

[CONTRIBUTION FROM THE RESEARCH LABORATORIES OF THE ETHYL CORPORATION]

The Partial Additive Chlorination of the Benzene Ring. III. Pentachlorocyclohexene and Hexachlorocyclohexene

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The photochlorination of monochlorobenzene and of *o*-dichlorobenzene, in the presence of iodine, results in part in the formation of the partial addition products, 1,3,4,5,6-pentachlorocyclohexene-1, and 1,2,3,4,5,6-hexachlorocyclohexene-1, respectively. Four steric isomers of each of these compounds have been separated chromatographically and characterized by chemical analysis and one or more of the following reactions: oxidative cleavage to tetrachloroadipic acid, alkaline dehydrochlorination to chlorobenzene isomers and comparison with chlorocycloolefins prepared by the monodehydrochlorination of benzene hexachloride or of heptachlorocyclohexane.

The photochlorination of benzene, in the presence of catalytic quantities of iodine or of iodine-releasing compounds, was shown¹ to proceed by three simultaneous processes, substitution chlorination, partial additive chlorination and normal additive chlorination, whereby chlorobenzene isomers, 3,4,5,6-tetrachlorocyclohexene-1 (benzene tetrachloride, BTC) and benzene hexachloride (BHC), respectively, were formed. In addition, isomers of 1,3,4,5,6-pentachlorocyclohexene-1 ($C_6H_5Cl_5$) were recovered from the reaction product.^{1,2} The formation of the later cycloolefin was attributed to the addition of chlorine to monochlorobenzene which was co-formed in the reaction. Confirmation of this explanation is now provided by the recovery of pentachlorocyclohexene in good yield from the iodine-catalyzed photochlorination of monochlorobenzene. That the "partial additive chlorination reaction" may be extended to other benzenoid compounds has been demonstrated by the synthesis of 1,2,3,4,5,6-hexachlorocyclohexene-1 ($C_6H_4Cl_6$) from *o*-dichlorobenzene by the same general procedure. From the products of the partial additive chlorination of monochlorobenzene and *o*-dichlorobenzene, respectively, four isomers each of pentachlorocyclohexene and hexachlorocyclohexene have been separated.

The decomposition of the hexachlorides of benzoic and chlorobenzoic acids to yield penta- and hexachlorocyclohexenes, respectively, has been reported by van der Linden.³ The rather unusual stability of the pentachlorocyclohexene (m.p. 103–104°) prepared by him is unexpected and in sharp contrast with the properties of the 2,3,4,5,6-pentachlorocyclohexene-1 synthesized by partial additive chlorination. Whereas van der Linden's product was not decomposed on heating with aluminum chloride or with alkaline permanganate solution, pentachlorocyclohexene prepared by the partial additive chlorination of monochlorobenzene undergoes dehydrochlorination with aluminum chloride in benzene, slowly at room temperature and rapidly under reflux conditions, to yield trichlorobenzene isomers; the double bond is oxidized readily with permanganate at room temperature with diol formation, as indicated by electrometric titration with aqueous permanganate in alcoholic solution; at higher temperatures or on standing, the ring is

cleaved and tetrachloroadipic acid (2,3,4,5-tetrachlorohexanedioic acid)¹ is formed.

γ -Hexachlorocyclohexene gives a positive permanganate test for unsaturation by the procedure of Ipatieff.⁴ Under conditions required for ring cleavage, such as prolonged refluxing with aqueous dichromate solution (0.36 *M* $Na_2Cr_2O_7$, 3.1 *M* H_2SO_4), dehydrochlorination and further oxidative degradation were observed. With alcoholic alkali, hexachlorocyclohexene is dehydrochlorinated rapidly to yield a mixture of tetrachlorobenzene isomers.

Recently, Nakazima and co-workers⁵ succeeded in effecting the partial dehydrochlorination of γ - and β -benzene hexachloride. From the former, a liquid isomer, γ -pentachlorocyclohexene (b.p. 123–124° at 11 mm.) was obtained, while from the latter a crystalline product, δ -pentachlorocyclohexene (m.p. 68–69°) was recovered. The same procedure was utilized by these investigators for the synthesis of three isomers of hexachlorocyclohexene (α , m.p. 147–148°; β , m.p. 126–127°; and γ , m.p. 100–101°).^{5,6}

