pressures. A longer time is usually required than with chlorinated methylbenzenes, as fluorination catalysts, such as antimony pentachloride, seem to have no effect on fluorination rate. The chlorinated methylpyridines are apparently not fluorinated with antimony trifluoride at atmospheric pressure.

PROPERTIES OF COMPOUNDS

Although these compounds are derivatives of pyridine, they have no basic properties. No hydrochloride precipitates when hydrogen chloride is bubbled through a benzene solution of the chlorinated or fluorinated methylpyridine. These compounds are not hydrochlorides or hydrofluorides, as shown by their insolubility in water and solubility in organic liquids such as ether, benzene, and petroleum ether. 2,6-Bis(trifluoromethyl)pyridine is a solid fluoro compound with interesting solubility properties, being soluble in alcohols as well as ethers and hydrocarbons. Chloro-2,6-bis(trifluoromethyl)pyridine is completely miscible with 95% ethyl alcohol. Table I gives the chemical analysis and properties of the compounds.

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(FLUORINATED HETEROCYCLIC COMPOUNDS)

(*Perhaloalkyl*)*triazines*

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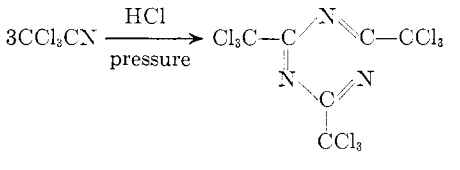
2,4,6-TRIS(trichloromethyl)-1,3,5-triazine was prepared by polymerizing trichloroacetonitrile with anhydrous hydrogen chloride at a pressure of 800 pounds per square inch. Trichloroacetonitrile was produced from trichloroacetamide made by ammonolysis of ethyl trichloroacetate. 2,4,6-Tris(trichloromethyl)-1,3,5-triazine was fluorinated with hydrogen fluoride and antimony pentachloride both at atmospheric and superatmospheric pressure. Eight new 2,4,6-tris(chlorofluoromethyl)-1,3,5-triazines were obtained. Physical constants and experimental data are reported.

TRIAZINES have been reported to exhibit exceptional stability to heat and hydrolysis (*2*), and it was believed that introduction of fluorine should increase stability and result in nonflammable compounds with a wide liquid range which might be suitable as heat transfer agents. The allylic nature of the chlorine atoms to be substituted made the known 2,4,6-tris(trichloromethyl)-1,3,5-triazine relatively easy to fluorinate. The series of reactions used in the preparation of this intermediate follows:

$$\mathrm{CCl_3CO_2H + EtOH \xrightarrow{HCl} CCl_3CO_2Et + H_2O} \tag{1}$$

$$\mathrm{CCl_3CO_2Et + NH_3 \xrightarrow{ether} CCl_3CONH_2 + EtOH} \tag{2}$$

$$\mathrm{CCl_3CONH_2 + P_2O_5 \longrightarrow CCl_3CN} \tag{3}$$



(4)

The 2,4,6-tris(trichloromethyl)-1,3,5-triazine was fluorinated with anhydrous hydrogen fluoride and antimony pentachloride at both atmospheric and superatmospheric pressures. Table I gives the compounds prepared, their physical properties, and their halogen analyses.

2,4,6-TRIS(TRICHLOROMETHYL)-1,3,5-TRIAZINE

The series of reactions outlined previously is described, and optimum yields are reported. Twenty-two hundred fifty grams (13.8 moles) of trichloroacetic acid and 3200 grams (70 moles) of absolute ethanol were placed in a 12-liter flask equipped with a reflux condenser. Ten milliliters of concentrated hydrochloric acid were added, and the flask was heated for 6 hours at reflux temperature. The reaction mixture was then distilled at atmospheric pressure through a short Vigreux column. The fraction boiling at 162–165° C. (750 mm. mercury) was collected as ethyl trichloroacetate, boiling at 164.0° C. Twenty-one hundred seventy-five grams (11.4 moles) of the ester were obtained; the yield and conversion were 83%.

Twenty-one hundred seventy-five grams (11.4 moles) of ethyl trichloroacetate were dissolved in 2 liters of anhydrous diethyl ether, and the solution was placed in a three-neck 5-liter flask equipped with a gas inlet tube. The solution was cooled to ice temperature, and anhydrous ammonia was bubbled slowly into the reaction mixture over a period of 20 hours. Trichloroacetamide separated immediately from solution. The flow of ammonia was then stopped and the remaining liquid removed by distillation. Sixteen hundred thirty grams (10.4 moles) of trichloroacetamide were obtained; the yield and conversion were 91%.

