nitrosation, a small volume of 2% aqueous hydrochloric acid be added to the acetic acid solution to dissolve the condensation product completely.

Anal. Calcd. for $C_{12}H_{21}N_3O_2$: C, 60. 22; H, 8.85; N, 17.56. Found: C, 60.39; H, 8.80; N, 17.74.

DL-*cis*-2-Cyclohexylidene-1-nitroso-1-(2-hydroxycyclohexyl)-hydrazine (*cis*-IV).—Condensation of *cis*-I with V followed by nitrosation was carried out exactly like the preparation of *trans*-II. The condensation product, DL-*cis*-2-cyclohexylidene-1-(2-hydroxycyclohexyl)hydrazine, was recrystallized from benzene, m.p. 102–104° dec., 90% yield.

Anal. Calcd. for $C_{12}H_{22}N_2O$: C, 68.53; H, 10.54; N, 13.32. Found: C, 68.44; H, 10.48; N, 13.24.

The nitrosated product, *cis*-IV, was recrystallized from ethanol as colorless plates, m.p. 120–121° dec., 83% yield.

Anal. Calcd. for $C_{12}H_{21}N_3O_2$: C, 60.22; H, 8.85; N, 17.56. Found: C, 59.81; H, 9.04; N, 17.56.

Acidic Hydrolysis of *trans*-II. The Formation of DL-*trans*-2-Aminocyclohexanol Hydrochloride (*trans*-VI·HCl).—A suspension of *trans*-II (0.58 g.) in 20% ethanolic hydrochloric acid solution (2 ml.) went slowly into clear solution while standing at room temperature. After 3 hr., ethanol (10 ml.) was added to the solution, and the solution was distilled. The treatment was repeated until cyclopentanecarboxaldehyde (III) was not found in the distillate. The oily residue crystallized with ice cooling to yield 0.065 g. (20%) of colorless needles, m.p. 172–173° after recrystallization from ethanol–ether. The product was identified as *trans*-VI·HCl by a mixture melting point and infrared spectrum determinations.

Acidic Hydrolysis of *cis*-IV. The Formation of DL-*cis*-2-Aminocyclohexanol Hydrochloride (*cis*-VI·HCl).—After work-up just like the foregoing item, 1.60 g. of *cis*-IV was converted to 0.06 g. (7%) of *cis*-VI·HCl, which was recrystallized from ether–ethanol as colorless needles, m.p. 181–182°. The identification depended upon a mixture melting point and infrared spectrum determinations.

Reaction of DL-*trans*-2-Hydroxycyclohexylhydrazine (*trans*-I) with Nitrous Acid. (1). The Simultaneous Formation of *trans*-II and III.—To 11 ml. of 10% aqueous acetic acid solution containing 0.73 g. (5.6 mmoles) of *trans*-I was added dropwise 5.6 ml. of 1 *N* aqueous sodium nitrite (5.6 mmoles) at 5–10° while stirring. The solution was stirred for 30 or more minutes causing the precipitation of crystals. Filtration followed by recrystallization from benzene gave colorless needles, 0.15 g. (22.4%) yield, m.p. 70–71° dec. alone and on admixture with authentic *trans*-II. The infrared spectrum was completely superimposed on that of *trans*-II. The filtrate was neutralized with sodium carbonate, and sodium chloride was added. The solution was extracted with ether, dried over anhydrous sodium sulfate, and evaporated to dryness. The residue was converted by the usual method to the 2,4-dinitrophenylhydrazone which was recrystallized from ethanol furnishing pale yellow scales, 0.08 g. (5%) yield, m.p. 152–154° dec. alone and on admixture with authentic III 2,4-dinitrophenylhydrazone.

(2). **The Formation of III.**—*trans*-I was treated essentially as in method 1, except 28.0 mmoles of sodium nitrite per 5.6 mmoles of the material was used. Consequently, the reaction furnished only a carbonyl compound which was converted to the 2,4-dinitrophenylhydrazone; the yield was 1.06 g. Recrystallization from ethanol gave pale yellow scales, 0.85 g. (53%) yield, m.p. 156–158° dec. alone and on admixture with authentic III 2,4-dinitrophenylhydrazone.

