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HALOGENATION

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Commercial production of chlorine and chlorinated organic compounds is still at a relatively high level but some decreases are evident especially in the area of insecticides and aromatics. In the field of chlorination research, the emphasis is still on improvements in techniques and processes especially in the categories of benzene hexachloride and of monomers and polymers. Fluorination research during the past year has been devoted primarily to hydrocarbons and olefins. The polymerization of chlorotrifluoroethylene has been studied quite extensively and a number of new polymers are described. The area of bromination is again concerned primarily with aliphatic and aromatic hydrocarbons. Several interesting investigations of the use of N-bromoamides and imides as brominating agents are described. Iodination still remains the least explored area of halogenation with only a few diversified investigations reported.

THE production of chlorine, hydrogen chloride, and hydrogen fluoride has maintained a steady high level as shown in the comparative total tonnages (Table A) for the years 1951 and 1952 (*77A*).

(Table A)	1951 (tons)	1952 (tons)
Cl_2	2,517,913	2,595,528
HCl	693,541	678,378
HF	43,660	41,085

However, the production of chlorinated organic compounds, in some instances, has dropped below the previous level as shown in the comparative monthly production statistics (*78A*).

This decrease in the production of certain chlorinated materials can be reflected, perhaps, in the increase in production of other compounds which are newly listed (Table B) (*78A*).

The general picture is one of continuing high activity in the commercial area (Table C).

(Table B)	January 1952 (lb.)	January 1953 (lb.)
CCl_4	24,076,124	19,075,423
C_6H_5Cl	38,079,061	30,228,619
D.D.T.	9,938,441	7,052,006
2,4-D	2,703,013	2,929,568
$C_6H_6Cl_6$	11,493,170	5,594,479
Gamma isomer	1,597,745	1,045,406

(Table C)	January 1953 (lb.)
C_2Cl_4	11,172,306
C_2HCl_3	24,229,044
2,4,5-T	541,084 (February 1953)

CHLORINATION

PARAFFIN HYDROCARBONS

The chlorination of methane (*47A*) was accomplished in high yield by passing methane mixed with chlorine through a bed of silica sand at 430° to 550° C. with sufficient pressure to fluidize the catalyst. A combined photochemical and catalytic process (*61A*) for the chlorination of methane comprised passing a mixture of chlorine and the hydrocarbon at 305° C. through an irradiated zone followed by passage of the effluent gases over activated carbon at 450° C. The product is principally carbon tetrachloride.

Ethane (*27A*) was chlorinated at 500° C. in the presence of nitrogen to form ethyl chloride in high yield. In the presence of an activated alumina catalyst (*33A*) ethane gave ethyl chloride in 78% yield. Chlorofluoroethanes (*7A*) can be chlorinated in the presence of iron at 200° to 400° C. to form higher chlorinated products as well as olefins resulting from dehydrofluorination.

The chlorination of hydrocarbons (*19A*) at 400° to 800° C. using excess chlorine gave hexachlorobutadiene in 60% yield. Similarly, photochemical chlorination (*17A*) at a maximum of 700° C. formed chlorinated cyclopentadienes in good yield. The reaction of paraffin (*75A*) with chlorine was studied and found to be relatively unaffected by temperature or catalysts. The rate of reaction was slowed considerably after the chlorine content of the product reached 50%.

AROMATIC HYDROCARBONS

The manufacture of benzene hexachloride is still receiving attention. The chlorination of benzene (*43A*) in the presence of iron salts and light was found to produce the hexachloride in good yield. Other materials that can be used as catalysts are organic acids and salts. Chlorination (*57A*) in the presence of acetic acid and light at 35° C. produced a product containing 45% of the gamma isomer. A continuous process (*50A*) was described which consisted of reacting a mixture of chlorine and benzene at 30° to 60° C. followed by washing with dilute caustic and then passing the organic layer through a bed of glass fiber to remove any emulsion formed. The solution remaining was then separated from the benzene hexachloride and recycled. Another process (*60A*) involved photochemical chlorination of benzene at 50° to 80° C. with stirring until the chlorine to benzene ratio reached 2:1, followed by distillation to remove the unreacted benzene. Chlorination (*2A*) of benzene at 0° to —30° C. in the presence of light and a catalytic amount of benzothiazole gave benzene hexachloride containing over 17% of the delta isomer. A product (*69A*) containing 97% of the gamma isomer was obtained by first chlorinating benzene at 80° C. followed by a crystallizing period of 36 hours. The objectionable odor and color of $C_6H_6Cl_6$ (*67A*, *68A*) were found to be due to oxygen dissolved in the benzene and could be controlled by treating the benzene with carbon dioxide before use.

