Methyl *n*-hexyl ketone, methyl ethyl ketone and diethyl ketone reacted violently but produced no solid and the products seemed to decompose as fast as they were formed.

Benzophenone was treated with selenium oxychloride in carbon disulfide solution in the presence of anhydrous aluminum chloride and heated for several days. Hydrogen chloride was given off slowly. After standing for two weeks, most of the solvent evaporated, leaving a crystalline mass. It was extracted with chloroform and on the evaporation of the chloroform crystals separated. They were placed on a porous plate but decomposed as soon as the protecting layer of chloroform evaporated.

Summary

1. The reaction between selenium oxychloride and certain ketones has been studied.

2. Condensation reactions took place between two molecules of the ketones and one molecule of selenium oxychloride.

3. New organic compounds of selenium have been prepared and studied.

West Lafayette, Indiana

[Contribution from the Chemical Laboratory of Harvard University]

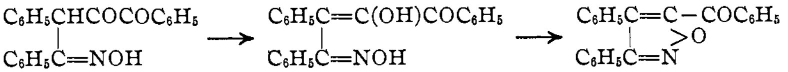
CYCLIC NITRONES

By E. P. Kohler and C. R. Addinall

Received November 26, 1929 Published April 7, 1930

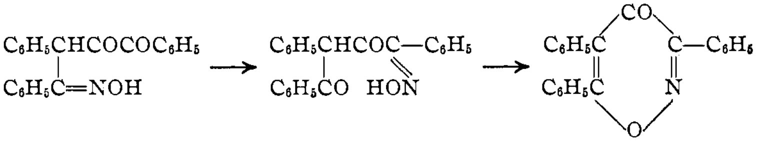
In earlier papers of this series there is mention of a "purple anhydride" which appeared in small quantities whenever solutions of triphenyl butane trione oxime became acid. Like benzoyl diphenyl isoxazole, previously investigated, this purple compound is a monomolecular anhydride of the oxime. It is, therefore, a surprisingly simple compound to have such a rich, deep purple color. This wide contrast between color and complexity was one of the reasons for the investigation.

Another incentive for investigating the purple compound arose from the difficulty of accounting for more than one monomolecular anhydride. The oxime is so constituted as to make an open-chained anhydride impossible, and the evidence is conclusive that the isoxazole derivative represents the anhydride of the only possible enolic modification of the open-chained oxime



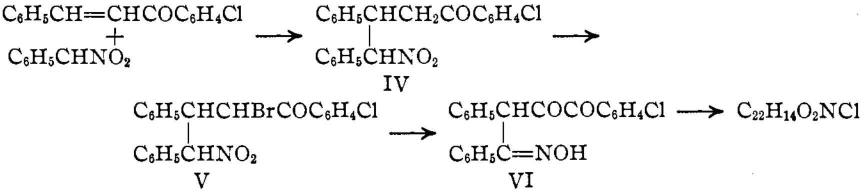
$$\begin{matrix} C_6H_5CHCOCOC_6H_5 \\ | \\ C_6H_5C{=}NOH \end{matrix} \longrightarrow \begin{matrix} C_6H_5C{=}C(OH)COC_6H_5 \\ | \\ C_6H_5C{=}NOH \end{matrix} \longrightarrow \begin{matrix} C_6H_5C{=}C-COC_6H_5 \\ | \quad >O \\ C_6H_5C{=}N \end{matrix}$$

In view of these facts it seemed probable that the formation of the purple compound is preceded by a rearrangement of the oxime. Since the slightest imaginable acidity leads to the appearance of the substance, a rearrangement involving the carbon chain is unlikely, but an interchange of the oximido group and the oxygen of a more active carbonyl is not improbable. A shift like this would be favored by an acid medium, and it would lead to a new anhydride



I II III

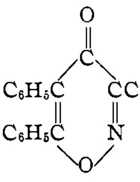
An attempt to determine by ozonization whether III is a possible formula for the purple anhydride failed because the products—benzoic acid and benzonitrile—are not sufficiently significant. In order to employ this method successfully it was necessary to secure an analogous compound in which either the *α*- or the *γ*-phenyl group could be identified by a substituent. Such a compound was, therefore, prepared in accordance with the scheme



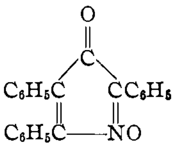
$$\begin{array}{l}C_6H_5CH{=}CHCOC_6H_4Cl\\ \quad + \\ C_6H_5CHNO_2\end{array} \longrightarrow \begin{array}{l}C_6H_5CHCH_2COC_6H_4Cl\\ \quad|\\ C_6H_5CHNO_2\\ \quad\text{IV}\end{array} \longrightarrow$$

$$\begin{array}{l}C_6H_5CHCHBrCOC_6H_4Cl\\ \quad|\\ C_6H_5CHNO_2\\ \quad\text{V}\end{array} \longrightarrow \begin{array}{l}C_6H_5CHCOCOC_6H_4Cl\\ \quad|\\ C_6H_5C{=}NOH\\ \quad\text{VI}\end{array} \longrightarrow C_{22}H_{14}O_2NCl$$

The ozonization products of this new purple compound were benzoic acid and *p*-chlorobenzonitrile—products which showed conclusively that in these purple compounds the nitrogen is attached to the *γ*-carbon, and which also reduced the number of plausible formulas to two



III



VII

In order to get a basis for distinguishing between these two formulas, the purple compound was treated with methyl magnesium iodide in an apparatus with which it is possible to determine both the volume of any gas that may be evolved and the amount of reagent that is consumed by a given weight of substance.[1] It was found that one mole of the anhydride liberated one mole of gas and consumed about 3 moles of reagent. Since there seems to be no reason why an orthoxazine derivative like III should liberate gas from methyl magnesium iodide, while isoxazoline oxides invariably do so, this result is evidence for the nitrone formula VII.

[1] Kohler, Stone and Fuson, This Journal, **49**, 3181 (1927).