Two of the $C_6H_5Cl_5$ isomers prepared by the partial additive chlorination of monochlorobenzene are identical with the γ - and δ -isomers, respectively, which have been synthesized by Nakazima⁵ and Cristol⁷ by monodehydrochlorination of the corresponding benzene hexachlorides. Our γ - $C_6H_5Cl_5$ (b.p. 115–116° at 4.0 mm., n_D^{20} 1.5630) gave the same infrared spectrum as a sample of material (from γ -BHC) provided by Prof. Nakazima. The δ -isomer, m.p. 68°,⁸ (from δ -BHC), obtained from Prof. Cristol, produced no depression in a mixed melting point determination with our isomer (m.p. 68.2–68.6°, cor.). The two remaining pentachlorocyclohexenes, which have not been previously reported, have been designated as alpha (m.p. 58.2–58.8°, cor.) and beta (m.p. 70.5–71.3°, cor.) in the order of their characterization. The nomenclature adopted here does not imply any structural relationship to α - and β -BHC. Although the assignment of Greek letter designations to γ - and δ - $C_6H_5Cl_5$ was intended⁵ to denote steric relationship with the parent compounds, γ - and δ -BHC, re-

(4) V. N. Ipatieff, W. W. Thompson and H. Pines, *THIS JOURNAL*, **70**, 1658 (1948).

(5) M. Nakazima, T. Okubo and Y. Katamura, *Botyu-Kagaku*, **14**, 10 (1949).

(6) *Ibid.*, **15**, 97 (1950).

(7) S. J. Cristol, N. L. Hause and J. S. Meek, *THIS JOURNAL*, **73**, 674 (1951).

(8) Melting points reported by Nakazima and Cristol are not corrected values.

(1) G. Calingaert, M. E. Griffing, E. R. Kerr, A. J. Kolka and H. D. Orloff, *THIS JOURNAL*, **73**, 5224 (1951).

(2) H. D. Orloff, A. J. Kolka, G. Calingaert, M. E. Griffing and E. R. Kerr, *ibid.*, **75**, 4243 (1953).

(3) T. van der Linden, *Rec. trav. chim.*, **53**, 45, 703, 779 (1934).

spectively, this system of nomenclature cannot be adopted for general usage because more than one pentachlorocyclohexene may be related theoretically to each of the BHC isomers other than beta.

Three of the four $C_6H_4Cl_6$ isomers prepared by partial additive chlorination of *o*-dichlorobenzene are identical with hexachlorocyclohexenes synthesized⁶ by monodehydrochlorination of pure heptachlorocyclohexane isomers. No depression was observed in mixed melting point tests of the following hexachlorocyclohexene preparations.

Isomer	M.p., °C.	
	Nakazima (uncor.)	This investig. (cor.)
α	147-148	146.8-147.5
β	126-127	124.5-125.0
γ	100-101	101.0-101.6

The fourth $C_6H_4Cl_6$ isomer, delta (m.p. 139.8-140.4°, cor.), obtained by the iodine-catalyzed chlorination technique, has not been previously reported.

In addition to these hexachlorocyclohexenes, we have isolated a new isomer of octachlorocyclohexane, m.p. 103.4-104.0° (cor.), from the chlorination products of *o*-dichlorobenzene. The only previously reported octachlorocyclohexane⁹ obtained from *o*-dichlorobenzene melted at 149°. Both compounds are presumably steric isomers of 1,1,2,2,3,4,5,6-octachlorocyclohexane.

In view of the method of preparation, identical with that of the benzene tetrachlorides,¹ and of the identity of two penta- and three hexachlorocyclohexene isomers prepared by partial additive chlorination with products of monodehydrohalogenation of BHC and heptachlorocyclohexane, respectively, it is concluded that only one chlorine substituent is present on each carbon atom. Further confirmation is provided by the fact that the identical tetrachloroadipic acid is formed by oxidative cleavage of γ -pentachlorocyclohexene and α -benzene tetrachloride.

The partial additive chlorination of mono- and *o*-dichlorobenzene appears to be somewhat more favored than that of benzene. The improved yield of penta- and hexachlorocyclohexene (based on amount of chlorine reacted) compared with that of BTC may be attributed in part to the decreased rate of substitution chlorination of mono- and *o*-dichlorobenzene.

Steric Structure.—The assignment of the configurations (Table I) of the chlorocycloolefins^{5,6,10} is based upon the mechanism of their formation by monodehydrochlorination of hexa- and heptachlorocyclohexanes of known structure. This mechanism involves the postulation, which is confirmed by

TABLE I
CONFIGURATIONS OF PENTA- AND HEXACHLOROCYCLO-
HEXENES

Isomer	Conformation	Isomer	Conformation
α - $C_6H_5Cl_5$	Unknown	α - $C_6H_4Cl_6$	$\bar{e}e\bar{e}e\bar{e}e$
β - $C_6H_5Cl_5$	Unknown	β - $C_6H_4Cl_6$	$pe\bar{e}e\bar{e}e$
γ - $C_6H_5Cl_5$	$\bar{e}e\bar{e}pp$	γ - $C_6H_4Cl_6$	$pp\bar{e}e\bar{e}e$
δ - $C_6H_5Cl_5$	$\bar{e}e\bar{e}e\bar{e}e$	δ - $C_6H_4Cl_6$	Unknown

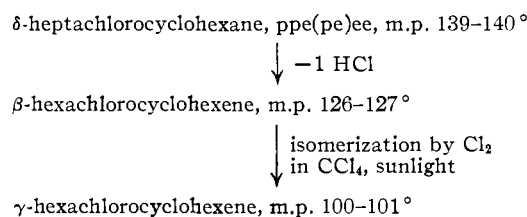
(9) T. van der Linden, *Ber.*, **45**, 414 (1912); T. Oiwa, R. Yamada, M. Hamada, M. Inouye and M. Ohno, *Botyu-Kagaku*, **15**, 32 (1950).

