turn yellow. When dissolved in alcohol and treated with alcoholic ferric chloride, a bluish-green color was produced; an alcoholic solution of the substance also decolorized indophenol. On standing, two other changes were observed: a very dull but deep orange-colored crystalline substance was formed after twenty to thirty minutes; when it was filtered it slowly oiled out viscous and brown and crystallized as a deep yellow substance, which upon recrystallization from methanol, melted at 106°.

Anal. Calcd. for $C_{18}H_{18}O_4$: $-OCH_3$, 10.00. Found: $-OCH_3$, 9.99.

Summary

We have reported the preparation and properties of the enolic modification of mesityl-*p*-methoxybenzylglyoxal (VII), and have shown that the mono- and diacetates (IX) and (X) upon hydrolysis go by way of autoxidation of the acetylene glycol (XI) to *p*-methoxyphenyl mesityl triketone (XII).

WASHINGTON, D. C. RECEIVED AUGUST 7, 1943

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY AND CHEMICAL ENGINEERING OF THE UNIVERSITY OF PENNSYLVANIA]

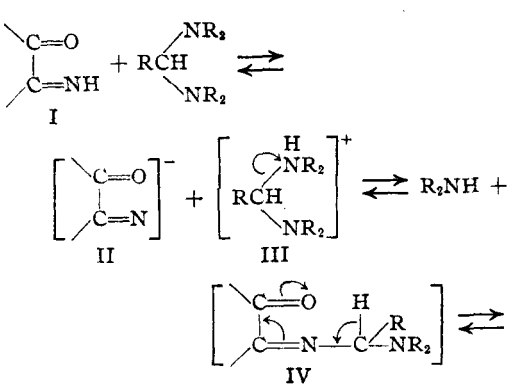
Reaction of Ortho Quinonimines with Alkylidenebisamines and Hydrobenzamide

BY GEORGE MCCOY[1] AND ALLAN R. DAY

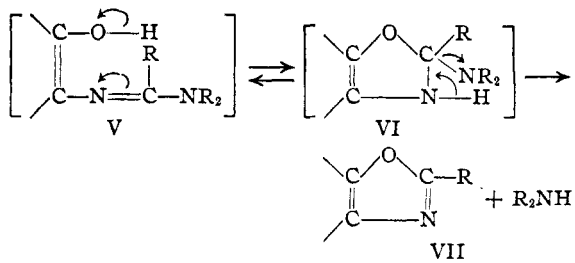
The validity of the structural analogy between aldehydes, Schiff bases, alkylidenebisamines, and hydrobenzamide was demonstrated by Knoevenagel in 1898.[2] He showed that benzaldehyde, benzalaniline, benzalbispiperidine and hydrobenzamide react with malonic acid to yield cinnamic acid as the final product in each case.

Stein and Day[3] have shown that the hydrogen atom of the imino group in retenequinonimine and phenanthraquinonimine is an active hydrogen. The quinonimines as a result undergo an aldol-type of addition with aldehydes or Schiff bases with the subsequent formation of 2-substituted retenoxazoles and phenanthroxazoles.

It seemed desirable to complete the above noted analogy by studying the reactions of the quinonimines with alkylidenebisamines and to re-examine the reaction of retenequinonimine with hydrobenzamide which is known to produce retenoxazoles.[4] It was found that retenequinonimine reacts readily with benzalbispiperidine and methylenebismorpholine to give almost quantitative yields of 2-phenylretenoxazole and retenoxazole, respectively. The reaction probably proceeds according to the course



I II III IV



V VI VII

In this series of reactions, the bisamine acts as a proton acceptor. The addition of the proton by displacing the electronic system toward the proton creates a tendency to cleave between the nitrogen atom and the *alpha* carbon atom. The electron deficiency on the alpha carbon atom may then be satisfied by union with the anion II. It will be noted that the intermediate IV is similar to that postulated by Stein and Day[3] for the intermediate formed by the interaction of retenequinonimine and a Schiff base.

Hydrobenzamide may be regarded both as a Schiff base and as an alkylidenebisamine. Kreps and Day[4] have shown that retenequinonimine reacts rapidly with hydrobenzamide to form 2-phenylretenoxazole. Their postulated mechanism, which was based on fewer facts than are now available, does not fit in entirely with the known general relationships between the aquo and the ammono systems. For this reason it was decided to re-examine the reaction.

