

## NEW PRODUCTS FROM FISH OILS

### Part IV - Preliminary Investigations on Alkyl Halides, Silicones, and Quaternary Ammonium Salts

By Edward H. Gruger, Jr. \*

#### ABSTRACT

LONG-CHAIN ALKYL HALIDES WERE PREPARED FROM PURE CETYL ALCOHOL, N-OCTADECYL ALCOHOL, AND OLEYL ALCOHOL. SOME ALKYL HALIDES WERE PREPARED FROM ALCOHOLS DERIVED FROM MENHADEN AND PILCHARD OILS. THESE COMPOUNDS WERE USED TO PREPARE SILICONES AND QUATERNARY AMMONIUM SALTS.

THE SILICONES PREPARED RESULTED FROM THE HYDROLYSIS AND SUBSEQUENT DEHYDRATION OF CHLOROSILANES OF THE TYPE  $RSiCl_3$ . THESE ALKYLTRICHLOROSILANES WERE PRODUCTS OF ALKYL MAGNESIUM HALIDE REACTIONS WITH SILICON TETRACHLORIDE.

THE QUATERNARY AMMONIUM SALTS ARE A COMBINATION OF THE ALKYL HALIDES AND TRIETHYLAMINE. THE LONG-CHAIN, POLYUNSATURATED ALKYLTRIETHYLAMMONIUM BROMIDES FROM FISH OIL ARE BEING TESTED AS ORE-FLOTATION COLLECTORS AND AS FUNGICIDES FOR THE CITRUS INDUSTRY.

#### INTRODUCTION

There is great need for research and development of derivatives <sup>1/</sup> prepared from fish-oil fatty acids. In the past, relatively little work has been done on these derivatives as compared with that done on the derivatives from the fatty acids of vegetable and animal oils.



Fig. 1 - Ultraviolet absorption measurements being made on long-chain fatty alcohols used to prepare alkyl halides.

Fish oils are known to be unique in containing a high percentage of long-chain fatty acids with many double bonds. These unique properties of fish oils make them potentially valuable for the manufacture of many industrial and pharmaceutical products (Stansby 1956). The present paper is one in a series reporting the research now being carried out at the Seattle Technological Laboratory on these potential products from fish oils.

Polyunsaturated fatty alcohols (Gruger 1956) have been prepared from fish oils and are being used as the starting material in the preparation of other derivatives. Polyamino fatty acids (McDonald and Gruger 1956), alkyl halides, silicones, and quaternary ammonium salts are presently the compounds being studied in the research program.

**ALKYL HALIDES:** The alkyl halides prepared from fish oils are the products of direct reaction of the fatty alcohols with an appropriate halogenating agent. Special

\*ORGANIC CHEMIST, FISHERY TECHNOLOGICAL LABORATORY, BRANCH OF COMMERCIAL FISHERIES, U. S. FISH AND WILDLIFE SERVICE, SEATTLE, WASH.

<sup>1/</sup>THE TERM DERIVATIVE IS USED IN ITS BROADEST SENSE. THUS, ANY GROUP OF COMPOUNDS THAT CAN BE PREPARED FROM FATTY ACIDS, EITHER DIRECTLY OR INDIRECTLY, IS CONSIDERED AS A FATTY-ACID DERIVATIVE. NOTE: "PART I - INTRODUCTION" APPEARED IN THE AUGUST 1956 (P. 1) ISSUE; "PART II - POLYAMINO FATTY ACIDS DERIVED FROM FISH OILS" IN SEPTEMBER 1956 (P. 7) ISSUE; AND "PART III - PREPARATION AND SEPARATION OF FATTY ALCOHOLS MADE FROM FISH OILS--A PRELIMINARY STUDY" IN THIS ISSUE (P. 13) OF COMMERCIAL FISHERIES REVIEW.

attention is being given to the long-chain polyunsaturated alkyl halides, although the preliminary work has been centered on saturated compounds that are commercially available in a relatively high state of purity.

