the refrigerator, when 1.8 g. of solid separated. This was dissolved in 8 cc. of warm 85% alcohol, and on cooling a white solid was deposited which weighed 1.1 g. and melted sharply at 113–114°.

Anal. Calcd. for $C_6Cl_6F_4$: F, 21.1; Cl, 59.0; mol. wt., 361. Found: F, 20.9, 21.0; Cl, 59.0, 59.1; mol. wt. in benzene, 378, 381.

Hexafluorohexachlorocyclohexane.—The portion boiling at 100–115° at 7 mm. (see above) weighed 30 g. When a 5-g. sample of this oil was emulsified vigorously with 1 cc. of water and the mixture allowed to stand in the cold, a small amount of solid separated. A solution of this in warm 85% alcohol deposited a white solid melting at 94–96°.

Anal. Calcd. for $C_6Cl_6F_6$: F, 28.6; Cl, 53.4; mol. wt., 399. Found: F, 28.7, 28.8; Cl, 53.3, 53.6; mol. wt. in benzene, 387, 353.

The analytical method used has been referred to previously[1] but it has been improved somewhat by means of slight modifications. As a further check the fluorine content of pure *p*-fluorobenzoic acid, m. p. 181–182°, has been determined with the following results.

Anal. Calcd. for $C_7H_5O_2F$: F, 13.6. Found: F, 13.8, 13.7, 13.5.

Summary

Hexachlorobenzene has been fluorinated in carbon tetrachloride solution at 0°. Small quantities of tetrafluorohexachlorocyclohexene, $C_6Cl_6F_4$ (m. p. 113–114°), and hexafluorohexachlorocyclohexane, $C_6Cl_6F_6$ (m. p. 94–96°), have been isolated.

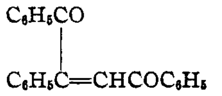
DURHAM, N. C. RECEIVED OCTOBER 20, 1934

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF HOWARD UNIVERSITY]

The Reaction between Phenyldibenzoylethylene and Hydroxylamine Hydrochloride—A Cyclic Hydroxy Nitrone

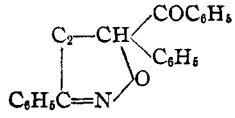
BY A. H. BLATT

In 1914 Oliveri-Mandalà and Calderaro[1] reported the results of a study of the reaction between *cis*-phenyldibenzoylethylene (I) and hydroxylamine hydrochloride. They obtained from this reaction a yellow crystalline product which had the composition of a monoxime of the diketone and which they considered, because of its almost complete lack of reactivity, to be an isoxazoline—either II or III. Quite incidentally we came across this same yellow product and made some preliminary experiments with it before we were aware of Oliveri-Mandalà and Calderaro's conclusions. Our experiments indicated that the material was unusually reactive. This marked reactivity of the yellow product, its intense color and the fact that it is formed in an acid solution are all difficult to reconcile with its formulation as an isoxazoline. These inconsistencies, coupled with the fact that no information could be found on the behavior of unsaturated 1,4-diketones toward hydroxylamine hydrochloride, have led us to a further study of the reaction between phenyldibenzoylethylene (I) and this typical ketone reagent. Certain of the results of that study are reported in the following paragraphs.

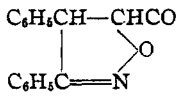


$C_6H_5CO-C(C_6H_5)=CHCOC_6H_5$

I



II



III

It should be stated at the outset that the chemical behavior of the yellow product formed from phenyldibenzoylethylene and hydroxylamine hydrochloride is far more complex than was indicated by the earlier work done with it. This product exists in two isomeric forms: one modification, that described by Oliveri-Mandalà and Calderaro, is bright yellow in color, is stable in neutral and acid solution and is easily obtained in a pure condition; the other modification, a very pale yellow solid, is stable only in alkaline or pyridine solution, but it can be obtained in an impure state by careful acidification of its alkaline solutions. We shall consider the alkali stable modification first. This substance is the monoxime of phenyldibenzoylethylene (IV). On this point the evidence is quite explicit. Sodium hydroxide or pyridine solutions of the oxime (IV) on treatment with benzoyl chloride furnish a benzoate (V, R = C_6H_5) which can be hydrolyzed to regenerate the oxime (IV). Pyridine solutions of the oxime furnish with acetyl chloride an acetate