There are only a few published examples involving the reaction of hydrobenzamide with active hydrogen compounds. Busch[5] treated hydrobenzamide, in dry alcohol–benzene solution, with hydrogen chloride and isolated benzaldimine hydrochloride and benzaldehyde diethylacetal. This reaction was repeated, in the present work, in dry ether solution and two moles of benzaldimine hydrochloride were obtained for each mole of hydrobenzamide. The cleavage of the two carbon to nitrogen linkages is undoubtedly initiated by proton addition to nitrogen.

(1) Present address: University of Pennsylvania, Philadelphia, Pa.

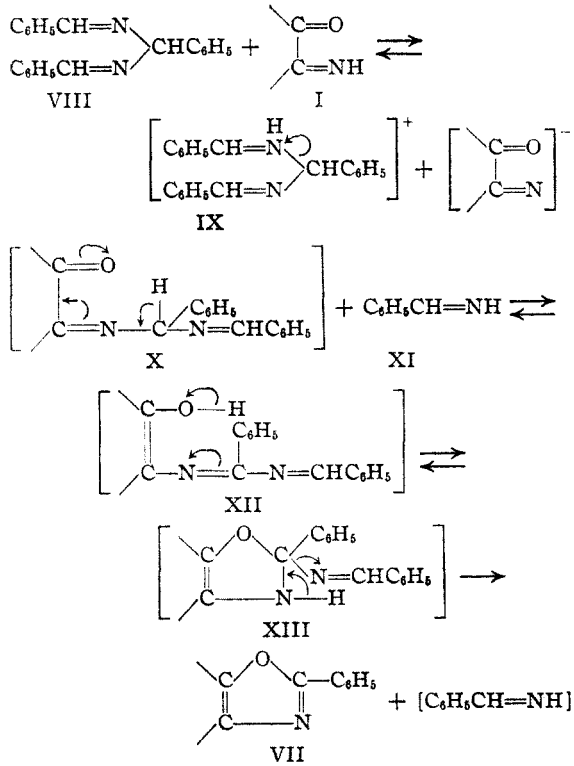
(2) Knoevenagel, *Ber.*, **31**, 2596 (1898).

(3) Stein and Day, THIS JOURNAL, **64**, 2567, 2569 (1942).

(4) Kreps and Day, *J. Org. Chem.*, **6**, 140 (1941).

(5) Busch, *Ber.*, **29**, 2143 (1896).

It may be assumed that any compound containing active hydrogen theoretically would be capable of reacting with hydrobenzamide in a similar manner. Thus the reaction of retenequinonimine with hydrobenzamide to form retenoxazole may be formulated as follows

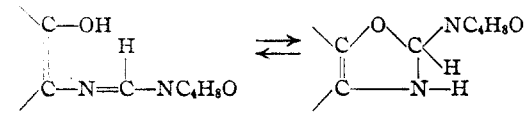


The two moles of benzaldimine liberated may react with two more moles of retenequinonimine, according to the mechanism outlined by Stein and Day[3] for Schiff bases, to form two more moles of retenoxazole and ammonia. It is impossible to state at present whether the latter happens or whether the benzaldimine reverts to hydrobenzamide and ammonia and the above course of reaction continues. In either case the over-all effect would be the same, namely, the reaction of of three moles of retenequinonimine with one mole of hydrobenzamide to form three moles of retenoxazole and two moles of ammonia. Actually, the experimental yield of 2-phenylretenoxazole was close to three moles and the formation of two-thirds of a mole of ammonia for each mole of oxazole was determined previously.[4]

Excellent evidence for the first step in the above reaction (VIII to X) may be found in a paper by Dougherty and Taylor.[6] They isolated and identified benzalphenylmercaptobenzylamine from the interaction of thiophenol and hydrobenzamide. This product could have been formed only through an addition and cleavage similar to that postulated above.

(6) Dougherty and Taylor, THIS JOURNAL, **55**, 4588 (1933).