A review of (*11A*) nuclear halogenation of aromatic compounds with *N*-halogenated amines furnishes an excellent description of the reaction. The rates of chlorination (*62A*) of various monosubstituted benzenes were given as follows: dimethylaniline, 10^{-18}; phenol, 10^{8}; bromobenzene, 10^{-1}; and nitrobenzene, 10^{-6}. Chlorobenzene (*37A*) was prepared in good yield by passing it as a film down an externally cooled vertical iron pipe, countercurrently to a stream of chlorine. A compact apparatus (*40A*) for the chlorination of benzene comprised a jacketed column filled with iron Raschig rings. Benzene and chlorine were introduced into the lower end, and the products were removed as gaseous materials from the upper end.

Toluene (*41A*) was chlorinated using liquid chlorine at —32° C. in the presence of iron chloride to produce highly nuclear chlorinated products. Nuclear chlorination (*32A*) of *p*-nitrotoluene in the presence of silver sulfate and sulfuric acid afforded a 96% yield of 2-chloro-4-nitrotoluene. Side-chain chlorination (*4A*) of toluene in a silent electrical discharge gave principally benzotrichloride as compared to a photochemical, vapor-phase reaction which produced mainly benzyl chloride. An apparatus (*26A*) for the preparation of benzyl chloride in high yield was described consisting of a distilling column packed with Raschig rings. Toluene was volatilized upward through the column and mixed with irradiated chlorine in the middle portion. The chlorination of toluene (*72A*) was found to be catalyzed by camphor and a 91% yield of benzyl chloride was obtained from this reaction. In the temperature range 50° to 115° C., the following reaction mechanism (*51A*) and rate equation were proposed:

$$Cl_2 + h\nu \xrightarrow{k_1} Cl + Cl$$

$$Cl + \phi CH_3 \xrightarrow{k_2} \phi CH_2Cl + H$$

$$H + Cl_2 \xrightarrow{k_3} HCl + Cl$$

$$Cl + Cl \xrightarrow{k_4} Cl_2$$

$$dx/dt = KI^{1/2}\ [\phi CH_3]\ [Cl_2]^{1/2}$$

$$K = k_2(k_1/k_4)^{1/2},\ I = \text{light intensity}$$

The application of *N*-chlorosuccinimide (*34A*, *35A*) to the chlorination of toluene has shown the reagent to be applicable to moderate side-chain substitution.

The chlorination (*8A*) of *o*-xylene at —10° C. in the presence of iron gave both the 4,5-dichloro- and 3,6-dichloro-*o*-xylenes. Ring-chlorinated alkylbenzenes (*42A*) were further chlorinated on the side chain by reaction with chlorine at 60° to 70° C. in the presence of iron chloride. The reactions were conducted at autogenous pressures and gave almost quantitative yields of the monochlorinated product. The nuclear chlorination (*45A*) of (perfluoroalkyl)benzenes was accomplished by a vapor-phase reaction at 200° C. in the presence of activated carbon impregnated with iron chloride.

The reaction of naphthalene (*65A*) with liquid chlorine produced the gamma isomer of 1,2,3,4-tetrachloro-1,2,3,4-tetrahydronaphthalene. A study of the chlorination (*36A*) of naphthalene as to reaction temperature and other factors for the production of chloronaphthalene is described. The chlorination (*48A*) of benz(α)anthracene with phosphorus pentachloride produced the 7-chloro derivative in 26% yield.

OLEFINS AND POLYMERS

Ethylene (*14A*) was chlorinated at 300° to 500° C. in the presence of a fluidized bed of activated carbon to produce a product containing 90% of both trichloro- and tetrachloroethylenes. The burning of ethylene (*18A*) by chlorine in an iron tube produced perchloroethylene in 90% yield. A mixture (*76A*) composed of C_2H_4, C_2H_6, CO, CO_2, H_2, and N_2 was treated with chlorine at 500° to 600° C. in the presence of coke to give vinyl chloride in 51% yield. Perchloroethylene (*21A*) was formed in good yield from the thermal decomposition of carbon tetrachloride at 500° to 1000° C. in the presence of a hydrocarbon capable of reacting with the chlorine formed—i.e., C_2H_2 or CH_4.