(10) T. Oiwa, R. Yamada and M. Ohno, *ibid.*, **16**, 11 (1951).

kinetic, stereochemical and X-ray data,^{7,11} that the major product will be that resulting from 1,2-*trans*-elimination of a polar hydrogen and chlorine pair.

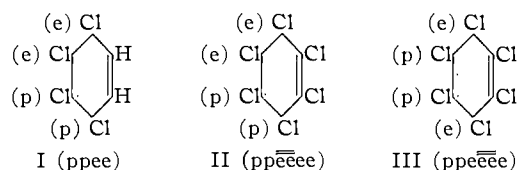
The nomenclature employed in this paper for the steric conformations is based on that described in ref. 2. Polar (p) and equatorial (e) orientations of the chlorine substituents are those in the chair-formed saturated chlorocyclohexane precursor (BHC or heptachlorocyclohexane). A bracketed designation (pe) denotes the presence of two chlorine substituents on one carbon atom. The double horizontal line in a cycloolefin (Table I) refers to the position of the double bond with reference to the structure of the saturated precursor while the short dash under the double line indicates the absence of chlorine from that position. Thus, δ -pentachlorocyclohexene ($\bar{e}e\bar{e}e\bar{e}e$) is structurally related to two possible BHC precursors, $pe\bar{e}e\bar{e}e$ and $e\bar{e}e\bar{e}e$. β -Hexachlorocyclohexene ($pp\bar{e}e\bar{e}e$) bears an analogous relationship to two heptachlorocyclohexenes, $pp(e)\bar{e}e\bar{e}e$ and $pp\bar{e}(e)\bar{e}e$. A chlorine substituent remaining on a carbon attached to the double bond, indicated in pentachlorocyclohexene as the single letter e and in hexachlorocyclohexene as the double letter e under the double horizontal line ($\bar{e}e\bar{e}e\bar{e}e$ and $pp\bar{e}e\bar{e}e$, respectively), actually has no steric significance in the cycloolefin itself. The conformation of a pentachlorocyclohexene, $\bar{e}e\bar{e}e\bar{e}e$, is undistinguishable from that described as $\bar{e}p\bar{e}e\bar{e}e$. When the molecule becomes saturated, for example, by addition of a chlorine molecule to the double bond the chlorine originally present on the unsaturated carbon atom or atoms may become either equatorial or polar. The orientations of the remaining substituents, however, do not change with respect to each other. We have therefore adopted the convention of indicating the presence of a chlorine substituent at the double bond by the letter e placed under the double horizontal line.

The synthesis of the β - and γ -isomers of hexachlorocyclohexene was reported by Nakazima⁶ according to the following sequence of reactions



Theoretically, δ -heptachlorocyclohexene can yield two hexachlorocyclohexenes possessing the structures $pp\bar{e}e\bar{e}e$ and $pp\bar{e}e\bar{e}e$. Nakazima assigned the former conformation to the β -, and the latter to γ -hexachlorocyclohexene. Oiwa and co-workers⁹ have subsequently established the structure $pp\bar{e}e\bar{e}e$ for the γ -isomer. The latter conformation was anticipated as more probable from the results of our investigation. Since the major partial addition product (>50%) of benzene is α -BTC,^{1,2} I, a similar structure, II, would be expected for γ - $C_6H_4Cl_6$, the predominant cycloolefin formed from *o*-dichlorobenzene.

(11) (a) W. Huckel, W. Tappe and G. Legutke, *Ann.*, **543**, 191 (1940); S. J. Cristol, *This Journal*, **69**, 338 (1947); (b) R. A. Pasternak, *Acta Cryst.*, **4**, 316 (1951).



The conformation of β -hexachlorocyclohexene, therefore, is ppeeēē (III) or its ring conversion form eepēēp.

