approximately 100° was maintained by having the latter two tubes in a bath of molten sodium nitrate at about 500° C., while the former were located in another bath maintained at a lower temperature. Propane was introduced into the first tube through a preheater, and chlorine was introduced into the first and second tubes through glass jets sealed into 7-mm. Pyrex tubing and arranged concentric to the nickel tubes. The jets were prepared as described previously (*7*) and the pressure on the chlorine line was varied from about 50 to 80 pounds per square inch.

Reaction products passed from the reactor into a 3-liter, 3-necked flask to which was attached a water scrubber packed with Raschig rings. Chlorine and volatile organic products passed through the scrubber and were collected in a receiver cooled by dry ice. Chlorine was separated from the organic product by rectification. The organic residue was combined with that collecting in the 3-liter flask and the mixture was steam distilled. The dried steam distillate was rectified and the fractions identified by boiling points. The residue from steam distillation was identified as hexachlorobenzene.

Data from several experiments are summarized in Table II. These data show that carbon tetrachloride and tetrachloroethylene may be produced satisfactorily by this procedure. These two compounds constituted about 90% of the product. It is believed, however, that the two-step process discussed earlier in the paper is to be preferred for commercial practice.

ACKNOWLEDGMENT

Thanks are hereby extended the Hooker Electrochemical Company for sponsoring this investigation as Purdue Research Foundation Fellowship 173. The assistance of W. E. Burt and A. N. Johnson in the chlorination studies, and of Z. D. Welch in the preparation of this manuscript is gratefully acknowledged.

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Received January 12, 1948. Abstracted from the Ph.D. thesis of L. W. Devaney, presented to the faculty of Purdue University. Contribution from Purdue Research Foundation and Department of Chemistry, Purdue University.

Production of Hexachlorocyclopentadiene

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High temperature chlorinations of polychlorocyclopentanes, polychloroisopentanes, and polychloro-*n*-pentanes at atmospheric pressure gave hexachlorocyclopentadiene as a product in yields as high as 75%. Polychloroneopentanes gave chlorinolysis products rather than hexachlorocyclopentadiene. Polychloro-*n*-hexanes, polychloroisohexanes, and polychloro-2-methylpentanes were also converted to hexachlorocyclopentadiene by this process. Polychloropentanes having a specific gravity of about 1.63 to 1.70 were found to be the most suitable charging stock for the production of hexachlorocyclopentadiene at a chlorination temperature of about 470° C. The most favorable mole ratio of chlorine to polychloropentanes having the specific gravity of 1.64 was 5.71 to 1.

THE chlorocarbons, carbon tetrachloride, tetrachloroethylene, and hexachloroethane, have been produced by chlorination and chlorinolysis of polychlorohydrocarbons. Hexachlorobutadiene has been produced by thermal chlorination of polychloro butanes. The present investigation is an extension of the previously reported chlorination techniques to include the polychloropentanes and polychlorohexanes (*1*, *2*).

PRODUCTION OF HEXACHLOROCYCLOPENTADIENE

High yields of hexachlorocyclopentadiene are produced from polychlorocyclopentanes and, contrary to expectations, good yields of hexachlorocyclopentadiene were also obtained by chlorination of polychloroisopentanes and polychloro-*n*-pentanes. The first reported preparation of hexachlorocyclopentadiene was by chlorination of cyclopentadiene at 0° C. in petroleum ether in contact with a highly basic potassium hypochlorite solution (*4*). Hexachlorocyclopentadiene has also been prepared by refluxing a solution of 1,1,2,3,3,4,5,5-octachloro-1-pentene and dichloromethane in contact with aluminum chloride (*3*). In contrast to these preparations, the thermal chlorination of polychloropentanes at atmospheric pressure is a direct method for the preparation of hexachlorocyclopentadiene and also it is both economically and technologically practical.

