(twice the time theoretically required), the electrodes were removed and the catholyte and washings were collected. The isolation of the 2,3-bis-(*p*-aminophenyl)-2,3-butanediol dihydrochloride was accomplished by the method of Allen and Corwin,[1] with the exception that the temperature was kept under 50° (rather than 25°) in the evaporation of the final catholyte solution *in vacuo;* yield 10.2 g. (59%) of yellow-brown solid which decomposed slowly above 230°.

2,3-Bis-(*p*-aminophenyl)-2,3-butanediol.—Saturated aqueous potassium carbonate solution was added to a solution of 51.5 g. of the pinacol dihydrochloride in 300 ml. of water until the mixture was strongly alkaline. The solid precipitate was filtered and treated with hot acetone. The 2,3-bis-(*p*-aminophenyl)-2,3-butanediol separated from acetone as faintly yellow platelets, m.p. 239–242° dec. (reported[1] 248–249°), of analytical purity; yield 16.3 g. (40%).

THE CHEMICAL LABORATORIES
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The Preparation of Samarium Metal[1]

BY E. I. ONSTOTT

RECEIVED JUNE 8, 1953

In a recent communication to the editor, Daane, Dennison and Spedding[2] described the preparation of samarium metal of at least 98% purity by reaction of samarium oxide with lanthanum metal. They also mentioned that barium had been tried as a reductant with little success. In this Laboratory relatively pure samarium metal has been produced by reaction of barium with anhydrous samarium(III) bromide. The reaction is carried out in a tantalum crucible[3] in an argon atmosphere by heating the mixture to a temperature of 1650–1700° for a period of about 20 minutes. During this heating period the samarium metal is collected in the bottom of the crucible and the excess barium is distilled out. The yield of metal is about 10 g. or 50% for a 50-g. batch of bromide. This technique of heating the charge to a high temperature to facilitate separation of the metal in the massive state has been used previously by Spedding, *et al.*, in the preparation of other rare earth metals.[4]

The purity of samarium metal prepared in this manner is believed to be greater than 99.5%. Spectrographic analysis showed the metal to contain: Li, Na, Mg, Ca, Mn, Fe, Cu, each less than 0.001%; Ba, Si, Sn, each less than 0.01%; Bi, 0.001–0.1%. Europium content was about 0.08%, since the samarium oxide used to make the anhydrous bromide contained this amount of europium oxide, as determined by a combination of gravimetric, colorimetric[5] and tracer analysis. No other rare earths were detected by spectrographic analysis. The samarium oxide as received from the Société de Produits Chimique des Terres Rares contained 1.5% calcium and 1.5% europium oxide. Purification was made by two electrolyses according to the method of McCoy,[6] followed by two oxalate precipitations and ignition to the oxide.

An experiment in this Laboratory confirms the report of Daane, Dennison and Spedding[2] that samarium metal is relatively volatile. When recasting samarium metal at about 1700° in an atmosphere of argon, approximately 1 g. of metal distilled to the lid of the crucible in a period of 5–10 minutes.

The density of three samples of samarium metal was determined by weighing in air, then weighing while suspended in acetylene tetrabromide. Density data are as follows: massive metal as made, 7.499 g./cc.; recast metal, 7.509 g./cc.; distilled metal, 7.495 g./cc. Accuracy of these data, which compare favorably to the value of 7.53 g./cc. obtained by Daane, Dennison and Spedding,[2] is believed to be ±0.005 g./cc.

Acknowledgment.—Some of the analyses were performed by Richard Wilhelm, O. R. Simi and F. H. Ellinger. Valuable suggestions were made by Dr. Henry Taube, Dr. E. R. Jette, Dr. R. D Fowler and Dr. R. P. Hammond.

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[1] This work is a contribution from the Chemical and Metallurgical Research Division of the Los Alamos Scientific Laboratory, Los Alamos, New Mexico, under the auspices of the Atomic Energy Commission.

[2] A. H. Daane, D. H. Dennison and F. H. Spedding, THIS JOURNAL, **75**, 2272 (1953).

[3] A. H. Daane, *Rev. Sci. Instruments*, **23**, 245 (1952).

[4] F. H. Spedding and A. H. Daane, THIS JOURNAL, **74**, 2783 (1952).

[5] T. Moeller and J. C. Brantley, *Anal. Chem.*, **22**, 433 (1950).

[6] H. N. McCoy, THIS JOURNAL, **63**, 3432 (1941).

