[CONTRIBUTION FROM THE RESEARCH LABORATORIES OF THE ETHYL CORPORATION]

The Partial Additive Chlorination of the Benzene Ring. II. The Isomers of Benzene Tetrachloride[1]

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Five isomers of benzene tetrachloride, synthesized by the iodine-catalyzed photochlorination of benzene, have been isolated by vacuum rectification and partition chromatography, purified and characterized by melting point and infrared spectrophotometry. The steric structures of these isomers have been established by chlorination to benzene hexachloride. On the basis of the products thereby formed and of the structural relationships of the tetra- and hexachlorides, it has been possible to confirm chemically the reported configurations of the benzene hexachlorides and to assign the following structures to the benzene tetrachlorides: α, eepp; β, peep; γ, eeep; δ, eeee; ε, eepe. The photocatalytic addition of chlorine to the cycloolefinic double bond has been shown to proceed by two *cis* and two *trans* mechanisms, yielding products in which the chlorine substituents thus introduced are oriented ep or pe, and ee or pp, respectively. Chemical evidence was obtained for ring conversion.

The photochlorination of benzene in the presence of iodine results, in part, in the formation of the partial addition product, benzene tetrachloride (3,4,5,6-tetrachlorocyclohexene-1, here abbreviated to BTC), one steric isomer of which, α-benzene tetrachloride, has been isolated previously.[3] The present paper deals with the separation and identification of four additional isomers, designated in the order of their characterization as β, γ, δ and ε. While α-BTC may be separated readily by rectification, partition chromatography employed in conjunction with infrared spectrophotometry was necessary for the resolution of the remaining isomers. Table I records physical data for the five presently known benzene tetrachlorides.

TABLE I

PHYSICAL PROPERTIES OF THE BENZENE TETRACHLORIDES

Isomer	M.p., cor., °C.	B.p., 15 mm., °C.
α	33.2–33.5	126
β	79.2–79.7	133
γ	88.2–88.8	142
δ	51.7–52.0	135
ε	98.7–99.3	142

The chlorination of the five isomers of BTC to known isomers of benzene hexachloride (BHC) by both *cis* and *trans* addition, has provided a valuable tool for the investigation of the mechanism of free radical chlorination of a cycloölefinic double bond and has facilitated the determination, by chemical methods alone, of the steric structures of the BTC isomers.

Stereochemical Relationships.—By adapting the modern stereochemical concepts[4-6] of saturated cyclohexane derivatives to six-membered rings containing one double bond, the steric relationships of the benzene tetra- and hexachlorides can be clarified. Whereas the carbon skeleton in saturated cyclohexane derivatives has been established[7] as essentially chair-formed, that of BTC is presumably a deformed chair, undoubtedly similar to δ-pentachlorocyclohexene.[8] In BTC (Fig. 1), the allylic (C_3, C_6) and the unsaturated (C_1, C_2) carbon atoms are considered to be coplanar, and the two remaining carbon atoms (C_4, C_5) to be situated one above and one below the plane.

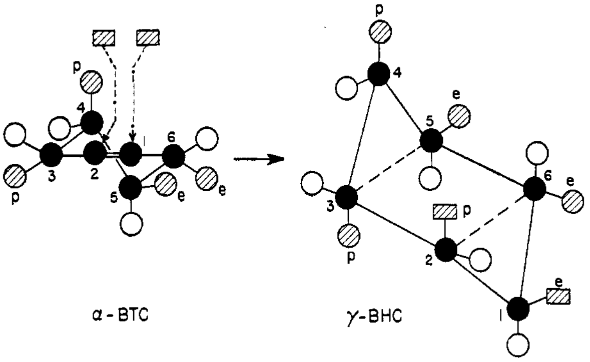

Fig. 1.—Formation of γ-BHC by *cis* addition of chlorine to α-BTC: ●, carbon; ○, hydrogen; ◍, chlorine present in original BTC molecule; ▨, chlorine introduced in addition process.

