[Contribution from the Chemical Laboratory of Harvard University]

PSEUDO BASES AND THEIR SALTS IN THE ISOXAZOLE SERIES

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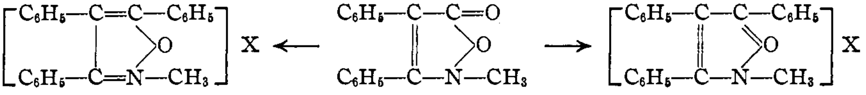
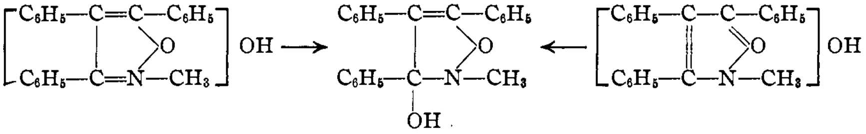
In a preceding paper[1] it was shown that when diphenyl isoxazolone is methylated by any method that is applicable it always yields an N-methyl derivative. Since this methyl isoxazolone does not have the hydrogen necessary for enolization, it would be expected to react with organic magnesium compounds to form salts of the corresponding hydroxy isoxazoline. These should be interesting because hydroxy isoxazolines are so constituted as to be capable of forming isomeric ammonium and oxonium salts.



II I III

Opinions might differ with regard to the possibility of this kind of isomerism, but all would agree, doubtless, that in the absence of color it would be difficult to identify isomers that bear this relation to each other, and also that the corresponding ammonium and oxonium hydroxides would readily undergo rearrangement to the same pseudo base.



IV

We have studied these relations with the salts of methyl triphenyl hydroxy isoxazoline (IV). Since these salts can be obtained by the action of methylating agents on triphenyl isoxazole as well as by the reaction between phenyl magnesium bromide and N-methyl diphenyl isoxazolone, there is no question about the position of the methyl and phenyl groups. Of the various salts of the isoxazoline, the sparingly soluble ferric chloride "double salt" proved to be the most satisfactory for the purpose of isolation. This salt was obtained in almost the calculated quantity by treating triphenyl isoxazole with dimethyl sulfate, hydrolyzing the resulting methyl sulfate with strong hydrochloric acid and adding ferric chloride to the solution. It was also obtained by digesting N-methyl diphenyl isoxazolone with phenyl magnesium bromide, acidifying the product with hydrochloric acid and adding ferric chloride to the aqueous layer.

From the ferric chloride double compound other salts can be made at will by liberating the corresponding base and treating it with acids. The

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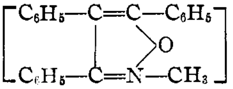
[1] Kohler and Blatt, This Journal, 50, 504 (1928).

most interesting of these salts is the bromide. This separates in a crystalline form when the Grignard product is acidified with hydrobromic acid and, when it is obtained in this manner, is lemon yellow in color. It retains this color when recrystallized from acetone and ether or from methyl alcohol and ether, and when the base formed by treating it with sodium hydroxide is dissolved in hydrobromic acid, the product again is yellow.

A colorless bromide can be made by an indirect method. Like many other bromides of pseudo bases, the yellow salt readily combines with bromine to form an orange-colored perbromide which is sparingly soluble and easily purified. This perbromide is capable of brominating acetone and its solution in acetone on addition of anhydrous ether deposits a colorless bromide which can be recrystallized without acquiring color.

Unfortunately both the yellow and the white bromides are difficult to handle, and neither could be obtained in a form in which it gave consistent analytical results; mean values for bromine agreed closely with the calculated, but individual values obtained with different preparations ranged nearly 2%. These bromides constitute the only indication that isomerism of the type represented by formulas II and III is possible and here the evidence is manifestly quite inadequate. A somewhat similar observation was made by Mumm and Münchmeyer[2] while studying the methylation product of phenyl isoxazole, but in that case also the evidence is inadequate.