Hexachlorocyclopentadiene which contains two chlorine atoms in a position allylic to two double bonds should find application in a number of fields since it is a reactive chemical intermediate and should prove to be a valuable addition to the list of commercially available chlorocarbons. Reactions of hexachlorocyclopentadiene are being published elsewhere.

PREPARATION OF POLYCHLOROHYDROCARBONS

Polychlorohydrocarbons for use as a starting material in thermal chlorinations were produced by the photochemical chlorination of the respective hydrocarbons following the continuous mixed-phase chlorination technique described previously (*1*). Chlorine was introduced into a chlorinator filled with polychlorohydrocarbons through a sintered-glass disk. The hydrocarbon was introduced as a liquid from a buret into the bottom of the chlorinator through a multiple-jet inlet arranged below the dispersion disk. Polychlorohydrocarbons of the desired specific gravity were withdrawn continuously. Dissolved chlorine and hydrogen chloride were removed by blowing air through the mixture before thermal chlorination. In industrial practice, this step is not necessary.

A convenient method for determining approximately the average chlorine content of mixtures of polychloro compounds is to determine the specific gravity of the mixture. Thus, a mixture of polychloropentanes having an average composition of $C_5H_{5.25}Cl_{6.75}$ may be identified by its specific gravity of 1.64. This method of identification is used in the tables as well as in the following discussion.

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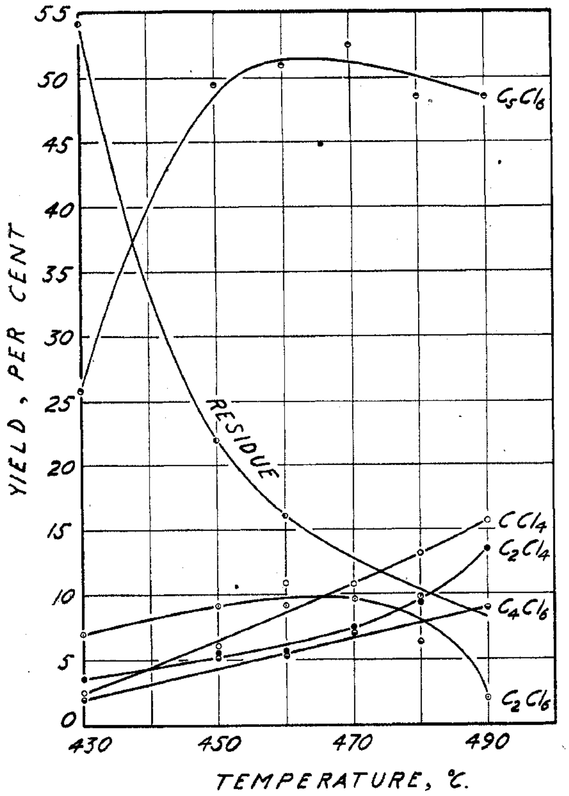

Figure 1. Effect of Temperature on Yield of Chlorocarbons from Polychloro-*n*-Pentanes

THERMAL CHLORINATIONS

The polychlorohydrocarbons were subjected to thermal chlorination at atmospheric pressure in the apparatus described previously (*1*). The apparatus was swept free of air at the start of each experiment by chlorine. Polychlorohydrocarbons were introduced into the chlorine stream at the desired rate from a buret and the mixture was led into a reactor made from a coil of Pyrex tubing having a diameter of 12 mm. where it was heated by immersing it in a bath of molten sodium nitrate. Reaction products were collected in a receiver at ambient temperatures. Volatile materials passed through a water-cooled condenser and were collected in a receiver cooled by dry ice. Hydrogen chloride and any other material which did not condense at dry ice temperature were vented into a water scrubber.

