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

Some Reaction Products of Aromatic Amidines with Diketones, Dialdehydes and their Monoximes

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1. Phenanthrenequinone, suspended in an equimolecular solution of the amidine hydrochloride, was dissolved on addition of excess 50% alkali. Neutralization with dilute acid and subsequent dilution gave the condensation product. Recrystallized from alcohol; crystals, insoluble in water, soluble in usual organic solvents; yields, 80 and 90%.

TABLE I

PHENANTHRENEQUINONE

Amidine		Benz-	*m*-Tolenyl	*o*-Tolenyl
M. p., °C.		277–278	269–270	287.5–288
Formula		$C_{21}H_{14}N_2O$	$C_{22}H_{16}N_2O$	$C_{22}H_{16}N_2O$
C, %	Calcd.	81.26	81.44	81.44
	Found[a]	81.39	81.69	81.64
H, %	Calcd.	4.55	4.98	4.98
	Found	4.79	5.21	5.30
N, %	Calcd.	9.03	8.64	8.64
	Found	8.97	8.49	8.66

[a] Results in this and following tables are averages of two satisfactory determinations.

2. Addition of 50% alkali to a mixture of most concentrated water solutions of the diacetyl monoxime with the amidine hydrochloride in twice the molecular proportion gave an immediate separation of yellow plates; recrystallized from toluene; soluble in the usual organic solvents. In the case of *m*-tolenylamidine similar chloroform solutions of the monoxime and the free amidine (prepared by Pinner's method[1]) were mixed and the solution concentrated by evaporation on the steam-bath, yielding a yellow oil which soon solidified; recrystallized from benzene–ligroin. Dissociation in solution was proved in each case by the formation with the appropriate reagent of known derivatives of either the oxime or the amidine, the one obtained from benzamidine by Kunckell and Bauer[2] being shown to be benzamidine benzoate.

TABLE II

DIACETYLMONOXIME

Amidine		Benz-	*m*-Tolenyl
M. p. (uncorr.), °C.		105–107	94–96
Formula		$C_{15}H_{22}N_4O_4$	$C_{16}H_{24}N_4O_4$
C, %	Calcd.	55.88	57.10
	Found	55.89	57.43
H, %	Calcd.	6.88	7.20
	Found	6.84	7.22
N, %	Calcd.	17.39	16.67
	Found	17.17	16.78

3. Equimolecular portions of phenanthrenequinonemonoxime partially dissolved in amyl alcohol and the amidine hydrochloride in chloroform containing an excess of potassium hydroxide were mixed. The oxime dissolved and, after the alcohol and chloroform had been partly evaporated off, the compound crystallized out; recrystallized from amyl alcohol; slowly and partially soluble in water, more rapidly in alkali, insoluble in ether and benzene; yields, 65 and 80%.

TABLE III

PHENANTHRENEQUINONEMONOXIME

Amidine		Benz-	*m*-Tolenyl	*p*-Tolenyl
M. p. (uncorr.), °C.		186	165–166	182–183
Color		[a]	Dark red	Dark red
Formula		$C_{21}H_{17}N_3O_2$	$C_{22}H_{19}N_3O_2$	$C_{22}H_{19}N_3O_2$
C, %	Calcd.	73.44	73.91	73.91
	Found	73.45	73.83	74.13
H, %	Calcd.	4.99	5.36	5.36
	Found	5.15	5.55	5.57
N, %	Calcd.	12.25	11.77	11.77
	Found	12.15	11.72	11.72

[a] Color: dark green in daylight; violet in artificial light.

4. The method of preparation was the same as in the case of phenanthrenequinonemonoxime; yield 59%, m. p. 145.6°; yellow plates. *Anal.* Calcd. for $C_{15}H_{16}N_3O_2$: C, 68.29; H, 5.38; N, 14.95. Found: C, 68.37, 68.12; H, 5.33, 5.63; N, 14.79, 14.81.

Similar attempts failed with beta-benzilmonoxime, with ω-isonitrosoacetophenone and with cyclohexene-1-dione-4,6-dioxime (tautomeric form dinitrosoresorcinol).

5. The following improved method for the preparation of substituted 2,4-diphenyl-5-hydroxypyrimidines (benzoyl glyoxalines)[3] from a glyoxal-amidine addition product was devised.

Five cubic centimeters of 50% potassium hydroxide solution was added to a 50-cc. alcohol

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(1) Pinner, *Ber.*, **22**, 1607 (1889).

(2) Kunckell and Bauer, *ibid.*, **34**, 3030 (1901).

(3) Ekeley and Ronzio, THIS JOURNAL, **57**, 1353 (1935).

