

Note on the Structures of the Gallium and Indium Trihalides

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Brode² recently published the results of an electron-diffraction investigation of the structures of the so-called trihalides of aluminum, gallium and indium. We believe that the interatomic distances which he reported (given in row *a* of the table) have been falsified by his application of an unsuitable "correction,"³ and that the values given below in rows *b* and *c* are significantly more reliable. Row *b* gives the values found by Brode with the use of the usual correlation method⁴ (omitting the Wierl correction), while those of row *c* are the ones we have obtained by the appli-

ima of the radial distribution functions substantiate Brode's conclusion that under the conditions of his experiments gallium tri-iodide is monomeric and coplanar, whereas the five other trihalides are dimeric. Inasmuch as we could not take account of the minima, for which Brode reported no measurements, the radial distribution functions tend to show spurious features, in these cases beyond the first two peaks, and we can draw no conclusions with regard to the conformation of the dimers.

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TABLE I

AVERAGE M-X BOND LENGTHS IN THE TRIHALIDES OF GALLIUM AND INDIUM

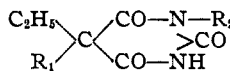
		Cl	Br	I
Ga	^a	2.16	2.35	2.40 ^d
	^b	2.22	2.41	2.48
	^c	2.22	2.34	2.50
In	^a	2.39	2.49	2.67
	^b	2.46	2.56	2.76
	^c	2.46	2.58	2.76

^a Brode's "corrected" value. ^b Brode's uncorrected value. ^c From the first peaks of the radial distribution functions. ^d GaI₃, coplanar equilateral triangle.

TABLE I

1-ARALKYL-5-ETHYL-5-ALKYL BARBITURIC ACIDS

R ₁	R ₂	M ₀ p. °C.	Formula	Analyses, %			
				Calcd.		Found	
				C	H	C	H
<i>n</i> -C ₄ H ₉	C ₆ H ₅ CH ₂	64	C ₁₇ H ₂₂ O ₃ N ₂	67.50	7.34	67.79	7.59
<i>n</i> -C ₄ H ₉	C ₆ H ₅ CH ₂ CH ₂	74	C ₁₈ H ₂₄ O ₃ N ₂	68.31	7.64	68.76	7.83
<i>i</i> -C ₄ H ₁₁	C ₆ H ₅ CH ₂	87-88	C ₁₈ H ₂₄ O ₃ N ₂	68.31	7.64	68.38	7.56
<i>i</i> -C ₄ H ₁₁	C ₆ H ₅ CH ₂ CH ₂	106-107	C ₁₉ H ₂₆ O ₃ N ₂	69.05	7.93	69.18	7.87



cation of the radial distribution method⁵ to his data. These two sets of values agree reasonably well except in the case of Ga₂Br₆.

The bond angle values (\angle XMX) indicated by the relative positions of the first and second max-

(1) Present address, Shell Development Company, Emeryville, California.

(2) Brode, *Ann. Physik*, **37**, 344 (1940).

(3) The correction is one due to Wierl (*ibid.*, **8**, 521 (1931)), and implies a procedure of measurement different from that which has been found suitable by Pauling and his co-workers. Almost certainly this correction should not have been applied to Brode's measurements, for his measurements on aluminum chloride agree well with those reported by Palmer and Elliott (*THIS JOURNAL*, **60**, 1852 (1938)).

(4) L. Pauling and L. O. Brockway, *J. Chem. Phys.*, **2**, 867 (1934).

(5) L. Pauling and L. O. Brockway, *THIS JOURNAL*, **57**, 2684 (1935); V. Schomaker, A. C. S. meeting, Baltimore, Md., April, 1939.

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Chaulmoogryl Quaternary Salts¹

Since favorable bacteriological results have been obtained with methiodides and benzochlorides from mixtures of chaulmoogryl and hydncarpyldimethylamines, it was decided to prepare some pure substances of this type.

Chaulmoogryl bromide² was heated in a bomb-tube at 105-110° with 33% methanolic dimethylamine in excess.

(1) Dittmar, *Z. Krebsforsch.*, **49**, 515 (1939), mentions a "Chaulmoogryl Zephirol." So far as the authors know these compounds have not been described.

(2) Sacks and Adams, *THIS JOURNAL*, **48**, 2397 (1926).

TABLE I
 CHAULMOOGRYL AND OCTADECYLTRIALKYLAMMONIUM IODIDES, $R_1R_2Me_2NI$

R ₁	R ₂	Appearance	M. p., °C.	Formula	Analyses, %			
					Calcd.		Found	
					C	H	C	H
C ₈ H ₇ (CH ₂) ₁₃	CH ₃	Irregular plates	> 170 (dec.)	C ₂₁ H ₄₂ NI	57.89	9.73	57.83	10.00
C ₁₈ H ₃₇	CH ₃	Platelets	227-230 (dec.)	C ₂₁ H ₄₆ NI	57.37	10.54	57.29	10.54
C ₈ H ₇ (CH ₂) ₁₃	C ₆ H ₅ CH ₂	Yellow leaflets ^a Yellow needles ^b	99	C ₂₇ H ₄₆ NI	63.36	9.07	63.20	9.05
C ₁₈ H ₃₇	C ₆ H ₅ CH ₂	Elongated plates	93	C ₂₇ H ₅₀ NI	62.86	9.78	62.92	9.91

^a From benzene. ^b From water.