ANALYSIS AND IDENTIFICATION OF PRODUCTS. Dissolved hydrogen chloride and excess chlorine were allowed to vaporize from the chlorocarbon mixture. The product was washed three times with a 10% sodium bicarbonate solution and twice with distilled water to remove residual chlorine and hydrogen chloride. After drying over anhydrous calcium chloride, rectification of the chlorocarbon mixture gave the following materials: carbon tetrachloride, tetrachloroethylene, hexachloroethane, hexachlorobutadiene, hexachlorocyclopentadiene, octachlorocyclopentene, and a residue. Hexachlorobenzene was crystallized from a benzene solution of the residue. Carbon tetrachloride and tetrachloroethylene were rectified at atmospheric pressure, other compounds at a pressure of 4 mm. of mercury.

Carbon tetrachloride, tetrachloroethylene, hexachloroethane, hexachlorobutadiene, octachlorocyclopentene, and hexachlorobenzene (*1*) were identified by their physical properties. Hexachlorocyclopentadiene was identified by chemical analysis and by a comparison of its physical properties with those of a sample prepared from cyclopentadiene using the method of Straus, Kollek, and Heyn (*4*). Chlorine determinations gave values of 77.9 and 77.9% compared to a calculated value of 77.99%. The molecular weights, determined by the Victor Meyer vapor-density method, were 270 and 273 compared to a calculated value of 272.8. Other determinations gave values of 21.92 and 22.32% for carbon which compare favorably with the calculated value of 22.01%. Additional proof of structure for hexachlorocyclopentadiene was found in the addition of chlorine. Hexachlorocyclopentadiene and chlorine were sealed in a Carius tube at a mole ratio of 2 to 1 and illuminated for 6 hours at room temperature and for an additional 4 hours at 85° C. The product was 42% octachlorocyclopentene.

Hexachlorocyclopentadiene has the following properties: boiling point (4 mm.), 83° to 84° C.; boiling point (760 mm.), 236° to 238° C.; melting point, 7.8° to 8.2° C.; n_D^{20}, 1.5652; and d_4^{20}, 1.7119.

TEMPERATURE. Investigation of the effect of temperature upon the chlorination of polychloro-*n*-pentanes having a specific gravity of 1.64 at a mole ratio of chlorine to polychlorohydrocarbons of 6 to 1 (Table I, Figure 1) revealed that the best yields of hexachlorocyclopentadiene were obtained at temperatures in the range of 450° to 490° C., the optimum temperature being about 470° C. At lower reaction temperatures, a large residue of material boiling at a higher temperature than hexachlorocyclopentadiene was obtained, while at higher temperatures, chlorinolysis products were substantially increased with resultant reduction in the quantity of hexachlorocyclopentadiene. The residue obtained by chlorination below 450° C. contained a substantial amount of octachlorocyclopentene which is converted to hexachlorocyclopentadiene at the higher temperature by loss of chlorine.

TABLE I. EFFECT OF TEMPERATURE ON CHLORINATION OF POLYCHLORO-*n*-PENTANES

Experiment No.	B-121	B-125	B-130	B-131	B-129	B-134
Temperature, ° C.	430	450	460	470	480	490
Time, minutes	64	64	64	64	64	54
Volume of reactor, ml.	275	275	275	275	275	300
Polychloropentanes, grams[a]	264	267	273	271	267	250
Chlorine, liters/hour	116	116	116	116	116	126
Product, grams	219	171	214	215	215	212
Composition, % by weight						
CCl_4	2.3	5.9	10.8	10.7	12.1	15.6
C_2Cl_4	3.4	5.3	5.6	7.4	9.7	13.7
C_2Cl_6	7.1	8.2	8.4	9.7	9.7	1.8
C_4Cl_6	2.1	5.3	5.1	7.4	6.1	8.9
C_5Cl_6	26.0	49.7	50.9	52.6	48.4	48.6
Residue	53.8	21.5	16.4	10.6	13.6	8.5

[a] Specific gravity of the polychloropentanes was 1.64.