Acetylene (*15A*) was chlorinated in the presence of a mercury salt and iron chloride to produce 1,1,2-trichloroethane in good yield. In a similar manner, the reaction (*16A*), conducted in an inert solvent, gave 1,2-dichloroethylene. Chlorination of acetylene (*70A*) in the presence of a mixture of C_2HCl_3, $C_2H_2Cl_4$, C_2HCl_5, and $FeCl_3$ formed C_2Cl_4 and C_2HCl_3 as the principal products. In this manner, two commercially important chloroolefins can be produced simultaneously.

Vinyl chloride (*6A*) was formed in high yield by reaction of acetylene with hydrogen chloride in the presence of an aqueous cuprous salt at 90° C. The use of a mercuric halide catalyst (*25A*) at 80° C. afforded a nearly quantitative yield of vinyl chloride. By using a series of catalyst chambers (*3A*) the life of the catalyst was considerably increased and a more uniform reaction temperature was possible. Another process (*30A*) described the reaction of acetylene with hydrogen chloride at 140° to 200° C. in the presence of calcium chloride to produce vinyl chloride in high yield. The use of an inert solvent (*20A*) and a catalyst composed of iron and mercury chlorides gave vinyl chloride in 95% yield. A continuous process (*49A*) was described in which acetylene and hydrogen chloride were passed over activated carbon, at 185° C., impregnated with mercuric chloride in the presence of water vapor. A 90% conversion to vinyl chloride was claimed. Hydrochlorination of acetylene (*22A*) in the presence of mercuric chloride and antimony pentachloride below 50° C. in a solvent such as trichloroethane gave 1,1-dichloroethane in good yield. Reaction of dimethylacetylene (*66A*) with sulfuryl chloride formed 1,2,3,4-tetramethyl-3,4-dichlorocyclobutene in 15% yield.

Chlorination of butadiene (*13A*) at 180° to 240° C. in the presence of fluidized coke gave a mixture of 1,4-dichloro-2-butene and 3,4-dichloro-1-butene in 80% yield. Reaction of butadiene (*23A*) with chlorine at 250° to 350° C. formed 1,4-dichloro-2-butene in 95% yield. Pentachlorobutadiene (*63A*) when chlorinated at 200° C. in the presence of light yielded both 1,1,2,3,3,4,4-heptachloro-1-butene and 1,1,2,3,4,4,4-heptachloro-1-butene. Additive chlorination (*81A*) of 2,3-dichloro-1,3-butadiene at 10° to 60° C. in chloroform gave 1,2,2,3,3,4-hexachlorobutane in 73% yield.

Isobutylene (*44A*) was reacted with hydrogen chloride in a glass apparatus at room temperature to form *tert*-butyl chloride in 98% yield. Methallyl chloride (*54A*) was obtained in 94% yield by chlorination of isobutylene at 462° C. Chlorination (*73A*) of a polyethylene polymer of molecular weight 18,000 to 20,000 in aqueous suspension at approximately 50° C. gave a product of 25 to 35% chlorine content which was reported to be superior in tensile strength and stiffness to those materials produced by solution chlorination.

OXYGEN-CONTAINING COMPOUNDS

Acetaldehyde (*58A, 59A*) or its polymer was chlorinated at 82° C. in the presence of antimony trichloride to produce chloral in 80% yield. By careful control of the reaction temperatures and ratio of reactants, the amount of dichloroacetaldehyde did not exceed 1 to 2%. Chlorination (*82A*) of trichloroacetone was accomplished by reacting it with chlorine in a bed of activated carbon at 150° to 160° C. The product, hexachloroacetone, was obtained in 78% yield. The polychloroacetone (*31A*) used above was prepared by chlorination of acetone dissolved in polychloroacetone at 30° to 100° C. The product contained both the di- and trichloro derivatives. Complete chlorination (*28A*) of simple aliphatic ketones can be easily accomplished in high yield by reaction at 130° to 140° C. for an extended period of time. In this manner, the perchloro derivatives of diethyl ketone, methyl propyl ketone, and methyl *tert*-butyl ketone were prepared. Camphor (*53A*) was treated with chlorosulfonic acid at low temperatures to form *dl*-γ-chlorocamphor in 30% yield.