When the isomeric bromides are treated with concentrated hydrochloric acid and ferric chloride, they give the same double chloride, and both lose methyl bromide readily when heated; the melting points obtained, therefore, by heating the individual bromides, mixtures of the two and mixtures with triphenyl isoxazole are the same as those obtained for the pure isoxazole. In the absence of any conclusive evidence as to their structure, we shall, for the present, represent all of the salts as cyclic ammonium compounds



$\cdot FeCl_4$, Br, Br_3, $OC_6H_2(NO_2)_3$

V VI VII VIII

These salts when treated with alkali yield an exceedingly unstable, colorless oil. Inasmuch as this oil is insoluble in water and readily soluble in ether, it cannot be the true base, and since it regenerates the salts when it is dissolved in acids it must be the pseudo base corresponding to these salts. Moreover, when the salts are treated with alkali in the presence of methyl alcohol, the product is a stable solid methyl ether which, like ethers of other pseudo bases, likewise regenerates the salts when

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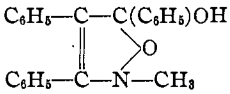
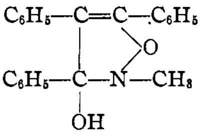
[2] Mumm and Münchmeyer, *Ber.*, **43**, 3340 (1910).

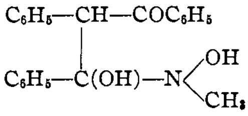
treated with acids. For the pseudo base three formulas are, *a priori*, equally probable:



IX

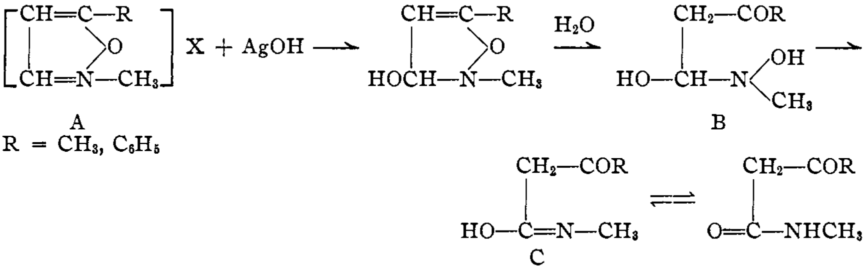


IV



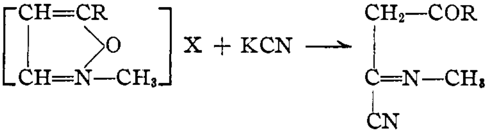
IVa

Formula IX represents the type of pseudo base that most frequently occurs in condensed ring systems[3] but which is found also in some mononuclear compounds, particularly in the bases formed from the simpler oxonium salts of dimethyl pyrone.[4] While the properties of our base could be reconciled with it, this formula is inconsistent with the behavior of the salts of less highly substituted isoxazolines. Thus, Claisen[5] found that silver hydroxide converts the methyl iodide addition product of 5-methyl isoxazole into aceto-acet methylamide, and Mumm and Münchmeyer[6] obtained the corresponding benzoyl-acet methylamide by the action of sodium hydroxide on the methyl sulfate addition product of 5-phenyl isoxazole. These results can be accounted for only if the intermediate pseudo base has an hydroxyl group in the 3-position, in which case the mechanism of these transformations is the following.



R = CH_3, C_6H_5

In accordance with this mechanism Mumm and Bergell[7] found that potassium cyanide converts these same salts into the nitriles corresponding to the enolic modification of the acid amide.



When this mechanism, which accounts for the observed behavior of all known isoxazoles and alkali, is applied to our substances it becomes

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[3] Decker, *J. prakt. Chem.*, [2] **45**, 195 (1892).

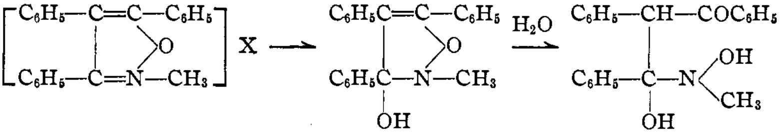
[4] Baeyer and Piccard, *Ann.*, **384**, 208 (1911); **407**, 332 (1915).

[5] Claisen, *Ber.*, **42**, 67 (1909).

[6] Ref. 2, p. 3344.

[7] Mumm and Bergell, *Ber.*, **45**, 3049 (1912).

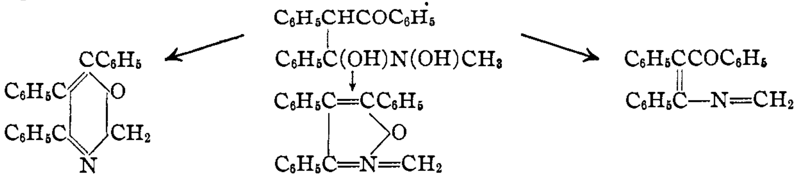
evident why here, for the first time in the isoxazole series, it has been possible to obtain a pseudo base and its ethers. For, in our substances, the presence of a phenyl group instead of a hydrogen atom in the 3-position makes impossible the loss of water corresponding to the passage of the open chained hydroxylamine derivative B into the enolic form of the acid amide C.