The reaction between methyl magnesium iodide and the purple compound supplied valuable information but the physical properties of the product made it unsuitable for further investigation. We, therefore, turned to phenyl magnesium bromide. Here a fresh difficulty arose. The product of the reaction between phenyl magnesium bromide and the purple anhydride is stable only in solid form. In solution it changes too rapidly for a reliable determination of its molecular weight; and by analyses alone it is not possible to determine how many molecules of the magnesium derivative are involved in the reaction. This difficulty was met by using bromo phenyl magnesium bromide in one experiment; a determination of bromine in the product showed that the reaction involves but one molecule of reagent for one of anhydride.

With this much established, we undertook to ascertain the mode of addition of the Grignard reagent by ozonization of the product, but found that it changed with sufficient rapidity to impair the value of the results. Cautious oxidation with chromic acid proved to be more helpful because, in addition to benzoic acid, it gave a substance which was identified as $C_6H_5COCOC(C_6H_5)_2OH$. These oxidation products, even though they are inadequate to establish the structure of the substance, nevertheless showed conclusively that the Grignard reaction does not consist in addition to **a** carbonyl group.

From the experiments that have been described it became evident that in order to use the Grignard reaction as a means of determining the structure of the purple compound, it was essential to stabilize the Grignard product before undertaking its degradation. It was, therefore, converted into its methyl ether. The ether is stable, easily obtained in a perfectly pure condition, and in every way admirably adapted for structural work. Its composition and molecular weight are represented by the formula $C_{29}H_{23}O_2N$, and its relation to the purple compound by the equation

$$C_{22}H_{15}O_2N + C_6H_6 + CH_2 = C_{29}H_{23}O_2N$$

The ether is insensitive to both acids and bases. By very cautious oxidation with chromic acid it was possible to add two atoms of oxygen without disrupting the molecule—the oxygen atoms, doubtless, taking the place of a double linkage. The oxidation product was readily attacked by bases, which cleaved it smoothly into phenyl glyoxylic acid and a nitrogenous compound which contained the rest of the molecule

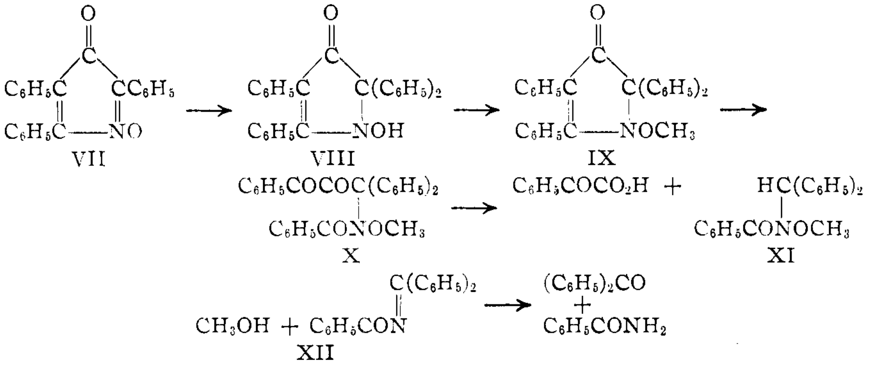
$$C_{29}H_{23}O_4N + H_2O \longrightarrow C_6H_5COCO_2H + C_{21}H_{19}O_2N$$

When the nitrogenous compound was heated above its melting point, it lost methyl alcohol, passing into a new nitrogen compound. This new product was hydrolyzed by acids to benzophenone and benzamide

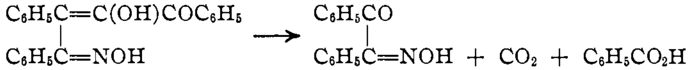
$$\text{I} \quad C_{21}H_{19}O_2N = C_{20}H_{15}ON + CH_3OH$$

$$\text{II} \quad C_{20}H_{15}ON + H_2O = (C_6H_5)_2CO + C_6H_5CONH_2$$

When all these facts are fitted together, they constitute a very complete proof that the purple anhydride is the cyclic nitrone VII

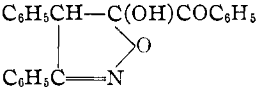


Concerning the mechanism by which the purple compound is formed from the oxime, it is not possible as yet to speak with any confidence. The open-chained formula of the oxime is based largely on its oxidation to α-benzil monoxime by sodium peroxide

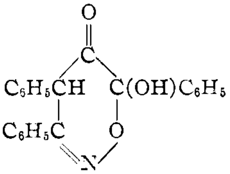


$$\begin{matrix} C_6H_5C{=}C(OH)COC_6H_5 \\ | \\ C_6H_5C{=}NOH \end{matrix} \longrightarrow \begin{matrix} C_6H_5CO \\ | \\ C_6H_5C{=}NOH \end{matrix} + CO_2 + C_6H_5CO_2H$$

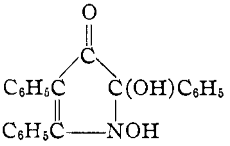
It would be difficult to reconcile these oxidation products with any other formula, but not a single open-chained derivative of the oxime is known. All reagents that do not disrupt the molecule transform the substance either into a cyclic isomer or into derivatives of cyclic isomers which belong to one of the following types



A

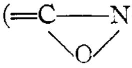


B

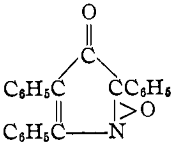


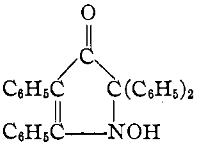
C

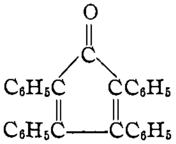
It is quite possible that all of these forms are present in solutions of this extremely active substance. If that be the case, then the formation of the purple nitrone merely represents the dehydration of the cyclic modification C.