The nomenclature adopted here for the benzene tetrachlorides is essentially that which has been employed successfully for a wide variety of halocyclohexane isomers.[4,9] Equatorial (e) and polar (p) orientations of the substituents are recognizable at C_4 and C_5, the carbon atoms opposite to the double bond of BTC. Although, strictly speaking, neither substituent at the allylic carbons is equatorial or polar, they may be so designated on the basis of the orientation which they will assume as a result of the formation (Fig. 1) of the chair-formed BHC molecule by chlorine addition to the double bond. This nomenclature clearly designates both the tetra- and hexachlorides and at the same time clarifies their mutual relationships.

Applying the current stereochemical concept of ring conversion among cyclohexane derivatives[10]

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

[4] O. Hassel, *Research*, **3**, 504 (1950); a review.

[5] C. W. Beckett, K. S. Pitzer and R. Spitzer, THIS JOURNAL, **69**, 2488 (1947).

[6] D. H. R. Barton, *Experientia*, **6**, 316 (1950).

[7] O. Hassel and H. Viervoll, *Acta Chem. Scand.*, **1**, 149 (1947); C. W. Beckett, N. K. Freeman and K. S. Pitzer, THIS JOURNAL, **70**, 4227 (1948).

[8] R. A. Pasternak, *Acta Cryst.*, **4**, 316 (1951).

[9] J. M. Bijvoet, *Rec. trav. chim.*, **67**, 777 (1948).

[10] O. Hassel, *Tids. Kjemi Bergvesen Met.*, **3**, 32 (1943).

and by analogy with the scheme proposed by Bijvoet[9] and Hassel[11] for reducing the thirteen theoretical steric isomers of BTC to eight separable forms, the ten theoretically possible conformations of BTC are reduced to six forms, the predominant configurations of which are considered to be those shown in the first column of Table II.[12] Strong evidence for these equilibrium relationships is provided from the present and related[12b] disclosures from this Laboratory and by the results of calculations based on dipole moment and electron diffraction investigations[13] of the five BTC isomers.

TABLE II

EQUILIBRIUM RELATIONSHIPS BETWEEN THE ISOMERS OF BENZENE TETRACHLORIDE

eeee $\rightleftarrows$ pppp
eeep $\rightleftarrows$ pppe
eepe $\rightleftarrows$ ppep
peep $\rightleftarrows$ eppe
eepp ($\rightleftarrows$ ppee, *i.e.*, identity)
epep ($\rightleftarrows$ pepe, *i.e.*, identity)

The procedure employed for establishing the steric configurations of the benzene tetrachlorides involved the photochlorination of individual BTC isomers to yield BHC. The products of the reaction may be differentiated by the orientation of the chlorine substituents in the resulting BHC molecule: ep or pe from *cis* addition, and ee or pp from *trans* addition. The maximum of four different steric isomers of BHC from a single BTC is possible only in the case of the two tetrachlorides, eeep and eepe. For example, *cis* (ep or pe) addition to eeep-BTC should yield the hexachlorides eeepep (a hitherto unknown BHC) and eeeppe (= eeeepp, α-BHC), whereas *trans* (ee or pp) addition should give the hexachlorides eeepee (= eeeeep, δ-BHC) and eeeppp (γ-BHC). In the case of the remaining tetrachlorides, two of the four products will be identical. Thus, ep and pe addition to eeee- BTC can only give δ-BHC (eeeeep). A reduction from the maximum number also may result as a consequence of ring conversion. Of the two products formed by ee and pp addition to eepp-BTC, namely, eeeepp- and eepppp-BHC, respectively, only the former, the lower energy conformation of α-BHC, has been found.

Utilizing the configurations reported[14] for the five known isomers of BHC (α, eeeepp; β, eeeeee; γ, eeeppp; δ, eeeeep; ϵ, eepeep), and making allowance for the possible formation of three hitherto unknown hexachlorides, η(eeppep), θ(eeepep) and ι(epepep),[15] it has been possible to tabulate the theoretical relationships between the benzene tetra- and hexachlorides (Table III).

