alpha,\beta$-dihydroxy Propane, IX.—These two substances are always formed together when either

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[17] *Cf.* Troell, Ref. 10, p. 2502, who gives 189° with decomposition.

the glyoxylic ester or the monohydroxy ester VII is added to a large excess of phenyl magnesium bromide, and the mixture is either allowed to remain for several days at the ordinary temperature or boiled for three or four hours, before it is decomposed with iced acid. In order to separate the mixture successfully it is necessary to proceed with great caution because the dihydroxyl compound is very readily cleaved into four other products, and when this happens the separation is almost hopeless. The most satisfactory procedure was as follows. A solution obtained by adding 20 g. of the hydroxy ester VII to an excess of phenyl magnesium bromide was boiled for three hours, then diluted with twice its volume of low-boiling petroleum ether and cooled in a freezing mixture for several hours. The top layer was treated separately with iced acid, but it contained little besides diphenyl and excess of phenyl magnesium bromide. The bottom layer was mixed with fresh ether, then likewise decomposed with iced acid. The ethereal solution was washed and dried, then allowed to evaporate in an open vessel. It left a pale yellow oil.

The oil was repeatedly extracted with low-boiling ether until the undissolved portion finally solidified. The solid was recrystallized from acetone and methyl alcohol and was thus readily purified. It crystallized in long truncated columns melting with decomposition at about 190°.

Anal. Calcd. for $C_{33}H_{28}O_2$: C, 86.8; H, 6.2. Found: C, 86.7; H, 6.3.

This substance is the glycol IX, as was established in the following manner. When it was treated with methyl magnesium iodide in the machine, it consumed two moles of reagent and liberated two moles of gas; therefore it contains two hydroxyl groups. When its solution in ethyl alcohol or, better, glacial acetic acid, was boiled for a few hours it decomposed, cleanly, into phenyl benzhydryl ketone and benzhydrol—both isolated and identified by comparison with samples in hand. And when it was kept a few degrees above its melting point for a short time it gave in addition to the two products already mentioned, smaller quantities of triphenyl ethyl alcohol and benzophenone, which were separated by fractional steam distillation and likewise identified by comparison with authentic samples.

I $(C_6H_5)_2CHC(C_6H_5)OHC(C_6H_5)_2OH \longrightarrow (C_6H_5)_2CHCOC_6H_5 + (C_6H_5)_2CHOH$

II $(C_6H_5)_2CHC(C_6H_5)OHC(C_6H_5)_2OH \longrightarrow (C_6H_5)_2CHCHOHC_6H_5 + (C_6H_5)_2CO$

The petroleum ether extracts were allowed to evaporate spontaneously. They gradually deposited along with a small quantity of the glycol another solid which separated in flat needles and after recrystallization from ether–petroleum ether melted at 123°.

Anal. Calcd. for $C_{27}H_{22}O_2$: C, 85.7; H, 5.8. Found: C, 85.7; H, 6.1.

This substance must be the hydroxy ketone VIII, because when it was boiled for three hours with a slight excess of phenyl magnesium bromide it was converted into the glycol IX.

The Glycolic Ester, X.—As was stated earlier, the crude glycidic ester, when distilled with steam, left a residue which solidified during the distillation. The solid was recrystallized from alcohol in fine lustrous needles melting at 130°.

Anal. Calcd. for $C_{17}H_{18}O_4$: C, 71.3; H, 6.3. Found: C, 71. 6; H, 6.5.

The corresponding methyl ester, obtained in a similar manner, likewise crystallized in silky needles and melted at almost the same temperature as the ethyl ester, 130–131°. A mixture of the two, however, melted at 110°.

Anal. Calcd. for $C_{16}H_{16}O_4$: C, 70.6; H, 5.9. Found: C, 70.8; H, 5.9.

Summary

1. When organic magnesium compounds react with α-oxido ketones, they combine with the carbonyl group only. By operating at a low tem-

perature and decomposing the product immediately, it is possible to secure the corresponding oxido carbinol; otherwise, the unstable magnesium derivatives decompose spontaneously into magnesium derivatives of aldehydes, and ketones which may subsequently be transformed into tertiary alcohols.

2. Organic magnesium derivatives first transform α-oxido esters into α-oxido ketones; the final products are therefore the same as those obtained with these ketones. Other results have been reported but the substance used in these cases was an α-ketonic ester and not the supposed isomeric α-oxido ester.

3. Oxido carbinols are reactive substances which show unexpected properties.

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STUDIES IN AUTO-OXIDATION REACTIONS. II. THE MECHANISM OF THE AUTO-OXIDATION OF CERTAIN ETHERS

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Introduction

In previous publications[2] from this Laboratory a general theory has been advocated, which, if properly applied, seems to account for the various phenomena and mechanism of auto-oxidation reactions. Briefly stated, the theory assumes the addition of molecular oxygen to compounds containing molecular valence electrons comparable to valence electrons of atoms. As a direct consequence of this theory, one would expect molecular oxygen to add directly onto the bivalent oxygen atom present in alcohols, ethers, ketones, aldehydes, etc., or onto the bivalent sulfur atom present in thio-alcohols, thio-ethers, thio-phenols, thio ketones, etc., or onto the trivalent nitrogen atom present in primary, secondary and tertiary amines, hydrazones and the like to form highly unstable dative peroxides which either rearrange or hydrolyze to yield other relatively more stable peroxides. Certain ethers were chosen for the present investigation because of the existence of diversity of opinion regarding the fundamental mechanism of their auto-oxidation.

The auto-oxidation of ethyl ether has been the subject of several investigations of which only two will be mentioned here. Clover[3] was the

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[2] Milas, (a) *J. Phys. Chem.*, **33**, 1204 (1929); (b) THIS JOURNAL, **52**, 739 (1930).

[3] Clover, *ibid.*, **44**, 1107 (1922).