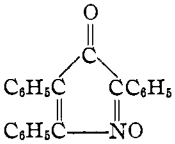
In whatever manner the anhydride may be formed, it manifestly belongs to a varied class of substances which are of especial interest at present in connection with modern theories of valence—a class that includes the N-ethers of oximes, the isatogens, the *aci*-nitro compounds and their ethers, and the isoxazoline oxides. The formulas with a carbazoxy ring  $(=C\text{——}N\text{—})$, which were formerly used extensively for representing these compounds, have now been generally abandoned in favor of those of the "nitrone" type ($>N=O$), although they are still occasionally regarded as possible alternatives in special cases.[2] We regard the evidence against the ring formulas as conclusive; they cannot be reconciled with the spectrochemical results of Brady[3] and of Auwers and Ottens,[4] the values for the parachor found by Sugden,[5] and the color of the isatogens and of our anhydrides.[6]

If these anhydrides had a carbazoxy ring (D), their color should not differ greatly from that of the addition products (E) all of which are yellow. Instead of this they have a very dark purple color which is scarcely distinguishable from that of Ziegler and Schnell's tetraphenyl cyclopentadienone (F.)[7]

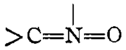

D


E


F


G

It is customary to represent the unsaturated system in nitrones with twinned double linkages analogous to those occurring in allenes, isocyanates and ketenes


$$>C=\overset{|}{N}=O \qquad >C=C=C< \qquad -N=C=O \qquad >C=C=O$$

The nitrones, however, not only bear but little resemblance to these other classes of unsaturated compounds, but also very rarely, if ever, form addition products in which the addends have taken the place of a double linkage. The list of substances which have been added to nitrones is both long and varied; it includes isocyanates,[8] organic magnesium compounds,[9] alcohols,[10] acetic acid, acetyl chloride, acetic anhydride,[10b] benzoyl chloride,[11] and diphenyl ketene.[8d] In the addition products which the various nitrones form with all of these substances—except possibly

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[2] Staudinger and Miescher, *Helv. Chim. Acta*, **2**, 554 (1919); Gabriel and Gerhard, *Ber.*, **54**, 1073 (1921); Ruggli, *Helv. Chim. Acta*, **6**, 594 (1923).

[3] Brady, *J. Chem. Soc.*, **105**, 2104 (1914).

[4] Auwers and Ottens, *Ber.*, **57**, 446 (1924).

[5] Sugden, *J. Chem. Soc.*, **127**, 1525 (1925).

[6] Pfeiffer, *Ann.*, **411**, 72 (1916).

[7] Ziegler and Schnell, *ibid.*, **445**, 266 (1925).

[8] (a) Beckmann, *Ber.*, **23**, 3395 (1890); (b) **27**, 1957 (1894); (c) Goldschmidt, *ibid.*, **24**, 2808 (1891); (d) Staudinger and Miescher, *Helv. Chim. Acta*, **2**, 554 (1919).

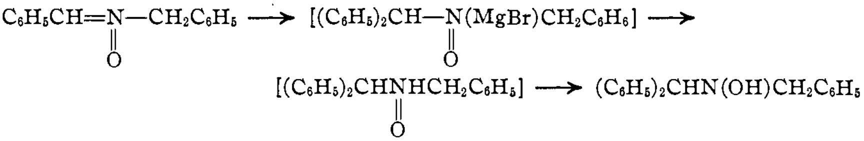
[9] Angeli, Alessandri and Aiazzi-Mancini, *Atti accad. Lincei*, [V] **20**, I, 546 (1911); Staudinger, *Helv. Chim. Acta*, **2**, 554 (1919).

[10] (a) Heller, *Ber.*, **55**, 474 (1922); (b) Ruggli, *ibid.*, **52**, 5 (1919); (c) Ruggli, Bollinger and Leonhardt, *Helv. Chim. Acta*, **6**, 594 (1923).

[11] Wieland and Kitasato, *Ber.*, **62**, 1251 (1929); *Ann.*, **475**, 42 (1929).

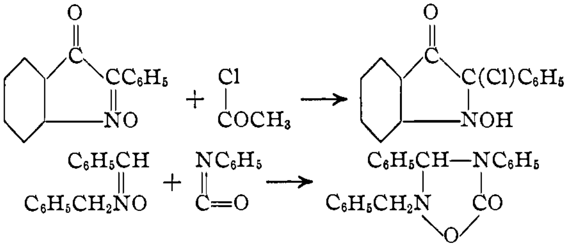
diphenyl ketene—the addends are invariably found at the ends of the unsaturated system.

Thus, in a typical example, the addition of phenyl magnesium bromide to the N-benzyl ether of benzaldoxime leads to the formation of benzyl-diphenyl methyl-hydroxylamine. In order to reconcile this result with the usual nitrone formula, Angeli[12] made the assumption that the reaction involves both addition and rearrangement



$$C_6H_5CH{=}\underset{\substack{\| \\ O}}{N}-CH_2C_6H_5 \longrightarrow [(C_6H_5)_2CH-\underset{\substack{\| \\ O}}{N}(MgBr)CH_2C_6H_6] \longrightarrow$$
$$[(C_6H_5)_2CH\underset{\substack{\| \\ O}}{N}HCH_2C_6H_5] \longrightarrow (C_6H_5)_2CHN(OH)CH_2C_6H_5$$

It is possible to account for the addition products that are obtained with alcohols and acetic acid in a similar manner, but not for those obtained with acid chlorides, acid anhydrides and phenyl isocyanide. Here the assumption that a 1,2-addition product would undergo rearrangement to a substance in which the addends are in the 1,3-position lacks all probability; the products must be due to 1,3-addition



From these examples it is evident that the unsaturated system in these nitrones is so constituted as to permit 1,3-addition and also that in every case in which it has been possible to establish the structure of the primary product, this has always been found to be a 1,3-addition product. There appears to be no good reason, therefore, for assuming a different mechanism in those cases in which 1,2-addition followed by rearrangement is conceivable; it seems much more probable that in substances of this type 1,3-addition is a normal process.

The customary method of representing the unsaturated system in nitrones neither suggests the possibility of 1,3-addition nor accounts for its occurrence. Moreover, the link between the nitrogen and the oxygen in these oxides certainly has nothing in common with that which is represented by the N=O group in nitroso compounds; it is of the type which has been called "semi-polar" or "coördinate." By resorting to electronic formulas it is easy to understand that 1,3-addition is possible in all systems in which such a "coördinate" link is twinned with a double linkage. Since

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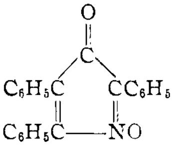
[12] Ref. 9 a, p. 548.