Reaction of DL-*cis*-2-Hydroxycyclohexylhydrazine (*cis*-I) with Nitrous Acid. (1). **The Simultaneous Formation of *cis*-II, III, *cis*-IV, and V.**—To 42 ml. of 10% aqueous acetic acid solution containing 3.0 g. (23 mmoles) of *cis*-I was added dropwise 23 ml. of 1 *N* aqueous sodium nitrite (23 mmoles) at 5–10° with good stirring. Stirring was continued for 30 or more minutes. An oily product which separated from the solution during the operation crystallized on standing. Filtration followed by repeated recrystallization from ethanol gave colorless plates, 0.56 g. (22%) yield, m.p. 120–121° dec. alone and on admixture with authentic *cis*-IV. Allowing the filtrate to stand for many hours caused the deposition of another crystalline product. Filtration followed by repeated recrystallization from ethanol gave colorless needles, 0.02 g. (0.7%) yield, m.p. 90–90.5° dec. alone and on admixture with authentic *cis*-II. Thereafter, the filtrate was treated as in 1 of the previous item to give a mixture of 2,4-dinitrophenylhydrazones. Fractional recrystallization gave pale yellow scales, m.p. 150–153° dec., 0.05 g. (0.71%) yield, and pale orange-yellow scales, m.p. 155–156° dec., 0.16 g. (2.4%) yield. The former and the latter scales were identical with III 2,4-dinitrophenylhydrazone and V 2,4-dinitrophenylhydrazone, respectively, by mixture melting point determinations.

(2). **The Simultaneous Formation of III and V.**—*cis*-I (11.5 mmoles) was treated with sodium nitrite (57.5 mmoles) in an aqueous acetic acid solution just like in 1 of this item. Only III and V were isolated as 2,4-dinitrophenylhydrazones from the reaction mixture to yield 0.16 g. (4.9%) and 0.61 g. (19%), respectively.

Acknowledgment.—The authors wish to acknowledge microanalysis and infrared spectrum determinations performed by the Analytical Section of this institute.

The Light-Induced Reactions of Iodine Trichloride with Cyclohexane[1]

WENDELL W. HESS,[2] EARL S. HUYSER, AND JACOB KLEINBERG

Department of Chemistry, University of Kansas, Lawrence, Kansas

Received September 3, 1963

Iodine trichloride and cyclohexane undergo a photochemically induced reaction. The products isolated are hydrogen chloride, chlorocyclohexane, iodocyclohexane, *trans*-1,2-dichlorocyclohexane, *trans*-1-chloro-2-iodocyclohexane, and molecular iodine. A free-radical chain sequence involving the $ICl_2\cdot$ radical is proposed to account for the formation of hydrogen chloride, chlorocyclohexane, and iodocyclohexane. Dehydrohalogenation of the halocyclohexanes produced in the chain sequence yields cyclohexene, the intermediate required for the formation of the 1,2-dihalocyclohexanes. Molecular iodine arises from reaction of hydrogen iodide with iodine trichloride.

A number of reports dealing with the halogenation of aromatic hydrocarbons by means of iodine trichloride have appeared in the literature.[3] Products were obtained in which both chlorine and iodine had been substituted on the aromatic ring, and the nature of the products indicated that the reaction proceeded by ionic mechanisms in the absence of illumination. The present paper is concerned with the light-induced reaction of iodine trichloride with the aliphatic hydrocarbon, cyclohexane. The results of our study are best interpreted in terms of a free-radical chain reaction involving the interhalogen radical $ICl_2\cdot$.

---

(1) This work was supported by a grant from the National Science Foundation. Support by this agency is gratefully acknowledged.

(2) This paper was taken from a portion of a thesis submitted by W. W. H. in partial fulfillment of the requirements for the Ph.D. degree from the University of Kansas, 1963.