Nine hundred seventy-two grams (6.0 moles) of trichloroacetamide and 284 grams (2.0 moles) of phosphorus pentoxide were intimately mixed, and the mixture was placed in a 3-liter distilling flask. The flask and contents were heated electrically with a Glascol heating mantle placed around the flask. The reaction proceeded smoothly, trichloroacetonitrile distilling from the reaction mixture as rapidly as formed. Additional amounts of phosphorus pentoxide were introduced during the reaction until a total of 994 grams (7.0 moles) had been added. Seven hundred

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TABLE I. NEW COMPOUNDS DERIVED FROM 2,4,6-TRIMETHYL-1,3,5-TRIAZINE

Compound	B.P., ° C. (748 Mm.)	F.P., ° C.	n_D^{20}	d_4^{26}	Mol. Wt. Theoretical	Mol. Wt. Found	% Cl Theoretical	% Cl Found	% F Theoretical	% F Found
$C_6H_3F_9$	98.3–98.5	−24.8	1.3231	1.5857	285	285	0.0	0.0	60.0	60.3
$C_6N_3F_8Cl$	119.0–119.2	−51.6	1.3540	1.6090	301.5	300	11.8	11.7	50.5	50.7
$C_6N_3F_7Cl_2$	145.1–145.3	−36.2	1.3827	1.6234	318	317	22.3	22.4	41.9	41.7
$C_6N_3F_6Cl_3$	166.6–166.8	−21.1	1.4129	1.6458	334.5	332	31.9	31.8	34.1	34.4
$C_6N_3F_5Cl_4$	194.2–194.4	− 9.4	1.4420	1.6656	351	348	40.5	40.5	27.1	27.2
$C_6N_3F_4Cl_5$	217.0–217.2	−10.2	1.4611	1.6860	367.5	365	48.2	48.1	20.7	20.6
$C_6N_3F_3Cl_6$	248.1–248.3	9.6	1.4920	1.7134	384	380	55.5	55.4	14.8	15.0
$C_6N_3F_2Cl_7$	274.5–274.7	14.0	1.5009	1.7400	400.5	...	62.0	61.9	9.5	9.8
$C_6N_3Cl_9$	...	96.0	...	...	433.5	...	73.9	74.0	...	...

thirty-four grams (5.1 moles) of trichloroacetonitrile boiling at 84° C. (760 mm.) were obtained. The yield and conversion were 85%.

Trichloroacetonitrile was polymerized in the presence of anhydrous hydrogen chloride following the directions of Dachlauer (*1*). Eleven hundred grams (7.4 moles) of trichloroacetonitrile were placed in a nickel-lined autoclave of one liter capacity. The reaction vessel was charged with anhydrous hydrogen chloride to 800 pounds per square inch pressure and rocked at room temperature for 100 hours before hydrogen chloride was allowed to escape and the vessel opened. The solid product was then removed from the autoclave with ether solvent. One thousand twenty-six grams (7.1 moles) of 2,4,6-tris(trichloromethyl)-1,3,5-triazine were obtained (melting point 96.0° C.). The yield and conversion were 96%. No unreacted nitrile was found. The yield and conversion to polymer, based on the trichloroacetic acid used, were 60%. Distillation of the nitrile prior to polymerization was necessary for obtaining high yields. Experiments conducted with crude trichloroacetonitrile gave little or none of the desired polymer.

FLUORINATION

The 2,4,6-tris(trichloromethyl)-1,3,5-triazine used as starting material in the fluorination experiments was the crude product from the polymerization reaction. It was found that recrystallization of the product was unnecessary before fluorination. The material had a melting range of 84° to 87° C.

