The **hydrochloride** was obtained from the picrate as colorless needles m. p. 206–207° (from methanol–ethyl acetate). *Anal.* Calcd. for $C_9H_{14}ClNO_2$: C, 53.1; H, 6.9. Found: C, 53.0; H, 6.8.

2-Hydroxy-3-methoxy-β-nitrostyrene.—A solution of 5.0 g. of freshly distilled 2-hydroxy-3-methoxybenzaldehyde, 2.5 ml. of nitromethane and 2 g. of ammonium acetate in 20 ml. of glacial acetic acid was refluxed for 2 hours. The cooled dark mixture was poured into water and the gummy product allowed to crystallize. The crude solid was recrystallized from benzene, with the aid of Norit. The yield of yellow needles, melting at 115–122° was 2.32 g. (37%). The analytical sample melted at 129–130°. *Anal.* Calcd. for $C_9H_9NO_4$: N, 7.2. Found: N, 7.2. Using a methanolic solution of methylamine as condensing agent only 18% of the nitrostyrene was obtained after seven days. The reaction failed using potassium hydroxide as condensing agent.

2-Hydroxy-3-methoxyphenethylamine.—The yield of the picrate of the amine obtained from 1.0 g. of 2-hydroxy-3-methoxy-β-nitrostyrene was 1.62 g. (81%), m. p. 168–170°; reported,[3b] m. p. 170°.

The **hydrochloride** crystallized from methanol–ethyl acetate as colorless plates, m. p. 177–178°; reported[3b] m. p. 175°.

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Praseodymium and Neodymium Complexes with 8-Quinolinol-5-sulfonic Acid

BY WILLIAM J. RAMSEY, DAVID L. DOUGLAS AND DON M. YOST

In a recent paper by Nakatsuka and Chang,[1] evidence is presented for the existence of higher oxidation states than three for praseodymium and neodymium in aqueous solution. They also present a method for the separation of these two neighboring rare earth elements. Because their findings would be of interest and significance, it was deemed important to repeat some of their experiments. Although we have not been able to confirm either the higher oxidation states or the separation method, there are constructive aspects to the chemistry involved that justify a brief note on it.

Nakatsuka and Chang subjected ammoniacal solutions containing 8-quinolinol-5-sulfonic acid and nitrates of praseodymium and neodymium to oxidation by the air and especially to anodic oxidation in a porous cup with a platinum anode. The solutions became dark reddish-brown in color; in the case of the more complete anodic oxidation, the solutions became opaque. For the separation, the oxidized mixtures were treated with sodium carbonate and glucose (reducing agent) and then heated, whereupon praseodymium(III) carbonate was reported to precipitate out, while the neodymium remained in solution.

In our own experiments an effort was made to confirm the separation method and to prepare, in solid form, the complex compounds that appear to exist in the mixtures indicated above.

Experimental

Reagents.—Samples of the light blue Nd_2O_3 and the jet black Pr_6O_{11}, each labeled 99% pure, were obtained from Research Chemicals, Incorporated, Burbank, California. Eastman Kodak Co. "white label" 8-quinolinol-5-sulfonic acid, recrystallized from 5% hydrochloric acid, was used throughout. All other chemicals were of Reagent Grade.

Tests for Higher Oxidation States.—To 100 cc. of 0.5 *N* ammonium hydroxide solution containing 1.5 g. of 8-quinolinol-5-sulfonic acid, was added 20 cc. of a solution containing 0.08 g. of praseodymium(III) as the nitrate; no precipitate formed. A similar blank solution containing no praseodymium was also prepared. On standing overnight exposed to the air both solutions became reddish-brown in color to about the same degree. Anodic oxidation for twenty minutes in a porous cup at 6 volts and 0.2 ampere caused both mixtures to become darkened to the extent of being opaque. No precipitate formed in either the test or blank solution.

It is evident that the color changes do not depend on the presence of praseodymium, and, therefore, no positive proof is provided at this stage that the praseodymium(III) was oxidized

Tests of Separation Procedure.—Solutions containing praseodymium, neodymium and mixtures of the two were prepared and treated as described above. To each such opaque solution were added 10 g. of sodium carbonate and 3 g. of glucose and the resulting mixture was heated for one and one-half hours on a steam-bath.