Alkyl halides have numerous applications. Employed in various coupling reactions they are used to prepare long-chain hydrocarbons. Alkyl magnesium halides--commonly called Grignard reagents--offer a means of producing many useful compounds of distinct chemical structures, such as silicones, primary alcohols, substituted secondary and tertiary alcohols, ketones, and sulfinic acids. Alkyl halides are also useful in undergoing displacement reactions to form such compounds as nitriles, ethers, and mercaptans. Each one of these products prepared from the alkyl halides have great potential utility.

**SILICONES:** Another field of investigation has been the silicones. McGregor (1954) defines a silicone as "a compound containing the elements of silicon, oxygen and organic groups, the silicon being present in sufficient amount to affect the properties measurably." Silicones are known to be quite stable at high temperatures, to be somewhat resistant to oxidation, and to have good lubricating and water-repellent properties. Silicones containing long-chain polyun-

saturated alkyl groups would probably possess special properties and would have interesting potential uses. There is a possibility that a highly stable drying oil or a tough resilient copolymer could result from this type of silicone.

**QUATERNARY AMMONIUM SALTS:** During the work on the alkyl halides, a satisfactory derivative was sought for use in the identification of the various long-chain alkyl halides that were being synthesized. Quaternary ammonium salts were chosen because of their relative ease of formation and reasonably sharp melting points. (With these compounds, a sharp melting point, however, does not necessarily indicate purity.) The quaternary ammonium salts have recently become commercially important as germicides and as surface-active agents in the textile field (Harwood 1952). Ralston (1948) has suggested their use in the production of disinfecting and preserving agents, detergents, fire-extinguishing foams, wetting agents, and flotation agents. Therefore the quaternary ammonium salts were studied somewhat extensively, with a view toward their eventual use with the unsaturated alkyl halides prepared from fish oils.

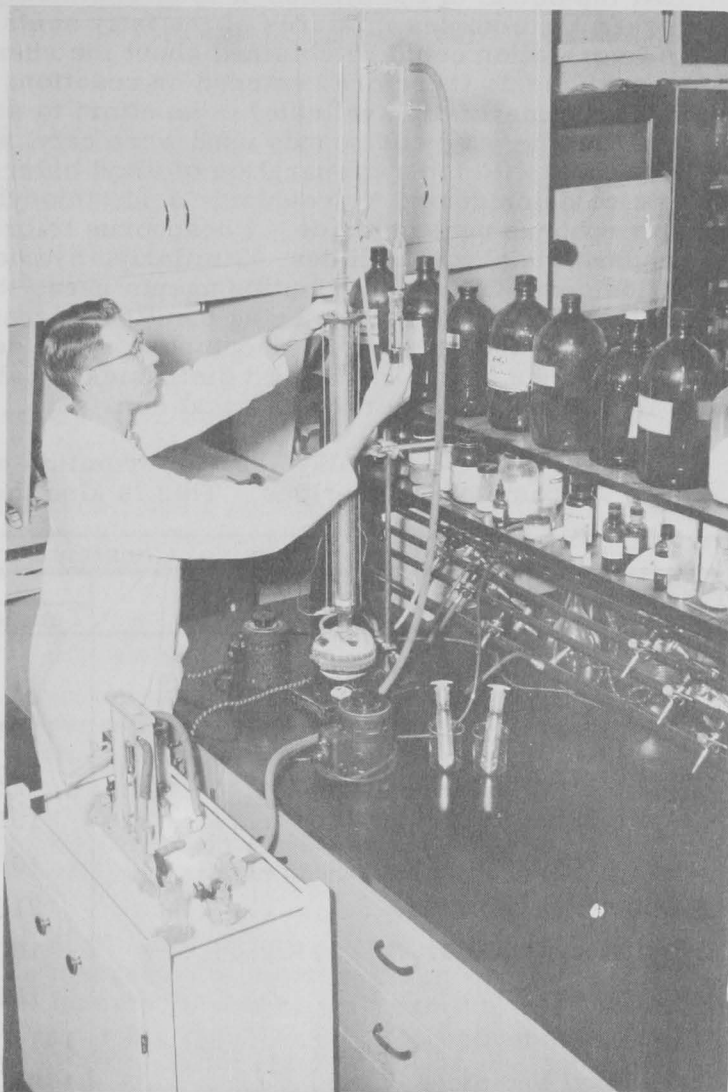


Fig. 2 - Fractional distillation of long-chain alkyl bromides prepared from fatty acids of fish oils.