TABLE III

THEORETICAL RELATIONSHIPS BETWEEN THE BENZENE TETRA- AND HEXACHLORIDES

	BHC isomers expected[a]		
BTC configuration	*cis* addition (ep or pe)	*trans* addition ee	pp
eeee	δ	β	α
eeep	α, θ	δ	γ
eepe	ϵ, θ	δ	η
peep (or eppe)	η	ϵ (or α)	$1/\alpha$ (or $1/\epsilon$)
eepp	γ, η	α	$1/\alpha$
epep	ι, η	θ	η

[a] The symbols indicated as reciprocals (*e.g.*, $1/\alpha$) designate the less favored and hence not isolated higher energy conformations.

Determination of Steric Structures.—The five pure isomers of BTC were subjected separately to photochlorination, and the resultant products were analyzed by infrared absorption, with the results given in Table IV. The identification of known BHC isomers was performed qualitatively by comparison with reference spectra; product distribution then was evaluated by quantitative methods. The spectrophotometric results were confirmed by recrystallization procedures[3] which served to separate partially the components of the reaction products and thereby to concentrate those present in small quantity. The resulting enriched fractions were examined spectrophotometrically and the absence of isomers which could not be accounted for theoretically, even in low concentration, was reliably established. The quantitative data in Table IV, based on infrared analyses, are in agreement with the results of partition chromatography[16] of the products of chlorination of individual BTC isomers.

TABLE IV

PRODUCT DISTRIBUTION FROM BTC CHLORINATION

	BHC isomers obtained in photochlorination (%)[a]						
BTC Isomer	α (eeeepp)	β (eeeeee)	γ (eeeppp)	δ (eeeeep)	ϵ (eepeep)	Other	BTC structure derived from these data
α	89	..	11	..	..	...	eepp
β	81	..	..	..	19	1[b]	peep or eppe
γ	39	..	40	11	..	1[b]	eeep
δ	70	13	..	17	..	...	eeee
ϵ	..	..	..	33	40	27[b]	eepe

[a] Per cent. of BHC formed. [b] By difference.

A remarkable agreement was observed between the products obtained and the theoretically possible results. Each one of the five tetrachlorides subjected to chlorination gave a different set of product hexachlorides, and each one of these sets corresponded exactly to the known BHC isomers theoretically obtainable from a BTC of a certain struc-

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[11] O. Hassel and B. Ottar, *Acta Chem. Scand.*, **1**, 929 (1947).

[12] On the basis of the older planar method of representation, the *cis–trans* relationships of the chlorine substituents in the BTC isomers may be indicated as follows: eeee (1,3/2,4), eeep (1,3,4/2), eepe (1,2,3/4), peep (1,2/3,4), eepp (1,4/2,3) and epep (1,2,3,4).

[12b] H. D. Orloff and A. J. Kolka, Abstracts, American Chemical Society, 121st Meeting, Buffalo, N. Y., March 24, 1952, 6K; to be published.

[13] (a) O. Bastiansen and J. Markali, *Acta Chem. Scand.*, **6**, 442 (1952); (b) O. Bastiansen, *ibid.*, **6**, 875 (1952).

[14] O. Bastiansen, Ø. Ellefsen and O. Hassel, *Research*, **2**, 248 (1949); *Acta Chem. Scand.*, **3**, 918 (1949).

[15] At the suggestion of Dr. E. J. Crane, Editor-in-chief, *Chemical Abstracts*, the latter hexachlorides have been designated as η, θ and ι, in order to avoid confusion with the so-called "ζ-BHC" which was recently shown to be an isomer of 1,1,2,4,4,5-hexachlorocyclohexane rather than of BHC, 1,2,3,4,5,6-hexachlorocyclohexane. (O. Bastiansen and O. Hassel, *Acta Chem. Scand.*, **1**, 683 (1947)); Ø. Ellefsen, O. Hassel and E. W. Lund, *ibid.*, **4**, 1145 (1950); G. Calingaert, A. J. Kolka and H. D. Orloff, THIS JOURNAL, **73**, 2359 (1951); R. Riemschneider, *Z. Naturforsch.*, **6b**, 339 (1951).