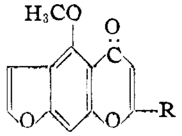
Furochromones and -Coumarins. VIII. Action of Hydrazine Hydrate and Hydroxylamine on Khellin, Khellol and Visnagin

BY ALEXANDER SCHÖNBERG AND MAHMOUD MOHAMED SIDKY

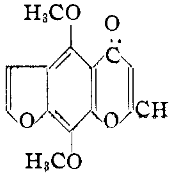
RECEIVED APRIL 10, 1953

The action of hydrazine hydrate on 2-methylchromone has been studied by Koenigs and Freund,[1] and on chromone itself by Baker, Harborne and Ollis.[2] Both groups of researches agree that the reaction products are pyrazole derivatives and not hydrazones of the chromones in question as previously believed. In the case of chromone itself, the product is 5(3)-*o*-hydroxyphenylpyrazole (IIId or IVd).

We have investigated the action of hydrazine hydrate on visnagin (Ia), khellol (Ib) and khellin (II), and believe that the reaction products are the pyrazole derivatives IIIa, IIIb and IIIc or IVa, IVb and IVc, respectively.



Ia, R = CH_3
Ib, R = CH_2OH



II

These substances are soluble in aqueous alkali, and their alcoholic solutions give a blue color with aqueous ferric chloride solution, and with titanium chloride a deep orange color is developed. From IIIa and IIIc—each containing one active hydrogen in the phenolic hydroxy group and one active hydrogen atom attached to a nitrogen atom—dibenzoyl derivatives were obtained when they were treated with benzoyl chloride (Schotten–Baumann).

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[1] E. Koenigs and J. Freund, *Ber.*, **80**, 143 (1947).

[2] W. Baker, J. B. Harborne and W. D. Ollis, *J. Chem. Soc.*, 1303 (1952).

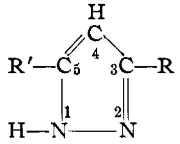
TABLE I

Reactants	Reacn.[a,b] prod.[a]	M.p., °C.	Color test, a, $FeCl_3$ b. $TiCl_3$	Formula of the reacn. prod.		Analyses, %
Hydrazine + Ib	[c]	181[i]	a, Blue	$C_{13}H_{12}O_4N_2$	Found	C, 59.8; H, 4.3; N, 10.7
			b, Deep orange		Calcd.	C, 60.0; H, 4.6; N, 10.8
Hydroxylamine + Ib	[d]	146	....	$C_{13}H_{11}O_5N$	Found	C, 60.0; H, 4.5
					Calcd.	C, 59.8; H, 4.2
Hydrazine + Ic	[e]	157[i]	a, Blue	$C_{14}H_{14}O_4N_2$[h]	Found	C, 61.4; H, 5.2; N, 10.6; $-OCH_3$, 22.4
			b, Deep orange		Calcd.	C, 61.3; H, 5.1; N, 10.2; $-OCH_3$, 22.6
Hydroxylamine + Ic	[f,g]	120–121	....	$C_{14}H_{13}O_5N$	Found	C, 61.2; H, 4.5; N, 4.8
					Calcd.	C, 61.1; H, 4.7; N, 5.1

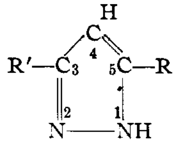
[a] Solvent for crystallization, dil. alcohol; yield above 85% in all reactions given. [b] The reaction products are colorless, soluble in aqueous sodium hydroxide (10%). [c] IIIb or IVb, 4-methoxy-5-[3(or 5)-hydroxymethyl-5(or 3)-pyrazolyl]-6-benzofuranol. [d] Vb or VIb, 4-methoxy-5-[5(or 3)-hydroxymethyl-3(or 5)-isoxazolyl]-6-benzofuranol. [e] IIIc or IVc, 4,7-dimethoxy-5-[3(or 5)-methyl-5(or 3)-pyrazolyl]-6-benzofuranol. [f] Vc or VIc, 4,7-dimethoxy-5-[5(or 3)-methyl-3(or 5)-isoxazolyl]-6-benzofuranol. [g] It is easily soluble in ethyl alcohol, but difficultly, soluble in light petroleum (b.p. 70–80°). [h] Active hydrogen, 0.7; calcd.: 0.7 (two active hydrogens). [i] Reaction with concd. sulfuric acid, yellow orange.