## PRELIMINARY INVESTIGATIONS OF LONG-CHAIN ALKYL HALIDES

At the outset of the studies of long-chain alkyl halides, it was quickly learned that when the complex mixtures of the fatty acids found in fish oil were used, very little information could be obtained about the chemistry of the substances reacting. The experiments therefore centered on reactions of single, pure, long-chain compounds (commercially available) in an effort to study the completeness of a given reaction. The pure compounds used were cetyl alcohol, n-octadecyl alcohol, and oleyl alcohol. For the preparation of alkyl chlorides, the halogenating agents used were zinc chloride and hydrochloric acid, thionyl chloride, phosphorus trichloride, and phosphorus pentachloride. Phosphorus tribromide was reacted with the alcohols to prepare the alkyl bromides. Similarly, hydriodic acid was used to prepare the alkyl iodides. Of the chlorinating agents used, thionyl chloride gave the best yield. When the alkyl halides were being purified by fractional distillation, the alkyl iodides showed a marked tendency to decompose. The decomposition was made evident by the appearance of iodine-colored distillates. Table 1 lists the halogen compounds prepared and their observed physical constants.

The relative ease of alkyl-halide formation was observed to be in the order: iodides > bromides > chlorides. This is also the order of reactivity of the corre-

Table 1 - Physical Constants for Alkyl Halides

Compound	Boiling Point		Refractive Index
	Temperature	Pressure	
	°C.	Mm. Hg	$n_D^T$
Cetyl chloride.....	191-194	15	-
Cetyl bromide.....	197-203	21	1.4593 <sup>20</sup>
Cetyl iodide.....	151-153	3	1.4389 <sup>49.9</sup>
n-Octadecyl chloride.....	195-203	12	-
n-Octadecyl bromide.....	213-216	14	1.4441 <sup>49.9</sup>
n-Octadecyl iodide.....	180-190	7	-
Oleyl chloride.....	153-163	3	1.4582 <sup>20</sup>
Oleyl bromide.....	141.7-147.7	1.0	1.4692 <sup>25</sup>
Satd. alkyl bromides <sup>1/</sup> .....	170.5-185.0	4.0	1.4619 <sup>24</sup>
Unsatd. alkyl bromides <sup>2/</sup> .....	181.0	9	1.4832 <sup>25</sup>
	201.0	0.57	

<sup>1/</sup>Prepared from menhaden oil.

<sup>2/</sup>Prepared from pilchard oil with boiling points at two different pressures.

sponding alkyl halides (Fieser and Fieser 1944). <sup>2/</sup> For the purpose of carrying out laboratory-scale experiments with alkyl halides, the bromides are most often chosen, since they are more reactive than are the chlorides and more economical to work with than are the iodides. Therefore, as the experiments in the Seattle laboratory progress with alkyl halides prepared from fish oil, only the bromides will be made. If any larger-than-laboratory-size quantities are made, the alkyl chlorides will probably be used, since they are cheaper to prepare than are the bromides.

## INVESTIGATION OF SILICONES DERIVED FROM FISH OIL

There are four commercial methods for preparing silicon compounds containing carbon. These methods are (1) the "direct process," (2) the Grignard method, (3) the olefin addition method, and (4) the sodium method (McGregor 1954). The Grignard

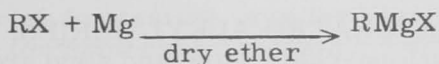
<sup>2/</sup>FOR A GIVEN ALKYL RADICAL, R, THE ORDER OF REACTIVITY OF ALKYL HALIDES IS RI > RBR > RCL. THEREFORE, THIS WOULD BE TRUE FOR ANY GIVEN LONG-CHAIN ALKYL HALIDE.

method is the one that has been studied at the Seattle laboratory. This method involves the substitution of an organic group for one or more of the chlorine atoms in silicon tetrachloride. In this way, compounds of the types  $RSiCl_3$ ,  $R_2SiCl_2$ ,  $R_3SiCl$  or  $R_4Si$  can be formed from  $SiCl_4$ , where R represents a group, such as the octadecyl group  $(-CH_2(CH_2)_{16}CH_3)$ .