In the case of praseodymium alone, it was found that praseodymium(III) carbonate would not precipitate quantitatively as claimed; from 10 to 50% of it remained in solution. The amount which precipitated was determined by converting the carbonate to the oxalate, by igniting the oxalate in a muffle furnace to the black oxide, Pr_6O_{11}, and by weighing this oxide. Also, it was not necessary to add glucose in order to precipitate part of the praseodymium carbonate. In the case of neodymium alone, it partially precipitated as the carbonate at the point in the procedure where praseodymium was supposed to precipitate quantitatively. The precipitates of neodymium(III) oxalate, on ignition, decomposed to form the light blue oxide, Nd_2O_3. In the case of the mixed sample, no semi-quantitative separation was observed. The oxides obtained from the ignition of the oxalates, which resulted from the conversion of the carbonate precipitate and from the filtrate from the carbonate precipitation, were the same shade of rust brown.

Thus the reported procedure for the separation of neodymium and praseodymium is impracticable, and constitutes no evidence for the existence, in solution, of higher oxidation states of these elements. Indeed, in view of recent work by Popov and Glockler[2] it appears that no stable compounds of neodymium in a higher oxidation state than three exist.

Preparation of Complex.—Our efforts to prepare solid samples of the praseodymium(III) derivative of the ammonium salt of 8-quinolinol-5-sulfonic acid were fruitless. The attempt to prepare this substance was made by adding a concentrated solution of $PrCl_3$ to a concentrated solution of the ammonium salt of the sulfonic acid in an excess of ammonium hydroxide, and by further concentrating the resulting solution by gentle heating and evaporation. The solid obtained, when analyzed for praseodymium, nitrogen and sulfur, gave compositions which corresponded to no simple compound. It is likely that the difficulty was the same as that encountered by Jackson at the University of Illinois[3] in his successful attempts to prepare the lanthanum derivative of 8-quinolinol, $La(C_9H_6NO)_3$. This difficulty was the partial hydrolysis and decomposition of the desired derivative either in concentrated, supersaturated solutions, or by heating in the presence of water.

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(1) Y. Nakatsuka and T. Chang, *Acta Chimica Taiwanica*, 1, 87 (1949).

(2) Popov and Glockler, THIS JOURNAL, 71, 4114 (1949).

(3) University of Illinois, N6-ori, Quarterly Progress Reports, Nos. 10, p. 33; 11, p. 26; 12, p. 33; (1948–1949).

From the above observations, it seems clear that Nakatsuka and Chang have found interesting complexes of praseodymium(III) and neodymium(III) which are stable in ammoniacal solutions without the precipitation of the hydroxides. However, their proposal of the existence, in solution, of oxidation states of praseodymium and neodymium greater than three does not appear tenable.

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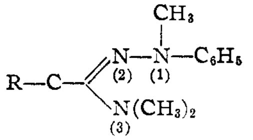
The Preparation of Some Tetrasubstituted Amidrazones

BY HENRY RAPOPORT AND ROBERT M. BONNER

We became interested in the preparation of tetrasubstituted amidrazones[1] of the general structure I as intermediates of possible value in another synthesis.



I

Both unsubstituted and monosubstituted amidrazones have been previously prepared by the reaction of the corresponding hydrazine with a nitrile, imido ester or imido chloride.[2] However, these methods are inapplicable to the synthesis of tetrasubstituted amidrazones, and no record of any completely substituted amidrazones could be found in the literature.

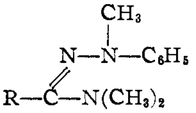
The synthesis of amidrazones of the type I has now been effected easily and in good yield by the condensation of the appropriately substituted amides and hydrazines in refluxing benzene in the presence of phosphorus oxychloride. In this manner, the N^1,N^3,N^3-trimethyl-N^1-phenylamidrazones of propionic, isobutyric and phenylacetic acids have been prepared; their characterization is summarized in Tables I and II.

Experimental

Dimethylamides.—The dimethylamides of propionic, isobutyric and phenylacetic acids were prepared by passing dry dimethylamine for two hours into a cooled, 50% solution of the respective acid chloride in benzene. The mixture was then filtered from dimethylamine hydrochloride, the precipitate washed with benzene, and the combined filtrate and washings distilled to give 90–95% yields of dimethylamide: **N,N-dimethylpropionamide**, b. p. 173–174°, n^{22}D 1.4402 (reported[3] b. p. 179.2–179.4° (765 mm.), n^{25}D 1.4371); **N,N-dimethylisobutyramide**, b. p. 178–179°,[4] n^{25}D 1.4388; **N,N-dimethylphenylacetamide**, b. p. 155° (10 mm.), m. p. 43–44° (reported[5] b. p. 155° (10 mm.), m. p. 43.5°).