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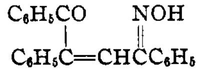
(1) Oliveri-Mandalà and Calderaro, *Gazz. chim. ital.*, **44**, [II] 85 (1914). The first study of this reaction was that of Japp and Klingemann, *J. Chem. Soc.*, **57**, 710 (1890), who employed quite drastic conditions and obtained what were evidently secondary products

(V, R = CH_3) which, like the benzoate, can be hydrolyzed to the oxime. The same acetate (V) is also formed by treatment with acetic anhydride of the unstable oxime (IV) obtained by careful acidification of its alkaline solutions. This conversion serves to link together the alkali stable oxime (IV) with its alkaline solutions. And, finally, both the pyridine and the alkaline solutions of the oxime on treatment with benzene sulfonyl chloride undergo a Beckmann rearrangement to furnish the anilide (VI), whose structure is established by its alkaline hydrolysis to desoxybenzoin, formic acid, ammonia and benzoic acid.

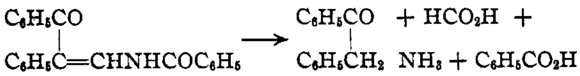


$$\overset{C_6H_5CO}{\overset{|}{C_6H_5C}}=CH\overset{NOH}{\overset{\|}{C}}C_6H_5$$

IV

$$\overset{C_6H_5CO}{\overset{|}{C_6H_5C}}=CH\overset{NOCOR}{\overset{\|}{C}}C_6H_5$$

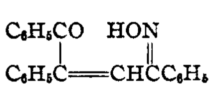
V



$$\overset{C_6H_5CO}{\overset{|}{C_6H_5C}}=CHNHCOC_6H_5 \longrightarrow \overset{C_6H_5CO}{\overset{|}{C_6H_5CH_2}} + HCO_2H + NH_3 + C_6H_5CO_2H$$

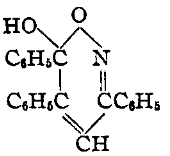
VI

The evidence for the structure of the acid stable isomer of the oxime (IV) is neither so direct nor so explicit as that for the oxime itself. However, the choice of probable formulas is relatively limited, for any formula to be satisfactory must take into account the ease of conversion of each isomer to the other. This single restriction limits the choice to either a stereoisomer (VII) of the oxime (IV) or to cyclic isomers of the oxime (IV). The stereoisomeric oxime (VII) is at once eliminated by the fact that a Beckmann rearrangement carried out in an acid medium furnishes the same anilide (VI) as does the alkaline rearrangement. We may, therefore, confine our attention to cyclic modifications of the oxime and of these only five need consideration: the isoxazoline (II),[2] the orthoxazines (VIII) and (IX), and the nitrones (X) and (XI).

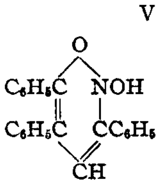


$$\overset{C_6H_5CO}{\overset{|}{C_6H_5C}}=CH\overset{HON}{\overset{\|}{C}}C_6H_5$$

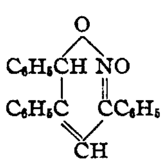
VII



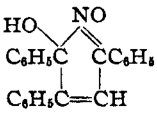
VIII



IX



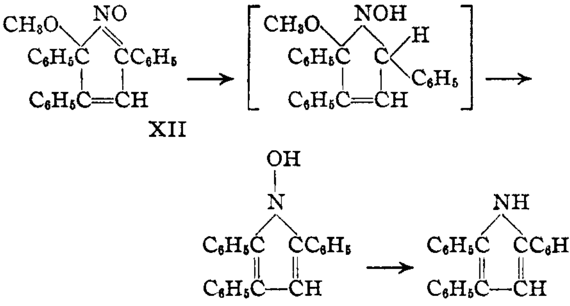
X



XI

A further restriction on the choice of a formula for the yellow, acid stable isomer is afforded by the fact that this isomer forms an O-methyl ether simply by boiling with methyl alcohol and hydrochloric acid. This behavior, characteristic of a tertiary carbinol, eliminates the isoxazoline (II) and the nitrone (X) and renders most unlikely the orthoxazine (IX). The decisive evidence for a final choice between the remaining structures is furnished by the reduction of the methyl ether with zinc and acetic acid to 2,3,5-triphenylpyrrole (XIII)—a transformation which fits only with the formulation of the acid stable isomer as the hydroxy nitrone (XI), and of its methyl ether as (XII).

