values since there is always considerable loss due to the incomplete combination of silicon with magnesium in the preparation of the silicide, the inability to get all of the silicide in contact with the ammonium bromide solution due to sticking to the walls of the tube, and to the decomposition of the silanes, especially disilane, in the water tube.

On the basis of the studies carried out in ammonia solution, it is suggested that such factors as the temperature of the reaction, the nature of the solvent and the composition of the silicide are of significance in determining the total yield of silanes as well as the yield of disilane. It appears that any mechanism proposed for the formation of the silanes must take these factors into consideration.

We are indebted to Prof. T. R. Hogness for assistance rendered in the construction of the apparatus and for invaluable suggestions offered in the course of the study.

Summary

Mono- and disilanes are prepared in large quantities and in yields ranging from 70 to 80% by allowing magnesium silicide to drop into a solution of ammonium bromide in liquid ammonia at low temperatures.

A study is made of the conditions favorable for the production of these silanes. On the basis of these studies certain suggestions are offered relative to the course of the reaction.

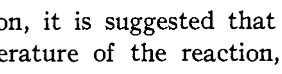
CHICAGO, ILLINOIS RECEIVED MAY 6, 1935

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

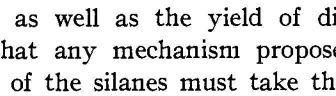
The Action of Aromatic Aldehydes upon the Addition Products Obtained from Aromatic Amidines and Glyoxal

BY JOHN B. EKELEY AND ANTHONY R. RONZIO

Diels and Schleich[1] have shown that benzamidine forms with diacetyl an addition product whose structure seems to be



since it reacts with benzaldehyde to form



We found, however, that, when benzamidine reacts with glyoxal,[2] although an addition product is formed, this reacts in quite a different manner from the one obtained from diacetyl. It forms a base with an alkaline reaction. The benzamidineglyoxal addition product dissociates in water solution yielding the osazone of glyoxal with phenylhydrazine and glyoxal disemicarbazone with semicarbazide. Warming the product with alkalies yields a brilliant red compound, which, in turn, splits off water, forming a magenta-red compound probably related to glyoxaline-red.[3] It is our intention to study this reaction more in detail, and report upon it in a later paper.

With aromatic aldehydes in alkaline solution this and similar addition products of other aromatic amidines condense forming compounds highly colored, yellow to red, with high melting points, and usually soluble in various organic solvents, which may be regarded either as hydroxypyrimidines or as benzoylphenylglyoxalines. They are soluble in cold alkalies, and stable in boiling concentrated alkalies. Often these alkaline solutions show fluorescence if alcohol is added, the fluorescence being intensified by the addition of a little ether. Evaporation of the solutions hydrolyzes the alkali salts. That the solubility of the compounds in alkalies is due to an OH group is shown by the fact that the compound from benzaldehyde and meta-tolenyl amidine upon treatment with a PCl_5–$POCl_3$ mixture gave a monochlorinated product in which the OH had been replaced by chlorine. No oxime, phenylhydrazone, or semicarbazone of the compound could be prepared. The compound with benzaldehyde is soluble in concentrated hydrochloric acid, but soon separates out as a crystalline hydrochloride of varying composition, having formed initially an unstable dihydrochloride. Hot alcohol hydrolyzes the chloride. Boiling with concentrated hydrochloric acid very slowly hydrolyzes the

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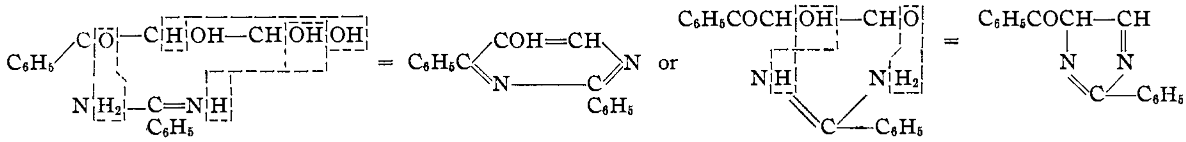
[1] Diels and Schleich, *Ber.*, **49**, 1711 (1916).

[2] We used Schuchardt's "polyglyoxal," a water soluble hydrated glyoxal containing some glyoxylic acid.