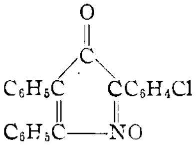
there is no accepted method for symbolizing such a coördinate link, we prefer to represent the unsaturated system in nitrones by $>C{=}\underset{|}{N}O$.[13]

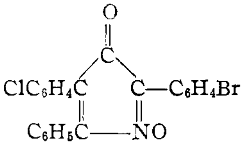
Experimental Part

Preparation of Materials

In the course of this investigation we studied three purple anhydrides


VII


XIII


XIV

The first of these substances was made from α, γ, δ-triphenyl butanetrione oxime which was prepared in the manner described in earlier papers.[14] In successful operations the crude dry product is sufficiently pure for nearly all purposes. When it is necessary to recrystallize it from acetone and ether it is essential to remove all trace of acid from the walls of the apparatus, to use only alcohol-free ether and acetone that has been distilled from permanganate and alkali, and to avoid contamination by acid in the air.

The second purple compound was made from the corresponding chlorinated oxime.[15] Inasmuch as the intermediates in the preparation of this oxime were obtained in the same manner as those employed in securing the halogen free oxime, it will be sufficient to tabulate their properties without describing the operations in detail.[16]

Substance	Melting point, °C.	Yield, %	Composition Calcd., % C	H	Found, % C	H
$C_6H_5CHCH_2COC_6H_4Cl$ | $C_6H_5CHNO_2$	176	93	69.6	4.7	69.0	4.9

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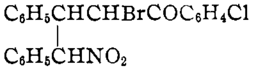
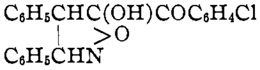
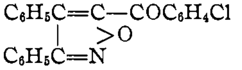
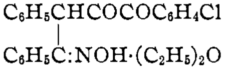
[13] The term "nitronic acid" which Bamberger [*Ber.*, **35**, 54 (1902)] proposed as a substitute for *aci*-nitro compounds is unfortunate because it implies a much closer analogy to carbonic acids than actually exists [Kuhn and Albrecht, *ibid.*, **60**, 1297 (1927)]. The term "nitrone" which was proposed by Pfeiffer for these unsaturated oxides seems almost equally unfortunate because, in reality, it is not the group $=\underset{|}{N}O$ but the entire unsaturated system $>C{=}\underset{|}{N}O$ that is equivalent to $>C{=}O$. And if the termination —nitrone— is to include this entire system, then it becomes extremely difficult to name individual substances. We have, therefore, used the term nitrone only as a general designation for all classes of substances that contain the unsaturated system $>C{=}\underset{|}{N}O$ and have named the individual substances as oxides.

[14] (a) Kohler, This Journal, **46**, 1733 (1924); (b) **47**, 3030 (1925).

[15] G. H. Reid, "Dissertation," Harvard University, **1926**.

[16] All experiments with the *p*-chloro compound, including the preparation of the purple compound and its ozonization, were performed by G. H. Reid.

Substance	Melting point, °C.	Yield, %	Composition Calcd., %		Found, %	
			C	H	C	H
 $\begin{array}{l} C_6H_5CHCHBrCOC_6H_4Cl \\ \vert \\ C_6H_5CHNO_2 \end{array}$	178	95	57.8	3.7	57.6	3.8
 $\begin{array}{l} C_6H_5CHC(OH)COC_6H_4Cl \\ \vert \quad >O \\ C_6H_5CHN \end{array}$	165	75	69.9	4.2	69.7	4.5
 $\begin{array}{l} C_6H_5C{=}C{-}COC_6H_4Cl \\ \vert \quad >O \\ C_6H_5C{=}N \end{array}$	164	75	73.2	3.7	73.2	4.1
 $\begin{array}{l} C_6H_5CHCOCOC_6H_4Cl \\ \vert \\ C_6H_5C{:}NOH \cdot (C_2H_5)_2O \end{array}$	112(eff.)	80	Cl 7.8		Cl 7.9	

In the preparation of the third purple compound from *p*-bromobenzal *p*-chloro-acetophenone, the sequence of reactions was the same as in the preceding cases, but none of the intermediates were purified or analyzed.

The Purple Compounds

For transforming the pure oximes into the purple compounds we found no better method than that mentioned in an earlier paper[17]—the action of hydrogen chloride on a solution of the oxime in chloroform. The procedure is as follows. The oxime is dissolved in chloroform which has previously been freed from alcohol, dried with phosphorus pentoxide, and saturated with dry hydrogen chloride. The solution immediately becomes purple in color and water soon collects in drops. It is saturated afresh with hydrogen chloride, which is passed through it for five minutes, then poured into a shallow dish and allowed to evaporate. To remove the last of the chloroform, the residue is mixed with dry ether, which is likewise allowed to evaporate. The residue is then collected on a filter and thoroughly washed with dry methyl alcohol, which removes the hydroxy isoxazoline (A) and leaves the purple compound. Pure oximes pass quantitatively into these two types of compound and these substances are formed in the proportion of 70–75% of purple anhydride to 25–30% of hydroxyl compound. When other substances turn up in the process, they are present in the oxime or due to other impurities in it.

This procedure is applicable to the crude oxime unless, owing to faulty operation, it is excessively impure. In that case, it is better to substitute phosphorus pentoxide for the hydrogen chloride. Thus the chloro bromo-oxime could not be obtained in crystalline form and, therefore, could not be freed from ether-soluble impurities; but pure anhydride was obtained from it by the following procedure.

The yellow paste obtained by treating 15 g. of α-bromo compound with alkalies in the usual manner was dissolved in a minimum of hot dry alcohol-free chloroform which was heated on a steam-bath. To the boiling solution phosphorus pentoxide was added until the mixture had a uniform purple color—about 2 g. was necessary. The chloroform was boiled off and the solid mass was repeatedly extracted with boiling water. In order to remove a high-melting yellow impurity, the crude product was dissolved in boiling benzene, the solution filtered and evaporated to dryness. The residue was freed from hydroxy isoxazoline by extraction with methyl alcohol, and finally recrystallized from chloroform and petroleum ether; yield, 7 g.

The three purple compounds resemble one another very closely; they crystallize well, melt without decomposition at a high temperature, are sparingly soluble in ether and in

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[17] Ref. 14 b, p. 3033.

the lower alcohols, and are readily soluble in acetone, in chloroform, in ethyl acetate and in boiling benzene. The color of the solutions is remarkably like that of a concentrated solution of potassium permanganate.