IIIb, differing from IIIa in having one more hydroxyl, furnished a tribenzoyl derivative.

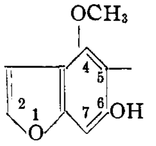
In contrast to the stability of visnagin (Ia), to hydroxylamine hydrochloride in acetic acid at room temperature,[3] we found that visnagin, khellol and khellin react rapidly with hydroxylamine hydrochloride in pyridine at the boiling point of the mixture. Flavone yields, under similar conditions, 3-*o*-hydroxyphenyl-5-phenylisoxazole[2] (V, R = phenyl, R′ = *o*-hydroxyphenyl).[2] By analogy, we give the reaction products obtained from Ia, Ib and II, the formulas Va, Vb and Vc, respectively, but do not wish to exclude the corresponding formulas VIa–c. The reaction products are soluble in aqueous alkali, their alcoholic solutions give a color reaction with aqueous ferric chloride solution. From Va (or VIa) and Vc (or VIc) monobenzoyl derivatives were obtained; Vb (or VIb) yields a dibenzoyl derivative (Schotten–Baumann). Va (or VIa) was recovered unchanged when boiled with 10% sodium hydroxide solution for one hour, followed by acidification. This stability toward alkali was to be expected, as according to Claisen,[4] 3,5-substituted isoxazoles are very resistant to alkali. The benzoyl derivative of Va (or VIa) was hydrolyzed to V or (VI) by the action of alkali.



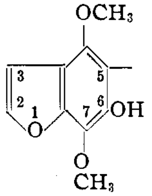
III



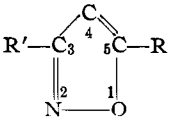
IV



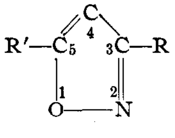
A



B



V



VI

IIIa, IVa, Va, VIa, R′ = A, R = CH_3
IIIb, IVb, Vb, VIb, R′ = A, R = CH_2OH
IIIc, IV, Vc, VIc, R′ = B, R = CH_3
IIId, IVd, R′ = *o*-HOC_6H_4, R = H

TABLE II

BENZOYL DERIVATIVES OF THE REACTION PRODUCTS MENTIONED IN TABLE I

Benzoyl deriv.[a] of	M.p., °C.	Solvent for cryst.	Formula of the benzoyl deriv.		Analyses, %
IIIb or IVb	129	MeOH	$C_{34}H_{24}O_7N_2$	Found	C, 71.7; H, 4.3; N, 5.0
				Calcd.	C, 71.3; H, 4.2; N, 4.9
Vb or VIb	132	MeOH	$C_{27}H_{19}O_7N$	Found	C, 69.0; H, 4.1; N, 3.1
				Calcd.	C, 69.1; H, 4.1; N, 3.0
IIIc or IVc	179	EtOH	$C_{28}H_{22}O_6N_2$	Found	C, 69.7; H, 4.5; N, 5.6
				Calcd.	C, 69.7; H, 4.6; N, 5.8
Vc or VIc	150	EtOH	$C_{21}H_{17}O_6N$	Found	C, 66.4; H, 4.3; N, 3.4
				Calcd.	C, 66.5; H, 4.5; N, 3.7

[a] The benzoyl derivatives obtained are colorless, insoluble in aqueous sodium hydroxide (10%).

Experimental[5]

Experiments with Hydrazine Hydrate. Visnagin (taken as an example).—Five grams of hydrazine hydrate in 10 ml. of warm alcohol was added to a solution of 1.2 g. of visnagin in 10 ml. of alcohol, and the mixture warmed for 15 minutes. The cooled mixture was diluted with water, the formed deposit was filtered and crystallized from benzene–light petroleum mixture, as colorless crystals, m.p. 142°. 4-Methyl-5-[3(or 5)-methyl-5(or 3)-pyrazolyl]-6-benzofuranol (IIIa or IVa) gives a blue color with ferric chloride, and a deep orange color with titanium chloride, dissolves in aqueous sodium hydroxide (10%), but is insoluble in hydrochloric acid (12%). It gives a yellow orange color reaction with concentrated sulfuric acid (Found: C, 64.3; H, 4.9; N, 12.3; $-OCH_3$, 12.7. $C_{13}H_{12}O_3N_2$ requires C, 63.9; H, 4.9; N, 11.5; $-OCH_3$, 12.7); yield about 85%.