Any hydrocarbon, except neopentane, containing five or six carbon atoms may be chlorinated directly to give hexachlorocyclopentadiene, provided that a sufficient quantity of chlorine is used. In the case of isopentane, hexachlorocyclopentadiene was obtained in 51.3% yield by chlorinating at 470° C. using a chlorine to hydrocarbon mole ratio of 60 to 1. However, polychloropentanes having a specific gravity of 1.62 or higher can be chlorinated at 470° C. with little or no excess chlorine to produce good yields of hexachlorocyclopentadiene.

In a series of experiments carried out to determine the effect of the chlorine content of starting polychloro-*n*-pentanes on the yield of hexachlorocyclopentadiene, the best yields were obtained by using polychloro-*n*-pentane mixtures having a specific gravity of 1.60 or less. Large amounts of chlorine were required to obtain high yields of hexachlorocyclopentadiene and to avoid the formation of hexachlorobenzene as a major organic product. Starting materials having a specific gravity above about 1.64 gave larger amounts of high boiling residue than obtained using materials having a lower specific gravity. The data are summarized in Table II and illustrated graphically in Figure 2. No attempt was made in this investigation to determine the effect of distribution or location of chlorine atoms in the *n*-pentane structure upon the yield of hexachlorocyclopentadiene.

MOLE RATIO. A study of the effect of chlorine to polychlorohydrocarbon mole ratios on the conversion of polychloro-*n*-pentanes having a specific gravity of 1.64 to hexachlorocyclopenta-

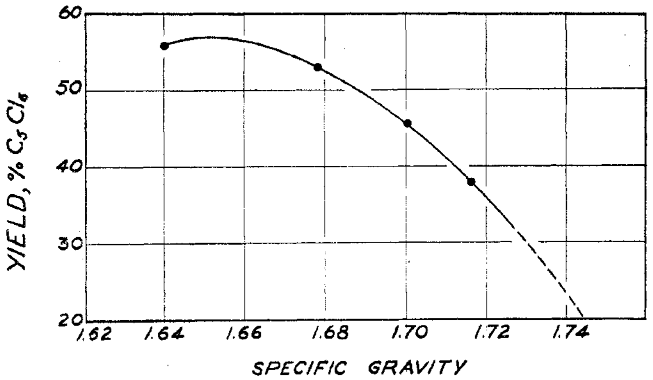

Figure 2. Effect of Degree of Prechlorination of *n*-Pentane

TABLE II. EFFECT OF DEGREE OF CHLORINATION OF STARTING POLYCHLORO-*n*-PENTANES[a]

Experiment No.	B-285	B-137	B-286	B-284	B-283
Time, minutes	4.5	55	64	57	63
Polychloro-*n*-pentanes, grams	20	249	300	268	298
Specific gravity	1.590	1.64	1.679	1.701	1.716
Chlorine, liters/hour	126	116	116	116	116
Product, grams	. . .	199	230	226	252
Composition, % by weight					
CCl_4	. . .	15.5	13.0	14.1	15.1
C_2Cl_4	. . .	6.0	10.0	11.1	10.3
C_2Cl_6	. . .	6.5	2.6	5.2	2.5
C_4Cl_6	. . .	5.0	5.2	8.0	10.3
C_5Cl_6	. . .	55.3	53.5	46.9	38.1
Residue	[b]	8.0	10.4	10.1	17.8

[a] Temperature was 470° C. in all experiments.
[b] Product from this experiment was essentially hexachlorobenzene.

diene was made at a temperature of 470° C. Mole ratios of chlorine to polychlorohydrocarbons below about 4.7 to 1 were ineffective in eliminating burning and carbonization. These undesirable features were absent at a ratio of 5.3 to 1. Although the maximum yield of hexachlorocyclopentadiene was obtained at a mole ratio of 5.7 to 1, the value is not significantly different from the yield obtained at slightly higher or lower mole ratios. The results indicate that the mole ratio has little if any effect upon the yield of hexachlorocyclopentadiene after a satisfactory ratio, above the burning or carbonization concentration, has once been attained. A compilation of these data appears in Table III.