3-Keto-2,4,5-triphenyl Pyrrolenine Oxide, VII.—The unhalogenated oxide crystallizes in double pyramids and melts at 175–177°.

Anal. Calcd. for $C_{22}H_{15}O_2N$: C, 81.2; H, 4.7; mol. wt. 325. Found: C, 81.1; H, 4.8; mol. wt. 330.

In the "machine"[18] one mole of the substance liberated 0.9 mole of gas and consumed 3.3 moles of reagent.

3-Keto-2-(4-chlorophenyl)-4,5-diphenyl Pyrrolenine Oxide, XIII.—The chloro anhydride crystallizes in stout needles and melts at 201°.

Anal. Calcd. for $C_{22}H_{14}O_2NCl$: C, 73.3; H, 3.9; mol. wt., 360. Found: C, 73.5; H, 3.8; mol. wt., 327.

3-Keto-2-(4-bromophenyl)-4-(4-chlorophenyl)-5-phenyl Pyrrolenine Oxide, XIV.—The chloro-bromo oxide crystallizes in very minute prisms and begins to sinter at 180°.

Anal. Calcd. for $C_{22}H_{13}O_2NClBr$: C, 60.1; H, 3.0. Found: C, 60.0; H, 3.4.

Ozonization

A current of ozonized oxygen containing about 6% of ozone was passed through a suspension of 10 g. of the unhalogenated anhydride. Ozone appeared in the effluent gas immediately, but the solid gradually dissolved and the purple color then began to fade. It disappeared completely after eight hours, leaving a colorless paste suspended in a pale yellow solution. The paste disappeared when the mixture was shaken with water. Tests for aldehydes and for phenyl glyoxylic acid in the resulting solution were negative. The solution was, therefore, freed from chloroform, the residual paste dissolved in ether, the ethereal solution dried and evaporated. It left a pale yellow paste with a strong odor of benzonitrile. A portion that was heated on the steam-bath first gave off benzonitrile, which was turned into benzamide for identification, and then a sublimate of benzoic acid. All attempts to isolate a solid product from the oil were unsuccessful. When left to itself it very slowly but persistently turned into benzonitrile and benzoic acid.

Three grams of *p*-chloro oxide when ozonized in the same manner gave a similar result, the only difference being that instead of benzonitrile, one of the products was *p*-chlorobenzonitrile. This melted at 94° and addition of an authentic sample caused no depression of the melting point.

Reaction with Grignard Reagents

Since the anhydrides are very sparingly soluble and the Grignard products both sensitive and difficult to purify, it is important to start with pure materials, use a large excess of Grignard reagent, and operate as rapidly as possible. As a result of many experiments we adopted the following procedure.

A solution of phenylmagnesium bromide, made from 4 g. of magnesium in a 1-liter flask that is provided with an effective stirrer, is cooled in ice water. To this solution is added, rapidly and with vigorous stirring, a solution of 10 g. of the anhydride in 100 cc. of hot benzene. The purple color should disappear immediately. After ten minutes, the flask—which, depending upon the relative quantities of ether and benzene, may contain either a clear yellow solution or a suspension of solution and yellow paste—is cooled in a freezing mixture. The solution is then diluted with 400–500 cc. of cooled, low-boiling

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[18] Kohler, Stone and Fuson, THIS JOURNAL, 49, 3181 (1927).

petroleum ether, which completes the precipitation of the pasty, yellow magnesium derivative.

After adequate dilution with petroleum ether, the solution is nearly colorless and contains nothing of value and hence is discarded; the yellow paste is composed mainly of addition product but contains a small quantity of phenyl magnesium bromide and other impurities. After the addition of 100 cc. of ether, it may be decomposed either with iced hydrochloric acid or with ammonium chloride. When it is decomposed with iced acid the result is a lemon-yellow ethereal solution which immediately begins to deposit yellow crystals of the magnesium-free product; yield of crude dry product, about 85%.

When the yellow pasty magnesium compound is decomposed with 30 g. of ammonium chloride, it usually forms a crystalline ammonium compound which is insoluble in ether and in ammonium chloride solution. This compound is stable in the presence of ammonia, but it rapidly turns green after it has been washed with water and ether.

1-Hydroxy-2,2,4,5-tetraphenyl Pyrrolidone-3, VIII.—The pure dry Grignard product appears to be perfectly stable, but the crude material slowly turns green and all solutions of the substance, even those made by dissolving perfectly pure material likewise become green. This change of color takes place in the absence of air, but access of air appears to promote it. It takes place more rapidly in benzene than in acetone and more rapidly in the latter than in ether, and it is promoted by increase in temperature. Since the substance is sparingly soluble in ether, it is best to purify it by dissolving it in the minimum quantity of warm acetone and immediately diluting the solution with cold anhydrous ether. It is thus obtained in yellow plates or prisms that usually have a greenish cast.

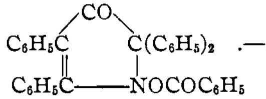
Anal. Calcd. for $C_{28}H_{21}O_2N$: C, 83.3; H, 5.2. Found: C, 83.4; H, 5.8.

Molecular weight determinations gave values ranging from nearly 800 in freezing benzene to 735 in dioxane. Since all solutions had turned to a vivid green during the operations, the significance of these values is uncertain. In a capillary tube the substance melts to a green liquid at about 184°, and shortly thereafter gives off a little gas as the melt resolidifies to a yellow solid. This high-melting, very sparingly soluble solid also constitutes the final product of the changes that occur in solution.

Oxidation with Permanganate.—A solution of the Grignard product in acetone, on treatment with potassium permanganate, first turned dark green in color and then became colorless. The acetone solutions, when manipulated in the usual manner, yielded a small quantity of a solid melting at 163°, benzoic acid and benzophenone.