A study (*29A*) of the chlorination of ethanol has shown that the reaction rate is best controlled by control of irradiation. By conducting the reaction in a quartz column containing sintered cross plates with intense irradiation, a high yield of chloroethanol can be obtained. Reaction of fluorine-containing alcohols (*46A*) with chlorine produced the corresponding aldehyde or ketone in good yield. Chlorination (*55A*) of *m*-benzylphenol in carbon tetrachloride solution gave nuclear-substituted products in good yield. Thionyl chloride can also be used as the chlorinating agent. The reaction of dodecyl alcohol (*38A,39A*) with concentrated hydrochloric acid in the presence of zinc chloride at reflux temperature produced the corresponding chloride in high yield.

Acetic acid (*71A*) was chlorinated at 85° to 130° C. at a pressure of 10 pounds per square inch in the presence of phosphorus trichloride to form both the mono- and dichloro derivatives. By careful control of the reaction temperature, a product containing 99% monochloroacetic acid was obtained. Chlorination (*24A*) of a mixture of glacial acetic acid and acetic anhydride at 95° to 150° C. gave a product containing 90% trichloroacetic acid. The advantage claimed for this process is a shorter reaction time. Reaction of γ-butyrolactone (*5A*) with chlorine at 140° to 160° C. gave primarily α-chloro-γ-butyrolactone in good yield. Chlorination (*56A*) of alpha fluoroethers was found to be directed in a manner so that the entering chlorine was on a carbon atom in a beta or further position from the fluorine grouping. Treatment of tetrabutyl titanate (*52A*) with chlorine in carbon tetrachloride solution resulted in degradation, forming butanol, dibutoxydichlorotitane, and similar products. Chlorination of aliphatic oximes (*10A*) can be successfully conducted at 80° C. giving the expected chloro derivatives.

SULFUR-CONTAINING COMPOUNDS

Methyl mercaptan (*64A*) was chlorinated at —15° C. in carbon tetrachloride solution to give methyl sulfur chloride in good yield. Reaction of *p*-nitrothiophenol (*79A*) with chlorine in glacial acetic acid gave *p*-nitrobenzene sulfonyl chloride in 80% yield. Dimethyl sulfide (*9A*) when treated with thionyl chloride in carbon tetrachloride solution at —20° C. produced chloromethyl sulfur chloride in 95% yield. A study (*74A*) of the chlorination of alkyl sulfides with both sulfuryl and thionyl chlorides indicated that both are satisfactory chlorinating agents with the former being more vigorous. Chlorination (*12A*) of thiophene at 30° to 40° C. produced tetrachlorothiolane in approximately 8% yield. Thiophane (*80A*) was chlorinated in aqueous acetic acid solution at 50° to 65° C. to give 4-chloro 1-butanesulfonyl chloride in 40 to 50% yield as well as cyclotetramethylene sulfone. Substituted benzenesulfonamides (*1A*) were chlorinated in dimethyl formamide at temperature below 60° C. to produce highly nuclear-substituted derivatives. It is postulated that the chlorine reacts initially with the solvent to form an active chlorinating agent.

FLUORINATION

A review (*31B*) of the field of industrial fluorochemicals as it stands at present is recommended to the reader.