CARBON STRUCTURE. A 74.5% yield of hexachlorocyclopentadiene was produced by the chlorination of polychlorocyclopentanes at 460° C. No carbon-carbon fission products boiling lower than hexachlorocyclopentadiene were obtained at this temperature. The highest yields of hexachlorocyclopentadiene obtained from polychloro-*n*-pentanes and polychloroisopentanes were 55.3 and 56.3%, respectively. It is to be expected that the yields of hexachlorocyclopentadiene would be best from polychlorocyclopentanes, as the mechanism for this transformation is less complicated than in the case of the other polychlorohydrocarbons studied.

Results obtained with polychloro-*n*-pentanes and polychloroisopentanes indicate that carbon skeletal rearrangement and cyclization can occur as readily in the polychloroisopentanes as in the polychloro-*n*-pentanes. Polychloroneopentanes did not yield any hexachlorocyclopentadiene upon chlorination. Instead, carbon tetrachloride and tetrachloroethylene were obtained in yields of 51.9 and 31.0%, respectively, indicating that the neocarbon structure is more susceptible to the chlorinolysis reaction than to carbon skeletal rearrangements. Carbon tetrachloride and tetrachloroethylene were obtained in 30.8 and 21.8%, yields, respectively, by the chlorination of polychloroneohexanes, further substantiating this observation. However, the polychloroneohexanes also gave an 18.8% yield of hexachlorocyclopentadiene. This indicates that, if upon carbon-carbon fission an isopentane or a *n*-pentane structure can be produced, hexachlorocyclopentadiene will result. This observation is substantiated by the fact that 19.7, 21.3, and 17.2% yields of hexachlorocyclopentadiene were obtained from the chlorination of polychloro-*n*-hexanes, polychloroisohexanes, and polychloro-3-methylpentanes, respectively. Data from this series of determinations are summarized in Table IV.

DISCUSSION

The formation of hexachlorocyclopentadiene by the action of chlorine on polychloropentanes at high temperatures and atmospheric pressure arouses considerable interest concerning the mechanism of the reaction. At the present time, however, sufficient data are not available for a positive or accurate interpretation of the mechanism.

The production of hexachlorocyclopentadiene from polychlorocyclopentanes must involve at least the mechanisms of chlorination, dehydrochlorination, and possibly dechlorination. The additional mechanism of cyclization occurs during the chlorination of polychloro-*n*-pentanes. The chlorination of polychloroisopentanes involves still another mechanism—namely, carbon skeletal rearrangement. Hexachlorocyclopentadiene is produced from polychlorohexanes by the previously mentioned mechanisms, and, in addition, by carbon-carbon fission. The most advantageous starting material from the standpoint of yields is cyclopentane. However, the more ready availability of isopentane and *n*-pentane make these two hydrocarbons the most promising materials for industrial application of the process. Chlorination of polychloroneopentanes did not produce any hexachlorocyclopentadiene, chlorinolysis taking precedence over carbon skeletal rearrangement in this case.

TABLE III. EFFECT OF MOLE RATIO OF REACTANTS ON CHLORINATION OF POLYCHLORO-*n*-PENTANES[a]

Experiment No.	B-147	B-146	B-137	B-131	B-136	B-135
Mole ratio, Cl_2:polychloropentanes	4.7	5.3	5.7	6.0	6.6	7.2
Volume of reactor, ml.	300	300	300	275	300	300
Time, minutes	58	55	55	64	55	55
Polychloropentanes, grams	258	249	249	271	249	251
Chlorine, liters/hour	94	107	116	116	133	148
Product, grams	224	219	199	215	206	207
Composition, % by weight						
CCl_4	10.3	12.3	15.5	10.7	11.6	13.0
C_2Cl_4	11.1	5.0	6.0	7.4	7.8	5.3
C_2Cl_6	6.3	6.4	6.5	9.7	7.8	10.6
C_4Cl_6	5.3	2.7	5.0	7.4	5.3	3.9
C_5Cl_6	51.3	51.6	55.3	52.6	51.5	52.1
Residue	10.3	17.3	8.0	10.6	10.7	9.7

[a] Temperature was 470° C. and specific gravity of polychloropentanes 1.64. ($C_5H_{6.75}Cl_{5.25}$).