The reduction of the methyl ether (XII) to the pyrrole (XIII) probably proceeds *via* 1,3 addition of hydrogen to the nitrone system, C═NO, followed by 1,4 elimination of methyl alcohol to form a 1-hydroxypyrrole (XIV) which is then further reduced, by the addition of hydrogen and the elimination of water, to the oxygen-free pyrrole (XIII). The process would be as follows



XII

XIV

XIII

Support for this interpretation, as well as for the original hydroxy nitrone structure, is afforded by the stepwise reduction of the methyl ether (XII). When this ether is treated with sodium–potassium alloy or with methylmagnesium iodide, ethylmagnesium bromide or phenylmagnesium bromide, the same product results. This product is formed from the ether by loss of a methoxyl group and addition of one hydrogen atom. It contains one active hydrogen atom, forms a monomethyl ether and a monoanisoate and is, therefore, to be formulated as the 1-hydroxypyrrole (XIV). On further reduction, this time with zinc and acetic acid, the hydroxypyrrole yields 2,3,5-triphenylpyrrole (XIII). This behavior is consistent with the few facts available concerning 1-hydroxypyrroles. Thus Blaise[3] found that 1-hydroxy-2,5-

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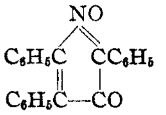
[2] The isomeric isoxazoline (III) is eliminated because of the different location of the nitrogen atom.

[3] E. E. Blaise, *Compt. rend.*, 158, 1686 (1914).

dimethylpyrrole is reduced by zinc and hydrochloric acid to 2,5-dimethylpyrroline. In this case the reduction proceeds past the pyrrole stage, for 2,5-dimethylpyrrole is likewise reduced by the same reagents to 2,5-dimethylpyrroline. In the present case, however, 2,3,5-triphenylpyrrole is not reduced by zinc and acetic acid and the reduction of the hydroxypyrrole, therefore, stops at the pyrrole stage.

The formulation of the yellow acid stable isomer of the oxime (IV) as the hydroxy nitrone (XI) is in agreement with the formation as well as the properties of the material. Thus, the configuration of the oxime (IV) is such that the hydroxyl group is spatially distant from the carbon atom involved in ring closure, so that for any ring system other than that present in the nitrone (XI) a *trans* ring closure must be assumed. This is not necessary with the nitrone (XI), however, for ring closure involves the nitrogen atom and a shift of the oximino hydrogen atom. The color, also, of the acid stable isomer, which is so intense as to be incompatible with an orthoxazine or an isoxazoline structure, fits admirably with the nitrone formula, for Kohler and Addinall[4] have shown that the nitrone (XV), which contains a carbonyl group in addition to the unsaturation present in the nitrone (XI), is very highly colored, while Pfeiffer's[5] isatogens are likewise highly colored.



XV

In the discussion of the structure of the nitrone (XI), only those reactions of the substance have been cited which are pertinent to the point at issue. The nitrone, however, is an exceedingly reactive compound and undergoes a number of other reactions, many of which result in the formation of nitrogen-free products. Because of their complexity these other reactions are being reserved for a separate presentation.