IV IVa

Whether our liquid pseudo base corresponds to IV or to the open-chain hydrolysis product IVa could not be established but since the composition of our ethers corresponds to derivatives of the cyclic form IV this doubtless represents a step in the process.

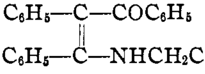
The presence of the phenyl group in position 3 in our pseudo base prevents the loss of water in the fashion observed in the unsubstituted isoxazolines, so with this pseudo base water is lost in a different manner and an entirely different set of consequences ensues. Thus, ethereal solutions of the pseudo base gradually deposit a colorless solid of which the composition and molecular weight correspond to those of a substance formed from IVa by the loss of two molecules of water. This anhydro compound combines with picric acid and with methyl alcohol to form substances which are isomeric with the picrate and methyl ether of the pseudo base. The process by which the anhydro compound is formed is not reversible, and neither the anhydro compound itself nor any of its derivatives can be transformed into salts of the pseudo base. Instead, the anhydro compound and all of its derivatives when treated with acids lose their nitrogen and yield phenyl dibenzoyl methane. These substances, therefore, belong to an entirely different class of compounds. Since a part of the hydrogen lost as water is necessarily contributed by the methyl group the number of possible formulas is limited.



X XI XII

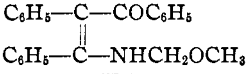
Few metoxazines (X) have been made and little is known about them except that they are easily hydrolyzed to open chained compounds. By assuming that the ring is opened in the proper manner by alcohol, alcoholates, halogen acids, picric acid and organic magnesium compounds, it would be possible to interpret most of the reactions of the anhydro compound with formula X. This formula, however, does not account for the most characteristic property of the substance—its autoxidation in moist air with liberation of formaldehyde.

Formulas XI and XII represent new types of compounds. All the facts at present available can be explained equally well with either of these formulas. Thus, ozonization results in equivalent quantities of benzil and benzoic acid; hydrolysis gives phenyl dibenzoyl methane; and phenyl magnesium bromide leads to an addition product which gives benzil when ozonized and phenyl dibenzoyl methane and benzyl amine when hydrolyzed. It is evident from these results that in order to distinguish between formulas XI and XII it will be necessary to prepare an anhydro compound in which the hydrocarbon residue in the 3-position is not a phenyl group. For the present we shall tentatively adopt formula XII and therefore represent the addition products as follows.



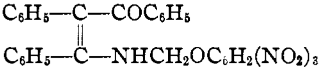
$$\begin{array}{l} C_6H_5\text{—}C\text{—}COC_6H_5 \\ \qquad\ \ \| \\ C_6H_5\text{—}C\text{—}NHCH_2C_6H_5 \end{array}$$

XIII



$$\begin{array}{l} C_6H_5\text{—}C\text{—}COC_6H_5 \\ \qquad\ \ \| \\ C_6H_5\text{—}C\text{—}NHCH_2OCH_3 \end{array}$$

XIV



$$\begin{array}{l} C_6H_5\text{—}C\text{—}COC_6H_5 \\ \qquad\ \ \| \\ C_6H_5\text{—}C\text{—}NHCH_2OC_6H_2(NO_2)_3 \end{array}$$

XV

In solutions these addition products may be in equilibrium with the anhydro compound or with their tautomeric modifications, but owing to the mode of addition they cannot regenerate an hydroxylamine derivative and therefore cannot revert to the pseudo base and the salts.

The formation of the anhydro compound and of addition products isomeric with derivatives of the pseudo base is a novelty in the chemistry of ammonium and oxonium compounds. Other pseudo bases are unstable: some are so easily oxidized that only the corresponding ketones can be isolated;[8] others lose water and form ethylenic derivatives;[9] many pass into open chained compounds.[10] All known pseudo bases of the isoxazole series are unstable; they combine with water to form open chained disubstituted hydroxylamines, and when these are so constituted that they cannot lose water in any other way they pass into a highly unsaturated, completely conjugated anhydro compound.