(3) (a) E. Campaigne and J. R. Leal, *J. Am. Chem. Soc.*, **75**, 230 (1953); (b) G. Calingaert, M. E. Griffing, E. R. Kerr, A. J. Kalka, and H. D. Orloff, *ibid.*, **73**, 5224 (1951); (c) V. Arrequine, Jr., and E. B. Garcia, *Anales asoc. quim. Arg.*, **9**, 121 (1921); (d) V. Thomas and P. Depuis, *Compt. rend.*, **143**, 282 (1906); (e) H. Muller, *J. Chem. Soc.*, **15**, 41 (1862).

Results and Discussion

In a typical experiment, a stirred mixture of iodine trichloride with a large excess of cyclohexane was illuminated with a 275-watt sun lamp at 14–15° for 90 min. After a few minutes of illumination, the formation of molecular iodine and the evolution of hydrogen chloride were noted. Upon conclusion of illumination, three products—chlorocyclohexane, iodocyclohexane, and *trans*-1,2-dichlorocyclohexane—were isolated and identified by gas chromatographic retention times on two different columns and by comparison of their infrared and n.m.r. spectra with those of authentic samples. Gas chromatographic analysis of the original reaction mixture indicated the presence of a fourth organic component which decomposed when isolation by column chromatography was attempted. The gas chromatographic retention times of this fourth component on two columns were identical with the retention times of an authentic sample of *trans*-1-chloro-2-iodocyclohexane. Quantitative determination of the four organic products was made from their respective gas chromatographic peak areas. The quantities of iodine and hydrogen chloride produced were found by standard methods. The results of analyses for four separate reactions are shown in Table I.

TABLE I

DATA FROM REACTIONS BETWEEN IODINE TRICHLORIDE AND CYCLOHEXANE[a]

Run no.	ICl_3	$C_6H_{11}Cl$[b]	$C_6H_{11}I$	$C_6H_{10}Cl_2$	$C_6H_{10}ICl$	HCl	I_2
1[c]	9.91	2.77	0.59	2.41	2.52	16.44	3.20
2[d]	12.23	2.66	.81	3.40	2.92	20.48	3.91
3[d]	12.02	2.96	.75	3.50	2.80	20.88	3.87
4[d]	12.96	3.61	.78	3.81	2.88	21.65	4.58

[a] All numbers are expressed in millimoles. [b] See Experimental for accuracy of determination. [c] Organic products determined on diethylene glycol succinate column. [d] Organic products determined on E-600 column.

It is quite likely that in cyclohexane medium iodine trichloride is somewhat dissociated into iodine monochloride and molecular chlorine,[4] and the possibility that this dissociation plays a role in the formation of the products noted above must be considered. When this possibility is taken into account, two alternative paths offer themselves for the light-induced reaction of iodine trichloride with cyclohexane. One of these mechanistic pathways (A) involves iodine trichloride as the source of the halogens, and the other path (B) requires the dissociation of the trichloride into iodine monochloride and chlorine molecules (eq. 1–18).

