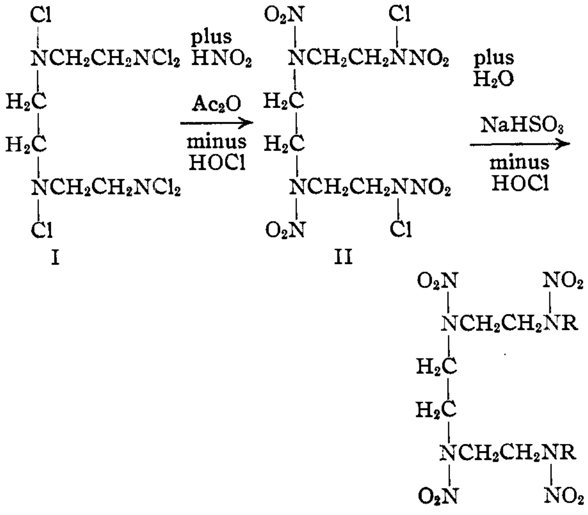
sensitive linkage (RNClR > $RNCl_2$) is known to decompose largely to the amine hydrochloride. The amine hydrochloride linkage has been found to revert to the chloramine in the presence of nitric acid in acetic anhydride.[1]

No attempt was made therefore to isolate the N-hexachlorotriethylenetetramine, I, from the chloroform solution in which it was prepared. Direct nitration in acetic anhydride solution yielded N^1,N^4-dichlorotriethylenetetranitramine, II, in fair yield, and this was converted readily to triethylenetetranitramine by means of aqueous sodium sulfite.



I

II

III (R = H)

IV (R = C_2H_5)

The alkali soluble III was characterized by conversion to N^1,N^4-diethyltriethylenetetranitramine, IV, with diazoethane.

Experimental[4]

Chlorination of Triethylenetetramine.—A solution of 49 g. (0.3 mole) of triethylenetetramine and 252 g. (3.0 moles) of sodium bicarbonate in 1500 cc. of water was combined with 100 cc. of chloroform and treated at 25° with a rapid stream of chlorine for ten hours. The chloroform layer was separated and dried with calcium chloride. This chloroform solution was used for the nitration described subsequently. Analysis showed that it contained five-sixths of the expected electropositive chlorine.

Dichlorotetranitrotriethylenetetramine.—One-half of the chloroform solution (assumed to be 0.15 mole of N-hexachlorotriethylenetetramine) was added proportionately with 36.3 ml. (0.9 mole) of 98% nitric acid to 143 ml. (1.5 mole) of acetic anhydride over one hour. The temperature was maintained at 40° during addition and subsequently for one hour. After the mixture was chilled to 0° for nine hours it was filtered to remove 25 g. of material melting roughly at 114–116°. This crude product when analyzed for electropositive chlorine seemed to be a mixture of N^1-chloro and N^1,N^4-dichlorotriethylenetetranitramine. If it were the latter compound the yield would be 42% of theoretical.

Triethylenetetranitramine.—When the crude reaction product (25 g.) was suspended in 250 cc. of cold stirred half-saturated sodium sulfite solution for nine hours the electropositive chlorine was consumed. The suspension was then filtered to remove 17.5 g. (36% yield from triethylenetetramine), melting at 159–160°. This material was dissolved in alkali (*p*H 8) and filtered. It was reprecipitated (m. p. 168°) by acidification to *p*H 4 with dilute hydrochloric acid. Final purification (m. p. 174.1°) was effected by two crystallizations from hot nitromethane (10 cc. per g.). The compound gave a positive Franchimont test for a nitramine. It formed an insoluble silver salt and a relatively insoluble pyridine salt.

Anal. Calcd. for $C_6H_{14}N_8O_8$: C, 22.1; H, 4.30; N, 34.4. Found: C, 22.4; H, 4.25; N, 33.9.

N^1,N^4-Diethyltriethylenetetranitramine.—A suspension of 0.5 g. of triethylenetetranitramine in an ether solution containing 0.25 g. of diazoethane evolved gas rapidly. Evaporation of the ether left a sirup which gradually solidified during four days. It was crystallized from ethanol to melt at 68–70° (yield 50% of theoretical). A recrystallization raised this melting point to 96.5–96.8°. The compound was insoluble in alkali, and it gave a positive Franchimont test for a nitramine.

Anal. Calcd. for $C_{10}H_{22}N_8O_8$: C, 31.5; H, 5.82; N, 29.3. Found: C, 31.9; H, 5.85; N, 29.1.

