[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF COLORADO]

The Glyoxalines. III. A Study of the Reactions between Phenylglyoxal and Aliphatic Amidines

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Phenylglyoxal has been shown to react with aminoguanidine,[3] urea,[4] and benzamidine[5] to yield triazines, hydantoins and glyoxalines, respectively. The reactions of phenylglyoxal with acetamidine, propionamidine and butyramidine have been studied and are here reported.

When equimolar quantities of acetamidine hydrochloride and phenylglyoxal hydrate reacted in water solution in the presence of the calculated amount of base, a compound having the formula $C_{24}H_{19}O_5N$ (I) precipitated in a few minutes. After removing the precipitate the filtrate slowly deposited, over a period of several days, a voluminous solid having formula $C_{10}H_{10}ON_2$ (II). Acidifying the solution after removal of the solid yielded an amorphous precipitate of indefinite composition. Removing the solid, heating the filtrate a short time, and again allowing to stand several days precipitates an amorphous solid from which was isolated a compound having formula $C_{17}H_{14}N_2$ (III).

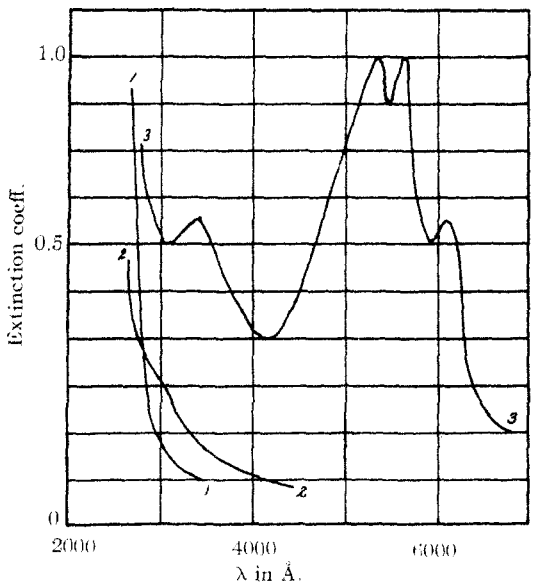

Fig. 1.—Curve 1, $C_{10}H_{10}ON_2$, 1.50 mg./50 ml. of abs. ethanol, 1 cm. cell; Curve 2, $C_{24}H_{19}O_5N$, 3.89 mg./50 ml. of dioxane, 1 cm. cell; Curve 3, $C_{25}H_{18}O_2N_2$, 0.61 mg./50 ml. of glacial acetic acid, 1 cm. cell.

It was found that in the presence of an excess of base the principal product, Compound (II), was obtained in good yield and without side reactions.

Only small quantities of Compound (I) were obtained. The same compound was isolated from the reaction using propionamidine but not with butyramidine. Since the identical compound was isolated using different amidines, the product is evidently the reaction of phenylglyoxal and fragments of the amidines. That the aliphatic amidines increase in stability with increase in molecular weight may explain why only small amounts of the compound form with propionamidine and none when butyramidine was used.

On the basis of chemical evidence, and analogy to reactions of phenylglyoxal previously reported,[4,5] the structure assigned to Compound (II) is that of 2-methyl-4-phenyl-5-hydroxyglyoxaline.

Propionamidine and butyramidine yielded analogous compounds.

Compound (III) was obtained in small yield when the reaction was carried out in water solution having only enough base to free the amidine. The carbon–hydrogen values clearly indicate that a cyclic compound was formed. A pyrimidine structure was suspected. The absorption spectrum of Compound (III) was compared with the spectra of several known pyrimidines. A compound, 2,4-diphenyl-6-methyl-pyrimidine,[6] having the same melting point as Compound (III) is recorded but the description, although meager, does not seem to conform to Compound (III).[7]

An analogous compound was obtained when propionamidine was used but none with butyramidine.