Mechanistic Path A

Initiation

$$ICl_3 \xrightarrow{h\nu} ICl_2\cdot + Cl\cdot \quad (1)$$

Chain sequence

$$C_6H_{12} + Cl\cdot \longrightarrow C_6H_{11}\cdot + HCl \quad (2)$$

$$C_6H_{11}\cdot + ICl_3 \longrightarrow C_6H_{11}Cl + ICl_2\cdot \quad (3)$$

$$ICl_2\cdot + C_6H_{12} \longrightarrow C_6H_{11}\cdot + ICl + HCl \quad (4)$$

$$C_6H_{11}\cdot + ICl \longrightarrow C_6H_{11}I + Cl\cdot \quad (5)$$

Secondary reactions

$$C_6H_{11}I \xrightarrow{HCl} C_6H_{10} + HI \quad (6)$$

$$C_6H_{11}Cl \xrightarrow{HCl} C_6H_{10} + HCl \quad (7)$$

$$3HI + ICl_3 \longrightarrow 2I_2 + 3HCl \quad (8)$$

$$2C_6H_{10} + ICl_3 \longrightarrow C_6H_{10}Cl_2 + C_6H_{10}ICl \quad (9)$$

Mechanistic Path B

$$ICl_3 \rightleftharpoons ICl + Cl_2 \quad (10)$$

Initiation

$$ICl \xrightarrow{h\nu} I\cdot + Cl\cdot \quad (11)$$

$$Cl_2 \xrightarrow{h\nu} 2Cl\cdot \quad (12)$$

Chain sequence

$$C_6H_{12} + Cl\cdot \longrightarrow C_6H_{11}\cdot + HCl \quad (13)$$

$$C_6H_{11}\cdot + ICl \longrightarrow C_6H_{11}I + Cl\cdot \quad (14)$$

$$C_6H_{11}\cdot + Cl_2 \longrightarrow C_6H_{11}Cl + Cl\cdot \quad (15)$$

Secondary reactions

$$C_6H_{11}I \xrightarrow{HCl} C_6H_{10} + HI \quad (6)$$

$$C_6H_{11}Cl \xrightarrow{HCl} C_6H_{10} + HCl \quad (7)$$

$$HI + ICl \longrightarrow I_2 + HCl \quad (16)$$

$$C_6H_{10} + Cl_2 \longrightarrow C_6H_{10}Cl_2 \quad (17)$$

$$C_6H_{10} + ICl \longrightarrow C_6H_{10}ICl \quad (18)$$

It is to be noted that the chain sequences for both paths A and B lead to the same stoichiometry.

$$2C_6H_{12} + ICl_3 \xrightarrow{h\nu} C_6H_{11}Cl + C_6H_{11}I + 2HCl \quad (19)$$

It is only a comparison of the relative quantities of products formed in the secondary reactions with those predicted from paths A and B that the more likely mechanism can be determined. This comparison can be justifiably made since the iodine trichloride was completely utilized in the reaction and accounted for adequately in the products formed, as is shown by the data of Table II. Although we cannot completely eliminate the possibility that both paths may be operative, our data indicate strongly that path A must be by far the predominant one. Our arguments for this conclusion follow.

First let us compare the quantities of hydrogen iodide required to produce the experimentally determined amount of iodine in terms of mechanistic paths A and B. Using the data from run number 3 in Table I, we find for mechanism A that 5.8 mmoles of hydrogen iodide would be required according to eq. 8 to produce the observed 3.87 mmoles of iodine, whereas for mechanism B, according to eq. 16, only 3.87 mmoles of hydrogen iodide would be required. The total amount of cyclohexyl iodide (and cyclohexyl chloride) initially formed must be equal to the sum of the quantity of hydrogen iodide calculated and that of cyclohexyl iodide found experimentally. For mechanism A this sum is 6.55 mmoles and for mechanism B 4.62 mmoles. The total quantity of olefin that could be produced must be equal to the sum of the total amount of each cyclohexyl iodide and cyclohexyl chloride initially produced minus the amounts of these substances observed experimentally. For path A the *total* olefin *potentially available* turns out to be 9.39 mmoles and for path B 5.53 mmoles. Since a total of 6.30 mmoles of olefin are re-

---

(4) R. D. Whitaker and G. B. Fozzard, *Virginia J. Sci.*, **14**, 6 (1963).

TABLE II

MASS BALANCE CALCULATIONS

	Chlorine, g.-atoms		Iodine, g.-atoms	
Run no.	Calcd.[a]	Found[b]	Calcd.[c]	Found[d]
1	29.73	26.55	9.91	9.51
2	36.69	32.86	12.23	11.55
3	36.06	33.64	12.02	11.29
4	38.88	35.76	12.96	12.82

[a] Calculation based on 3 g.-atoms of chloride/molecule of ICl_3. [b] Summation of yields of chlorine-containing compounds, with the number of atoms of chlorine in each type of molecule taken into account. [c] Equal to the amount of iodine trichloride introduced. [d] Summation of yields of iodine-containing compounds, with the number of atoms of iodine in each type of molecule taken into account.

quired for the formation of the dihalides actually found (run 3, Table I), path A can give rise to a sufficient quantity of olefin, whereas path B obviously cannot.

