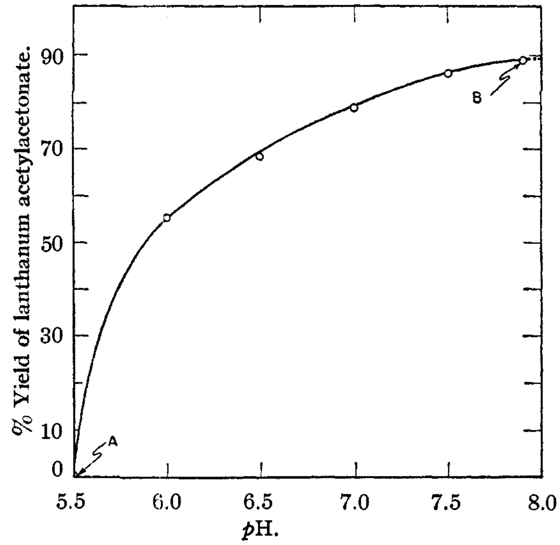

Fig. 1.—Point A represents *p*H of solution at first noticeable yield. Point B represents highest *p*H used for precipitation in order to prevent formation of lanthanum hydroxide.

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 *p*H of the reaction mixture was maintained at all times at a value just below that of the *p*H 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.	*p*H	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[4]	
Y	3.67	6.2	93	89	131–132	131[3]	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 *p*H of the solution was determined by a series of experiments in which the amount of rare earth acetylacetonate formed in a solution of known *p*H 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 *p*H of the solution.

CONTRIBUTION FROM THE
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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.

TABLE I

NUCLEAR HALOGENATED α,α-DIHYDROXYMALONANILIDE AND INTERMEDIATES

Derivative	Formula	M. p., °C.	Yield, %	Analyses, %					
				Carbon		Hydrogen		Nitrogen	
				Found	Calcd.	Found	Calcd.	Found	Calcd.
Nuclear Halogenated Isonitrosomalonanilide (II)									
4,4'-Dichloro	$C_{15}H_{11}N_3O_3Cl_2$	215	80	51.5	51.2	3.0	3.2	11.8	11.9
2,2',4,4'-Tetrachloro	$C_{15}H_9N_3O_3Cl_4$	215	67	42.7	42.8	2.0	2.1	10.1	10.0
4,4'-Dibromo	$C_{15}H_{11}N_3O_3Br_2$	226	38	41.0	40.8	2.6	2.5	9.4	9.5
N-Methyl Ether of Nuclear Halogenated Isonitrosomalonanilide (III)									
4,4'-Dichloro	$C_{16}H_{13}N_3O_3Cl_2$	185	69	52.7	52.5	3.6	3.6	11.8	11.5
2,2',4,4'-Tetrachloro	$C_{16}H_{11}N_3O_3Cl_4$	198	83	44.7	44.2	2.6	2.6	9.6	9.7
4,4'-Dibromo	$C_{16}H_{13}N_3O_3Br_2$	186	44	42.5	42.2	2.8	2.9	9.0	9.2
Nuclear Halogenated α,α-Dihydroxymalonanilide (IV)									
4,4'-Dichloro	$C_{15}H_{12}N_2O_4Cl_2$	208	21	51.0	50.7	3.2	3.4	8.2	7.9
2,2',4,4'-Tetrachloro	$C_{16}H_{10}N_2O_4Cl_4$	190	19	42.7	42.5	2.2	2.4	6.7	6.6
4,4'-Dibromo	$C_{16}H_{12}N_2O_4Br_2$	166	50	40.6	40.5	2.6	2.7	6.4	6.3
O-Methyl Ether of 4,4'-Dibromo-isonitrosomalonanilide (V)									
	$C_{16}H_{13}N_3O_3Br_2$	219	10	42.3	42.2	3.1	2.9	8.8	9.2

hydrogen chloride was passed through for one hour. The yellow solid gave way to a white precipitate. The solid (IV) was filtered off and crystallized from glacial acetic acid. The chloroform filtrate contained an additional quantity of IV. This was recovered by removing the solvent under reduced pressure on the water-bath and crystallizing the residue from glacial acetic acid.

In the preparation of 4,4'-dibromo-α,α-dihydroxymalonanilide a second compound was isolated in 16% yield from the chloroform filtrate. After removing the solvent under reduced pressure on the water-bath, the residue was crystallized from alcohol. There was obtained as colorless crystals a compound melting at 219°. Its chemical composition indicated the conversion of some N-methyl ether to the O-methyl form (V). This conversion was similar to that reported by Plowman and Whitely[1] in the preparation of mesox p-toluidide.

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Branched Structure of Guaran

BY ROY L. WHISTLER, TSIANG KWANG LI AND WILLIAM DVONCH

The principal polysaccharide of guar endosperm has been shown to be homogeneous[1] as to composition and to consist of anhydrogalactose and anhydromannose units in the ratio of one to two.[1,2] For convenience in designation, this particular polysaccharide has been given the name guaran.[1,3] Its triacetate can be formed into strong films which can be elongated 550% and thereby become birefringent, but they do not develop crystallinity which can be detected by X-ray examination. This has been taken to indicate the presence either of linear molecules in which a random distribution of anhydrogalactose and anhydromannose units occur or of a chain predominantly linear but with branches of very short length.[1] Recently Swanson[4] has shown that the galactose units occur principally as chain ends since from the methylated polysaccharide approximately 90% of the galactose can be recovered as 2,3,4,6-tetramethylgalactose. Consequently, one galactopyranoside end unit occurs for approximately two anhydromannose units. On oxidation of guaran with periodate Moe, Miller and Iwen[2] found that one mole of oxidant is consumed for each anhydrosugar unit present. This led them to conclude that the polysaccharide contained 1,4-glycosidic units although the possibility of branching was not eliminated.

The structure suggested by Swanson[4] is supported by work reported here on the periodate oxidation of guaran. In agreement with Moe, Miller and Iwen it is found that one mole of oxidant is consumed for each anhydrosugar unit present; but, in addition, it is found that by use of the oxidation method of Hirst, *et al.*,[5] one mole of formic acid is produced for approximately 2.7 anhydroglycosidic units. This indicates a large number of pyranosidic non-reducing end units or about one for two units of the main chain. Hence, one way to account for both the yield of formic acid and the fact that the polysaccharide consumes but one mole of oxidant for each anhydroglycosidic unit is to assume that guaran consists predominantly of a chain of anhydroglycosidic units one-half of which bear a glycopyranoside unit in conformity with the structure proposed by Swanson. Such a structure would require that on periodate oxidation the single unit side chains are split twice with the formation of one molecule of formic acid, that one-half of

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[1] E. Heyne and R. L. Whistler, THIS JOURNAL, **70**, 2249 (1948).

[2] O. A. Moe, S. E. Miller and M. H. Iwen, *ibid.*, **69**, 2621 (1947).

[3] R. L. Whistler, *Chem. Ind.*, **62**, 60 (1948).

[4] W. Swanson, paper presented before the Division of Sugar Chemistry and Technology at the 112th meeting of the American Chemical Society, New York, 1947.

[5] F. Brown, S. Dunstan, T. G. Halsall, E. L. Hirst and J. K. N. Jones, *Nature*, **156**, 785 (1945); T. G. Halsall, E. L. Hirst and J. K. N. Jones, *J. Chem. Soc.*, 1399 (1947); and private communication from Dr. E. L. Hirst.