Experimental

The amidines used in this research were prepared by the method of Ronzio and Ekeley.[8] After several recrystallizations, the purity was checked by analysis for chlorine and also by microscopic examination. All the melting points reported are corrected and were obtained with calibrated thermometers.

Compound (I), $C_{24}H_{19}O_5N$.—To a solution of 30.4 g. (0.2 mole) of phenylglyoxal hydrate and 18.9 g. (0.2 mole) of acetamidine hydrochloride in a liter of water was added 15 ml. (0.2 mole) of 50% potassium hydroxide. The solution became yellow and a precipitate gradually formed. After ten minutes the flocculent orange-yellow precipitate was filtered off and was washed with water, (A), yield, 2.23 g. After extracting the dried powder with hot methanol, the residue was dissolved in the minimum quantity of hot cyclohexanol, diluted with an equal volume of 95% alcohol and allowed to stand several hours. A fine crystalline powder formed; yield, 0.41 g.; m. p. 226.5–227.5°.

(1) Now with Goodyear Tire and Rubber Company, Inc., Akron, Ohio.

(2) Now with The Institute of Paper Chemistry, Appleton, Wisconsin.

(3) Carlson, Ekeley and Ronzio, *Rec. trav. chim.*, **59**, 496 (1940).

(4) Fisher, Ekeley and Ronzio, THIS JOURNAL, **64**, 1434 (1942).

(5) Waugh, Ekeley and Ronzio, *ibid.*, **64**, 2028 (1942).

(6) Ashina and Kuroda, *Ber.*, **47**, 1818 (1914).

(7) An analogous compound, $C_{22}H_{16}N_2$, to which no structure was assigned was obtained from the reaction of phenylglyoxal with benzamidine.[5]

(8) Ronzio and Ekeley, "Organic Syntheses," Coll. Vol. 1, John Wiley and Sons, Inc., New York, N. Y., revised ed., 1941, p. 6.

The compound was insoluble in water, dilute acid and in dilute base. It was slightly soluble in the usual organic solvents. The compound dissolved in concentrated sulfuric acid with the formation of a yellow-green fluorescence. Dilution with water removed the color.

Anal. Calcd. for $C_{24}H_{19}O_3N$: C, 71.8; H, 4.77; N, 3.49. Found: C, 71.5, 71.5; H, 5.06, 5.10; N, 3.49, 3.50.

Compound (II), 2-Methyl-4-phenyl-5-hydroxyglyoxaline.—The filtrate from the above experiment (A) was allowed to stand for about thirty hours. The resulting flocculent orange precipitate was filtered off and washed with water (B); yield, 12.37 g. This product was first extracted with several small portions of hot methanol, then recrystallized from methanol. The yield was 3.3 g. of colorless, shiny crystals which changed to an opaque crystalline powder on drying. It was slightly soluble in the lower alcohols and in acetone but insoluble in water, ether, ligroin and benzene. The high boiling solvents caused decomposition of the compound. Soluble in dilute base but insoluble in 50% potassium hydroxide or in 10% sodium carbonate solution. The compound darkened at 185° and decomposed at 190–192°. A methyl alcohol solution containing a trace of potassium hydroxide showed a blue-green fluorescence. The compound added bromine with the formation of hydrogen bromide. An alcoholic solution of the compound was colored a faint purple with ferric chloride. Many attempts to form an acetyl derivative were unsuccessful. The compound did not form either an oxime or a phenylhydrazone.

Anal. Calcd. for $C_{10}H_{10}ON_2$: C, 69.0; H, 5.79; N, 16.09. Found: C, 69.1, 69.2; H, 5.54, 5.60; N, 15.93, 16.10.

A picrate formed easily in alcohol solution, and, recrystallized from alcohol, melted at 185.5–186.5° dec.

Anal. Calcd. for $C_{10}H_{10}ON_2 \cdot C_6H_3O_7N_3$: C, 47.7; H, 3.25; N, 17.37. Found: C, 47.8, 47.8; H, 3.53, 3.73; N, 17.30.