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The Rare Earth Metals and their Compounds. VIII. An Improved Method for the Synthesis of Some Rare Earth Acetylacetonates[1a]

BY JOSEPH G. STITES, C. N. MCCARTY AND LAURENCE L. QUILL

Methods reported in the literature[1-7] for the preparation of the acetylacetonates of the rare earths involve, for the most part, the addition of a solution of sodium or ammonium acetylacetonate to a dilute acid solution of the rare earth nitrate. The yields are either unreported or are low.

This study was undertaken to observe the effect of changing the acidity on the formation of the rare earth acetylacetonates since (a) acetylacetone is a weak acid and (b) completeness of precipitation of many rare earth compounds is *p*H dependent. Also, since acetylacetone is so easily oxidized it was thought that part of the lower yield resulting when the nitrates of the rare earths are used was due to an oxidation effect and, consequently, that the chlorides might give better results.

Experimental

A weighed quantity of rare earth oxide was dissolved in the minimum amount of dilute hydrochloric acid and the *p*H of the solution adjusted by the addition of dilute ammonium hydroxide to a value of approximately 5.0 as measured by the glass electrode. A solution of ammonium acetylacetonate was prepared by adding concen-

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(4) All melting points have been corrected against known standards.

(1a) Presented before the Division of Physical and Inorganic Chemistry of the American Chemical Society at the Chicago meeting April 1948.

(1) W. Biltz, *Ann.*, **331**, 334 (1904).

(2) G. Jantsch and E. Meyer, *Ber.*, **53B**, 1577–1587 (1920).

(3) G. Urbain, *Bull. soc. chim.*, [3] **15**, 338–347 (1896).

(4) G. Urbain, *Ann. chim. phys.*, [7] **19**, 223 (1900).

(5) R. C. Young and J. Kovitz, "Inorganic Syntheses," Vol. II, McGraw-Hill Book Co., New York, 1947, p. 123.

(6) R. A. Staniforth, L. L. Quill and J. P. McReynolds, Thesis, Ohio State University, 1943, unpublished.

(7) J. K. Marsh, *J. Chem. Soc.*, 1084 (1947).

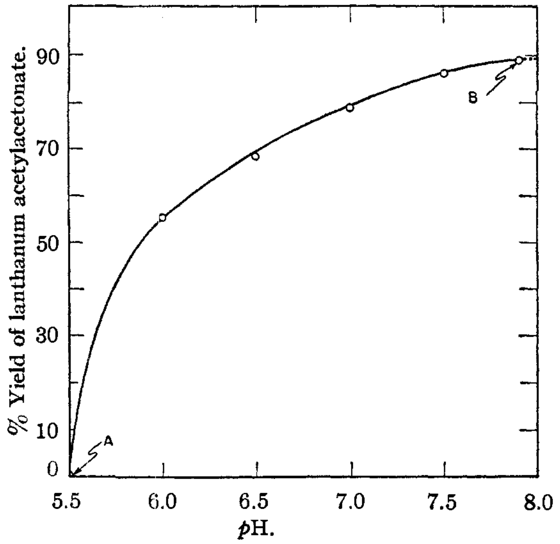

Fig. 1.—Point A represents pH of solution at first noticeable yield. Point B represents highest pH used for precipitation in order to prevent formation of lanthanum hydroxide.

trated ammonium hydroxide together with sufficient water for solution to an amount of freshly distilled acetylacetone which was 50% in excess of that required for complete reaction with the rare earth oxide. The solution of ammonium acetylacetonate was added slowly with stirring to the rare earth chloride solution. The pH of the reaction mixture was maintained at all times at a value just below that of the pH of precipitation of the corresponding rare early hydroxide[8] by the addition of either dilute ammonium hydroxide or hydrochloric acid as required. The mixture was stirred for twelve hours to insure conversion of any basic acetylacetonate to the normal compound and to allow for completeness of reaction. Crystalline precipitates of the rare earth acetylacetonates were obtained which were filtered, air dried for twenty-four hours, and then placed over magnesium perchlorate for four days. The precipitates were then weighed and their melting points obtained. For comparison of yields the same compounds were prepared using nitric acid in place of hydrochloric acid. The following table shows typical experimental data obtained from both nitrate and chloride solution.