Two additional points only require consideration in this article. First, why does cyclic nitrone formation take place with the oxime of phenyldibenzoylethylene? The answer seems to be the *cis* configuration of the unsaturated diketone, for with this configuration the two benzoyl groups are spatially adjacent and ring formation is stereochemically possible. The stable phenyldiacylethylenes are in general *cis* isomers and all those which we have tried furnished, on treatment with hydroxylamine hydrochloride, products analogous to the hydroxy nitrone (XI). To check this further, the behavior of *trans*-dibenzoylethylene and of *cis*-dibenzoylstilbene toward hydroxylamine hydrochloride has been examined. Of these two substances, the latter gave only tars and, therefore, furnished no useful information; the former, however, gave not a cyclic nitrone but instead, a normal dioxime. The second point is the divergence between the experimental results reported in this paper and those reported by the earlier workers.[1] For this divergence we can offer no adequate explanation but only the suggestion that, since the hydroxy nitrone is so sparingly soluble, insolubility may have been mistaken for lack of reactivity.

Experimental

I. Dibenzoylethylene[6]

Reaction with Hydroxylamine Hydrochloride.—A solution of 7.0 g. of hydroxylamine hydrochloride in 25 cc. of hot water was added to 11.8 g. of dibenzoylethylene in 110 cc. of boiling alcohol and the reaction mixture was boiled for two hours, then left overnight. The first precipitate obtained weighed 5.9 g. and by concentrating the filtrate an additional 4.0 g. was secured; yield, 74%. The alcoholic filtrate had a decided odor of benzonitrile.

Anal. Calcd. for $C_{16}H_{14}O_2N_2$: C, 72.2; H, 5.3. Found: C, 72.3; H, 5.6.

The dioxime of dibenzoylethylene is only slightly soluble in the common solvents except glacial acetic acid and from this solvent it crystallizes well. The purified material melts at 210–211° with decomposition. On treatment with acetic anhydride the dioxime furnishes a diacetate. One gram of the dioxime was dissolved in 3 cc. of acetic anhydride and heated on a water-bath for a half hour. After cooling, the reaction mixture was poured into water and a quantitative yield of the crude diacetate was obtained. The product was crystallized from alcohol and melted, first to an opaque liquid at about 140°, then to a transparent liquid at 156°. On treatment with alcoholic alkali the diacetate is hydrolyzed to regenerate the dioxime.

Anal. Calcd. for $C_{20}H_{18}O_4N_2$: C, 68.6; H, 5.1. Found: C, 68.5; H, 5.2.

II. Phenyldibenzoylethylene

Reaction with Hydroxylamine Hydrochloride.—To a solution of 31.2 g. (0.1 mole) of phenyldibenzoylethylene in 325 cc. of boiling alcohol is added 14.0 g. (0.2 mole) of hydroxylamine hydrochloride dissolved in 75 cc. of hot water. The resulting almost colorless reaction mixture soon assumes an intense yellow color, and after ten to fifteen minutes of boiling a bright orange-yellow precipitate forms. Boiling is continued for an hour in all, then, after cooling,

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[4] Kohler and Addinall, THIS JOURNAL, **52**, 1590 (1930).

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

[6] We are indebted to Dr. R. E. Lutz for a supply of this material.

the precipitate is filtered and dried; weight 25.0 g. On standing overnight the filtrate furnishes an additional 1.0–1.5 g. of the same material, making a total yield of 26.0 g. or 80%. The filtrate invariably has a strong odor of benzonitrile and, by an appropriate ether extraction and washing, it is possible to secure a small amount of a neutral oil which furnishes ammonia and benzoic acid when it is boiled with alcoholic alkali. For analysis the yellow material is purified by solution in 5% sodium hydroxide, filtration to remove any alkali insoluble impurities, acidification and immediate crystallization of the precipitate from alcohol.

Anal. Calcd. for $C_{22}H_{17}O_2N$: C, 80.7; H, 5.2. Found: C, 80.7; H, 5.4.

2-Hydroxy-2,3,5-triphenylpyrrolenine oxide (XI)[7] melts at 179° and decomposes a few degrees above that temperature. It is only very slightly soluble in all the ordinary solvents with the exception of pyridine. It can be crystallized from pyridine by diluting its solutions in that solvent with acetone and water. When so crystallized, the material has the same composition as that crystallized from alcohol. (Calcd.: C, 80.7; H, 5.2. Found: C, 80.6; H, 5.3.) The crude nitrone invariably melts at a higher temperature than does the purified material. The crude nitrone melts and decomposes at the same temperature, while the purified material decomposes only after it has melted. Similarly, the crude nitrone is much more intensely colored than the purified material. This difference in color is apparently due to a difference in crystal size, for the crude product is obtained in large lozenge-shaped crystals while the purified material is obtained as very small crystals. When the crude nitrone is very finely powdered, the color difference between it and the purified nitrone disappears.