On the basis of the known conformation, ppee, of α -BTC,² the steric structure, IV, of tetrachloroadipic acid has been assigned. The formation of the same acid from γ - $C_6H_5Cl_5$ provides chemical confirmation of the configuration ēēēpp assigned to the latter cycloolefin by Nakazima.⁶ Although oxidation of $C_6H_4Cl_6$ isomers to the corresponding diacids and comparison of the resulting products with those derived from BTC isomers of known structure may be used to establish the conformations of the hexachlorocyclohexenes, similar treatment of $C_6H_5Cl_5$ isomers will only elucidate the configurations of the chlorines on the saturated carbon atoms but will not fix the position of the chlorine at the double bond. Structural investigations along such lines are not contemplated.

Acknowledgments.—The authors wish to express their grateful appreciation to Drs. S. J. Cristol and M. Nakazima for samples of penta- and hexachlorocyclohexene isomers, and to Miss Shirley L. Trapp and John P. Napolitano for valuable assistance with the experimental part of this investigation.

Experimental Part

Pentachlorocyclohexene. 1. Preparation.—Chlorine gas (950 g., 13.4 moles) was introduced over 13.5 hr. into a solution of 12.5 g. of iodine in 2750 g. (24.4 moles) of monochlorobenzene at 20–30°, according to the procedure reported for the partial additive chlorination of benzene.¹ After removal of unreacted monochlorobenzene at reduced pressure and deiodination, the residual portion of the reaction product (894 g.) was rectified in a 2 × 50-cm. column packed with 6-mm. Pyrex spheres. The distillate (478 g.) boiling below 70° (5 mm.) was primarily a mixture of di- and trichlorobenzenes. The pressure was reduced further and distillation continued until the temperature reached 110° (1 mm.). The latter distillate (379 g.) was a mixture of pentachlorocyclohexenes while the pot residue consisted largely of more highly chlorinated products. The extent of decomposition of an unidentified iodine-containing unstable component of the reaction mixture was less than that observed in the preparation of benzene tetrachloride.² After deiodination, the partially purified material was rerectified and the pentachlorocyclohexene isomers collected between 114 and 125° (4 mm.). On the basis of the distillation data, chlorine and infrared analyses, the product distribution has been calculated as

Product	Yield, % based on Cl ₂ reacted
Dichlorobenzene	34
Trichlorobenzene	2
Pentachlorocyclohexene	24
Higher chlorinated material	4
Hydrogen chloride	36

Some separation of isomers was achieved in the rectification. The portion boiling at 115–116° at 4.0 mm., n_D^{20} 1.5630 (110 g.) was found to be a single isomer, subsequently designated γ -pentachlorocyclohexene. *Anal.* Calcd. for

$C_6H_5Cl_5$: C, 28.33; H, 1.98; Cl, 69.69. Found: C, 27.96; H, 2.18; Cl, 69.82. Since this isomer was identical with one isolated by partition chromatography from the products of the iodine-catalyzed photochlorination of benzene,² it was concluded that pentachlorocyclohexene formed in the latter reaction resulted from the partial additive chlorination of monochlorobenzene which was co-formed in the reaction. Since four pentachlorocyclohexene isomers were isolated in the course of separation of the components of the reaction product obtained by the iodine-catalyzed photochlorination of benzene, no attempt was made to separate $C_6H_5Cl_5$ isomers from the remainder of the distillation fractions obtained from the chlorination of monochlorobenzene.

On rectification of the crude benzene tetrachloride-pentachlorocyclohexene mixture,² approximately 15–20% of each of the ten highest boiling cuts (b.p. 133–145° at 8.0 mm.) crystallized and the crystals were separated by filtration. That the crystalline fractions were a single isomer was confirmed by infrared spectrophotometry. Recrystallization from hexane yielded a purified material, m.p. 68.2–68.6° (cor.),¹² which was shown by mixed melting point to be identical with δ -pentachlorocyclohexene obtained by Cristol⁷ by monodehydrohalogenation of δ -BHC. *Anal.* Calcd. for $C_6H_5Cl_5$: Cl, 69.69. Found: Cl, 69.28.

2. Partition Chromatography.—Two of the $C_6H_5Cl_5$ isomers were recovered from the chromatographic separation of a chlorocycloolefin distillate from the iodine-catalyzed photochlorination of benzene (Table VIII, ref. 2). The first was a colorless oil which did not crystallize. Its infrared spectrum was identical with that of the distillate (b.p. 115–116° at 4.0 mm., n_D^{20} 1.5630) obtained in the rectification of the product of partial additive chlorination of monochlorobenzene and with that of γ -pentachlorocyclohexene obtained by Nakazima by monodehydrochlorination of γ -BHC. The other $C_6H_5Cl_5$ isomer, recrystallized from hexane and melting at 58.2–58.5° (cor.) was designated α -pentachlorocyclohexene. *Anal.* Calcd. for $C_6H_5Cl_5$: Cl, 69.69. Found: Cl, 69.64.