Table 2 - Analytical Data for Alkyl Trichlorosilanes

Alkyl Trichlorosilane ( $RSiCl_3$ )	Boiling Point		Amount of Silicon in $RSiCl_3$	
	Temperature	Pressure	Experimental	Theoretical
	$^{\circ}C.$	Mm. Hg	Percent	Percent
Dodecyl trichlorosilane . .	154.0-157.0	10.0	35.32	35.01
Cetyl trichlorosilane . . .	199.0-201.0	10.0	27.21	27.56
Oleyl trichlorosilane . . .	166.0-167.0	1.5	29.63	29.55

**GRIGNARD METHOD:** In the Grignard method, the Grignard reagent (alkyl magnesium halide) is first prepared. This reagent is made by placing magnesium chips and an appropriate dry solvent--usually ethyl ether--into a reaction vessel equipped with a stirrer and reflux condenser. Next, an alkyl halide (the long-chain alkyl bromides, in the present case), diluted in the same solvent, is allowed to drip into the stirred mixture of magnesium and solvent, while protecting the reaction mixture from the moisture in the air. This reaction is represented by the following general equation (where X represents the halogen):

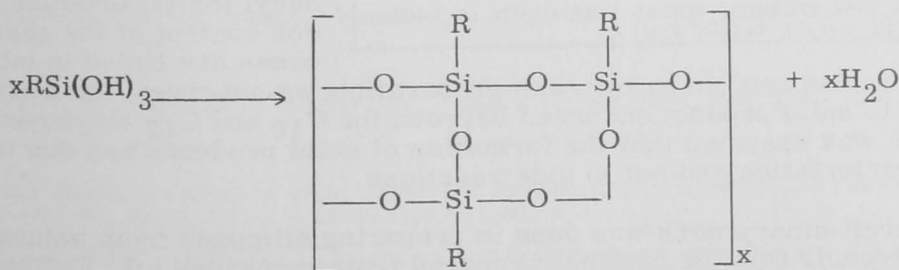
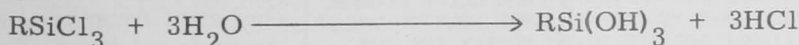


The next step in the synthesis involves the reaction of the Grignard reagent and silicon tetrachloride. The Grignard reagent is added, with stirring, to the silicon tetrachloride in dry ether. This reaction is represented as follows:



It is evident from the equation that, by varying the ratio of amounts of Grignard reagent to silicon tetrachloride, the other types of compounds ( $R_2SiCl_2$ ,  $R_3SiCl$ , and  $R_4Si$ ) may be formed.

**ALKYL CHLOROSILANES:** The alkyl chlorosilanes, as they are called, have a marked reactivity toward compounds containing a hydroxylic group or groups. Therefore, by reacting alkyl chlorosilanes with water, for example, one can form compounds called alkyl silanols. (This is the reaction that has been investigated most in the Seattle laboratory in the study of silicones.) Because low-molecular weight alkyl silanols dehydrate readily to form silicon polymers or silicones, it was decided that this same reaction should be tried in the preparation of long-chain alkyl silanols. One type of reaction involved can be expressed, generally, as follows:



(a resinous cross-linked polymer)

Thus far, the only type of alkyl chlorosilane that has been produced in the Seattle laboratory is of the  $RSiCl_3$  type (table 2). The type  $R_2SiCl_2$  was attempted; however, the analyses indicated that only one mole of Grignard reagent reacted instead of two moles, in all the chlorosilanes made here. Apparently, there is too much steric hindrance in the  $RSiCl_3$  formed for it to react with a second mole of the Grignard reagent. In any case, more severe reaction conditions are necessary.