[16] A. J. Kolka, H. D. Orloff and M. E. Griffing, Abstracts, American Chemical Society, 121st Meeting, Buffalo, N. Y., March 24, 1952, 5K; to be published.

ture by straightforward *cis* and *trans* addition. This agreement made possible the unequivocal assignment of structure to the BTC isomers (Table IV) and serves to substantiate the structures of the BHC isomers accepted on the basis of physical data.[14] The results obtained failed to provide evidence for rearrangement and hence may be considered as confirmation of the basic premise that rearrangement or isomerization did not take place.

The sixth theoretically possible BTC (which has not been found) is the one possessing the configuration epep. Its absence may be attributed to the fact that, assuming 1,2- and/or 1,4-addition, the configuration epep can result from the chlorination of benzene only by an all-*cis* mechanism. The probability of such a mechanism appears small. It is interesting to note (Table III) that theoretically the additive chlorination of this sixth isomer can only give rise to hitherto unknown benzene hexachlorides.

Mechanism of Chlorine Addition.—In addition to establishing the structures of the isomers, the data in Table IV shed considerable light on the mechanism of addition chlorination. Few instances of both *cis* and *trans* halogen addition to cyclic olefins could be found in the literature. Although the formation of *cis* and *trans* dichlorides by the direct chlorination of cyclohexene, in the presence of a copper catalyst, has been reported,[17] the claim could not be verified.[18] Recent investigations by Nakazima, *et al.*,[19] on the chlorination of pentachlorocyclohexene isomers resulted in the isolation of two heptachlorocyclohexanes; one was stated to be the product of *cis* addition, the other of *trans* addition. Hassel and Lunde[20] obtained three isomers of 1,2,3,4-tetrabromocyclohexane from 1,4-dibromocyclohexene-2, but indicated that isomerization rather than different addition mechanisms may have been involved.

In the first communication of this series,[3] the photochlorination of pure α-BTC was reported to yield a mixture of α- and γ-BHC. It is impossible to explain the formation of the two latter products from a single BTC isomer of any structure by *cis* addition only or by *trans* addition only. If, as seems now established beyond any doubt, the configurations assigned[14] to α- and γ-BHC are correct, then both *cis* and *trans* addition must have been involved in the chlorination. An ionic mechanism should lead only to *trans* addition products.[21] A mechanism consistent with the formation of both *cis* and *trans* addition products and with the observation that chlorination of BTC does not proceed at moderate temperatures in the absence of light, is a free radical process in which, theoretically, it should be possible for chlorine to add from one side of the double bond by *cis* addition, and from both sides by *trans* addition. In view of the extent of *cis* addition which has been found, a hybrid intermediate radical of the type postulated by Goering, *et al.*,[22] for the addition of hydrogen bromide to 1-bromocyclohexene, analogous to the halonium ion involved in ionic addition, does not appear applicable to the free radical chlorination of BTC.

From the structures of the three BHC isomers which were obtained by the chlorination of δ-BTC (Table IV), it is possible to attribute the formation of δ-BHC to a *cis* mechanism (ep or pe) and of α- and β-BHC to a *trans* mechanism (pp and ee, respectively). That both *trans* processes take place is indicated by the formation of the three pairs of known BHC isomers, α and ε, δ and γ, α and β, from the chlorination of β-, γ- and δ-BTC, respectively. Three known BHC isomers were obtained from each of the tetrachlorides, γ and δ. On the basis of the spectrophotometric data alone, it was not possible to establish the *simultaneous* occurrence of the two *cis* mechanisms or the formation of four BHC isomers from a single BTC, because in each such case a hitherto unknown hexachloride is involved. Complete interpretation of the results of the chlorinations of γ- and particularly of ε-BTC, which alone can give rise to four different addition products, was hampered by the presence of unidentified products. The results of an investigation of the latter products indicate[17] that all four modes of addition take place.