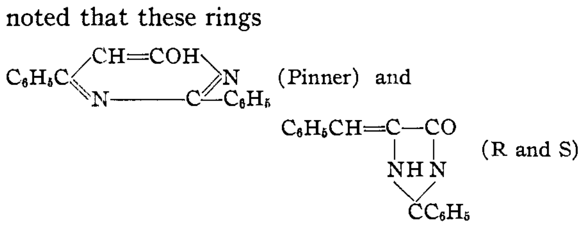
[3] Ruhemann and Stapleton, *Proc. Chem. Soc.*, **16**, 121 (1900).

substance with the formation of benzaldehyde. It forms a chloroplatinate. Careful oxidation with alkaline potassium permanganate yields benzamide, benzoic acid, and phenylpyruvic acid (m. p. 154–157°), but no phthalic acid. Oxidation with acid potassium permanganate yields only benzoic acid.

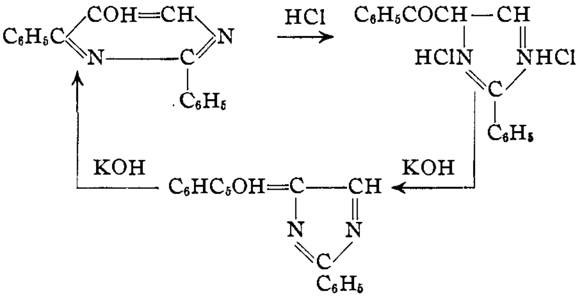
Since the compound from benzaldehyde and the benzamidine-glyoxal addition product has the empirical formula $C_{16}H_{12}N_2O$, and since the same product is formed when equimolecular portions of the aromatic aldehyde, glyoxal, and benzamidine are brought together in potassium hydroxide solution, the reagents have combined in the ratios of one to one to one. In order that such a combination should take place, the most probable explanation would be that the aromatic aldehyde and the glyoxal have reacted to form C_6H_5CO-CHOHCHO or $C_6H_5CHOHCOCHO$, which in turn reacted with benzamidine with the elimination of two molecules of water to form either the hydroxypyrimidine or 3-benzoyl-1-phenylglyoxaline. All other possible structures contain a phenylene group which on oxidation would yield phthalic acid, and hence are eliminated.



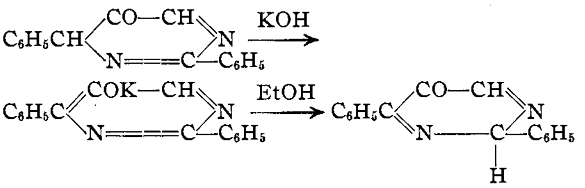
Ruhemann and Cunnington[4] obtained a benzalphenylglyoxalidone from benzamidine and phenylpropiolic acid. This substance in alcoholic potassium hydroxide solution shows a yellow-green fluorescence. It dissolves in concentrated hydrochloric acid, but soon separates out in the form of an unstable hydrochloride. Ruhemann and Stapleton[5] obtained from the same reagents a second compound which was identical with Pinner's[6] diphenylhydroxypyrimidine. It will be noted that these rings



differ from ours chiefly in the positions of the COH and the CO groups. We therefore conclude that the reaction between benzamidine, benzaldehyde, and glyoxal yields a diphenylhydroxypyrimidine which is stable in alkaline solution, but which rearranges in hydrochloric acid solution to benzoylphenylglyoxaline.



Another explanation of the fluorescence might be assumed as follows. The original compound is in the keto form and, in the presence of an alkali, it changes to the enol form. The addition of alcohol then causes rearrangement to the quinonoid structure.



Experimental Part

Aromatic Amidine Glyoxal Addition Product.—Saturated (below 5°) aqueous solutions of the amidine hydrochloride and polyglyoxal in molar proportions are mixed, and 50% potassium hydroxide is added to alkalinity with litmus. After fifteen minutes the reaction product is filtered off, when successive 0.5-cc. portions of the potassium hydroxide solution are added at fifteen-minute intervals, followed by filtration. The crystalline product is washed with ice water, and if vacuum dried over sulfuric acid, after several weeks acquires a pink color. These compounds dissociate in water solution, that with benzamidine yielding glyoxal osazone (m. p. 170°) with phenylhydrazine (*Anal.* Calcd. for $C_{14}H_{14}N_4$: C, 70.59; H, 5.84; N, 23.53. Found: C, 71.00; H, 6.03; N, 23.9), and glyoxalcarbazone (m. p. above 250°) with carbazide (*Anal.* Calcd. for $C_4H_8N_6O_2$: N, 48.85. Found: N, 48.85, 49.13).