Experimental Part

I. Salts

The ferric chloride double salt is most conveniently obtained from the addition of triphenyl isoxazole and dimethyl sulfate, the yellow bromide from the reaction between methyl-diphenyl isoxazolone and phenyl magnesium bromide, and the picrate from the methyl ether of the pseudo base. Methylation of the isoxazole presents no complications, but the Grignard reaction yields two products, of which one remains in the

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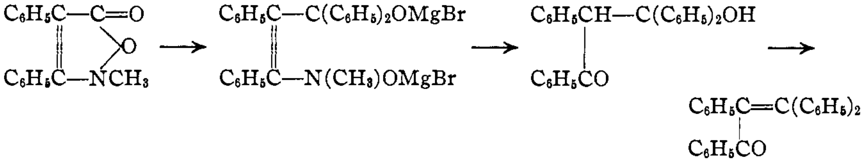
[8] Ref. 3, p. 161.

[9] Decker and Hock, *Ber.*, **37**, 1564 (1904); Decker and Pschorr, *ibid.*, p. 3396.

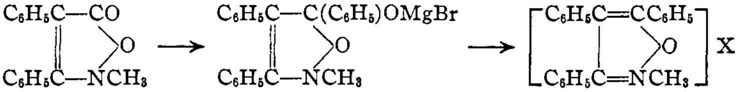
[10] Zincke, *Ann.*, **330**, 361 (1903); **333**, 296 (1904).

ethereal layer after the magnesium derivatives have been decomposed with acids while the other enters the aqueous solution as a salt.

Two products are formed in this case because the Grignard reaction may start either by opening the ring or by adding to the carbonyl group. When it starts by opening the ring the primary product is a ketone which immediately combines with a second molecule of the reagent, and when the resulting magnesium derivative is acidified it yields diphenyl benzalacetophenone.



When the Grignard reagent combines with the carbonyl group of the isoxazolone it forms a magnesium derivative that yields a salt when acidified.



In accordance with this interpretation we found that the yield of diphenyl benzalacetophenone (10–15%) is not increased either by the use of a large excess of reagent or prolonged heating.

The Ferric Chloride Double Salt, V.—Ten g. of pure triphenyl isoxazole was added, in portions, to 30 g. of pure dimethyl sulfate. The mixture was heated on a steam-bath until the isoxazole had dissolved completely and did not reprecipitate on cooling, then cooled and treated with half-concentrated hydrochloric acid in order to decompose the excess of reagent and convert the addition product into a water-soluble salt. Next ferric chloride solution (two parts of chloride to one of water) was added until the double salt was precipitated. The crude product was washed with a little water and then recrystallized from glacial acetic acid.

Anal. Calcd. for $C_{22}H_{18}ONFeCl_4$: C, 51.8; H, 3.6; Cl, 27.8. Found: C, 51.4; H, 3.6; Cl, 27.8.

The salt crystallizes well from all common solvents except ether and petroleum ether in which it is very sparingly soluble. In glacial acetic acid it is very soluble at the boiling point and very slightly soluble at the ordinary temperature. It separates in sulfur-yellow needles and melts at 162°.

The Grignard Reaction.—When an ethereal solution of 2-methyl-3,4-diphenyl isoxazolone is added to phenyl magnesium bromide it forms a white, curdy precipitate which on stirring turns into a heavy, dark green oil. If the mixture is decomposed at this point it regenerates the methyl isoxazolone, and if it is heated immediately the yield of Grignard products is poor. Our procedure, therefore, was as follows. A solution of 5 g. of the isoxazolone in 100 cc. of ether was added in the course of several minutes, at room temperature and with stirring, to a solution of phenyl magnesium bromide containing 2.4 g. of magnesium. The mixture was stirred for an hour at the ordinary temperature, then boiled until the dark green oil had changed into a yellow powder. Solution and powder were then poured into a mixture of 50 cc. of hydrobromic acid (40%) and 100 g. of ice and the ether and water layers separated.

The ether layer was distilled with steam to remove ether, bromobenzene and diphenyl. The residue was an oil, and a dried ethereal solution on evaporation also left an oil, but when this was dissolved in methyl alcohol, the solution gradually deposited a solid. This was recrystallized from methyl alcohol, from which it separated in small, colorless prisms melting at 149–150°. An analysis led to the formula $C_{27}H_{20}O$ and the substance was identified as α,β-diphenyl benzalacetophenone by comparison with a specimen on hand;[11] yield, 0.7–1 g.