Benzoylation.—The general procedure for carrying out a Schotten–Baumann reaction has been followed. The dibenzoyl derivative crystallizes slowly from alcohol as colorless crystals, m.p. 150°. It is insoluble in aqueous sodium hydroxide (10%) (Found: C, 71.2; H, 4.5; N, 6.0. $C_{27}H_{20}O_5N_2$ requires C, 71.1; H, 4.4; N, 6.2).

Experiments with Hydroxylamine Hydrochloride. Visnagin (taken as an example).—A mixture of 0.15 g. of hydroxylamine hydrochloride in 0.5 ml. of water, and 0.1 g. of visnagin in 1 ml. of pyridine was refluxed for 4 hours. The cooled mixture was acidified with dilute acetic acid; the deposit formed was filtered and crystallized from benzene–light-petroleum mixture, as colorless crystals, m.p. 146°. 4-Methoxy-5-[5(or 3)-methyl-3(or 5)-isoxazolyl]-6-benzofuranol (Va or VIa) is insoluble in water and soluble in aqueous sodium hydroxide (10%). The yield is *ca.* 85% (Found: C, 63.5; H, 4.8; N, 5.2. $C_{13}H_{11}O_4N$ requires C, 63.7; H, 4.5; N, 5.7.). It was recovered unchanged or almost unchanged when its solution in aqueous sodium hy-

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(3) *Cf.* preceding page 4992.

(4) L. Claisen, *Ber.*, 36, 3672 (1903).

(5) The color reactions with ferric chloride were carried out by dissolving the substance in alcohol and adding a small amount of dilute aqueous ferric chloride solution. The color reactions with titanium trichloride were carried out similarly. The reagent was titanium trichloride (15%), free from iron (E. Merck, Darmstadt, Germany). The hydrazine hydrate was 50%.

droxide (10%) was refluxed for one hour followed by cooling and acidification with dilute hydrochloric acid.

Benzoylation.—The benzoyl derivative (Schotten–Baumann method) was crystallized slowly from alcohol, as colorless crystals, m.p. 111°. It is insoluble in aqueous sodium hydroxide solution (10%) (Found: C, 68.3; H, 4.3; N, 3.5. $C_{20}H_{15}O_5N$ requires C, 68.8; H, 4.3; N, 4.0.). The benzoyl derivative was refluxed with aqueous sodium hydroxide solution (10%) for one hour, allowed to cool and acidified with dilute hydrochloric acid, the deposit was crystallized from benzene–petroleum-ether mixture and proved to be (Va or VIa) (m.p. and mixed m.p.).

The syntheses of the other substances mentioned in the theoretical part are listed in the Tables I and II.

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The Osmotic and Activity Coefficients of Calcium, Strontium and Barium Perchlorate at 25°

BY R. A. ROBINSON, C. K. LIM AND K. P. ANG

RECEIVED JUNE 23, 1953

Nicholson[1] has deduced the activity coefficients of magnesium, calcium, strontium and barium perchlorate from freezing point measurements; his results for the magnesium salt are in good agreement with those derived[2] from isopiestic vapor pressure measurements at 25°, the latter being higher by 0.003 in γ at 0.1 *m*. If the two sets of data are adjusted relative to the same value of $\gamma = 0.587$ at 0.1 *m*, the isopiestic values at other concentrations are higher, the difference rising to 0.043 at 1 *m*. Some time ago we made isopiestic measurements on calcium perchlorate and we have recently made measurements on the strontium and barium salts which can be compared with the data of Nicholson.

The stock solutions were prepared by adding a slight excess of the carbonate to perchloric acid (of "analytical" purity), filtering off the excess of carbonate and analyzing for the metal. Isopiestic measurements were made with calcium chloride as reference salt (Table I) and the osmotic and activity coefficients (Table II) calculated in the usual way. It proved very difficult to get reproducible results with the barium salt at concentrations less than 1 *m* and the results in this region should be accepted with caution. These solutions seemed to have a very low rate of evaporation and gave a degree of difficulty we have not experienced with any other solutions. The activity coefficients are of the magnitude we would expect for highly dissociated and hydrated salts. The curves for the calcium and strontium salts resemble those plotted from Nicholson's data at the freezing point but the barium salt exhibits a large temperature variation. For example, recalculating the freezing point data to refer to $\gamma = 0.523$ at 0.1 *m*, the activity coefficient of 0.512 at 1 *m* and 25° contrasts with 0.434 at the freezing point.