Next let us examine the quantity of hydrogen chloride found with the amounts expected from paths A and B. In both mechanisms there are three sources of this gas; these are (a) the free-radical chain sequence summarized in eq. 19; (b) the reaction of hydrogen iodide with iodine trichloride (eq. 8) or with iodine monochloride (eq. 16); and (c) the dehydrohalogenation of cyclohexyl chloride (eq. 7). In the previous paragraph it was shown that 6.55 mmoles each of cyclohexyl chloride and iodide would be formed initially through mechanism A in run 3. This corresponds to the evolution of 13.10 mmoles of hydrogen chloride. On the basis of the amount of iodine observed in run 3, reaction of hydrogen iodide with iodine trichloride would yield another 5.80 mmoles of hydrogen chloride. From the amount of cyclohexyl chloride found experimentally and that expected (6.55 mmoles) another 3.59 mmoles of hydrogen chloride would arise. Thus, the total quantity of hydrogen chloride which could be formed by path A is 22.49 mmoles. Similar calculations for path B with the data of run 3 yield 14.77 mmoles as the expected quantity of hydrogen chloride. Experimentally, 20.88 mmoles of this gas were observed. Here again, it is apparent that path A is more consistent with the data than is path B.

The above calculations show unequivocally that mechanistic path B cannot supply sufficient olefin to account for the quantities of dihalocyclohexanes formed nor does it account for the amount of hydrogen chloride which was observed experimentally. On the other hand, in terms of the quantities of products isolated path A offers a reasonable mechanism. However, our data do not completely eliminate the possibility that the reactions shown in mechanism B occur to a small extent. Similar calculations to those described for run 3, with the data of runs 1, 2, and 4 (see Table I), lead to the same conclusions. Finally, it should be emphasized that pathway A requires the generation of a new inorganic free radical, namely $ICl_2\cdot$.

Experimental

Chemicals.—Iodine trichloride was prepared according to the method of Booth and Morris.[5]

Anal. Calcd. for ICl_3: I, 54.39; Cl, 45.61. Found: I, 53.88; Cl, 45.61.

The compound can be kept for several weeks in a high state of purity if maintained under a chlorine atmosphere at temperatures below 10°. Freshly prepared iodine trichloride was used where any doubt existed concerning the purity of any sample at hand.

Iodine monochloride was made by direct union of the elements in a 1:1 molar ratio as described by Cornog and Karges.[6] The liquid product was gradually cooled until about 50% had solidified and then the remaining liquid was decanted and discarded. The solid was liquefied and the cooling and decantation process was repeated. The solid obtained was placed in a tightly stoppered flask, liquefied, and stored in a refrigerator. The crystals which formed on storage were used as needed.

Spectroquality grade cyclohexane was purchased from Matheson, Coleman and Bell Chemical Co. Gas chromatographic analysis showed the purity of the compound to be greater than 99%. The material was stored under an inert atmosphere in the presence of a desiccant and used without further purification.

Cyclohexene of "chromatoquality" was obtained from Matheson, Coleman and Bell Chemical Co. and used without purification. The material came packed under an inert atmosphere and had a reported purity of 99+ mole %.

Cyclohexyl chloride was made by the photochemical chlorination of cyclohexane. The compound was distilled from the reaction mixture and then redistilled through a 60-cm. Vigreux, column, the fraction boiling at 140–141° being collected. Gas chromatographic analysis showed the compound to be pure.

Cyclohexyl iodide was prepared according to the method described by Vogel.[7]

trans-1,2-Dichlorocyclohexane was prepared in the following manner. Chlorine was bubbled slowly into a solution of cyclohexene in carbon tetrachloride in the presence of ultraviolet light. Distillation of the reaction mixture yielded the crude dichloro compound which was purified by redistillation; b.p. 88–89° (30 mm.). The infrared spectrum of the compound was identical with that published by Stevens and Grummitt[8] for *trans*-1,2-dichlorocyclohexane.

trans-1-Chloro-2-iodocyclohexane was obtained as follows. Iodine monochloride dissolved in glacial acetic acid and cyclohexene in the same solvent were brought together in a 1:1 molar ratio.[9] The crude product separated as a heavy white oil and had to be distilled three times before high purity was obtained; b.p. 117–118° (14 mm.). Prior to use, the compound was stored in a refrigerator in order that decomposition be retarded.