The Yellow Bromide, VI.—The water layer from the Grignard reaction gradually deposited a yellow salt which was collected and air dried. The substance changed in color when exposed to light and air, and it decomposed on drying under reduced pressure. Purification was attempted by solution in warm acetone and reprecipitation with ether, and also by solution in methyl alcohol and precipitation with ether, but it was not possible to get consistent analytical results.

Anal. Calcd. for $C_{22}H_{18}ONBr$: Br, 20.4. Found: Br, 20.7, 19.1.

When heated the substance loses methyl bromide at comparatively low temperatures, then melts at 209–210°—the melting point of triphenyl isoxazole. A specimen heated to constant weight at 135° until it was colorless and free from bromine lost 27.5% instead of 24.2% calculated.

The Perbromide, VII.—When the aqueous layer obtained by decomposing the Grignard product with ice and hydrobromic acid was treated with excess of bromine it deposited the perbromide in minute, orange-colored crystals. The salt was readily recrystallized from hot methyl alcohol; m. p. 152°; yield from 5 g. of the isoxazolone, 8–9 g.

Anal. Calcd. for $C_{22}H_{18}ONBr_3$: C, 47.8; H, 3.3; Br, 43.5. Found: C, 47.2; H, 3.3; Br, 43.5.

The Colorless Bromide, VI.—When the methyl alcoholic filtrates from the perbromide are diluted with ether they deposit a colorless salt. This is more conveniently obtained by dissolving the perbromide in acetone and gradually diluting the solution with ether. The acetone solution is yellow and has the odor of bromo acetone; on standing and on continuous dilution with ether its color fades and it precipitates a colorless salt. The colorless bromide decomposes at comparatively low temperatures and turns yellow on exposure to light. Attempts to purify it were no more successful than with the yellow bromide.

Anal. Calcd. for $C_{22}H_{18}ONBr$: Br, 20.4. Found: Br, 20.4, 21.2, 19.2. Loss in weight at 135°: 25.2 instead of 24.2 calcd. for CH_3Br.

The solubilities of the yellow and white bromides appear to be the same and both form the same ferric chloride double salt and the same perbromide.

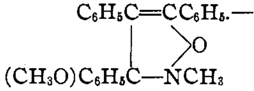
The Picrate, VIII.—The picrate is deposited as a yellow powder when an ethereal solution of picric acid is added to a solution of the methyl ether of the pseudo base in the same solvent. By recrystallization from methyl alcohol or ethyl acetate containing picric acid, it is obtained in yellow needles melting at 174°.

Anal. Calcd. for $C_{28}H_{20}O_8N_4$: C, 62.2; H, 3.7. Found: C, 62.3; H, 3.8.

II. The Pseudo Base and its Ethers

The pseudo base was obtained only as an oil that rapidly changed to other substances. Its composition and character are inferred from those of its ethers, which may be obtained either by dissolving the oil in alcohols or, better, by treating the salts with alcoholates or alcoholic solutions of sodium hydroxide.

The Methyl Ether,



.—When a 5% solution of sodium in methyl alcohol was added to the yellow bromide considerable heat was evolved and the

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[11] Kohler, *Am. Chem. J.*, **38**, 559 (1907).

mixture soon became a stiff paste. This was diluted with water and then extracted with ether. The ethereal solution was freed from methyl alcohol with a saturated solution of calcium chloride, then dried and concentrated. It deposited a solid in stout prisms. After recrystallization from methyl alcohol the solid melted, with decomposition, at 135°.

Anal. Calcd. for $C_{23}H_{21}O_2N$: C, 80.4; H, 6.2; OCH_3, 9.0. Found: C, 80.1; H, 6.4; OCH_3, 9.3.

The methyl ether dissolves in strong hydrochloric acid and gives a clear solution which on addition of ferric chloride precipitates the double chloride melting at 162°. It dissolves also in 15% hydrobromic acid and this solution deposits the yellow bromide.

The ethyl ether was obtained as a micro-crystalline powder melting at 118°.

Anal. Calcd. for $C_{24}H_{23}O_2N$: C, 80.7; H, 6.4. Found: C, 80.4; H, 6.6.

The ethyl ether reacts with acids like the methyl ether and forms the same salts. When its solution in boiling methyl alcohol is cooled it deposits the methyl in place of the ethyl ether.