TABLE IV. EFFECT OF CARBON STRUCTURE ON YIELD OF HEXACHLOROCYCLOPENTADIENE

Experiment No.	B-137	B-234	B-225	B-85	B-103	B-105	B-106	B-80
Carbon structure	*n*-C_5	Iso-C_5	Neo-C_5	Cyclo-C_5	*n*-C_6	Iso-C_6	3-Me-C_5	Neo-C_6
Temperature, ° C.	470	470	470	460	465	465	465	470
Time, minutes	55	70	70	105	71	81	98	120
Volume of reactor, ml.	300	300	300	275	275	275	275	275
Chlorohydrocarbons, grams	249	340	396	310	297	225	360	357
Specific gravity	1.64	1.62	1.56	1.67	1.73	1.75	1.78	1.74
Chlorine atoms per molecule	6.75	6	8	8	11	11	11	9
Chlorine, liters/hour	116	145	116	85	115	115	115	94
Mole ratio, Cl_2:polychlorohydrocarbon	5.7	6	10	8	7	10	9.5	9.3
Product, grams	119	318	313	251	110	77	95	234
Composition, % by weight								
CCl_4	15.5	12.9	51.9	. .	9.6	18.5	7.8	30.8
C_2Cl_4	6.0	10.0	31.0	. .	4.8	14.8	10.0	21.8
C_2Cl_6	6.5	3.4	10.6	. .	3.0	Trace	1.7	3.4
C_4Cl_6	5.0	2.8		. . .	3.0	4.6	5.6	8.1
C_5Cl_6	55.3	56.3	. .	74.5	19.7	21.3	17.2	18.8
Residue	8.0	11.9	6.4	23.1	44.9	35.2	53.9	10.2

ACKNOWLEDGMENT

The authors are indebted to the Hooker Electrochemical Company for defraying expenses of this investigation as a Purdue Research Foundation Fellowship.

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RECEIVED January 12, 1948. Presented before the Division of Industrial and Engineering Chemistry at the 111th Meeting of the AMERICAN CHEMICAL SOCIETY, Atlantic City, N. J. Abstracted from the Ph.D. thesis by Charles F. Baranauckas, presented to the faculty of Purdue University. Contribution from Purdue Research Foundation and Department of Chemistry Purdue University.

Production of Hexachlorobutadiene

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In a continuation of chlorination-chlorinolysis studies, hexachlorobutadiene has been produced as the principal product of the chlorination of polychlorobutanes at high temperature and atmospheric pressure. Simultaneous chlorinolysis yields some carbon tetrachloride, tetrachloroethylene, hexachloroethane, and hexachlorobenzene. Starting materials were prepared from butane or chlorobutanes by photochemical chlorination. Polychlorobutanes thus produced were passed, with chlorine, through a hot tube and the products recovered. The hot tube chlorination process was studied extensively to determine optimum conditions for the production of hexachlorobutadiene. Yields in excess of 75% of this interesting chlorocarbon having conjugated double bonds may be obtained by the new process.

THE chlorination and dehydrochlorination of hexachlorobutene in the presence of various metallic chloride catalysts, such as ferric or antimony, at temperatures of 70° to 140° C. to yield hexachlorobutadiene are the subject matter of several patents (*3, 4*).