Fluorinations were conducted with anhydrous hydrogen fluoride and antimony pentachloride at both atmospheric and superatmospheric pressures. For the fluorination conducted at atmospheric pressure, 417 grams (0.97 mole) of 2,4,6-tris(trichloromethyl)-1,3,5-triazine and 75 grams (0.25 mole) of antimony pentachloride were placed in a vertical vessel constructed of 2-inch nickel pipe, 21 inches in length. The bottom end was closed, and the top was fitted with a thermocouple well and water-cooled condenser of 1/2-inch nickel pipe, 13 inches long. An inlet tube was provided so that hydrogen fluoride could be introduced below the surface of the material to be fluorinated. The exit end of the condenser was connected by a 1/2-inch copper tube to a series of cooled nickel traps. The reactor was placed in an electric heater and the reaction temperature held between 100° and 125° C. Five hundred grams (25.0 moles) of anhydrous hydrogen fluoride were bubbled into the mixture over a period of 12 hours. The product was then aerated and poured from the reactor. The material was treated with aqueous sodium hydroxide to neutralize any acids present and steam-distilled. The distillate was dried with calcium sulfate and rectified. Five distinct fractions were obtained and identified as: 2,4,6-(trichlorohexafluorotrimethyl)-1,3,5-triazine, 2,4,6-(tetrachloropentafluorotrimethyl)-1,3,5-triazine, 2,4,6-(pentachlorotetrafluorotrimethyl)-1,3,5-triazine, 2,4,6-(hexachlorotrifluorotrimethyl)-1,3,5-triazine, and 2,4,6-(heptachlorodifluorotrimethyl)-1,3,5-triazine. One hundred ninety-six grams of crude fluorinated product were obtained; yield and conversion were 47%.

Fluorinations conducted at superatmospheric pressure were conducted as follows: Two hundred seventeen grams (0.5 mole) of 2,4,6-tris(trichloromethyl)-1,3,5-triazine and 50 grams (0.17 mole) of antimony pentachloride were placed in a nickel-lined autoclave of one liter capacity. Two hundred grams (10.0 moles) of anhydrous hydrogen fluoride were distilled into the reaction vessel from a small steel container, and the reactor was placed in a mechanical rocker. A reaction temperature of 169° C. was maintained for 24 hours, the pressure rising to 2300 pounds per square inch. The autoclave was cooled to room temperature, and gases were bled off into an aqueous sodium hydroxide solution. The reaction product was poured from the autoclave, treated with aqueous sodium hydroxide, and steam-distilled. The distillate was dried with calcium sulfate and rectified. Five fractions were obtained and identified as: 2,4,6-(dichloroheptafluorotrimethyl)-1,3,5-triazine, 2,4,6-(trichlorohexafluorotrimethyl)-1,3,5-triazine, 2,4,6-(tetrachloropentafluorotrimethyl)-1,3,5-triazine, 2,4,6-(pentachlorotetrafluorotrimethyl)-1,3,5-triazine, and 2,4,6-(hexachlorotrifluorotrimethyl)-1,3,5-triazine. One hundred seventy-eight grams of crude fluorinated product were obtained; the yield and conversion were 85%.

An experiment similar to the preceding was performed at 240° C.; reaction time was 24 hours, and the pressure reached 3500 pounds per square inch. Rectification of the reaction product yielded four fractions: 2,4,6-tris(trifluoromethyl)-1,3,5-triazine, 2,4,6-(chloro-octafluorotrimethyl)-1,3,5-triazine, 2,4,6-(dichloroheptafluorotrimethyl)-1,3,5-triazine, and 2,4,6-(trichlorohexafluorotrimethyl)-1,3,5-triazine. One hundred forty grams of crude fluorinated product were obtained; the yield and conversion were 75%.

PROPERTIES

Fluorination of tris(trichloromethyl)triazines is apparently accomplished as readily as fluorination of tris(trichloromethyl) benzenes. The material was successfully fluorinated in the crude state without further purification.

The 2,4,6-tris(chlorofluoromethyl)-1,3,5-triazines had some apparent physiological effects. A burning sensation in the upper respiratory system was experienced upon inhalation of the compounds, but no further investigation of this phenomenon was attempted.

All of the compounds were insoluble in acids. This is due to the substitution of halogen for hydrogen atoms on the carbons adjacent to the nitrogen atoms, which results in a reduction of basicity to the point where the heterocyclic compounds, if basic at all, are no longer sufficiently basic to form hydrochlorides.

The compounds give preliminary evidence of utility in the desired capacity as heat transfer agents.

In each case, the sample used for determination of physical properties and halogen analyses was purified by rectification in a Podbielniak Hyper-Cal column. The boiling range of any sample was not more than 0.2° C.

ACKNOWLEDGMENT

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