The hydroxy nitrone dissolves in cold concd. sulfuric acid to furnish a dark brown solution which gives an amorphous brown precipitate when it is poured onto ice. The brown precipitate decomposes on treatment with organic solvents and a strong odor of benzonitrile is noticeable. From the action of hot concd. nitric acid on the hydroxy nitrone no definite products could be isolated.

The hydroxy nitrone suspended in dry ether and treated with phosphorus pentachloride furnishes the same rearrangement product (VI) which is obtained by the action of benzene sulfonyl chloride on the sodium or pyridine derivative of the oxime (IV). This product is described in detail under the reactions of the open-chain isomer.

A. Reactions of the Hydroxy Nitrone (XI)

Preparation of the Methyl Ether (XII).—When 13.0 g. of the hydroxy nitrone was suspended in 145 cc. of methyl alcohol to which 5 cc. of concd. hydrochloric acid had been added, and the reaction mixture was boiled for three hours, all of the solid dissolved. The clear solution was made alkaline by the addition of 75 cc. of 5% sodium hydroxide and on cooling it deposited 11.0 g. of the methyl ether. Additional material could be obtained from the filtrate by suitable concentration and extraction, but this recovery was not a profitable operation. For analysis the ether was crystallized from ethyl alcohol and from chloroform and petroleum ether.

Anal. Calcd. for $C_{23}H_{19}O_2N$: C, 80.9; H, 5.6; OCH_3, 9.1. Found: C, 81.0; H, 5.6; OCH_3, 8.8.

2-Methoxy-2,3,5-triphenylpyrrolenine oxide (XII) occurs as small, bright yellow crystals which melt at 172°. It is readily soluble in acetone, benzene, chloroform, acetic acid and ethyl acetate, less soluble in methyl and ethyl alcohols and ether, and insoluble in petroleum ether. There are indications that this ether forms a methyl alcohol addition product for occasionally on crystallizing the material from methyl alcohol samples have been obtained which melted with effervescence at about 130°, resolidified and melted again at 172°. The volatilized material was shown to be methyl alcohol, but we have not been able to find the experimental conditions which will furnish this low melting ether regularly.

The formation of the methyl ether is reversible for when it is dissolved in methyl alcohol containing hydrochloric acid and water and boiled the hydroxy nitrone is regenerated.

Reduction of the Methyl Ether (XII) to 2,3,5-Triphenylpyrrole (XIII).—A solution of 6.5 g. of the methyl ether in 100 cc. of glacial acetic acid, containing a crystal of copper sulfate and a drop of concd. hydrochloric acid, was heated to 90° for five hours, during which time 10 g. of zinc dust was added in small portions. The hot, pale yellow solution was filtered into cold water and the resulting white precipitate was filtered and dried. It weighed 5.0 g. and, after crystallization from dilute acetic acid or alcohol and water, melted at 142°. It was identified as 2,3,5-triphenylpyrrole by means of a mixed melting point with a known sample of that material prepared according to the procedure of Japp and Tingle.[8]

Reduction of the Methyl Ether (XII) to 1-Hydroxy-2,3,5-triphenylpyrrole (XIV).—One gram of the methyl ether and 0.5 g. of liquid sodium–potassium alloy, suspended in 25 cc. of absolute ether in a flask in which the air had been displaced by nitrogen, were shaken for twenty-four hours. During this time the methyl ether dissolved and a precipitate of a pale yellow metallic derivative separated. The excess alloy was removed and the metallic derivative was decomposed by the successive addition of moist ether, alcohol and water. The ether layer when dried, concentrated and diluted with petroleum ether deposited a colorless solid which was purified by crystallization from benzene and from chloroform and petroleum ether.