HYDROCARBONS

A reactor (*47B*) for the fluorination of hydrocarbons with cobalt trifluoride was described consisting of a copper tube fitted with a paddle stirrer made of nickel. A study (*5B*) of reaction variables using a cobalt trifluoride fluorinating agent indicated that the optimum temperature was 300° to 350° C. with the hydrocarbon feed rate depending on the size and geometry of the reactor. Fluorination (*73B*) of *o*-dichlorobenzene with cobalt trifluoride at 35° C. produced 1,2-dichloroperfluorocyclohexane in 20% yield. A chlorinated oil (*16B*) was reacted with cobalt trifluoride at 117° to 245° C. to yield a stable halocarbon oily material. This process is also applicable to the stabilization of polymers of chlorotrifluoroethylene. Fluorination of alkylbenzenes (*45B*) was accomplished by reaction with silver difluoride (AgF_2) at 150° to 350° C. to form the corresponding fluorocarbons in fair yield. Reaction of a lubricating oil fraction (*20B*) of average molecular weight of 300 with ceric fluoride (CeF_4) at 300° to 425° C. gave a fluorocarbon product having the same carbon structure as the starting hydrocarbon. A polyalkylnaphthalene (*74B*) was fluorinated with silver difluoride (AgF_2) at 200° to 400° C. to produce a highly fluorinated product suitable for use as a lubricant. An electrolytic process (*76B*) was developed for the fluorination of chlorohydrocarbons which comprised electrolysis of a mixture of the chloro compound, hydrogen fluoride, and lithium fluoride. From CH_2Cl_2, there was obtained CF_4, CF_3Cl, CF_3H, CH_2F_2, $CHClF_2$, CCl_2F_2, $CHFCl_2$, and CCl_3F. Fluorination (*18B*) of a 1,1,1,3-polyhalogenated olefin with hydrogen fluoride and mercuric oxide at 105° C. produced a fluorinated hydrocarbon with increased chain length. A description (*61B*) of the use of a mixture of hydrogen fluoride and chlorine trifluoride as a fluorinating agent was given with the conclusion that the agent is applicable to a wide variety of starting materials. The reaction (*17B*) of chlorine trifluoride with benzene at 0° C. in a nitrogen atmosphere gave nuclear-substituted products containing both chlorine and fluorine.

Several pyrolytic reactions have been studied. Vinylidene fluoride (*12B*) when heated with chlorine at 775° to 800° C. gave CCl_2F_2 in 83% yield and CCl_3F in 27% yield. Some CCl_4 and C_2Cl_4 were also formed. Pyrolysis (*71B*) of short chain fluorocarbons on a platinum filament at 1000° to 1400° C. caused degradation to occur. Perfluoroethane formed CF_4 and a polymer while C_3F_8 yielded C_2F_6, C_3F_6, and C_4F_8. Perfluorodicyclohexyl (*6B*) on reaction with chlorine at 650° C. formed chloroperfluorocyclohexane in good yield. Reaction with toluene gave dibenzyl and undecafluorocyclohexane.

The physical properties of liquid chlorine trifluoride (*4B*) were given. Other listings of physical properties (*52B*, *60B*, *68B*,*72B*, *75B*) describe some interesting observations on the differences caused by fluorine substitution. The use of benzotrifluoride (*23B*) as a cryoscopic solvent for fluorinated compounds was found satisfactory with a molal freezing point depression constant of 4.90 ± 0.05°.

OLEFINS AND POLYMERS

Tetrafluoroethylene (*41B*) was prepared in high yield by heating a metal salt of trifluoroacetic acid with an alkali metal hydroxide at 200° C. Synthesis of vinyl fluoride (*13B*) was accomplished by heating a mixture of acetylene and hydrogen fluoride at 160° C. in the presence of cuprous cyanide. A 40% conversion of the acetylene was obtained. Another procedure (*33B*) comprised passing a mixture of hydrogen fluoride and acetylene over an alumina catalyst at 300° C. In this case, a conversion of 95% was achieved. Hexafluorobutadiene (*26B*) was prepared in 60% yield from chlorotrifluoroethylene by first reaction with iodine monochloride followed by dehalogenation with zinc. Pyrolysis of octafluorocyclobutane (*55B*) at 700° C. produced perfluoroisobutene in 50% conversion. The olefin, $C_5HCl_7F_2$, was prepared (*67B*) in 71% yield by reaction of 1,1,2, 3,3,4,5,5,5-nonachloropentene with hydrogen fluoride at 140° C. at autogenous pressures. Several fluorinated styrenes (*14B*, *64B*) were synthesized in which the fluorine was substituted in the vinyl group. These formed polymers of higher softening points than polystyrene itself.