A hydrochloride was formed by saturating an acetic acid solution of the compound with hydrogen chloride gas; m. p. 251–254° dec.

Anal. Calcd. for $C_{10}H_{10}ON_2 \cdot HCl$: N, 13.30. Found: N, 13.32, 13.24.

The filtrate (B) was neutralized with hydrochloric acid and allowed to stand for three days. The orange ppt. formed was filtered off and washed with water (C); weight, 1.88 g. The precipitate could not be recrystallized without decomposition from any of the solvents tried. The only purification used was solution in chloroform followed by precipitation with petroleum ether. Analytical values obtained for the product are C, 69.3, H, 5.57, N, 7.90. Further precipitations followed by analyses for nitrogen gave values of 6.67 and 7.09.

The filtrate (C) was made slightly acid and boiled for thirty minutes, then again allowed to stand. After three days the resulting yellow precipitate was washed with water and dried. Solution in chloroform followed by precipitation with petroleum ether (D) yielded 1.65 g. of yellow powder. The product possessed no definite melting point. Analytical values obtained for the well-dried product were C, 69.4, H, 5.51, N, 7.96. Further precipitations followed by analyses for nitrogen gave the values 6.86 and 6.24.

The instability of the products obtained, the inconsistent analytical values and the carbon–nitrogen ratio clearly indicate that these precipitates are unstable, loosely bound fragments of the original reacting compounds. These were not investigated further.

Compound (III), $C_{17}H_{14}N_2$.—This compound of unknown structure was isolated when the chloroform–petroleum ether filtrate (D) was evaporated to dryness. The residue consisted of fine needles in a red tar; weight, 2.44 g. Recrystallization from methanol yielded 0.90 g. of white needles melting at 94°. The compound was insoluble in water but soluble in the usual organic solvents.

Anal. Calcd. for $C_{17}H_{14}N_2$: C, 82.9; H, 5.74; N, 11.38. Found: C, 82.9, 82.9; H, 5.81, 5.85; N, 11.40, 11.44.

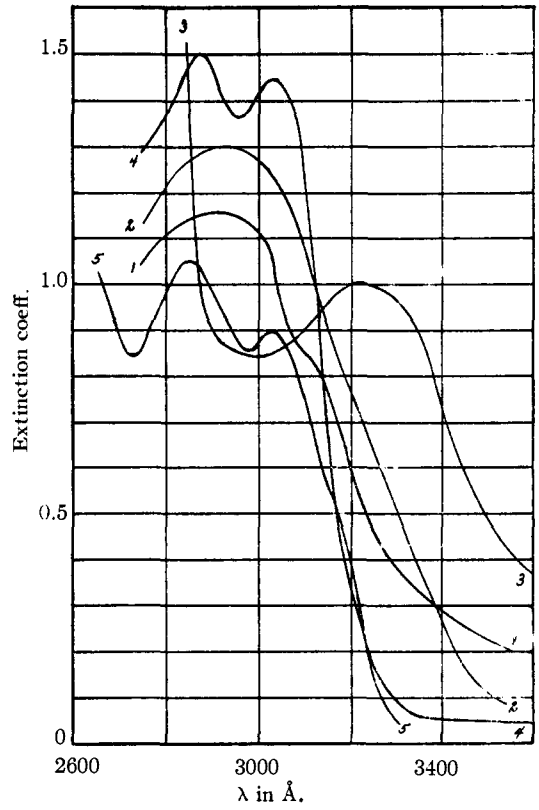

Fig. 2.—Curve 1, 2-methyl-4-phenyl-6-hydroxypyrimidine, 1.11 mg./50 ml. of abs. ethanol, 1 cm. cell; Curve 2, 2-phenyl-4-methyl-6-hydroxypyrimidine; 1.48 mg./50 ml. of abs. ethanol, 1 cm. cell; Curve 3, 2,4-diphenyl-6-hydroxypyrimidine[9]; 1.70 mg./50 ml. of dioxane, 1 cm. cell; Curve 4, $C_{18}H_{16}N_2$, 1.07 mg./50 ml. of abs. ethanol, 1 cm. cell; Curve 5, $C_{17}H_{14}N_2$, 0.68 mg./50 ml. of abs. ethanol, 1 cm. cell.