Oxidation with Chromic Acid.—A solution of 4 g. of the Grignard product in 100 g. of hot glacial acetic acid was treated, gradually, with a solution of chromic acid that was made by dissolving 4 g. of the anhydride in 4 cc. of water and diluting with 10 g. of glacial acetic acid. Each addition of the oxidizer produced a dark green color which rapidly disappeared on shaking. When further addition no longer affected the color, the solution was cooled and poured into water. The resulting suspension was filtered, the pasty solid thoroughly washed with water, and then dissolved in ether. From the ethereal solution sodium carbonate extracted approximately one equivalent of benzoic acid. The dried, acid-free ethereal solution on evaporation left a yellow oil that partially solidified when rubbed with methyl alcohol. The solid was identified as $C_6H_5COCOC(C_6H_5)_2OH$ by comparison with a sample on hand.[19]

The Benzoate of the Grignard Product,



$$\begin{array}{lcl} & CO & \\ C_6H_5C & & C(C_6H_5)_2 \\ \| & & | \\ C_6H_5C & \text{——} & NOCOC_6H_5 \end{array}$$

.—As a first attempt at stabilizing the Grignard product we turned it into the benzoate. Sodium

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[19] Kohler, This Journal, **47**, 3036 (1925).

hydroxide converts the hydroxyl compound into a crystalline yellow sodium salt which is rapidly hydrolyzed by water but is stable in 5% sodium hydroxide solution. This sodium salt reacts with benzoyl chloride to form the benzoate but the yield is poor. Better results were obtained with pyridine. To a solution of 2 g. of the substance in hot dry pyridine was added 2 g. of benzoyl chloride. The mixture was set aside for eighteen hours, during which it deposited 1.3 g. of large greenish-yellow crystals. By recrystallization from boiling benzene the product was obtained in colorless rhomboidal plates, sparingly soluble in ether and in alcohol, and melting at 225°. From the benzene the benzoate crystallized with a molecule of solvent.

Anal. Calcd. for $C_{35}H_{25}O_3N\cdot C_6H_6$: C, 84.1; H, 5.3. Found: C, 84.0; H, 5.0.

The molecular weight which in boiling benzene was found to be 542 instead of 507 calcd. indicated that the Grignard product was monomolecular, but beyond this the benzoate was useless for our purpose.

The Methyl Ethers and Their Degradation

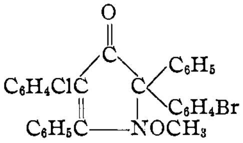
The yellow sodium salt of the Grignard product reacts readily with dimethyl sulfate and forms the corresponding methyl ether in almost the calculated quantity. The most satisfactory method of getting this ether is as follows.

The solution obtained in the Grignard reaction is transferred to a separating funnel in which it is cooled and diluted with petroleum ether. After decanting the petroleum ether layer and adding ordinary ether, the pasty yellow magnesium derivative is decomposed with iced hydrochloric acid in the usual manner. The aqueous layer is drawn off, the ethereal layer washed with water and then immediately shaken with excess of 10% sodium hydroxide. The crystalline yellow sodium compound thus formed is collected on a sintered glass suction funnel and washed with ether and with 5% sodium hydroxide.

The relatively pure sodium salt thus obtained is transferred immediately to a flask containing 150 cc. of 3% sodium hydroxide and treated with 15 g. of dimethyl sulfate. This gradually transforms it first to an oil and then to a solid. After decomposing the excess of dimethyl sulfate by warming on a steam-bath, the solid is collected in a funnel, thoroughly washed with hot water and dried. The yield of crude dry product is 13 g. The ether is readily purified by recrystallization from acetone and methyl alcohol; yield, 12.2 g. of pure ether from 10 g. of the purple anhydride.

Anal. Calcd. for $C_{29}H_{23}O_2N$: C, 83.5; H, 5.6; OCH_3, 7.4; mol. wt., 417. Found: C, 83.3; H, 5.8; OCH_3, 6.0; mol. wt., 416.

The methyl ether is moderately soluble in ether and in methyl alcohol, readily soluble in acetone and in chloroform. Its solutions in all solvents are deep yellow but it crystallizes in needles that are all but colorless. It melts at about 185°, with effervescence due to loss of formaldehyde, then resolidifies to the same waxy solid that is formed by melting the hydroxyl compound.



1-Methoxy-2(4-bromophenyl)-4-(4-chlorophenyl)-2,5-diphenyl Pyrrolidone-3.—When the dihalogenated purple compound (XIV) was treated with phenyl magnesium bromide, it yielded a product very similar to that obtained from the halogen-free compound.

Anal. Calcd. for $C_{28}H_{19}O_2NBrCl$: C, 65.0; H, 3.7. Found: C, 65.6; H, 3.7.

The methyl ether, made like the corresponding halogen-free compound, crystallizes in very pale yellow needles and melts with decomposition at about 158°. In all common organic solvents it is more soluble than the unhalogenated ether.

Anal. Calcd. for $C_{29}H_{21}O_2NClBr$: C, 65.5; H, 4.0; OCH_3, 5.8. Found: C, 65.4; H, 4.1; OCH_3, 5.3.

Ozonization.—A current of ozonized oxygen was passed through a suspension of 5 g. of the unhalogenated ether in ethyl bromide for six hours, during which time all of the ether dissolved. Water was added to the clear pale yellow solution and the solvent was evaporated in a current of air. The residual yellow paste was distilled with steam until only a discolored film remained in the flask. The distillate was extracted and the contents of the ethereal solution were separated into acidic and indifferent components. The acidic portion gave 2 g. of pure benzoic acid. The non-acid portion was left, on evaporation of the ether, as a pale yellow oil which partially solidified when rubbed with methyl alcohol.

The composition, melting point (60°) and the hydrolysis products indicated that the solid was the methyl ether of benzophenone oxime. The identification was completed by comparing the substance with a sample of this ether which was obtained by methylating the oxime with dimethyl sulfate. The formation of this uncommon type of ozonization product showed that the methyl ether contains the group $—C(C_6H_5)_2—N(OCH_3)—$ and, therefore, that the phenyl group of the Grignard reagent enters the 2-position.

Oxidation with Chromic Acid, X.—Three 5-g. lots of the ether were dissolved, separately, in 100 cc. of glacial acetic acid at 90°. To each solution 3 g. of chromic anhydride, dissolved in 3 cc. of water and 10 cc. of glacial acetic acid, was added as rapidly as the initial precipitate could be made to disappear by vigorous shaking. Each solution was then immediately poured into 500 cc. of cold water. The resulting suspensions were filtered, and pasty precipitates washed and dissolved in ether. The ethereal solutions were extracted with bicarbonate until free from acetic acid, then dried and concentrated to small volume. They gradually deposited 12 g. of crude solid oxidation product.