When phenanthraquinonimine was treated with benzalbispiperidine under the same conditions as used in the retene series, a practically quantitative yield of 2-phenylphenanthroxazole was obtained. However, with methylenebismorpholine, instead of the expected phenanthroxazole, 2-morpholinophenanthroxazole was obtained. The reason for this anomolous behavior is not known at present. However, if one examines the intermediate formed in this case, it is readily seen how this might happen.



If a molecule of hydrogen is eliminated from the last intermediate, according to the course of reaction established for the reaction of retenequinone with a primary amine,[7] 2-morpholinophenanthroxazole would result. However, if morpholine were to split out the reaction-product would be phenanthroxazole. Benzalbispiperidine behaved similarly in both cases and it is only with methylenebismorpholine that this difference was noted.

Phenanthraquinonimine reacts with hydrobenzamide to give 2-phenylphenanthroxazole, under the same conditions as noted previously for retenequinonimine.

Experimental

Preparation of Retenequinonimine and Phenanthraquinonimine.—The methods used were noted in previous papers in this series.[3]

Reaction of Retenequinonimine with Benzalbispiperidine.—Two grams (0.0076 mole) of retenequinonimine and 2 g. (0.0076 mole) of benzalbispiperidine[8] were dissolved in 30 cc. of hot, dry alcohol and refluxed for fifteen minutes. The 2-phenylretenoxazole obtained by cooling the mixture was recrystallized from alcohol and water; yield 2.7 g. (100%); m. p. 174–176°. A mixed melting point determination with a sample prepared by Stein and Day[3] showed no depression.

Reaction of Retenequinonimine with Methylenebismorpholine.—Two grams (0.0076 mole) of retenequinonimine and 1.4 g. (0.0076 mole) of methylenebismorpholine[9] were dissolved in 30 cc. of hot, dry alcohol and refluxed for one hour. The hot mixture was diluted with water and the crude retenoxazole removed and recrystallized from alcohol and water; yield 1.8 g. (83%); m. p. 108–108.8°. A mixed melting point determination with a sample prepared by Jaffe and Day[10] showed no depression.

Reaction of Hydrobenzamide with Hydrogen Chloride.—Eight grams (0.027 mole) of hydrobenzamide was dissolved in 500 cc. of dry ether, cooled in a salt–ice mixture and treated with dry hydrogen chloride until no more precipitate formed. The benzaldimine hydrochloride was dried in a vacuum desiccator overnight and then further dried for four hours at 70°; yield 7.45 g.; m. p. 174–176°. Theory calls for 3.8 g. for one equivalent and 7.6 g. for two equivalents.

Reaction of Retenequinonimine with Hydrobenzamide.—Six grams (0.0228 mole) of retenequinonimine and 2.3 g. (0.0076 mole) of hydrobenzamide were dissolved in 250 cc. of dry alcohol and refluxed for thirty minutes. The mixture was diluted with water, cooled and the 2-phenylreten-

(7) McCoy and Day, *ibid.*, **65**, 1956 (1943).
(8) Laun, *Ber.*, **17**, 675 (1884).
(9) Feldman and Wagner, *J. Org. Chem.*, **7**, 31 (1942).
(10) Jaffe and Day, *ibid.*, **8**, 43 (1943).

oxazole removed by filtration. It was recrystallized from dioxane and water; yield 7.4 g.; m. p. 175–176°. The yield based on three moles of oxazole per mole of hydrobenzamide was 92.5%.

Reaction of Phenanthraquinonimine with Benzalbispiperidine.—One gram (0.0048 mole) of phenanthraquinonimine and 1.24 g. (0.0048 mole) of benzalbispiperidine were dissolved in 30 cc. of hot, dry alcohol and refluxed for fifteen minutes. After cooling, the 2-phenylphenanthroxazole was removed by filtration; yield 1.37 g. (98%); m. p. 205–206°. A mixed melting point determination with a sample prepared by Stein and Day[3] showed no depression.

Reaction of Phenanthraquinonimine with Methylenebismorpholine.—Two grams (0.0097 mole) of the quinonimine and 1.8 g. (0.0097 mole) of methylenebismorpholine were dissolved in 30 cc. of hot dry alcohol and refluxed for one hour. After dilution with water and cooling, the precipitate was removed and recrystallized from alcohol and water; yield 1.5 g. (51%); m. p. 178–179°. Analysis indicated this compound to be 2-morpholinophenanthroxazole.