TABLE I

Rare earth	Oxide taken, g.	pH	Yield, % Chlor.	Nit.	M. p., °C. obs.	lit.	
La	5.3	7.8	89	75	142–143	142–143[6]	
Ce	11.5[a]	6.9	83	74	146–147	145[1]	
Pr	5.47	6.5	90	65	143–144	146[1]	138–139[6]
Nd	5.47	6.5	96	67	144–145	144–146[1]	143–144[6]
Sm	5.68	6.5	96	88	144–145	146–147[1]	143–144[6]
Eu	2.85	6.5	98	90	144–145	144–145[8]	
Y	3.67	6.2	93	89	131–132	131[2]	129–130[6]

[a] Oxalate converted to chloride or nitrate.

The agreement of melting points obtained as compared to those recorded in the literature[1–7] even after purification indicates a product of high purity.

In preparing these acetylacetonates it was observed that if the solution was too acidic no precipitate was formed and if too basic a gelatinous product was obtained. Melting points of different samples of the gelatinous type of material were not consistent.

The variation in the yield of rare earth acetylacetonates with change in pH of the solution was determined by a series of experiments in which the amount of rare earth acetylacetonate formed in a solution of known pH was determined. Below is a typical curve drawn from data obtained in the preparation of lanthanum acetylacetonate.

It is obvious from the curve that the yield of the acetylacetonate is a function of the pH of the solution.

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[8] T. Moeller and H. E. Kremers, *Chem. Rev.*, **37**, I, 97–159 (1945).

Some Nuclear Halogenated Derivatives of α,α-Dihydroxymalonanilide

BY BENJAMIN WITTEN AND HAROLD H. ROSEN

Plowman and Whitely[1] have described the synthesis of α,α-dihydroxymalonanilide and 4,4′-dimethyl-α,α-dihydroxymalonanilide. We have extended the series to include three nuclear halogenated derivatives, the 4,4′-dichloro-, the 4,4′-dibromo- and the 2,2′,4,4′-tetrachloro-, α,α-dihydroxymalonanilides, following essentially the method of Plowman and Whitely.

Experimental

Nuclear Halogenated Malonanilide (I).—These compounds were prepared by the method of Chattaway and Mason.[2] The conversion of these compounds to the corresponding nuclear halogenated isonitroso N-ether and α,α-dihydroxymalonanilide was based on the method of Whitely,[3] and Plowman and Whitely.[1]

Nuclear Halogenated Isonitrosomalonanilide (II).—Into a 500-ml. three-necked flask equipped with a mechanical stirrer, gas inlet tube and thermometer was placed 0.05 mole of I suspended in 200 ml. of chloroform. The suspension was cooled to 0° and nitrosyl chloride (approximately 10 g.) was passed into the mixture until the color of the liquid became reddish-brown (about one hour). The white solid gave way to a yellow precipitate. It was filtered and crystallized from a 1:1 mixture of dioxane and alcohol. Yellow crystals of nuclear halogenated isonitrosomalonanilide were obtained.

The nitrosyl chloride used in the above synthesis was prepared by the method of Coleman, Lillis and Goheen.[4] This procedure was modified by using a 500-ml. three-necked flask and mechanical stirring in the preparation. The nitrosyl chloride was used without purification.

N-Methyl Ether of Nuclear Halogenated Isonitrosomalonanilide (III).—Into a 1-liter three-necked flask equipped with a mechanical stirrer, thermometer and dropping funnel was suspended 0.04 mole of II in 300 ml. of ether. The reaction was carried out at 0°. A solution of diazomethane, which was prepared from 13 g. of nitrosomethylurea[5] in 100 ml. of ether, was added dropwise. Nitrogen was evolved during the reaction. The mixture was allowed to warm up to room temperature. The yellow solid was filtered off and crystallized from absolute ethanol.

Nuclear Halogenated α,α-Dihydroxymalonanilide (IV).—Into a 500-ml. 3-necked flask, equipped with a mechanical stirrer and gas inlet tube, was suspended 0.02 mole of III in 150 ml. of chloroform. A stream of hydrogen chloride was allowed to pass first through glass wool saturated with water and then through the suspension. The

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[1] Plowman and Whitely, *J. Chem. Soc.*, **125**, 587 (1924).

[2] Chattaway and Mason, *ibid.*, **97**, 341 (1910).

[3] Whitely, *ibid.*, **83**, 34 (1903).

[4] H. S. Booth, Ed., "Inorganic Syntheses," Vol. I, McGraw-Hill Book Co., Inc., New York, N. Y., 1939.

[5] Gattermann and Wieland, "Laboratory Methods of Organic Chemistry," The Macmillan Company, New York, N. Y., 1937.