Three factors appear to be controlling in determining the preferred mode of introduction of chlorine substituents: (1) the mechanism of addition, whether *cis* or *trans;* (2) a so-called "entry factor" resulting from the structure of the BTC molecule and involving steric and/or electrostatic influences; (3) the steric strains and thermodynamic stability of the product hexachloride. *trans*-Addition of chlorine to the double bond appears to be the predominant mechanism. In the case of the α-, β- and δ-isomers, this mode accounts for over 80% of the reaction products (Table IV). In the remaining two isomers, however, the ratio of *trans* to *cis* addition approaches unity. The insecticidally active γ-BHC, which may be considered less favored thermodynamically because of the meta polar strain of the 1p, 3p chlorine substituents, can be formed only from two benzene tetrachlorides, α and γ, both of which can also give rise to the less strained α-BHC. α-BTC yields α-BHC by *trans* addition and γ-BHC by *cis* addition in a ratio of 8:1. The preference for α-BHC appears logical for thermodynamic reasons and because *trans* rather than *cis* addition is involved. However, γ-BTC also yields α- and γ-BHC but by the reverse mechanism (α-BHC by *cis* and γ-BHC by *trans* addition) and in approximately equal amounts. The increased γ:α BHC ratio resulting from the chlorination of γ-BTC suggests that in this case at least, where thermodynamic factors would be expected to lead to the opposite result, the mechanism of addition (*trans versus cis*) has been controlling.

The ratio of *trans* to *cis* addition was increased appreciably by performing the chlorination of α-

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[17] S. Komatsu and T. Kawamoto, *J. Chem. Soc. Japan*, **52**, 685 (1931).

[18] B. Carroll, D. G. Kubler, H. W. Davies and A. M. Whaley, THIS JOURNAL, **73**, 5382 (1951); H. C. Stevens and O. Grummitt, *ibid.*, **74**, 4876 (1952).

[19] M. Nakazima, T. Okubo and Y. Katumura, *Botyu-Kagaku*, **15**, 97 (1950).

[20] O. Hassel and K. Lunde, *Acta Chem. Scand.*, **4**, 1597 (1950).

[21] I. Roberts and G. E. Kimball, THIS JOURNAL, **59**, 947 (1937); S. Winstein, *ibid.*, **64**, 2792 (1942).

[22] H. L. Goering, P. I. Abell and B. F. Aycock, *ibid.*, **74**, 3588 (1952).

BTC at an elevated temperature in the absence of light. As previously reported,[3] no reaction was observed after 24 hours at room temperature. However, after 700 hours in a sealed tube at 100°, a mixture of α- and γ-BHC was obtained in a 15:1 ratio, almost double that (8:1) from a photochlorination at room temperature. The fact that both *cis* and *trans* addition products were obtained indicates that a free radical mechanism was still taking place. The increase in *trans*:*cis* addition may have resulted from a temperature effect on the free radical process or to some degree of ionic addition.

Evidence of Ring Conversion.—The theoretical basis[10,23] for ring conversion has been substantiated by physical evidence[4] and by the fact that the number of steric isomers of cyclohexane derivatives actually observed may be adequately accounted for by this mechanism. We are not aware that direct chemical experimental evidence has previously been presented showing that such a conversion takes place.

The chlorination of β-BTC, which may be represented as a thermolabile equilibrium mixture, eppe $\rightleftarrows$ peep, provides such direct chemical evidence for ring conversion. In view of the fact that this isomer, as separated by partition chromatography from a complex isomeric mixture, did not undergo any detectable change in infrared spectrum during the separation and subsequent recrystallization, it is reasonable to presume that the material thus obtained was either the eppe or the peep conformation,[24] or an equilibrium mixture of constant composition.

If conversion does not take place, the following results may may be expected:

Conformation of BTC	BHC expected on chlorination		
	cis addition (ep or pe)	*trans* addition	
		ee	pp
eppe	η	α	$1/\epsilon$
peep	η	ϵ	$1/\alpha$

Actually, both α- and ϵ-BHC were obtained (Table IV) with no evidence of the presence of the higher energy conversion forms $1/\alpha$ or $1/\epsilon$. Unless ring conversion has taken place, either in the case of the original tetrachloride or of the resultant BHC isomers, it would not have been possible to obtain both α- and ϵ-BHC.