The resulting tertiary amine boiled at 170° (0.5 mm.) and solidified in the refrigerator.

Chaulmoogryldimethylamine reacted with methyl iodide in absolute ether to form the methiodide, which is soluble in hot alcohol, sparingly soluble in cold alcohol, water, ethyl acetate and benzene, and insoluble in ether.

Attempts to prepare quaternary salts from the reaction of chaulmoogryldimethylamine with benzyl chloride, *p*-chlorobenzyl chloride and α -menaphthyl chloride resulted only in the formation of oils which presumably were in the main the desired quaternary salts but did not crystallize. Chaulmoogryldimethylbenzylammonium iodide, however, prepared from the chloride and sodium iodide, crystallized readily. It is soluble in alcohol, hot benzene, ethyl acetate and acetone, sparingly soluble in water and cold benzene, insoluble in ether and hexane.

For purposes of comparison octadecyltrimethylammonium iodide³ and octadecyldimethylbenzylammonium iodide were prepared, the latter from the tertiary amine and benzyl iodide. Data on these and the preceding compounds are presented in Table I.

(3) Mentioned, but not described, by Shelton, Van Campen and Nisonger, at the Boston meeting of the Am. Chem. Soc., Sept., 1939.

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1,1,1-Trichloro-2-hydroxy-3-nitroalkanes and their Reduction Products

The halogenated nitroalcohols were made by a procedure essentially the same as that described by Nicodemus and Wulff.¹ Four-tenths of a mole (66.2 g.) of chloral hydrate was dissolved in a mixture of 200 cc. of water and 15 cc. of concentrated hydrochloric acid, in a 500-cc. round-bottomed, three-necked flask equipped with a mechanical stirrer and a thermometer dipping below the surface of the solution. A slight excess of nitroparaffin was added and the stirrer was started. A saturated aqueous solution of potassium carbonate was added until the mixture was just alkaline to litmus. The mixture was heated in a water-bath at a temperature of 50-52° for two hours (six hours when 1-nitropropane was used), with constant stirring. The dark yellow lower layer was removed and fractionally distilled under reduced pressure. The results are summarized in Table I.

(1) Nicodemus and Wulff, U. S. Patent 2,123,556 (1938).

The halogenated nitroalcohols were reduced at room temperature using 0.1 mole of the nitro compound dissolved in 150 cc. of absolute ethyl alcohol, 9 g. of freshly prepared Raney nickel catalyst² and starting with an initial hydrogen pressure of about 55 pounds per square inch. The catalyst was removed by suction filtration and the dark green filtrate was concentrated by distilling the alcohol under reduced pressure. Attempts to remove the color by treatment with decolorizing carbon were unsuccessful. Consequently, the dark brown or black solids were treated with benzoyl chloride in alkaline solution. The benzoyl derivatives were washed well with water and recrystallized by dissolving in hot ethyl acetate and then adding ligroin to the cooled solution. The time required for practically complete reduction, the melting points and analyses of the benzoyl derivatives are also given in Table I.

TABLE I

Nitroparaffin	Nitromethane	Nitroethane	1-Nitropropane
Reduction time, hours	2	2	20
Yield, %	63	53	36
B. p. { °C.	138-146 ^a	134-140 ^b	136-142
{ Mm.	13	9	10
Nitrogen, % { Calcd.	6.70	6.29	5.92
{ Found	6.75 6.68	6.21 6.19	5.86 5.82
Benzoyl deriv., m. p., °C., cor.	167.4	182.5	195.2
Nitrogen, % { Calcd.	4.96	4.72	4.51
{ Found	5.01 4.98	4.77 4.79	4.59 4.53

^a M. p., 44.7-45.7°, cor.; Henry,³ 42-43°; Chattaway and Witherington,⁴ b. p. 119° (3 mm.). ^b Chattaway, Drewitt and Parkes,⁵ b. p. 115° (2 mm.).

In an attempt to obtain some pure 1,1,1-trichloro-2-hydroxy-3-aminopropane, it was found that the addition of acetone to a concentrated alcoholic solution of the amine resulted in the precipitation of an almost white solid. Repeated washing of the solid with acetone followed by recrystallization from a mixture of xylene and absolute alcohol and spontaneous evaporation of the solvent yielded white crystals which melted at 167.4-167.7° (cor.). The losses involved in this method of purification were enormous.

Anal. Calcd. for C₃H₆Cl₃NO: N, 7.84. Found: N, 7.69, 7.80.

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(2) Covert and Adkins, *THIS JOURNAL*, **54**, 4116 (1932).

(3) Henry, *Bull. soc. chim.*, **32**, 17 (1896).

(4) Chattaway and Witherington, *J. Chem. Soc.*, 1178 (1935).

(5) Chattaway, Drewitt and Parkes, *ibid.*, 1294 (1936).