The present investigation included the chlorination of polychlorobutanes at high temperature and atmospheric pressure in a hot tube without the employment of a catalytic agent. High yields of hexachlorobutadiene are obtained in this manner; minor proportions of carbon tetrachloride, tetrachloroethylene, and hexachloroethane were formed during the process by simultaneous and competitive chlorinolysis. Variables in the process were studied extensively to determine optimum conditions.

PREPARATION OF POLYCHLOROBUTANES

It has been shown (*2*) that a polychlorinated paraffin hydrocarbon may be produced by introduction of the hydrocarbon and chlorine through inlets maintained a relatively short distance apart into an irradiated body of liquid, preferably a body of material which is similar to the product to be produced by the chlorination reaction. In a detailed study of the process as applied to the chlorination of propane, it was found that the specific gravity of the product increased with a higher ratio of chlorine to propane, and that only small quantities of mono- and dichloropropanes were ever present in the reaction products. This procedure was applied to the preparation of polychlorobutanes for the present investigation.

The effect of various ratios of chlorine to butane on the continuous photochemical chlorination of butane was studied extensively. In general, the specific gravity of the product increased with a higher mole ratio of chlorine to butane up to a ratio of about 7 to 1. For example, with a chlorine to butane mole ratio of 6 to 1, the specific gravity of polychlorobutane product was 1.63; at a mole ratio of 7 to 1, the specific gravity was 1.68; but at a mole ratio of 8 to 1, the specific gravity was again 1.68. With the latter ratio, free chlorine was present in the exit gases. The chlorinations were generally carried out at about 80° C., as considerable chlorinolysis was found to occur at temperatures substantially above 90° C. In some instances, polychlorobutanes produced by the continuous process were chlorinated batchwise to products of higher specific gravity.

The capacity of the reactor (75 cm. × 75 mm.) (*2*) was determined at a temperature of approximately 80° C. under conditions at which substantially all of the chlorine and butane reacted. At a mole ratio of 6 chlorines to 1 butane, the capacity was 15 liters of butane and 90 liters of chlorine per hour; at a mole ratio of 7 to 1, the capacity was found to have decreased to 6 liters of butane and 42 liters of chlorine per hour.

The same photochemical chlorination technique as described for the conversion of butane to polychlorobutanes was applied successfully to butene with a substantial saving of chlorine. This is of commercial significance, as a mixture of butane and butenes is readily available from petroleum refineries.

CHLORINATION OF POLYCHLOROBUTANES

Although the reaction of chlorine and tetrachlorobutane at high temperatures and pressures has been shown to give high yields of hexachloroethane (*1*) alone or together with carbon tetrachloride, depending upon the exact conditions employed, and it has been shown that carbon tetrachloride and tetrachloroethylene (*2*) can be obtained in excellent yields by the treatment of polychloropropanes with chlorine at elevated temperatures and atmospheric pressure, application of the latter procedure to polychlorobutanes produced only small yields of these products. The principal product of the reaction between chlorine and polychlorobutanes at high temperatures and atmospheric pressure was found to be hexachlorobutadiene. Varying amounts of carbon tetrachloride, tetrachloroethylene, and hexachloroethane were produced by a competing chlorinolysis reaction, and the ratios of these chlorocarbons in the product depended upon the conditions of reaction. Small amounts of hexachlorobenzene were also produced.

APPARATUS. The production of hexachlorobutadiene was carried out in an apparatus similar to that described for the chlorinolysis of polychloropropanes (*2*).

Chlorine and polychlorobutanes were mixed at a tee and the mixture was introduced into the reactor consisting of coil made from 12-mm. Pyrex tubing and having a volume of 200 to 250 ml. The reactor was heated to 400° to 500° C. in a bath of molten sodium and potassium nitrate. The temperature of the bath was measured by a thermometer. Reaction products passed from the reactor into an air-cooled receiver and thence into a water scrubber. Unreacted chlorine and uncondensed organic products leaving the scrubber were collected in a receiver maintained at dry ice temperature. The organic products were combined and washed with a dilute sodium bicarbonate solution and dried.

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