Hydrochloride.—Evaporation of the hydrochloric acid solution of the benzamidine glyoxal product, subsequent solution in acetic acid, and precipitation with ether yielded the stable, colorless hydrochloride (m. p. 157–213° with dec.).

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[4] Ruhemann and Cunnington, *J. Chem. Soc.*, **75**, 954 (1899).

[5] Ruhemann and Stapleton, *ibid.*, **77**, 239 (1900).

[6] Pinner, *Ber.*, **22**, 1612 (1889).

Anal. Calcd. for $C_9H_{10}N_2O_2{\cdot}HCl$: Cl, 17.36. Found: Cl, 17.35, 17.45.

Hydroxypyrimidines (Benzoylphenylglyoxalines).—The powdered amidine glyoxal addition product was added to a little more than its equivalent of aromatic aldehyde dissolved in alcohol–water solution containing 1 cc. of 50% potassium hydroxide solution. If after an hour a yellow to orange color had not developed, an additional cc. of the potassium hydroxide brought the color change and within forty-eight hours yellow crystals separated out. Acidifying the filtrate with acetic acid increased the yield still further. After washing with ether, recrystallization from hot butyl acetate gave the pure compound.

Hydrochloride of the Pyrimidine.—Dry hydrogen chloride passed into an absolute alcohol suspension of the benzaldehyde benzamidine glyoxal product dissolved it completely and an excess of ether deposited crystals of an hydrochloride, which air-dried gave analyses lying between those for a mono and a dihydrochloride. The latter is evidently unstable.

Anal. Calcd. for $C_{16}H_{12}N_2O{\cdot}HCl$: Cl, 12.51. Calcd. for $C_{16}H_{12}N_2O{\cdot}2HCl$: Cl, 21.90. Found: Cl, 15.80.

Boiling the salt with alcohol (insoluble in water) completes the hydrolysis.

Platinum Double Salt.—An alcohol–hydrogen chloride solution of the pyrimidine yielded the platinum double salt by the usual method; red rosets, recrystallized from alcohol (m. p. 264° with dec.).

Anal. Calcd. for $(C_{16}H_{12}N_2O)_2{\cdot}H_2PtCl_6{\cdot}2H_2O$: Pt, 20.68. Found: Pt, 20.63, 20.80.

TABLE I

This table gives the amidine used, the formulas, m. p., etc., and the analytical data concerning the addition products with glyoxal.

Amidine used	Yield, %	M. p., °C. Elect. bloc Maquenne	Formula	Carbon, % Calcd.	Carbon, % Found		Hydrogen, % Calcd.	Hydrogen, % Found		Nitrogen, % Calcd.	Nitrogen, % Found	
Benz-	82	Pink 140, m. p. 160	$C_9H_{10}N_2O_2$	60.67	60.77	60.47	5.62	5.70	5.71	15.73	16.05	15.97
m-Tolenyl-	46	Gray 145, m. p. 148	$C_{10}H_{12}N_2O_2$	62.50	62.40	62.31	6.25	6.34	6.38	14.58	14.58	14.66
p-Tolenyl-	50	Gray 140, m. p. 164	$C_{10}H_{12}N_2O_2$	62.50	62.57	62.55	6.25	6.30	6.33	14.58	14.68	14.66
p-Chlorobenz-	63	Pink 157, m. p. 188	$C_9H_9ClN_2O_2$	50.84	50.60	50.87	4.24	4.23	4.39	13.18	13.46	
β-Naphtho-	45	Dec. 164 to 207	$C_{13}H_{12}N_2O_2$	68.39	67.92	Lost	5.31	5.47	5.66	12.28	12.26	12.15