A picrate formed readily in alcohol solution, which, recrystallized from alcohol, melted at 189°.

2-Ethyl-4-phenyl-5-hydroxyglyoxaline.—An analogous procedure using the same mole fractions of propionamidine hydrochloride and phenylglyoxal hydrate yielded 0.24 g. of Compound (I) (*Anal.* C, 71.6, 71.7; H, 4.90, 4.83; N, 3.54, 3.68), and 7.80 g. of the glyoxaline. The product recrystallized from methanol–ethyl acetate (plates) gradually decomposed at 165–175°.

Anal. Calcd. for $C_{11}H_{12}ON_2$: C, 70.2; H, 6.43; N, 14.90. Found: C, 70.0, 70.2; H, 6.59, 6.65; N, 14.96, 14.88.

A picrate gradually formed in alcohol solution, which, recrystallized from alcohol, melted with decomposition at 180.5–182°.

Anal. Calcd. for $C_{11}H_{12}ON_2 \cdot C_6H_3O_7N_3$: C, 48.9; H, 3.62; N, 16.79. Found: C, 49.0, 49.0; H, 3.82, 3.86; N, 16.70.

A monohydrochloride precipitated when an acetic acid solution of the compound was saturated with anhydrous hydrogen chloride gas.

Anal. Calcd. for $C_{11}H_{12}ON_2 \cdot HCl$: N, 12.47. Found: N, 12.54, 12.57.

An analogous orange precipitate was obtained at the stage in the procedure corresponding to (B) which, purified in the same manner, gave 7.30% N. Again reprecipitated in the same manner several times, the nitrogen con-

(9) Ekeley and Ronzio, THIS JOURNAL, 59, 1118 (1937).

tent dropped to 6.48%. The product had no melting point. The orange precipitate obtained at stage (C) weighed 1.20 g. Purified as before, the nitrogen content was found to be 7.57%. After several reprecipitations the nitrogen content found was 6.84%.

Compound $C_{18}H_{16}N_2$.—The residue left upon the evaporation of the chloroform–petroleum ether at stage (D) of the procedure, after recrystallization from methanol, yielded 0.54 g. of white plates melting at 82°; insoluble in water but soluble in the usual organic solvents.

Anal. Calcd. for $C_{18}H_{16}N_2$: C, 83.2; H, 6.21; N, 10.54. Found: C, 83.1, 83.1; H, 6.21, 6.29; N, 10.78, 10.84.

A picrate formed readily in alcohol solution which, recrystallized from alcohol, melted at 157°.

2-Propyl-4-phenyl-5-hydroxyglyoxaline.—To a solution of 9.12 g. (0.06 mole) of phenylglyoxal hydrate and 7.35 g. (0.06 mole) of butyramidine hydrochloride in 500 ml. of water was added 4.5 ml. of 50% potassium hydroxide solution (0.06 mole). The solution turned yellow and a precipitate gradually formed. After twenty-four hours the precipitate was filtered off (A). The precipitate, weighing 6.4 g., was recrystallized from a mixture of methanol and ethyl acetate. The colorless prisms obtained were slightly soluble in dilute base, the lower alcohols, butyl acetate and insoluble in water, ethyl acetate or the hydrocarbons. The compound gradually decomposed at 215–230°.

Anal. Calcd. for $C_{12}H_{14}ON_2$: C, 71.2; H, 6.98; N, 13.87. Found: C, 71.0, 70.9; H, 6.97, 6.99; N, 13.90, 13.94.

A picrate formed in alcohol solution and was recrystallized from alcohol; m. p. 183.5–184°.

Anal. Calcd. for $C_{12}H_{14}ON_2 \cdot C_6H_3O_7N_3$: C, 50.1; H, 3.95; N, 16.24. Found: C, 50.1, 50.3; H, 4.30, 4.34; N, 16.38.