After removal of the δ -pentachlorocyclohexene which crystallized on standing, a composite (45.88 g.) from the two highest boiling cuts (b.p. 143–145.5°, 8.0 mm.) in the rectification² of the reaction product from the iodine-catalyzed photochlorination of benzene was subjected to partition chromatography in a 5.1 × 195-cm. column packed with 1500

TABLE II

PARTITION CHROMATOGRAPHY OF $C_6H_5Cl_5$ DISTILLATE

Com- pos- ite no.	Vol. eluate (ml. × 10 ²)	Description	Composition based on infrared spectra	Wt. (g.)
1	1–20	Empty		0.00
2	21–22	Crystals	1,2,4,5-Trichloro- benzene; traces	0.18
			1,2,3,4-isomer and of 1,2,4- and 1,2,3- trichlorobenzene	
3	23	Oils	γ - $C_6H_5Cl_5$	6.83
4	35–36	Trace oils	γ - $C_6H_5Cl_5$	
	37	Empty		
	38	Trace crystals	α - $C_6H_5Cl_5$	
	39–40	Crystals + oils	α - $C_6H_5Cl_5$	11.75
	41–48	Crystals + oils	α - and δ - $C_6H_5Cl_5$	
5	49–61	Crystals	δ - $C_6H_5Cl_5$	6.44
6	62–67	Oils	β - and δ - $C_6H_5Cl_5$	11.07
7	68–73	Oils	β -, trace δ - $C_6H_5Cl_5$	5.29
8	74–76	Crystals	β - $C_6H_5Cl_5$	1.01
9	77–78	Oils	Chiefly, β - $C_6H_5Cl_5$	0.50
10	79–85	Oils	β - $C_6H_5Cl_5$, traces γ -, ϵ -BTC	
11	86–93	Crystals + oils	γ -, ϵ -BTC	0.28
12	94–125	Empty		0.00
				45.24

(12) All melting points obtained in this investigation were determined with a calibrated Anschütz thermometer and a temperature rise of 0.1°/min.

g. of silicic acid. A fourth pentachlorocyclohexene, beta, was separated from composites 7-9 (Table II). Recrystallization from hexane yielded 6.99 g., m.p. 70.5-71.3° (cor.). *Anal.* Calcd. for $C_6H_5Cl_5$: Cl, 69.69. Found: Cl, 69.77.

3. **Oxidation.**— γ -Pentachlorocyclohexene (50.9 g., 0.2 mole) was oxidized with potassium permanganate in 50% sulfuric acid according to the procedure previously reported.¹ The crude product (20.8 g., 37% yield) was recrystallized from acetone and melted at 269° (uncor.), with decomposition. The acid was established by infrared spectrophotometry to be identical with the tetrachloro-adipic acid (2,3,4,5-tetrachlorohexanedioic acid) obtained from α -benzene tetrachloride.¹ *Anal.* Calcd. for $C_6H_4Cl_4O_4$: Cl, 49.95. Found: Cl, 49.64. Titration of a sample with standard alkali indicated the presence of two carboxyl groups (milliequivalent weight: calcd., 0.1420; found, 0.1432).

4. **Dehydrochlorination.**—The β , γ - and δ -isomers of pentachlorocyclohexene were dehydrohalogenated with an excess of ethanolic potassium hydroxide by the procedure previously described.¹ Sufficient alpha isomer was not available for this reaction. The ratios of trichlorobenzene isomers formed were determined by infrared analysis¹³ of the organic phase (Table III). The aqueous solutions from the reactions of the γ - and δ -isomers were titrated argentometrically and the amount of potassium chloride formed was calculated as equivalent to the elimination of two molecules of hydrogen chloride from the starting material.

TABLE III

Iso-mer	Wt. (g.)	Trichlorobenzene (%)			KCl (g.)	
		1,2,4	1,2,3	1,3,5	Calcd.	Found
β^a	0.20	74	23	33
γ	5.38	84.9	4.7	10.4	3.15	3.07
δ	4.00	86.6	5.7	7.7	2.34	2.37

^a Precision of analyses lower because of small sample size.

TABLE IV

IDENTIFICATION OF PRODUCTS FROM *o*-DICHLOROBENZENE

Fraction no. ^a	Description	Wt. (g.)	M.p., °C. ^b	Anal., ^c Cl, %	Identification
1-8	Empty	0.00
9-11	Crystals	3.63	136.5-137.5	...	1,2,4,5-Tetrachlorobenzene ^d
12-15	Oils	13.37	Mixture
16-18	Crystals	2.58	103.4-104.0	78.51	Octachlorocyclohexane
19	Oil + crystals	0.13
20-23	Crystals	1.61	Mixt. α -, β - $C_6H_4Cl_6$
24-25	Oils + crystals	1.08
26-31	Crystals	4.63	139.8-140.4	74.18	δ - $C_6H_4Cl_6$
32-60	Empty	0.00

^a Each fraction represents 100 ml. of eluate. ^b Values corrected. ^c Calcd. for $C_6H_4Cl_6$: Cl, 73.67. Calcd. for $C_6H_4Cl_5$: Cl, 78.86. ^d Identified by infrared spectrum. Examination of solute from recrystallization of composite (no. 9-11) confirmed presence of 1,2,3,4-tetrachlorobenzene.