TABLE II

HYDROXYPYRIMIDINES FROM BENZAMIDINE AND POLYGLYOXAL

Aldehyde used	Yield, %	M. p., °C. Elect. bloc Maquenne	Formula	Carbon, % Calcd.	Carbon, % Found		Hydrogen, % Calcd.	Hydrogen, % Found		Nitrogen, % Calcd.	Nitrogen, % Found	
Benzal-	60	284	$C_{16}H_{12}N_2O_2$	77.42	77.46	77.44	4.83	4.91	5.03	11.29	11.67	11.38
p-Toluyl-	57	319	$C_{17}H_{14}N_2O$	77.86	77.99	77.73	5.34	5.35	5.41	10.69	10.64	10.68
Salicyl-	56	338	$C_{16}H_{12}N_2O_2$	72.36	72.36	72.05	4.55	4.85	4.42	10.60	10.60	10.68
p-Bromosalicyl-	40	335	$C_{16}H_{11}N_2O_2Br$	55.98	55.89	55.84	3.20	3.39	3.54	8.16	8.16	8.17
Anis-	25	307	$C_{17}H_{14}N_2O_2$	73.35	73.25	73.40	5.07	5.32	5.09	10.07	10.04	10.09
m-Nitrobenz-	43	262	$C_{16}H_{11}N_3O_3$	65.53	65.58	65.89	3.75	4.16	4.30	14.33	14.02	14.26
Terphthal-	73	292	$C_{17}H_{12}N_2O_2$	73.91	73.34	73.53	4.35	4.35	4.53	10.15	10.57	10.15
Isophthal-	52	241	$C_{17}H_{12}N_2O_2$	73.91	73.45	74.09	4.35	4.68	4.65	10.15	10.02	9.85
Furfural	61	293.5	$C_{14}H_{16}N_2O_2$	70.59	70.91	70.88	4.20	4.53	4.40	11.76	11.75	11.45
o-Methoxybenz-	33	283	$C_{17}H_{14}N_2O_2$	73.35	73.52	73.46	5.07	5.53	5.31	10.07	9.93	9.98

TABLE III

HYDROXYPYRIMIDINES FROM *p*-TOLENYLAMIDINE AND POLYGLYOXAL

Aldehyde used	Yield, %	M. p., °C. Elect. bloc Maquenne	Formula	Carbon, % Calcd.	Carbon, % Found		Hydrogen, % Calcd.	Hydrogen, % Found		Nitrogen, % Calcd.	Nitrogen, % Found	
Benz-	66	310	$C_{17}H_{14}N_2O$	77.86	77.77	77.63	5.34	5.31	Lost	10.69	10.88	10.50
p-Toluyl-	64	295	$C_{18}H_{16}N_2O$	78.44	78.82	78.75	5.80	5.83	5.96	10.15	10.19	10.13
Salicyl-	64	323.5 to 337	$C_{17}H_{14}N_2O_2$	73.38	73.61	73.69	5.04	5.38	5.60	10.07	10.13	10.10
m-Nitrobenz-	50	295	$C_{17}H_{13}N_3O_3$	66.45	66.50	66.65	4.24	4.42	4.53	13.68	13.79	13.78
p-Bromosalicyl-	46	344.5 to 351.5	$C_{17}H_{13}N_2O_2Br$	57.18	57.38	57.28	3.67	3.82	4.06	7.87	7.77	7.80
Furfural	55	310	$C_{15}H_2N_2O_2$	71.43	71.68	71.46	4.76	4.97	4.89	11.11	11.12	11.23

TABLE IV

Amidine used with glyoxal	Aldehyde used	Yield, %	M. p., °C. Elect. bloc Maquenne	Formula	Carbon, % Calcd.	Carbon, % Found		Hydrogen, % Calcd.	Hydrogen, % Found		Nitrogen, % Calcd.	Nitrogen, % Found	
p-Chlorobenz-	Benz-	55	331.5	$C_{16}H_{11}N_2OCl$	67.96	67.75	67.72	3.89	3.84	3.99	9.91	9.79	10.06
m-Tolenyl-	Benz-	40	258.5	$C_{17}H_{14}N_2O$	77.86	78.02	77.35	5.34	5.45	5.29	10.69	10.69	10.81
β-Naphtho-	Benz-	Not recorded	281	$C_{20}H_{14}N_2O$	68.39	67.92	Lost	5.31	5.66	5.47	9.39	9.24	9.16
p-Nitrobenz-	Benz-	Poor	326	$C_{16}H_{11}N_3O_3$	65.53	65.41	65.20	3.75	3.97	3.96	14.33	14.39	14.01

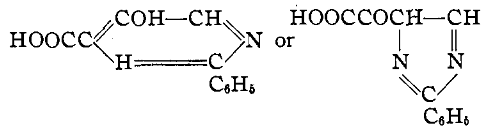
The Chloropyrimidine.—The product from benzaldehyde, glyoxal and *m*-tolenylamidine refluxed with a PCl_5-$POCl_3$ mixture for several hours gave a gum insoluble in water. This, after boiling with water several hours, was dissolved in alcohol. After several days a small yield of yellow crystals was obtained which, recrystallized from alcohol several times, melted at 285.5° (bloc Maquenne).