The polymerization of chlorotrifluoroethylene and the properties of the polymers have received increasing attention. One polymerization technique (*49B*) involved treating the monomer, C_2ClF_3, with barium peroxide at 0° to —30° C. to form a plastic polymer in rather low yield. Another method (*11B*) used a polymerization system of water, C_2ClF_3, boric acid, inorganic peroxide, iron salt, and sodium bisulfite. A different method (*77B*) employed a system of a halogenated acyl peroxide in a hydrocarbon solvent at 0° to 20° C. to produce a solid polymer. A liquid polymer (*53B*) for lubricant use was made by heating chlorotrifluoroethylene at 150° to 450° C. in the presence of a catalyst such as di-(*tert*-butyl) peroxide. A high-softening polymer (*66B*) was obtained by treating chlorotrifluoroethylene with a mixture of water, an organic peroxide, iron phosphate, and sodium bisulfite at temperatures below 35° C. Copolymers of chlorotrifluoroethylene with 1,1-chlorofluoroethylene (*59B*), methyl methacrylate (*58B*), and vinyl acetate (*36B*, *56B*) have been prepared in an effort to obtain properties suitable for use as films or fibers.

Polymerization (*50B*) of tetrafluoroethylene to form a polymer having a softening point above 350° C. was accomplished using a mixture of water, peroxide, iron salts, and sodium bisulfite at 0° to 35° C. A hydrolyzed copolymer (*57B*) of 1,1-chlorofluoroethene and vinyl acetate was found to be useful in filament formation. Polymerization (*48B*) of perfluoropropene and tetrafluoroethylene using trichloroacetyl peroxide gave a solid thermoplastic fluorocarbon. Extrusion properties (*42B*, *43B*) of polytetrafluoroethylene were presented in detail. It was found that the colloidally dispersed polymer could be extruded below its transition temperature.

The addition reactions of fluoro olefins have been studied somewhat extensively. 3,3,3-Trifluoropropyne (*25B*, *27B*) was found to be very reactive and, for example, reacted with water in the presence of a mercury salt to form both trifluoroacetone and trifluoropropanol. Chlorodifluoroethylene (*10B*) formed 1,2-dichloroperfluorocyclobutane on heating to 700° C. while reaction with mercaptans (*39B*) or alcohols (*40B*) in the presence of a base gave the corresponding ether. Similarly 1,1,2-trichlorotrifluoropropene (*54B*) formed ethers on reaction with alcohols. Tetrafluoroethylene (*3B*) in the presence of light and mercury vapor at 30° C. formed a polymer and the cyclic C_3F_6. However, the identity of the latter material was not conclusively shown. The synthesis (*46B*) of a number of chlorofluoro- and bromofluoroalkenes is described.

OXYGEN-CONTAINING COMPOUNDS

Fluorine-containing esters (*29B*) were prepared from both alcohols and acids containing fluorine and their physical properties were studied. Similarly thiol esters (*30B*) were synthesized from mercaptans and fluorocarbon acids. An extensive study (*19B*) of the diesters of fluorinated dibasic acids was made and the effect of fluorine substitution on their physical properties was reported. Vinyl esters (*65B*) of perfluoroacids were prepared by reaction of the acid with acetylene in the presence of mercuric oxide and sulfuric acid at 35° C. The esters were found to give both homo- and copolymers. A series of orthoesters (*34B*) was prepared by reaction of a simple ester of a perfluoroacid with a dialkyl sulfate in the presence of a base.

The chemistry of perfluoropropionic acid (*35B*) was well presented and several new fluorinated materials described as derivatives of this acid. The synthesis of perfluorosebacic acid (*22B*) was described and comprised electrolysis of the acid in liquid hydrogen fluoride. Similarly, perfluorocyclohexane carboxylic acid and perfluorocyclohexylacetic acid (*15B*) were obtained from the corresponding aromatic acids. Trifluoroacetic anhydride has been found useful as a catalyst in the esterification of fluorine-containing alcohols (*1B*) and, mixed with nitric acid, in the nitration of aromatic rings and the preparation of nitrate esters (*7B*). In the latter case, considerably less hydrolysis was encountered.

The synthesis (*44B*) of 3,3,3-trifluoropropylene oxide by dehydrobromination of the corresponding bromohydrin was described.