Hexachlorocyclohexene. 1. **Preparation.**—*o*-Dichlorobenzene (3110 g., 21.2 moles, 97% ortho isomer), containing 9.0 g. of dissolved iodine, reacted at 20-30° with 1000 g. (14.1 moles) of chlorine gas over 14.5 hr. The apparatus and procedure were similar to those reported for the chlorination of benzene¹ with the exception that a greater light intensity was employed: two 250-watt white glass infrared heat lamps and two 275-watt R.S. reflector sunlamps (General Electric Co.). Steam distillation of the reaction solution, which resulted in the liberation of a small quantity of free iodine, was continued until 1,2,4,5-tetrachlorobenzene crystallized in the condenser. At this point no further liberation of iodine occurred and the weight of organic distillate totaled 2750 g. The distillation residue was diluted with ether, dried with anhydrous sodium sulfate and the ether removed on the steam-bath. Thirty-six grams of 1,2,4,5-tetrachlorobenzene separated at room temperature, and an additional 13 g. after standing overnight in a refrigerator. The filtrate was allowed to stand at 25° for two weeks. Colorless crystals (121 g.) which formed were filtered on a büchner

(13) M. E. Griffing and R. L. Hudson, presented before the Pittsburgh Analytical Conference (A.C.S.), March, 1951; to be published.

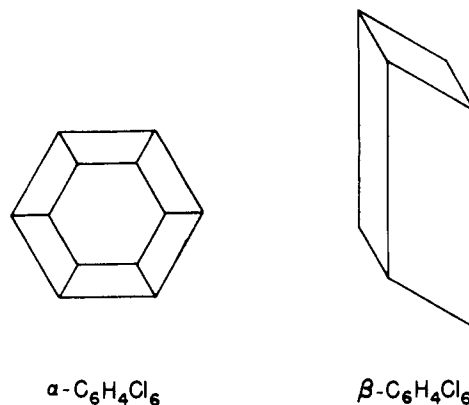


Fig. 1.—Diagrammatic representation of α - and β -hexachlorocyclohexene (from *n*-hexane at 25°).

funnel, washed with hexane and recrystallized twice from the latter solvent. The purified product (44.7 g., m.p. 101.0-101.6°, cor.), γ -hexachlorocyclohexene, gave no depression in a mixed melting point determination with a sample, m.p. 100-101°, obtained from the dehydrochlorination of δ -heptachlorocyclohexane by Prof. Nakazima. *Anal.* Calcd. for $C_6H_4Cl_6$: Cl, 73.65. Found: Cl, 73.70.

2. **Partition Chromatography of Hexachlorocyclohexene.** A 27.1-g. aliquot of the residual reaction product was subjected to partition chromatography² in a 4.5 × 185-cm. column packed with 1000 g. of silicic acid. The crystalline residues were recrystallized and identified by means of melting point, chlorine analysis and infrared spectra (Table IV). No attempt was made to identify the oily fractions (no. 12-15) which constituted almost half of the total weight and probably contain isomers of trichlorobenzene, tetrachlorobenzene and hexachlorocyclohexene.

On the basis of the experimental data, the product distribution from the partial additive chlorination of *o*-dichlorobenzene has been calculated as

Product	Yield, % based on Cl_2 reacted
Trichlorobenzene	18
Tetrachlorobenzene	10
Hexachlorocyclohexene	36
Octachlorocyclohexane	8
Hydrogen chloride	28
	100

3. **Separation of α - and β - $C_6H_4Cl_6$.**—In view of the imperfect separation of these isomers by partition chromatography, fractional crystallizations from *n*-hexane and manual separation were utilized, employing the technique developed³ for γ - and ϵ -benzene tetrachloride. Fractions 20-23 were combined with identical material from a second chromatographic run. The composite (2.81 g.) was dissolved in hexane and allowed to evaporate slowly at room