A hydrochloride, prepared in the manner described above, melted at 182–184°.

Anal. Calcd. for $C_{12}H_{14}ON_2 \cdot HCl$: N, 11.73. Found: N, 11.49, 11.48.

The filtrate (A) was neutralized and allowed to stand another twenty-four hours. A yellow precipitate weighing 0.22 g. was formed. The product dissolved in chloroform and precipitated with petroleum ether gave a pale yellow powder with no definite melting point (4.28% nitrogen). No other product could be isolated from the solution.

The following general procedure gives good yields of the glyoxalines only. To a water solution containing 0.1 mole of the amidine hydrochloride and 0.1 mole of phenylglyoxal hydrate in 750 ml. of water was added 37 ml. of 50% potassium hydroxide (0.5 mole). The solution was then allowed to stand from two to four hours at room temperature. The resulting yellow solution then was treated with carbon, filtered, and carefully neutralized with hydrochloric acid. A voluminous precipitate formed as the neutral point was approached. The precipitate was filtered off, washed with water and dried. The yield for acetamidine was 72%, for propionamidine was 69% and for butyramidine was 75%. The crude products were pure enough for ordinary purposes.

The absorption spectra data here reported were obtained using a Hilger E3 spectrograph and a Hilger sectorphotometer. A high frequency underwater spark served as a light source. The photographic plates were Eastman III-O and Panchromatic.

Summary

1. A 2-methyl-4-phenyl-5-hydroxyglyoxaline was prepared and derivatives characterized.

2. A 2-ethyl-4-phenyl-5-hydroxyglyoxaline was prepared and derivatives characterized.

3. A 2-propyl-4-phenyl-5-hydroxyglyoxaline was prepared and derivatives characterized.

4. A compound, $C_{17}H_{14}N_2$, probably a pyrimidine, was isolated and studied.

5. A compound, $C_{18}H_{16}N_2$, probably a pyrimidine, was isolated and studied.

6. A compound, $C_{24}H_{19}O_5N$, of unknown structure was isolated and derivatives prepared.

7. Absorption spectra data are reported.

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[CONTRIBUTION FROM UNIVERSAL OIL PRODUCTS CO.]

Hydrocarbon Reactions in the Presence of Cracking Catalysts. II.[1] Hydrogen Transfer

BY CHARLES L. THOMAS

While studying the practical applications of catalytic cracking, it was found that when an olefin-containing gasoline that had been produced by catalytic cracking was again brought in contact with the cracking catalyst the olefin content of the gasoline decreased whereas the isoparaffins and aromatics increased. This action suggested that hydroaromatic hydrocarbons were present in the gasoline and that these lost hydrogen to form the aromatic hydrocarbons while the hydrogen thus made available, reacted with isoolefins present to form isoparaffins. Consequently, the reaction was called *hydrogen transfer*. It was found that the hydrogen transfer reaction could be aided by adding higher boiling (above about 200°) petroleum fractions that should contain appreciable quantities of cycloparaffins.[2]

Certain of the results obtained with gasolines were not readily explainable by such a simple hypothesis. More hydrogen seemed to be used in saturating olefins than was available from the cycloparaffins present, so the cycloparaffins appeared to be helpful if present but not essential. Earlier work[1] had indicated that under some conditions minor proportions of paraffinic products could be formed from olefins in the presence of this type of catalyst. It was suggested that some of the hydrogen needed to convert the olefins to paraffins was made available by the formation of a hydrogen-deficient catalyst deposit.

The present article describes a test of this hypothesis which comprises subjecting *n*-octenes

(1) For the first article in this series see G. Egloff, J. C. Morrell, C. L. Thomas and H. S. Bloch, THIS JOURNAL, **61**, 3571 (1939).

(2) E. H. Kanhofer (to Universal Oil Products Co.) U. S. Patent 2,275,441 (March 10, 1942).