MISCELLANEOUS

The reaction of trifluoromethyl iodide (*9B*) with arsenic at 220° C. gave $(CF_3)_2As$ in 70% yield and CF_3AsI in 20% yield. Similarly, reaction with sulfur (*8B*) at 205° C. produced $(CF_3)_2S_2$ in 50% yield. The preparation (*70B*) of iodides of the type $C_nF_{2n+1}I$ by reaction of tetrafluoroethylene with iodine pentafluoride at 175° C. was described. Several workers (*24B*, *32B*, *62B*, *63B*) described the preparation and reactions of C_3F_7MgI in great detail. Reaction (*28B*) of the silver salt of perfluorobutyric acid with C_3F_7I at 300° C. gave a nearly quantitative yield of C_6F_{14}.

Fluorination (*51B*) of thiophene with a mixture of fluorine and nitrogen at 90° C. produced a nearly quantitative yield of SF_6 together with a mixture of fluorocarbons from CF_4 to C_4F_{10} as well as cyclic C_4F_8 and C_8F_{16}. Reaction (*69B*) of carbon disulfide with fluorine at 30° C. formed both SF_4 and CF_4 while an electrolytic fluorination gave only CF_3SF_5. A series (*2B*) of perfluoroalkyl isocyanates was prepared by reaction of the corresponding acid chloride with silver azide followed by decomposition with heat. An electrolytic fluorination (*38B*) of *N*-methylpyridine yielded the perfluoro-derivative, while a similar fluorination (*37B*) of tertiary amines gave the completely fluorinated product.

The preparation (*21B*) of fluorine-containing organosilanes is described and comprises reaction of an allyl silane with a fluoro olefin at approximately 150° C.

BROMINATION

The activity in this field is largely confined to the biochemical sciences and the reader is referred to the literature in that area for additional descriptions of brominations.

HYDROCARBONS AND OLEFINS

Pentane (*8C*) was brominated in the vapor phase at 80° C. to form polybrominated products. No carbon chain fission was detected. The kinetics (*5C*) of iodine-catalyzed aromatic brominations were studied and the following mechanism was proposed:

$$Br_2 + I_2 \rightleftarrows 2BrI \text{ (fast)}$$

$$C_6H_6 + Br_2 \rightleftarrows C_6H_6 - Br_2 \text{ (fast)}$$

$$C_6H_6Br_2 + BrI \longrightarrow C_6H_5Br + HBr + BrI \text{ (slow)}$$

Nuclear bromination (*13C*) of toluene was conducted with various halogenated *N*-bromoacetamides. The result indicates that the activity of the brominating agent, *R*CONHBr, increased in the order: $R = CH_3 < CCl_3 < CCl_2H < CClH_2 < CF_3$. Allylic bromination activity decreased in the order: $R = CH_3 > CCl_2H > CCl_3 > CClH_2 > CF_3$. Side-chain bromination (*17C*) of substituted toluenes with *N*-bromosuccinimide was conducted in carbon tetrachloride solution using a benzoyl peroxide initiator. The yields of the monobrominated products are as follows: 86% *o*-Cl, 90% *p*-Cl, 47% *o*-nitro, 78% *p*-nitro, 43% *o*-CN, 80% *p*-CN, 73% *o*-CO_2H, 95% *p*-CO_2H, and 46% *p*-MeO. A study (*15C*) of the mechanism of the reaction of 1,3-dibromo-5,5-dimethylhydantoin with toluene indicated that no reaction occurred in refluxing carbon tetrachloride in either light or dark. However, a trace of bromine was found to catalyze the reaction. Nuclear bromination (*7C*) of xylene was accomplished by passing a mixture of bromine, air, and xylene over a catalyst composed of $CuBr_2$, ThO_2, and CoO_2 at 150° to 300° C. By using a large excess of xylene over bromine, the product was principally monobromoxylene. Another nuclear bromination process (*1C*) comprised reaction of an aromatic compound with a mixture of bromine and chlorine in the presence of an iron halide. For example, nitrobenzene was converted to 1-bromo-3-nitrobenzene in 92% conversion at a reaction temperature of 70° C.

2-Methylnaphthalene (*3C*) was converted to 2-(bromomethyl) naphthalene in 75% yield by photochemical reaction with bromine in carbon tetrachloride solution. Bromination (*10C*) of 4-methylphenanthrene in acetic acid gave the 10-bromo derivative in good yield. Anthracene (*14C*) on treatment with 1,3-dibromo-5,5-dimethylhydantoin in refluxing carbon tetrachloride produced the 9-bromo derivative in 80% yield. On prolonged treatment, the 9,10-dibromo derivative was obtained in 60% yield. A similar reaction (*14C*) with phenanthrene produced the 9-bromo derivative in 50% yield.