The crude oxidation product is not easy to handle because it decomposes in high-boiling solvents, and it both dissolves in and separates from low-boiling solvents very slowly. It is best to purify it partially by dissolving it in ethyl bromide, boiling down the solution until it begins to separate, and then completing the precipitation by diluting with an equal volume of ether. After filtering and washing with ether, the fine yellow powder can now be dissolved by prolonged boiling with 50 times its weight of dry methyl alcohol. On cooling, this solution very slowly deposits the pure oxidation product in transparent yellow needles, which melt at 160° and lose formaldehyde at about 175°.

Anal. Calcd. for $C_{29}H_{23}O_4N$: C, 77.5; H, 5.1; OCH_3, 7.0. Found: C, 77.5; H, 5.1; OCH_3, 8.4.

Oxidation of the Halogenated Ether, $ClC_6H_4COCOC(C_6H_5)(C_6H_4Br)N(OCH_3)$-$COC_6H_5$.—The chloro-bromo ether on oxidation with chromic acid gave a diketone which was much more easily purified. It crystallized in transparent yellow needles and melted with loss of formaldehyde at about 170°.

Anal. Calcd. for $C_{29}H_{21}O_4NBrCl$: C, 61.8; H, 3.8. Found: C, 61.8; H, 3.9.

Action of Sodium Methylate on the Oxidation Products.—Seven grams of the finely ground halogen-free oxidation product was shaken with a cold solution of 4 g. of sodium in 175 cc. of methyl alcohol until all but a few coarse particles had dissolved. The colorless solution was then evaporated as rapidly as possible in a strong draught. The moist pasty solid residue was collected on a funnel, washed with water until free from alkali and then repeatedly with low-boiling petroleum ether.

A weighed portion of the aqueous solution was acidified with dilute hydrochloric acid and then warmed with an excess of phenylhydrazine hydrochloride. It deposited the phenyl hydrazone of phenyl-glyoxylic acid, which was identified by comparison with a sample on hand. The weight of the hydrazone obtained was equivalent to 3 g. in place of 3.7 g. possible from 7 g. of oxidation product.

The solid product weighed 4.2 g. By a tedious series of operations, partly mechanical, it was finally separated into 1.5 g. of a substance that melted, with effervescence, at 155–160°, 2.0 g. of a substance melting at 115°, and a small quantity of a third product that crystallized in fine silky needles, sparingly soluble in ether, and melting without decomposition at 165°.

Diphenylmethenyl Benzamide, XII.—The lowest melting cleavage product (115°) is readily soluble in all common organic solvents except low-boiling petroleum ether. It crystallizes in large colorless prisms.

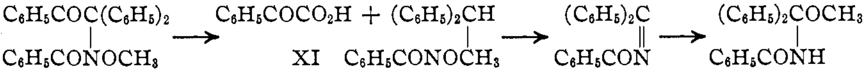
Anal. Calcd. for $C_{20}H_{15}ON$: C, 84.2; H, 5.3. Found: C, 84.0; H, 5.3.

The structure of this product was established by hydrolysis. The finely powdered substance dissolved readily in concentrated hydrochloric acid, forming a solution that almost at once became cloudy. Then the solution was diluted at this point and immediately extracted with ether; the ethereal layer contained benzophenone and benzamide, which were easily separated by evaporation to dryness and extraction with petroleum ether. Both substances were identified by comparison with authentic samples. When the acid solution was allowed to stand for some time before extraction, the products were benzophenone, benzoic acid and ammonium chloride.

The cleavage product that melts with effervescence at 155–160° is sparingly soluble in ether, moderately soluble in methyl alcohol and crystallizes in needles.

Anal. Calcd. for $C_{21}H_{19}O_2N$: C, 79.5; H, 6.0. Found: C, 79.4; H, 5.9.

The relation between this substance and diphenylmethyl benzamide is clear, because the effervescence above the melting point is due to evolution of methyl alcohol and the residue left after heating is the benzamide derivative. The detailed structure of the substance is, however, uncertain because, while it appears to be a direct cleavage product of the diketonic compound, it may none the less be an isomer formed by addition of sodium methylate to the unsaturated benzamide derivative



$$\begin{array}{ccccccc} C_6H_5COC(C_6H_5)_2 & & C_6H_5COCO_2H + (C_6H_5)_2CH & & (C_6H_5)_2C & & (C_6H_5)_2COCH_3 \\ | & \longrightarrow & | & \longrightarrow & \| & \longrightarrow & | \\ C_6H_5CONOCH_3 & & \text{XI}\quad C_6H_5CONOCH_3 & & C_6H_5CON & & C_6H_5CONH \end{array}$$

In the absence of any conclusive evidence we have tentatively formulated the substance as the cleavage product XI.

Cleavage of the Halogenated Oxidation Product.—A suspension of 1.8 g. of the finely powdered oxidation product in a cold solution of 1 g. of sodium in 25 cc. of dry methyl alcohol was shaken for three hours, during which time the powder was replaced by a mass of fine white needles. The mixture was cooled in a freezing bath, the solid collected on a filter, washed with water and with chilled methyl alcohol, and dried in the air; yield, 1.3 g. This solid cleavage product—$(C_6H_5)Br(C_6H_4)CHN(COC_6H_5)OCH_3$—is sparingly soluble in ether and in methyl alcohol, more readily soluble in acetone. It crystallizes in fine needles and begins to effervesce freely at about 140°.

Anal. Calcd. for $C_{21}H_{18}O_2NBr$: C, 63.4; H, 4.5. Found: C, 63.6; H, 5.1.

The Phenylhydrazone of 4-Chlorophenyl Glyoxylic Acid, $ClC_6H_4C(NNHC_6H_5)$-COOH.—The filtrates and washings from the solid cleavage product were combined and concentrated under diminished pressure at the ordinary temperature. The concentrated solution was thoroughly extracted with ether, then barely acidified with dilute acid. It deposited a sodium salt which was readily soluble in water, sparingly soluble in a saturated solution of sodium carbonate and crystallized in colorless plates. A solution of a small quantity of this salt was treated with phenylhydrazine hydrochloride. It promptly precipitated a lemon-yellow hydrazone which contained halogen. The hydrazone was recrystallized from aqueous methyl alcohol, from which it separated in needles melting at 188°.