Cyclohexyl bromide was prepared and purified by the method of Vogel.[10]

Oil-pumped dry nitrogen was employed without further purification to supply an inert atmosphere where needed.

Analytical Methods.—The organic products of reaction between iodine trichloride and cyclohexane were determined quantitatively by gas chromatography. The column found to be most suitable was composed of a polyglycol, E-600, obtained from the Dow Chemical Co., Freeport, Tex. Another substrate which was employed was diethylene glycol succinate. These substrates were put on acid-washed, 30–60-mesh Chromsorb support, obtained from the Johns Manville Co. The columns contained 10% by weight of the substrate. The E-600 column was 4 ft. in length and the succinate column 10 ft. long. The chromatograph employed was a Model A-90-P Aerograph. For the E-600 column a temperature between 80 and 90° was found to be suitable, and for the succinate column a temperature from 100 to 120° was used. Constant amounts of solution were injected by means of a Hamilton 10-μl. syringe. In all cases, at least three chromatograms of the reaction solution were taken, and the peak areas for each of the products were averaged.

In order to obtain quantitative data, an internal standard, cyclohexyl bromide, was employed. The addition of a known quantity of this compound to the reaction mixture after illumination permits one to determine the absolute quantities of the products present without knowledge of the volume of the reaction mixture. To do this, a reference solution which gave a chromatogram closely resembling that of the reaction mixture was prepared. This solution contained a known amount of the internal standard and of each of the products. Analysis of unknown reaction mixtures was immediately preceded and followed by similar analysis of the reference solution. The quantities of products in the reac-

---

(5) H. S. Booth and W. C. Morris, *Inorg. Syn.*, **1**, 167 (1939).

(6) J. Cornog and R. A. Karges, *ibid.*, **1**, 165 (1939).

(7) A. I. Vogel, "Practical Organic Chemistry," 3rd Ed., Longmans, Green and Co. Ltd., London, 1959, p. 284.

(8) H. C. Stevens and O. Grummitt, *J. Am. Chem. Soc.*, **74**, 4876 (1952).

(9) M. L. Brunel, *Ann. chim. phys.*, [8]**6**, 230 (1905).

(10) Ref. 7, p. 277.

tion mixture were determined by comparison of their peak areas with those of the compounds in the reference solution and with the use of the following equation.

$$\text{Moles } P_{\text{reac}} = \frac{\text{moles } (IS)_{\text{reac}}}{\text{area } (IS)_{\text{reac}}} \times \text{area } P_{\text{reac}} \left[\frac{\text{moles } P_{\text{ref}}}{\text{area } P_{\text{ref}}} \times \frac{\text{area } (IS)_{\text{ref}}}{\text{moles } (IS)_{\text{ref}}}\right]$$

where P_{reac} is the product sought, P_{ref} the product in the reference solution, $(IS)_{\text{reac}}$ the internal standard in the reaction solution, and $(IS)_{\text{ref}}$ the internal standard in the reference solution. The expression within the brackets constitutes a correction factor for the area of P_{reac} as compared to that of the internal standard; this correction factor usually had a value close to unity.

Separation of the organic products produced in the reaction was partially achieved by column chromatography on neutral Woelm alumina of varying water content. By this method, chlorocyclohexane, iodocyclohexane, and *trans*-1,2-dichlorocyclohexane were isolated and identified unequivocally by the identity of their infrared and n.m.r. spectra with those of the authentic samples. A fourth component in the reaction mixture, the presence of which was indicated by gas chromatographic analysis, was seen on the alumina columns, but attempts to elute it were unsuccessful since the compound decomposed. The fourth component had identical retention times on the two gas chromatographic columns noted above as an authentic sample of *trans*-1-chloro-2-iodocyclohexane prepared as described previously.[9]

Quantitative determination of the iodine formed was made on a Cary Model 14 spectrophotometer. Solutions containing known varying amounts of resublimed iodine dissolved in cyclohexane were prepared and their absorbance at 520 mμ measured. A plot of absorbance *vs.* concentration gave a straight line, and this plot was used as a calibration curve for the spectrophotometric determination of iodine in the reaction solution. New calibrations were made at suitable intervals to take into account minor changes that might have occurred in the instrument.