The Pseudo Base, IV or IVa.—The reaction between the salts and aqueous alkali is illustrated by the following experiment. Four g. of the yellow bromide was shaken in a separatory funnel with an excess of 5% sodium hydroxide in the presence of 75 cc. of alcohol-free ether. A part of the ether was removed after shaking for only a few minutes and while most of the salt still remained unattacked. This ethereal solution was washed with water, rapidly dried with sodium sulfate and concentrated in a current of air. The concentrated solution gave the methyl ether of the pseudo base when mixed with methyl alcohol, the picrate melting at 174°, and on complete evaporation left an oil which likewise gave the methyl ether melting at 135°.

The rest of the material in the separatory funnel was shaken until all of the salt had disappeared. The ethereal layer was washed with water, thoroughly dried with sodium sulfate, then concentrated in a current of air. A sample removed at this stage still gave the picrate melting at 174°, but when another sample was mixed with methyl alcohol and boiled until the ether had been expelled, it gave in place of the methyl ether melting at 135° an isomeric methoxyl compound melting at 104–105°. On further evaporation the ethereal solution deposited colorless needles of the anhydro compound.

The Anhydro Compound, XII.—The anhydro compound is formed whenever ethereal solutions of the pseudo base are prepared essentially as described in the preceding experiment. The yield appears to be independent of the concentration of the alkali and the time during which it is allowed to act. Thus the concentration of the base was varied between 5 and 40%, and the time between thirty minutes and twelve hours without appreciably affecting the yield, which in all cases was about 50%. The substance separates in colorless needles which rapidly turn yellow, superficially, when exposed to the air. It was purified by recrystallization from absolute ether and from acetone that had been distilled from permanganate. It then melted at 140–141°. A qualitative test proved the presence of nitrogen and a negative Zeisel determination showed the absence of alkoxyl groups.

Anal. Calcd. for $C_{22}H_{17}ON$: C, 84.9; H, 5.5. Found: C, 84.7; H, 5.8.

In freezing benzene the molecular weight was found to be 306 instead of the calcd. 311.

The anhydro compound is colorless but even the purest samples turn yellow in the air. The nature of the change has not been established; it is accompanied by the liberation of formaldehyde, the odor of which is always perceptible in the containers in which the substance is kept.

Hydrolysis by Acids.—Acids are incapable of regenerating the salts from the anhydro compound. Thus 15% hydrobromic acid turned the substance into a yellow oil which gradually solidified and finally when heated with the acid gave phenyl dibenzoyl methane melting at 146–147°. Similarly, when aqueous hydrochloric acid was added to a solution of 0.7 g. of the anhydro compound in methyl alcohol, the solution turned yellow, but the color faded on heating and the colorless solution, when cooled, deposited the calculated amount of phenyl dibenzoyl methane. This was identified by comparison with an authentic sample.

Reaction with Phenyl Magnesium Bromide, XIII.—A solution of 2 g. of the anhydro compound in anhydrous ether was added to phenyl magnesium bromide made from 1 g. of magnesium. The resulting clear green solution was boiled for half an hour, then cooled and poured into ice and ammonium chloride. The ethereal layer when dried and evaporated left a colorless solid which after recrystallization from methyl alcohol melted at 134°. The yield was quantitative.

Anal. Calcd. for $C_{28}H_{23}ON$: C, 86.4; H, 5.9. Found: C, 86.0; H, 6.1.

Hydrolysis of the Addition Product.—Ten cc. of pure, concentrated hydrochloric acid was added to a solution of 3.9 g. of the addition product in 30 cc. of methyl alcohol. The intensely yellow solution was heated on a steam-bath for five minutes during which it became colorless and deposited a heavy precipitate of phenyl dibenzoyl methane. After an hour's heating the mixture was cooled and filtered and the solid washed with methyl alcoholic hydrochloric acid. The filtrate was extracted with ether. The ethereal layer on evaporation gave a second crop of the diketone, making the total yield 2.85 g., equal to 95%.

The aqueous layer was evaporated to dryness; it left a discolored hydrochloride (1.49 g. instead of 1.43 g. calcd.). A solution of 1.6 g. of sodium hydroxide in 15 cc. of water was added to the dry hydrochloride; it liberated an oil which had the odor of benzyl amine and which rapidly changed to a granular solid when 2.1 g. of benzoyl chloride was added to the alkaline suspension. After washing and drying, the crude solid melted at 104–105°, and it caused no depression of the melting point of an authentic sample of benzoyl benzylamine. The yield was 2.05 g., equal to 97%.