TABLE IV

2,4-DIPHENYL-5-HYDROXYPYRIMIDINES FROM BENZAMIDINE AND GLYOXAL

Aldehyde used	Color	M. p., °C.	Formula	Analyses, % Carbon Calcd.	Carbon Found	Hydrogen Calcd.	Hydrogen Found	Nitrogen Calcd.	Nitrogen Found
Phthaldehydic acid	Lemon-yellow	259–260	$C_{17}H_{12}N_2O_3$	69.84	69.54	4.14	4.33	9.59	9.49
o-Chlorobenzaldehyde	Lemon-yellow	260	$C_{16}H_{11}N_2OCl$	67.95	67.66	3.92	4.07	9.92	9.87
p-Chlorobenzaldehyde	Yellow	305–306	$C_{16}H_{11}N_2OCl$	67.95	67.81	3.92	4.03	9.92	9.87
Dimethoxyresorcylaldehyde	Orange	248–249	$C_{18}H_{16}N_2O_3$	70.10	70.15	5.23	5.33	9.09	9.01
2,5-Dimethoxybenzaldehyde	Orange	268–269	$C_{18}H_{16}N_2O_3$	70.10	69.86	5.23	5.28	9.09	9.17
3,4-Dimethoxybenzaldehyde	Brown-orange	259–260	$C_{18}H_{16}N_2O_3$	70.10	70.45	5.23	5.31	9.09	9.30
p-Dimethylaminobenzaldehyde	Red-brown	277–278	$C_{18}H_{17}N_3O$	74.18	74.03	5.89	5.99	14.43	14.65
p-Ethoxybenzaldehyde	Lemon-yellow	292–293	$C_{18}H_{16}N_2O_2$	73.94	73.89	5.52	5.65	9.59	9.75
m-Hydroxybenzaldehyde	Yellow	265–265.5	$C_{16}H_{12}N_2O_2$	72.70	72.88	4.58	4.81	10.61	10.62
Dibromosalicyl aldehyde	Orange-red	311	$C_{16}H_{10}N_2O_2Br_2$	45.40	45.52	2.38	2.52	6.62	6.51
Homosalicyl aldehyde	Bright red	287–288	$C_{17}H_{14}N_2O_2$	73.35	73.49	5.07	5.24	10.07	10.09
5-Nitrosalicyl aldehyde	Red-brown	Above 300	$C_{16}H_{11}N_3O_4$	62.11	62.28	3.59	3.68	13.59	13.57
Cumenol	Orange	246–247	$C_{19}H_{18}N_2O$	78.58	78.53	6.25	6.35	9.66	9.85
4-Methoxy-3-methylbenzaldehyde	Orange-yellow	253–254	$C_{18}H_{16}N_2O_2$	73.94	73.71	5.52	5.67	9.59	9.47
Piperonal	Yellow-brown	285–287	$C_{17}H_{12}N_2O_3$	69.84	69.64	4.14	4.25	9.59	9.65
m-Toluyl aldehyde	Lemon-yellow	237–238	$C_{17}H_{14}N_2O$	77.82	77.75	5.38	5.38	10.69	10.68

TABLE V

5-HYDROXY-2-(3-TOLUYL)-PYRIMIDINES FROM *m*-TOLENYLAMIDINE AND GLYOXAL

Aldehyde used	Color	M. p., °C.	Formula	Analyses, % Carbon Calcd.	Carbon Found	Hydrogen Calcd.	Hydrogen Found	Nitrogen Calcd.	Nitrogen Found
Dimethoxyresorcylaldehyde	Orange	250–251	$C_{19}H_{18}N_2O_3$	70.77	70.60	5.63	5.74	8.70	8.97
2,5-Dimethoxybenzaldehyde	Orange-yellow	229–230	$C_{19}H_{18}N_2O_3$	70.77	70.74	5.63	5.88	8.70	8.87
3,4-Dimethoxybenzaldehyde	Orange-brown	238–239	$C_{19}H_{18}N_2O_3$	70.77	70.59	5.63	5.65	8.70	8.79
p-Ethoxybenzaldehyde	Yellow	237–238	$C_{19}H_{18}N_2O_2$	74.47	74.31	5.93	6.09	9.15	9.26
Cumenol	Yellow	263–264	$C_{20}H_{20}N_2O$	78.90	78.63	6.63	6.67	9.21	9.17
o-Methoxybenzaldehyde	Yellow	272–273	$C_{18}H_{16}N_2O_2$	73.94	73.87	5.52	5.57	9.59	9.68
Anisaldehyde	Lemon-yellow	227–229	$C_{18}H_{16}N_2O_2$	73.94	73.95	5.52	5.65	9.59	9.65
Piperonal	Yellow-brown	249	$C_{18}H_{14}N_2O_3$	70.56	70.70	4.61	4.80	9.15	9.18
4-Methoxy-3-methylbenzaldehyde	Orange	237–239	$C_{19}H_{18}N_2O_2$	74.47	74.37	5.93	5.95	9.15	9.14

solution containing 1 g. of glyoxal-amidine addition product, and from 10 to 20% excess of the calculated amount of aromatic aldehyde in a flask, the flask tightly stoppered and allowed to stand at room temperature for several days. The solution was then made slightly acid with acetic acid and the solid material filtered off, suspended in 25 cc. of alcohol, enough 50% potassium hydroxide solution added to dissolve it, the solution boiled with bone charcoal, and filtered. The filtrate was made slightly acid with acetic acid and the resulting precipitate filtered, boiled with water, filtered again, dried, recrystallized from ethyl benzoate, and the crystals washed with ether. This procedure gives a very pure product.

Summary

1. The reaction products of several aromatic amidines with various 1,2 dialdehydes, ketones and certain of their monoxides have been prepared, analyzed and described.

2. An improved method used in the preparation of a large number of 2,4-diphenyl-5-hydroxypyrimidines, resp., benzoyl glyoxalines has been described.

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