TABLE I

MOLALITIES OF ISOPIESTIC SOLUTIONS AT 25°

$CaCl_2$	Ca-$(ClO_4)_2$	$CaCl_2$	Ca-$(ClO_4)_2$	$CaCl_2$	Ca-$(ClO_4)_2$	$CaCl_2$	Ca-$(ClO_4)_2$
0.1176	0.1133	1.584	1.392	3.135	2.722	6.074	5.270
.2879	.2695	1.968	1.717	3.210	2.784	6.795	5.799
.3879	.3587	2.017	1.760	3.656	3.176	6.810	5.812
.5528	.5047	2.202	1.916	4.118	3.584	7.385	6.181
.6407	.5807	2.471	2.148	4.330	3.771	7.970	6.540
.8038	.7236	2.483	2.159	4.771	4.163	8.658	6.919
1.121	.9933	2.795	2.427	5.321	4.651		
$CaCl_2$	Sr-$(ClO_4)_2$	$CaCl_2$	Sr-$(ClO_4)_2$	$CaCl_2$	Sr-$(ClO_4)_2$	$CaCl_2$	Sr-$(ClO_4)_2$
0.1051	0.1038	1.066	0.9794	3.817	3.602	6.968	6.833
.1692	.1645	1.233	1.128	4.199	4.000	7.475	7.279
.2429	.2346	1.722	1.569	4.801	4.642	8.468	8.071
.3177	.3044	2.444	2.244	5.377	5.258	8.561	8.139
.4637	.4388	2.804	2.594	6.269	6.174	8.705	8.250
.8449	.7804	3.362	3.143				
$CaCl_2$	Ba-$(ClO_4)_2$	$CaCl_2$	Ba-$(ClO_4)_2$	$CaCl_2$	Ba-$(ClO_4)_2$	$CaCl_2$	Ba-$(ClO_4)_2$
0.2429	0.2409	1.611	1.665	2.437	2.641	3.828	4.502
.5100	.5041	1.917	2.017	2.757	3.053	4.462	5.462
.8711	.8651	2.163	2.319	3.303	3.766	4.629	5.694
1.270	1.292						

TABLE II

OSMOTIC AND ACTIVITY COEFFICIENTS AT 25°

	$Ca(ClO_4)_2$		$Sr(ClO_4)_2$		$Ba(ClO_4)_2$	
m	φ	γ	φ	γ	φ	γ
0.1	0.883	(0.565)	0.864	(0.532)	0.857	(0.523)
.2	.911	.540	.886	.497	.868	.480
.3	.942	.540	.915	.491	.884	.463
.4	.976	.552	.947	.497	.905	.458
.5	1.014	.573	.982	.511	.929	.461
.6	1.051	.598	1.017	.529	.954	.468
.7	1.089	.627	1.052	.550	.977	.476
.8	1.131	.664	1.090	.577	1.000	.486
.9	1.175	.706	1.130	.608	1.024	.499
1.0	1.219	.754	1.170	.643	1.046	.512
1.2	1.310	.866	1.249	.723	1.094	.544
1.4	1.405	1.007	1.329	.818	1.141	.580
1.6	1.503	1.179	1.413	.935	1.188	.621
1.8	1.605	1.393	1.492	1.067	1.233	.673
2.0	1.710	1.659	1.577	1.229	1.279	.717
2.5	1.992	2.66	1.789	1.767	1.394	.866
3.0	2.261	4.27	2.008	2.59	1.509	1.045
3.5	2.521	6.86	2.196	3.71	1.619	1.284
4.0	2.769	10.93	2.372	5.24	1.713	1.542
4.5	3.005	17.28	2.538	7.35	1.791	1.822
5.0	3.233	27.1	2.693	10.16	1.862	2.13
5.5	3.454	42.3	2.834	13.83	1.945	2.53
6.0	3.655	64.7	2.962	18.56	...	...
6.5	3.828	95.7	3.074	24.4	...	...
7.0	3.989	139.3	3.166	31.3	...	...
7.5	...	...	3.241	39.3	...	...
8.0	...	...	3.308	48.6	...	...

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[1] D. E. Nicholson (with W. A. Felsing), THIS JOURNAL, **72**, 4469 (1950); **73**, 3520 (1951).

[2] R. H. Stokes and B. J. Levien, *ibid.*, **68**, 333 (1946).