Action of Ozone.—Ozonized oxygen containing approximately 6% of ozone was passed for two hours through a solution of 2 g. of the Grignard product in carbon tetrachloride. Both the solid ozonide that separated and the oil left after the removal of the solvent were decomposed with water in the usual manner. The ethereal solution of the product deposited a solid which after recrystallization from methyl alcohol, melted at 92–94° and caused no depression in the melting point of pure benzil.

The Methyl Alcohol Addition Product, XIV.—A solution of 1 g. of the anhydro compound in 30 cc. of methyl alcohol was boiled for an hour, then concentrated and cooled. It deposited 0.85 g. of a compound melting at 104°. The same substance was obtained as one of the products formed by the prolonged action of sodium methylate on its isomer, the methyl ether of the pseudo base. In this case 2.9 g. of the methyl ether, when boiled for five hours with 10 cc. of a 4% solution of sodium methylate, gave 1.1 g. of the new methoxyl compound.

Anal. Calcd. for $C_{23}H_{21}O_2N$: C, 80.4; H, 6.2; OCH_3, 9.0. Found: C, 80.2; H, 6.1; OCH_3, 9.2.

The Picric Acid Addition Product, XV.—Toward mineral acids the methyl alcohol addition product behaves precisely like the Grignard product, forming a yellow solution which fades on warming and ultimately yields phenyl dibenzoyl methane. Toward picric acid, on the other hand, the addition product behaves like the anhydro compound itself. Thus when an ethereal solution of picric acid is added to a solution of the addition product in the same solvent a yellow solid separates, which contains no methoxyl, is identical with the product obtained from the anhydro compound, and is isomeric with the picrate of the pseudo base. After recrystallization from glacial acetic acid this yellow product melts at 184°. Like all the other addition products of the anhydro compound it is readily hydrolyzed to phenyl dibenzoyl methane.

Anal. Calcd. for $C_{28}H_{20}O_8N_4$: C, 62.2; H, 3.7. Found: C, 61.9; H, 3.8.

Summary

This paper contains the results of the study of the pseudo base 2-methyl-3,4,5-triphenyl-3-hydroxy isoxazoline and its salts. It is shown that this substance, in addition to the usual reactions of pseudo bases, undergoes a novel irreversible transformation into an open chained anhydro compound, the behavior of which has been explored. The results obtained in this work provide a basis for the formulation of a mechanism which correlates the behavior of all pseudo bases of the isoxazole series.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, MISSISSIPPI COLLEGE]

PREPARATION OF ALIPHATIC AND AROMATIC SULFONES WITH SODIUM HYPOCHLORITE[1]

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This paper represents a study of the conditions best suited for the oxidation of pure alkyl and aromatic sulfides. Birch and Norris[2] have made some observations relevant to the oxidation of organic sulfides previously dissolved in a light petroleum distillate. Birch and Norris reported the complete oxidation of ethyl, *n*-propyl, *iso*butyl and *iso*-amyl sulfides to the corresponding sulfones. Under similar conditions, Wood, Greene and Provine[3] reported the oxidation of ethyl, *n*-propyl and phenyl sulfides to the corresponding sulfones.

Experimental

Eastman's ethyl, *n*-propyl, *n*-butyl, *n*-heptyl, phenyl and benzyl sulfides were used without further purification.

Hypochlorite solutions 1, 2 and 3 were prepared by passing chlorine into solutions of pure sodium hydroxide. Hypochlorite solutions 4, 5 and 6 were prepared by passing chlorine into solutions containing both pure sodium hydroxide and pure sodium carbonate. The chlorinating solutions were kept below 27°. The alkalinity was determined by decomposing the sodium hypochlorite with hydrogen peroxide and titrating against standard hydrochloric acid with phenolphthalein and methyl orange as indicators. The available chlorine was determined by titrating the iodine liberated from potassium iodide against 0.1 *N* sodium thio-

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[1] A preliminary version of this paper was received on May 3, 1927.

[2] Birch and Norris, *J. Chem. Soc.*, **127**, 1934 (1925).

[3] Wood, Greene and Provine, *Ind. Eng. Chem.*, **18**, 823 (1926).