Anal. Calcd. for $C_{22}H_{17}ON$: C, 84.9; H, 5.5; N, 4.5; mol. wt., 311. Found: C, 84.8; H, 5.9; N, 4.2; mol. wt. (camphor), 319.

1-Hydroxy-2,3,5-triphenylpyrrole (XIV) melts at 196°. It is moderately soluble in ether, methyl and ethyl alcohols and chloroform, sparingly soluble in benzene and petroleum ether. On exposure to light the material turns superficially yellow. It is insoluble in 5% aqueous sodium hydroxide but dissolves readily in sodium methylate and is not affected by boiling its solutions in that reagent. In the Grignard machine the pyrrole shows one active hydrogen atom. It is attacked by permanganate and by nitrous acid, but no definite products could be isolated.

The same hydroxypyrrole is also obtained by treating the methyl ether (XII) with methylmagnesium iodide,

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[7] The system used in naming these compounds is that employed by Kohler and Addinall, Ref. 4.

[8] Japp and Tingle, *J. Chem. Soc.*, **71**, 1146 (1897).

ethylmagnesium bromide or phenylmagnesium bromide. When the ether was treated with a solution of the last named reagent, large quantities of diphenyl were formed along with the pyrrole. An aliquot portion of the reagent decomposed before the addition of the ether gave only insignificant quantities of diphenyl. The hydroxypyrrole is most conveniently prepared by treatment of the methyl ether with methylmagnesium iodide.

The hydroxypyrrole forms a monoanisoate on treatment with anisoyl chloride in pyridine, and forms a monomethyl ether when alkylated with methyl iodide and sodium methylate. Thus, 0.8 g. of the hydroxypyrrole in 10 cc. of pyridine and 1.0 g. of anisoyl chloride[9] gave an anisoate which melted at 139–140° after crystallization from alcohol. (*Anal.* Calcd. for $C_{30}H_{23}O_3N$: C, 80.9; H, 5.2; OCH_3, 6.97. Found: C, 81.0; H, 5.6; OCH_3, 7.16.) This anisoate, which like the parent compound turns yellow on exposure to light, is hydrolyzed to anisic acid and the hydroxypyrrole by alcoholic alkali.

The methyl ether of the hydroxypyrrole was formed in a quantitative yield when 1.5 g. of the pyrrole in 25 cc. of methyl alcohol containing 0.25 g. of sodium and 5.0 g. of methyl iodide was warmed for two hours. The ether crystallized on cooling and was purified by crystallization from methyl alcohol, in which it is very sparingly soluble. (*Anal.* Calcd. for $C_{23}H_{19}ON$: C, 84.9; H, 5.84; OCH_3, 9.55. Found: C, 85.2; H, 6.1; OCH_3, 9.11.) The methyl ether, which melts at 122–123°, turns yellow on exposure to light. It is unaffected by alcoholic alkali or acid, or by treatment with phenylmagnesium bromide.

Reduction of the Hydroxypyrrole (XIV) to 2,3,5-Triphenylpyrrole (XIII).—One gram of the hydroxypyrrole in 40 cc. of hot glacial acetic acid containing a crystal of copper sulfate and a drop of hydrochloric acid, was heated for four hours with 2.0 g. of zinc dust. The hot solution filtered into cold water gave a quantitative yield of 2,3,5-triphenylpyrrole which was identified by a mixed melting point with an authentic specimen.

Treatment of the Hydroxy Nitrone (XI) with Alkali. Preparation of the Impure Oxime (IV).—The crude and the purified hydroxy nitrone, though insoluble in alkali carbonates, dissolve readily in 5% sodium hydroxide or in dilute sodium methylate solutions. The purified nitrone is occasionally erratic in its behavior toward sodium hydroxide for some samples seem not to be wetted by the alkaline solution and dissolve only slowly and incompletely. These samples which are reluctant to dissolve in aqueous sodium hydroxide do dissolve rapidly, however, in sodium methylate. By using fairly concentrated sodium methylate solution it is possible to obtain a solid sodium derivative. Thus, when 3.27 g. of the hydroxy nitrone was dissolved in 20 cc. of sodium methylate solution containing 1.0 g. of sodium and filtered quickly, the filtrate soon deposited crystals of a pale yellow sodium salt whose composition indicated the replacement of one hydrogen atom by metal.