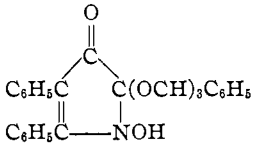
Anal. Calcd. for $C_{14}H_{11}O_2NCl$: C, 61.1; H, 4.0. Found: C, 61.2; H, 4.5.

Phenyl-(4-bromophenyl)-methenyl Benzamide, $(C_6H_5)(C_6H_4Br)C{=}NCOC_6H_5$.—The solid cleavage product begins to lose methyl alcohol below 140° but in order to get complete transformation it is necessary to heat it at a much higher temperature. Thus the residue left after heating 1.2 g. for ten minutes to 180–190° and then five minutes longer at 200° still contained some unchanged cleavage product which appeared after repeated extractions with low-boiling petroleum ether. The extracts deposited the unsaturated compound in small lustrous rhombs, readily soluble in organic solvents including petroleum ether.

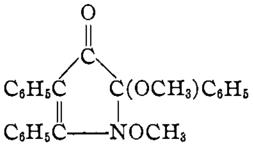
Anal. Calcd. for $C_{20}H_{14}ONBr$: C, 65.9; H, 3.9. Found: C, 65.8; H, 3.9.

When the substance was hydrolyzed with concentrated hydrochloric acid, it gave *p*-bromobenzophenone and benzamide—both identified by comparison with authentic samples.

The 1,3-addition reactions of nitrones are evidently subject to the same kind of hindrance as the 1,4-addition reactions of α,β-unsaturated ketones. For while the N-phenyl and N-benzyl ethers of diphenyl acetaldoxime no longer combine either with Grignard reagents or with alcoholates, these purple nitrones, although equally highly substituted, still combine readily with both. The methyl alcohol addition product—obtained by adding sodium methylate and acidifying—closely resembles the Grignard product in color and instability. Like the Grignard product also, it readily forms a very stable methyl ether. There seems to be no doubt, therefore, that the addition product and its ether are constituted like the corresponding Grignard products.



XV



XVI

Addition of Sodium Methylate to the Nitrone.—Six grams of the purple nitrone was dissolved in a warm solution of 1 g. of sodium in 130 cc. of dry methyl alcohol. Through the brilliant scarlet solution a current of sulfur dioxide was passed until the color changed to pale yellow. The excess of sulfur dioxide was swept out with a current of air and the slight remaining acidity neutralized with methyl alcoholic ammonia. The solution was then concentrated and finally allowed to crystallize by slow evaporation. It deposited 6 g. of a fine yellow powder. This powder was recrystallized from acetone, from which it separated in large greenish octahedra resembling the Grignard product.

Anal. Calcd. for $C_{23}H_{19}O_3N$: C, 77.3; H, 5.3; OCH_3, 8.7; mol. wt., 357. Found: C, 77.6; H, 5.6; OCH_3, 8.7; mol. wt., 360.

1-Hydroxy-2-methoxy-2,4,5-triphenyl Pyrrolidone-3 (XV).—The methyl alcohol addition product is soluble in all common solvents except petroleum ether. It melts with decomposition at 163–165°. Like the Grignard product it is sufficiently acidic to dissolve in aqueous ammonia and aqueous alkalies. The solutions have the same scarlet color as those obtained by dissolving the nitrone in methyl alcoholic sodium methylate.

The Methyl Ether, XVI.—A solution of 10 g. of the methyl alcohol addition product in 100 cc. of 10% potassium hydroxide to which had been added 200 cc. of methyl alcohol was cleared by filtration, then treated with 10 g. of methyl iodide and set aside until the scarlet color had disappeared. The pale yellow solution thus formed was extracted with ether, the ethereal solution dried over sodium sulfate and allowed to evaporate. It deposited a mixture of yellow needles and a pale yellow high-melting powder.

The yellow needles were extracted with cold acetone and ultimately purified by recrystallization from ether. Like the methyl ether of the Grignard product, this methyl ether of the methyl alcohol addition product loses formaldehyde at the melting point, 175-180°.

Anal. Calcd. for $C_{24}H_{21}O_3N$: C, 77.6; H, 5.7; OCH_3, 16.7. Found: C, 77.3; H, 5.8; OCH_3, 14.5.

Summary

1. The preparation of three purple anhydrides from the corresponding oximes is described.
2. These remarkably colored substances are shown to be highly phenylated pyrrolenine oxides—capable of addition to the $\rangle C{=}\underset{|}{N}O$ system.
3. The mode of addition with Grignard reagents to these compounds is studied and an analogous addition reaction with sodium methylate is reported.
4. The evidence in favor of a "nitrone" formulation as against the carbazoxy ring structure is summarized, support for the former proceeding from this study of the purple anhydrides.
5. The use of the term "nitrone" and the method of representing the unsaturated system in nitrones are discussed, preference being given to $\rangle C{=}\underset{|}{N}O$.

CAMBRIDGE, MASSACHUSETTS

[CONTRIBUTION FROM THE DEPARTMENTS OF CHEMISTRY AND CHEMICAL ENGINEERING OF IOWA STATE COLLEGE]

A DELICATE COLOR TEST FOR MICHLER'S KETONE AND A LESS SENSITIVE TEST FOR PHOSGENE AND DIALKYLANILINES

BY HENRY GILMAN, O. R. SWEENEY AND L. L. HECK

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Introduction

The delicate color test of Gilman, Schulze and Heck[1] for reactive organometallic compounds, involving as it does the use of Michler's ketone, suggested its application as a test for Michler's ketone, and for phosgene, which is used in the preparation of the ketone. The test, which has found its widest application with organomagnesium compounds, is readily carried out by adding a very small quantity of the reactive organometallic com-

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[1] (a) Gilman and Schulze, THIS JOURNAL, **47**, 2002 (1925); *Bull. soc. chim.*, [4] **41**, 1479 (1927); (b) Gilman and Heck, *Rec. trav. chim.*, **48**, 193 (1929); (c) Gilman and Heck, *Ber.*, **62**, 1379 (1929).