Anal. Calcd. for $C_{19}H_{16}N_2O_2$: C, 74.99; H, 5.30; N, 9.22. Found: C, 75.08; H, 5.46; N, 9.16.

Reaction of Phenanthraquinonimine with Hydrobenzamide.—This reaction was carried out in the manner described for the corresponding reaction with retenequinonimine. The crude 2-phenylphenanthroxazole was recrystallized from alcohol; yield, 86%; m. p. 206–207°. A mixed melting point determination with an authentic sample showed no depression.

Summary

1. It has been shown that retenequinonimine and phenanthraquinonimine react with alkylidenebisamines as well as hydrobenzamide to yield the corresponding retenoxazoles or phenanthroxazoles.

2. The probable mechanisms for these reactions have been formulated.

PHILADELPHIA, PA. RECEIVED MAY 27, 1943

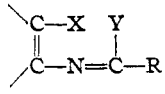
[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY AND CHEMICAL ENGINEERING OF THE UNIVERSITY OF PENNSYLVANIA]

Ortho Condensations which Lead to Oxazole or Imidazole Formation

BY GEORGE MCCOY[1] AND ALLAN R. DAY

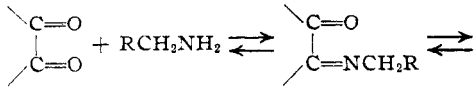
A comprehensive study of the reactions of ortho quinones and ortho quinonimines, which result in the formation of oxazoles and imidazoles, has been carried out in this Laboratory during the past few years. Retenequinone, phenanthraquinone and the corresponding quinonimines were used as examples of ortho quinones and quinonimines. These compounds are much more stable than the corresponding derivatives in the benzene or naphthalene series and are more readily available.

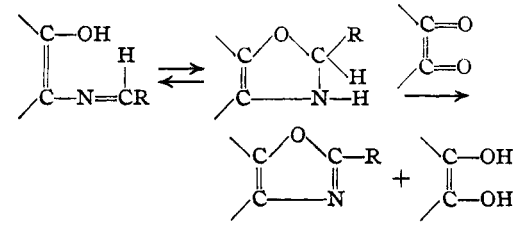
At the conclusion of this work, it was realized that it is possible to represent many if not all ortho condensations which lead to oxazole or imidazole formation by a common intermediate. Whether oxazole or imidazole results is determined by the nature of the groups X and Y



This may clearly be seen from a consideration of the following examples.

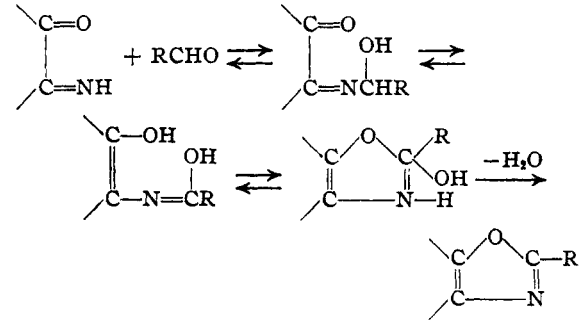
Oxazole Formation. 1. X = OH, Y = H.—It has been shown by McCoy and Day[2] that the interaction of retene- or phenanthraquinone with a primary amine gives this intermediate with the subsequent formation of a 2-substituted oxazole.





This same intermediate is formed in the reaction of aldehydes with *o*-aminophenols. For example, 9, 10-aminophenanthrol reacts rapidly with aldehydes to form 2-substituted phenanthroxazoles.[2]

2. X = OH, Y = OH.—Stein and Day[3] have shown that the interaction of retene- or phenanthraquinonimine with an aldehyde probably proceeds through this intermediate to give 2-substituted oxazoles.



Ladenburg[4] prepared 2-alkylbenzoxazoles from *o*-aminophenol and aliphatic acids and acid anhy-

(1) Present address: University of Pennsylvania, Philadelphia, Pa.

(2) McCoy and Day, THIS JOURNAL, **65**, 1956 (1943).

(3) Stein and Day, *ibid.*, **64**, 2567, 2569 (1942).

(4) Ladenburg, *Ber.*, **10**, 1124 (1877).