Anal. Calcd. for $C_{22}H_{16}O_2NNa$: Na, 6.6. Found: Na 6.4.

When a solution of the hydroxy nitrone in 5% sodium hydroxide is acidified without precautions, the product is deep yellow in color and only slightly soluble in organic solvents. (The analysis of such a sample which had been washed with water and dried after precipitation gave, C, 80.9; H, 5.35. Calcd. for $C_{22}H_{17}O_2N$: C, 80.7; H, 5.2.) If, however, the alkaline solution is kept cold and is acidified carefully with cold dilute hydrochloric acid, the precipitate is the oxime (IV), a very pale yellow, almost cream-colored, solid which is extremely soluble in organic solvents. On standing in contact with excess acid or, more rapidly, by warming or by rubbing against the walls of the containing vessel with a glass rod, the oxime rapidly turns the bright yellow of the hydroxy nitrone and its solubility decreases accordingly. The oxime can be isolated in an impure state by the incomplete acidification of its chilled alkaline solutions with cold dilute hydrochloric acid. The precipitate obtained by this treatment is allowed to stand for a half hour in an ice chest to coagulate. It is then filtered, washed with water containing a trace of sodium carbonate, and dried in vacuum over sodium hydroxide. This material always contains considerable amounts of sodium chloride. We have not been able to purify it by crystallization for, although the oxime is extremely soluble in the common organic solvents excepting petroleum ether, conversion to the very sparingly soluble hydroxy nitrone takes place too rapidly in solution. The evidence that the pale yellow material is the oxime (IV) and not the hydroxy nitrone is furnished by the reaction with acetic anhydride. With this reagent the crude oxime furnishes the acetate (V)—as described in the next paragraph—while the hydroxy nitrone gives a nitrogen free product.

B. Reactions of the Oxime (IV) or its Sodium and Pyridine Derivatives

Reaction with Acetic Anhydride.—When 0.5 g. of the crude oxime was warmed with acetic anhydride, all save traces of the solid went into solution at once. After thirty minutes on the water-bath, the solution was cooled and poured into water. The resulting colorless precipitate was crystallized from alcohol and from chloroform and petroleum ether.

Anal. Calcd. for $C_{24}H_{19}O_3N$: C, 78.0; H, 5.1. Found: C, 77.9; H, 5.1.

Phenyldibenzoylethylene monoxime acetate (V, R = CH_3) melts at 99°. It is very soluble in acetone and chloroform, moderately so in methyl and ethyl alcohols and insoluble in petroleum ether. On prolonged exposure to light it turns superficially yellow. The same acetate is obtained when a solution of the oxime in pyridine is acetylated with acetyl chloride. If the acetate is dissolved in alcohol and aqueous sodium hydroxide is added, the solution turns deep yellow and this color persists on heating. If the yellow alkaline solution is cooled and acidified, its behavior is that of a solution of the sodium salt of the oxime: first, a pale yellow precipitate is obtained, then this precipitate on standing turns bright yellow. The melting point of the precipitate is 178° and a mixed melting point shows that the material is the hydroxy nitrone.

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[9] We have found it very convenient in this and other work to replace benzoyl chloride with anisoyl chloride for acylation reactions. The anisoates thus obtained can be analyzed not only for carbon and hydrogen but also for methoxyl by the very convenient and accurate method described by Clark, *J. Assn. Off. Agr. Chem.*, **15**, 136 (1932). The methoxyl content gives at once the number of acyl groups which has been introduced; *cf.* Hill, THIS JOURNAL, **56**, 993 (1934).

Reaction with Benzoyl Chloride.—To a solution of 6.5 g. (0.02 mole) of the oxime in 25 cc. of pyridine was added 5.6 g. (0.04 mole) of benzoyl chloride. A precipitate formed at once. The reaction mixture was left overnight, then poured onto ice and an excess of dilute hydrochloric acid and the solid product separated by filtration. It weighed 7.7 g., a yield of 90%. For analysis it was crystallized from alcohol and from chloroform and petroleum ether.