Bromination (*11C*) of an ethylenic double bond was conducted using bromine together with pyridine hydrobromide. In this way, substitution reactions were considerably reduced and a more crystalline addition product was obtained. Styrene (*9C*) was converted to the dibromide in high yield by reaction with bromine in chloroform solution at −8° C. Reaction of 1-phenyl-1,3-butadiene (*6C*) with bromine in carbon tetrachloride gave both the dibromide and the tetrabromide.

MISCELLANEOUS

Nitromethane (*16C*) was brominated in aqueous sodium hydroxide solution at 25° to 30° C. to form bromonitromethane in yields up to 90%. Thiophene (*4C*) was reacted with 1,3-dibromo-5,5-dimethylhydantoin at reflux temperatures to give 2-bromothiophene in 71% yield. Similarly, carbazole (*4C*) in refluxing carbon tetrachloride produced 3-bromocarbazole in 37% yield. Bromination (*12C*) of 1,1,1-trifluoroacetone in an acid medium gave the dibromo derivative while, in a basic medium the tribromo derivative was obtained. Reaction (*2C*) of an acetal of heptanal with bromine in the presence of phosphorus trichloride at 30° C. gave α, α-dibromoheptanal in 43% yield.

IODINATION

During the past year, little activity has been reported in this area of halogenation.

A direct iodination (*1D*) of phthalic anhydride was accomplished using a mixture of iodine and oleum at 70° to 80° C. for a period of 6 days. The product was a mixture of the 3,6-diiodo- and 3,4,6-triiodophthalic acids. Iodination (*4D*) of *p*-aminobenzenesulfonamide with a mixture of iodine, ethanol, and water gave the monoiodo derivative. The method was claimed to be applicable to other sulfonamides. Reaction (*3D*) of 1-nonocosanol with iodine and red phosphorus at 145° C. gave 1-iodononocosane in good yield. 2-(iodoethyl)trimethylammonium iodide (*2D*) was prepared in 75% yield by reaction of the corresponding chloro compound with potassium iodide.

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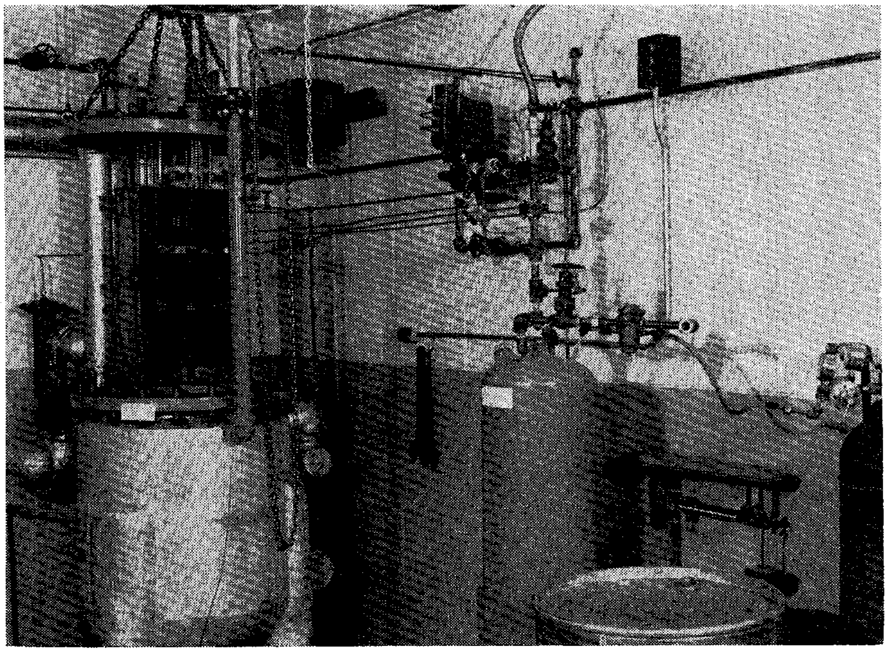

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Fluorination Cell (2000 Amp.) Prior to Assembly

COURTESY MINNESOTA MINING & MFG. CO.