Hydrogen chloride produced in a reaction was swept into a known volume of standardized sodium hydroxide solution by means of dry nitrogen. Aliquots of the resulting solution were titrated with standardized hydrochloric acid to a phenolphthalein end point, and from the amount of base which has been consumed the quantity of hydrogen chloride was determined.

Reaction between Iodine Trichloride and Cyclohexane.—A 200-ml., three-necked standard taper round-bottomed flask was equipped with a condenser, a ground-glass Teflon blade stirrer, and a nitrogen inlet tube. A standard taper joint connected the condenser to a gas absorption tower. The entire apparatus was made moisture-free by flaming it while a rapid stream of dry nitrogen was passed through. The apparatus was cooled and then was so adjusted that the flask was submerged in a constant temperature water bath. Water from the bath maintained at 14–15° was circulated through the condenser. Approximately 90 ml. of pure cyclohexane was added to the flask and the stirrer put into operation. The nitrogen inlet tube was extended below the surface of the liquid, and the gas was permitted to flow at such a rate that the cyclohexane was not swept through the condenser. One hundred milliliters of standard sodium hydroxide solution was added to the gas absorption tower.

A carefully dried 25-ml. erlenmeyer flask fitted with a ground-glass stopper was weighed on a triple beam balance and then cold iodine trichloride was added under a stream of nitrogen to give the approximate weight of this reagent desired. The flask was tightly stoppered and weighed on an analytical balance. The bottom was then chilled in a mixture of Dry Ice and Cellosolve, and the iodine trichloride added to the stirred, cooled cyclohexane by raising the nitrogen inlet tube and quickly inverting the erlenmeyer flask. The flask was stoppered immediately, permitted to come to room temperature, and weighed. The nitrogen inlet tube was replaced and the gas flow adjusted to about 5 bubbles per min. at the absorption tower. A 275-watt ultraviolet sun lamp was placed at the outside of the water bath within 2 in. of the reaction mixture, immediately following the addition of iodine trichloride. The reaction mixture, originally red-orange in color, darkened shortly after the light was turned on and within a few minutes the violet color of iodine became evident. The reaction was allowed to proceed for 90 min., after which time the light was removed and the nitrogen flow gradually increased for a period of 2 hr. until it approximated 20 bubbles per min.

The absorption tower was then removed, stirring discontinued, and the reaction flask taken from the constant temperature bath. The nitrogen flow was stopped, and the condenser and gas inlet tube were rinsed with cyclohexane, the rinsings being added to the reaction mixture. The contents of the reaction flask were transferred quantitatively into a dry 100-ml. volumetric flask; the reaction flask was rinsed repeatedly with small amounts of cyclohexane, the washings added to the volumetric flask, and the solution brought up to volume with cyclohexane.

One milliliter of the solution was removed by means of a pipet, added to a dry 25-ml. volumetric flask, and diluted to volume with cyclohexane. A suitable aliquot (2–4 ml.) was removed, added to a dry 10-ml. volumetric flask, and diluted to volume with cyclohexane. The absorbance of this solution was measured at 520 mμ and from a previously prepared Beer's law plot of concentration *vs.* absorbance, the concentration of iodine was determined.

The other 99 ml. of reaction solution was transferred quantitatively to a 125-ml. erlenmeyer flask, and cyclohexane was removed on a "Roto-vac" apparatus. The "distillate" from this operation was condensed in a cold trap cooled by means of a Dry Ice–Cellosolve mixture. Concentration was continued until the solution remaining yielded suitable peaks for the products on the gas chromatograph.