TABLE I

TETRASUBSTITUTED AMIDRAZONES,



$R-C(=N-N(CH_3)-C_6H_5)-N(CH_3)_2$

-R	Yield, %	B. p., °C.	B. p., Mm.	n^{25}D	Formula	Analyses, %[a] Carbon Calcd.	Carbon Found	Hydrogen Calcd.	Hydrogen Found	Nitrogen Calcd.	Nitrogen Found	Equiv. wt.[b] Calcd.	Equiv. wt.[b] Found	pK_a[b]
CH_3CH_2	82	134	3	1.5618	$C_{12}H_{19}N_3$	70.2	70.2	9.3	9.1	20.5	20.4	205	210	9.3
$(CH_3)_2CH$	57	127	2	1.5538	$C_{13}H_{21}N_3$	71.2	71.4	9.7	9.5	19.2	19.4	219	220	9.5
$C_6H_5CH_2$	40	[c]		1.6008	$C_{17}H_{21}N_3$	76.4	76.5	7.9	7.7	15.7	15.7	267	268	8.0

[a] Microanalyses by V. H. Tashinian of this Laboratory. [b] Apparent pK_a values and equivalent weights were obtained by potentiometric titration with 0.1 N hydrochloric acid of 1–1.5 millimoles of amidrazone in 15 ml. of ethanol and 10 ml. of water. [c] Ordinary distillation caused decomposition; consequently purification was effected through the picrate (see Table II). The free base was liberated from the picrate with lithium hydroxide, extracted into ether, and distilled in a cold-finger sublimation apparatus at 200° (1 mm.) as a viscous oil.

TABLE II

PICRATES[a] OF AMIDRAZONES OF TABLE I

-R	M. p.,[b] °C.	Formula	Analyses, % Carbon Calcd.	Carbon Found	Hydrogen Calcd.	Hydrogen Found	Nitrogen Calcd.	Nitrogen Found
CH_3CH_2	173–174	$C_{18}H_{22}N_6O_7$	49.8	49.6	5.1	5.1	19.4	19.5
$(CH_3)_2CH$	150–151	$C_{19}H_{24}N_6O_7$	50.9	51.1	5.4	5.2	18.7	19.1
$C_6H_5CH_2$	144–145	$C_{23}H_{24}N_6O_7$	55.6	55.5	4.9	4.7	16.9	17.1

[a] The picrates were prepared by adding a saturated ethanolic solution of picric acid to the amidrazone in ethanol and were recrystallized from ethanol. [b] Corrected.

Amidrazones.—The tetrasubstituted amidrazones listed in Table I were prepared by the following general procedure. To a solution of 15.4 g. (0.1 mole) of phosphorus oxychloride in 50 ml. of dry benzene, heated under reflux,

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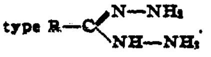
[1] This type of compound has also been referred to as a hydrazidine and as the hydrazone of an amide. Of the three possibilities, the amidrazone nomenclature appears to be the most concise and unambiguous. For example, the first compound in Table I (R = CH_3CH_2), in analogy with amidine nomenclature, would thus be named N^1,N^3,N^3-trimethyl-N^1-phenylpropionamidrazone. The hydrazidine designation could then be reserved for compounds of the type



$R-C(=N-NH_2)-NH-NH_2$.

[2] Wieland, "Die Hydrazine," Ferdinand Enke, Stuttgart, 1913, p. 192.

[3] Ruhoff and Reid, THIS JOURNAL, **59**, 401 (1937).

[4] *C. A.*, **40**, 3725[9] (1946), reports this compound as boiling at 175–176° (7 mm.). This is undoubtedly a typographical error; the original article [Gavrilov, Koperina and Klyucharova, *Bull. soc. chim. France*, [5] **12**, 773 (1945)] was unavailable.

[5] Taverne, *Rec. trav. chim.*, **16**, 33 (1897).