Anal. Calcd. for $C_{17}H_{13}N_2Cl$: Cl, 12.63. Found: Cl, 12.83, 12.89.

Phenylpyrimidine Carboxylic Acid.—The mother liquor from the benzamidine glyoxal product, after several weeks (red color) was neutralized with hydrochloric acid giving an orange-red precipitate which was separated mechanically from the red gum. Boiling with dilute potassium hydroxide and charcoal several times, reprecipitation with acid and recrystallization from dilute alcohol, gave flesh-colored crystals (m. p. 310°, electrical bloc Maquenne, 250° capillary tube).

Anal. Calcd. for $C_{11}H_8N_2O_3$: C, 61.11; H, 3.70; N, 12.95. Found: C, 61.50; H, 3.90; N, 12.82, 13.15.

Since "polyglyoxal" (Schuchardt) contains a small amount of glyoxylic acid, this has evidently reacted with the addition product to form



This acid is an isomer of an acid obtained by Pinner.[6]

Summary

1. A series of addition products of aromatic amidines and glyoxal has been prepared, analyzed and formulas determined. The hydrochloride of the benzamidine–glyoxal addition product has been prepared and analyzed.

2. A series of diphenylhydroxypyrimidines (benzoylphenylglyoxalines) have been prepared, analyzed and presumptive formulas ascribed to them.

3. A chloropyrimidine from phenyl-*m*-tolenylhydroxypyrimidine has been prepared and analyzed.

4. A phenylpyrimidine carboxylic acid has been prepared and analyzed.

BOULDER, COLORADO RECEIVED APRIL 29, 1935

[CONTRIBUTION FROM THE LABORATORIES OF THE ROCKEFELLER INSTITUTE FOR MEDICAL RESEARCH]

The Determination of Activity Coefficients from the Potentials of Concentration Cells with Transference. I. Sodium Chloride at 25°

BY ALFRED S. BROWN[1] AND D. A. MACINNES

In the determination of the activities of electrolytes in solution the method depending upon the measurement of concentration cells has certain decided advantages over the other available methods, which are, it will be recalled, the determinations of freezing points, of boiling points or of vapor pressures. The concentration cell method is superior to the first two of these alternative methods in that the measurements are isothermal and that they may be made at any temperature at which the existence of the cell is possible. The concentration cell method is also better than the other procedures mentioned in that the precision of the measurements does not decrease rapidly as the concentrations of the solutions are lowered. There is, however, a distinct limitation to a method depending upon the determination of electromotive forces in that reversible electrodes are necessary for the ion constituents involved. Thus, for sodium chloride solutions, a concentration cell without liquid junction, of which the following is a typical example

$$\text{Ag; AgCl, NaCl }(C_1)\text{: NaHg}_x - \text{NaHg}_x\text{; NaCl }(C_2)\text{, AgCl; Ag} \quad \text{(A)}$$

involves electrodes reversible to the chloride and sodium ion constituents, in this case silver–silver chloride and sodium amalgam electrodes. Amalgam electrodes, however, require elaborate experimental technique and are limited in the concentration range in which they can be used.

Although it is rarely possible to find electrodes for both ions of a binary electrolyte which are reversible and at the same time convenient to work with experimentally, suitable electrodes for one of the ion constituents are much more frequently available. With such electrodes, cells with liquid junctions can be set up. A cell of this type and the one that is the subject of this research is the following

$$\text{Ag; AgCl, NaCl }(C_1)\text{: NaCl }(C_2)\text{, AgCl; Ag} \quad \text{(B)}$$

If the transference number t_i is a constant in the concentration range C_1 to C_2 the activity ratio can be computed from the equation

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[1] National Research Council Fellow during the progress of this research.