Anal. Calcd. $C_{29}H_{21}O_3N$: C, 80.7; H, 4.9. Found: C, 80.6; H, 4.8.

Phenyldibenzoylethylene monoxime benzoate (V, R = C_6H_5) melts to a clear liquid at 148° after having melted first to an opaque liquid at 141°. It is quite soluble in acetone, benzene, chloroform and ethyl acetate, moderately soluble in methyl and ethyl alcohols and insoluble in petroleum ether.

The same benzoate may also be obtained by a Schotten–Baumann benzoylation of a solution of the sodium salt of the oxime in excess sodium hydroxide but this procedure is not so satisfactory as the benzoylation in pyridine.

When the benzoate is added to sodium hydroxide in alcohol and water it dissolves at once to furnish a yellow solution. If, after boiling for one-half hour, this solution is cooled, acidified and then made alkaline with sodium carbonate, filtration will separate the hydroxy nitrone whose identity is shown by a mixed melting point. The sodium carbonate filtrate on acidification furnishes benzoic acid.

Beckmann Rearrangement of the Oxime.—A solution of 6.5 g. (0.02 mole) of the oxime in 25 cc. of pyridine was cooled in water and shaken while 5.6 g. (0.04 mole) of benzene sulfonyl chloride was added. After one hour the reaction mixture was poured on ice and an excess of dilute hydrochloric acid. The yield of crude rearrangement product was quantitative. For analysis the material was crystallized from alcohol and from acetic acid.

Anal. Calcd. for $C_{22}H_{17}O_2N$: C, 80.7; H, 5.2; mol. wt., 327. Found: C, 80.3; H, 5.3; mol. wt. (camphor), 340.

The (β-benzoyl)-styryl amide of benzoic acid (VI) melts at 162°. It is moderately soluble in hot alcohol, acetone or benzene, but large losses are encountered when the material is crystallized from these solvents. Acetic acid is the most satisfactory medium for purifying the amide and from this solvent the material is obtained in stout yellow prisms often a centimeter in length.

The same rearrangement can be brought about by treatment of a solution of the sodium salt of the oxime with benzene sulfonyl chloride or by treatment of an ether suspension of the hydroxy nitrone itself with phosphorus pentachloride. These latter two methods are less satisfactory than the rearrangement in pyridine.

Hydrolysis of the Amide (VI).—To 1.63 g. of the amide suspended in 40 cc. of boiling alcohol there was added a solution of 2.2 g. of potassium hydroxide in 5 cc. of water. The reaction mixture was boiled for three and one-half hours, during which time its color changed from yellow to orange while ammonia was evolved. Water and ether were added and the ether layer separated and washed thoroughly with calcium chloride solution and water and dried over sodium sulfate. Methyl alcohol was then added and the ether was boiled off. On concentrating and chilling the solution 0.45 g. of desoxybenzoin (mixed m. p.) was obtained. Further concentration of the methyl alcohol filtrate gave only an oil.

The aqueous alkaline layer which had been separated from the ether extract was concentrated, cooled, acidified and filtered from the 0.6 g. of benzoic acid thus obtained. The acid filtrate from which the benzoic acid had been removed was made barely alkaline with sodium carbonate and concentrated until it solidified on cooling. It was then dissolved in the minimum amount of hot water, made just acid with hydrochloric acid and distilled. Samples of the distillate gave a positive test for formic acid by the mercuric oxide method of Mulliken.[10]

Summary

The product of the reaction between *cis*-phenyldibenzoylethylene and hydroxylamine hydrochloride is shown to be a cyclic hydroxy nitrone which is capable of reacting also in an isomeric form as an open chain oxime. The reactions of the oxime and hydroxy nitrone which are pertinent to the proof of their structures are presented, and the stereochemical factors involved in the ring closure are discussed.

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(10) Mulliken, "Identification of Pure Organic Compounds," John Wiley and Sons, Inc., New York, 1904, Vol. I, p. 83.