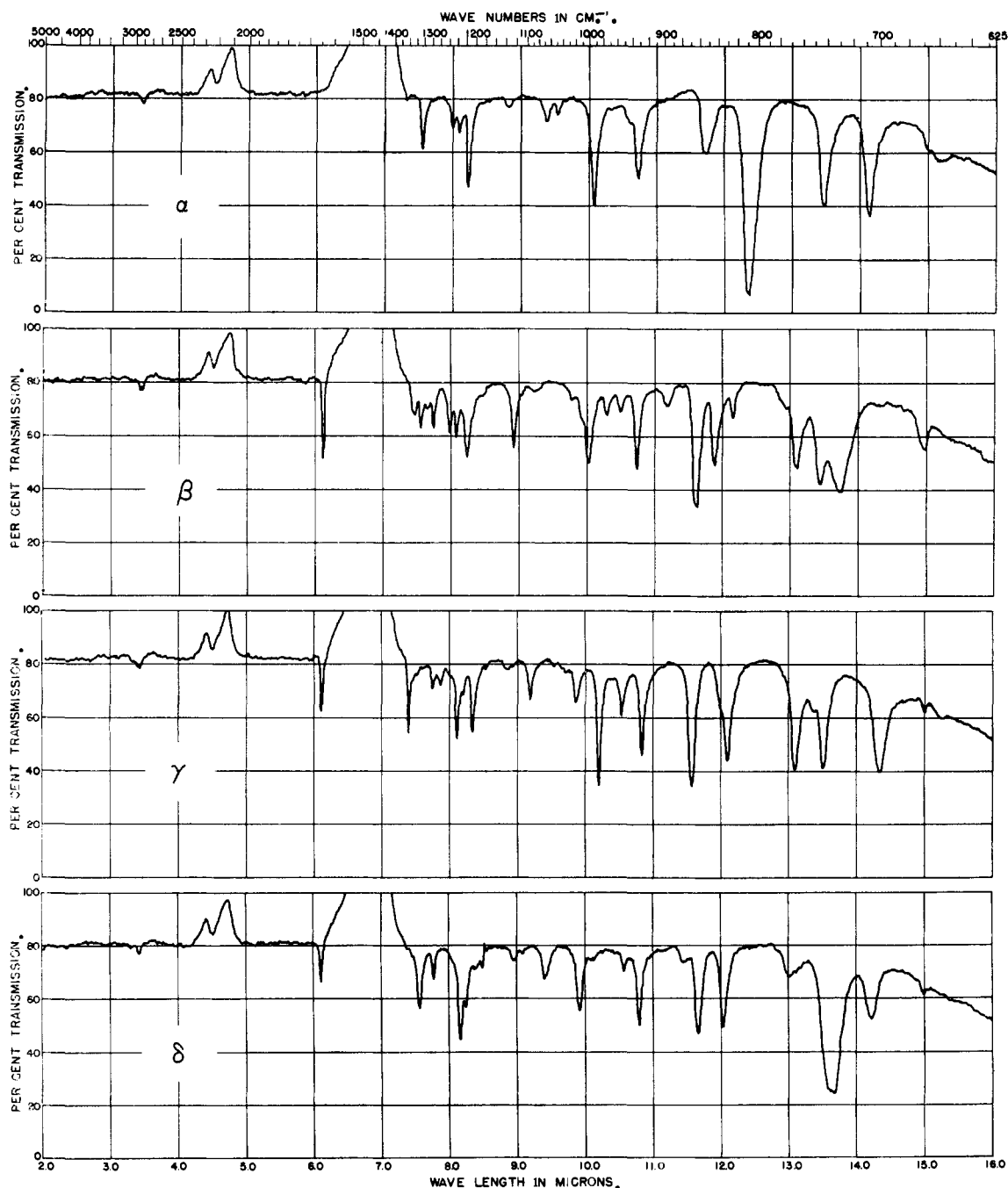


Fig. 2.—Infrared absorption spectra of pentachlorocyclohexene isomers; concentrations, g. per liter in carbon disulfide, as follows: alpha, 14.16; beta, 17.69; gamma, 14.82; delta, 14.33.

temperature. Successive crystal fractions were removed and separated manually with the aid of a hand lens. The higher melting α -isomer formed hexagonal plates whereas the β -isomer normally yielded needles (Fig. 1). The amount of α -isomer recovered was 0.87 g., while that of the β -isomer was 1.49 g. Recrystallization from hexane yielded 0.72 g. of α - $C_6H_4Cl_6$ (m.p. 146.8–147.7°, cor. *Anal.* Calcd. for $C_6H_4Cl_6$: Cl, 73.7. Found: Cl, 74.2) and 1.14 g. of β - $C_6H_4Cl_6$ (m.p. 124.5–125.0°, cor. *Anal.* Calcd. for $C_6H_4Cl_6$: Cl, 73.7. Found: Cl, 74.3).

4. **Dehydrochlorination.**—The four isomers were dehydrochlorinated with an excess of ethanolic potassium hydroxide. Argentimetric analysis of the aqueous solution obtained from the reaction of γ - $C_6H_4Cl_6$ confirmed the elimination of two molecules of hydrogen chloride. *Anal.*

Calcd.: KCl, 2.17 g. Found: KCl, 2.06 g. Since smaller quantities of the α -, β - and δ -isomers were available, the latter were dehydrochlorinated on a smaller scale (0.1–0.2 g.), and the organic reaction products, extracted with carbon disulfide, were analyzed spectrophotometrically. Because of the smaller samples available for analysis, the precision for the latter isomers is not as great as for γ - $C_6H_4Cl_6$.

$C_6H_4Cl_6$ isomer	Tetrachlorobenzene (%)		
	1,2,3,4	1,2,3,5	1,2,4,5
α	65	35	0
β	59	33	8
γ	47.2	52.6	0.2
δ	41	51	8

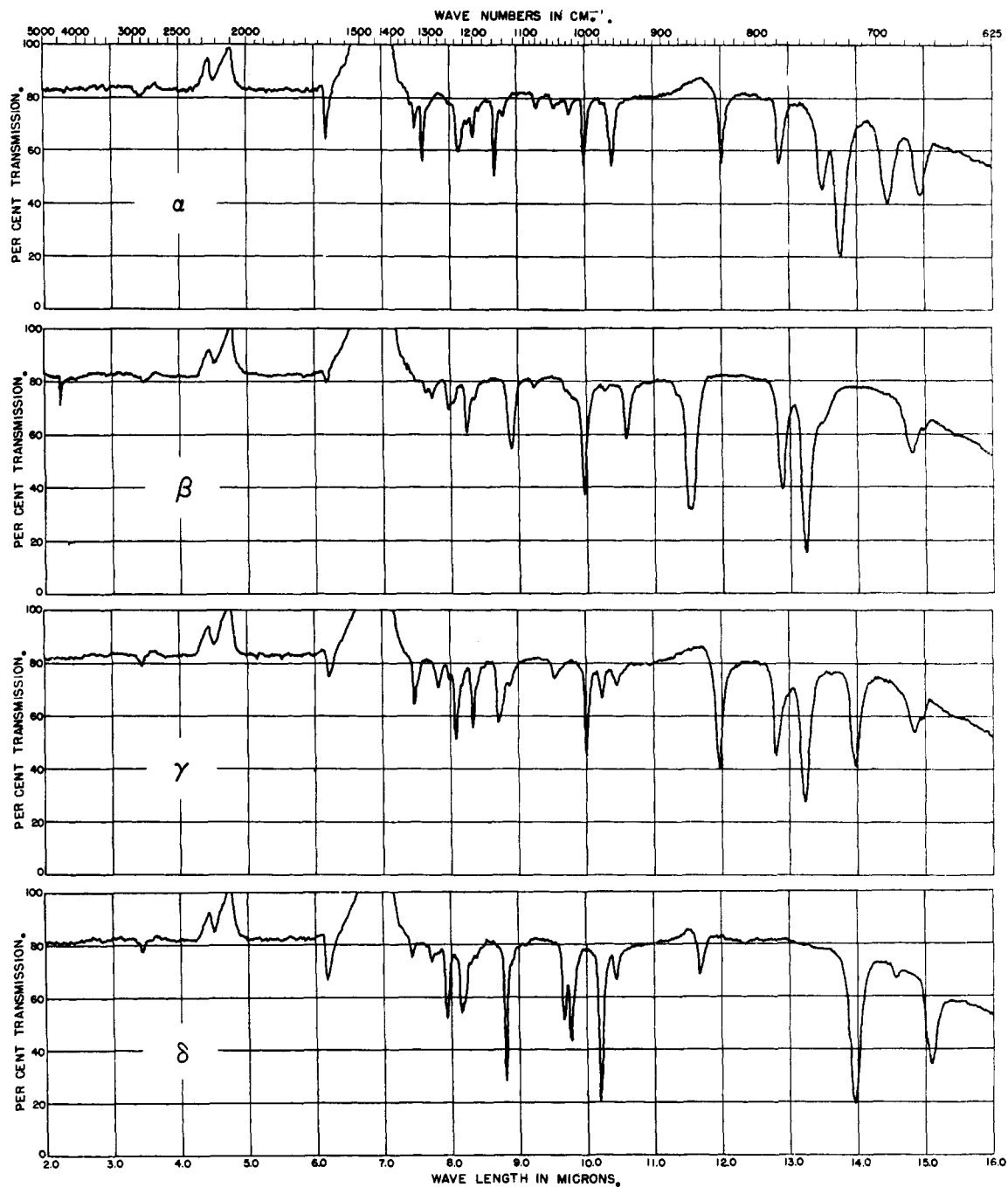


Fig. 3.—Infrared absorption spectra of hexachlorocyclohexene isomers; concentrations, g. per liter in carbon disulfide, as follows: alpha, 14.27; beta, 13.73; gamma, 14.01; delta, 15.54.

Infrared Data.—The infrared spectra, reproduced according to the procedures previously described,² are recorded in Figs. 2 and 3.

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