Bastiansen[13a] has shown, by dipole measurements, that under the conditions of his experimental procedure, the β-isomer exists as an equilibrium mixture in which the ratio of the conformations peep and eppe is 87:13. Assuming in the above tabulation that pp addition did not take place (since it can give rise only to the strained conformations $1/\epsilon$ and $1/\alpha$), the chlorination product of an equilibrium mixture eppe $\rightleftarrows$ peep, in which the latter predominates, should contain considerably more ϵ-BHC than α-BHC. The data in Table IV, however, show that the actual ratio of products obtained was 81% α-BHC, 19% ϵ-BHC.

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Experimental and Results

Preparation and Separation of Isomers.—Eighteen iodine-catalyzed photochlorinations of benzene were carried out by a modification of the procedure previously described.[3] In each run, 2.2 kg. of benzene containing 2.5–5.0 g. of iodine per liter reacted at 25–35° with 0.9–1.0 kg. of chlorine gas and then was steam distilled to remove monochlorobenzene and unreacted benzene. The distillates boiling below 95° and shown by infrared analysis to be free of BTC were discarded. The less volatile oily residues, which contained all the products of additive chlorination together with the higher boiling substitution products, were composited, extracted with aqueous sodium sulfite to remove free iodine, and dried over anhydrous sodium sulfate; yield 6680 g.

To accelerate the decomposition of an unidentified, unstable, iodine-containing substance,[3] the entire composite was vacuum distilled through a 2 × 50-cm. column packed with 6-mm. Pyrex spheres. The fractions boiling below 68° (5 mm.), 495 g., constituted a mixture of mono-, di- and trichlorobenzenes. The distillation of the bulk of the charge (5395 g.) was discontinued at 140° (5 mm.) when solid α-BHC began to crystallize in the stillhead. The pot residue, believed to consist primarily of a mixture of BHC isomers, was not investigated further.

After deiodination and drying, a portion (2874 g.) of the cycloölefinic concentrate was redistilled at 1–3 mm. to decompose the last traces of the unstable iodine compound. The operation was discontinued after 2739 g. had been collected. After the latter material was deiodinated and dried, no further liberation of iodine occurred.

For the separation of the α-isomer, a portion (2661 g.) of the twice-distilled crude was rectified in a 2 × 90-cm. column packed with 6-mm. Pyrex spheres, at a 20:1 reflux ratio and a 10 ml./hr. take-off rate. The twenty-one cuts were composited in four portions:

Cut. No	B.p., 0.5 mm., °C.	Amount, g.	Description
1	<62	105.7	Primarily trichlorobenzene; trace α-BTC
2–7	62–67	1265.4	Primarily α-BTC
8–15	67–85	778.6	Isomeric mixture (liquid)
16–21	85–95	476.1	Isomeric mixture (liquid from which crystals formed slowly)
Residue		18.5	
Distn. loss		16.7	

Cuts 2–7 were placed in a refrigerator for one week, which allowed the α-BTC to crystallize. The supernatant mother liquor (450 g.) from these fractions was decanted and combined with cuts 8–21 for rerectification in a 2.8 × 122-cm. column packed with $^3/_{32}$-inch multiple turn glass helices. Thirty fractions were removed at 8.0 mm. stillhead pressure, 20:1 reflux ratio and a take-off rate of 10 ml./hr. with no visible indication of decomposition other than a slight darkening of the pot charge. The rectification was discontinued when signs of decomposition became evident (pot temperature 163°). The distillation data indicated the separation of trichlorobenzenes in the material boiling below 110° (8.0 mm.) and the concentration of additional α-BTC in the distillate, b.p. 110–113° (8.0 mm.). Although the data suggested possible separation of some of the constituents in two fractions, b.p. 126–127.5° and 130.5–131.5° (8.0 mm.), subsequent investigations based on partition chromatography and infrared spectrophotometry established that the rectification did little more than concentrate the lower boiling (other than α-BTC) and higher boiling components at the beginning and end of the series of distillates. Each cut was a mixture of varying amounts of BTC and pentachlorocyclohexene[3] isomers.

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[23] W. A. Wightman. *Chemistry and Industry*. **58**, 604 (1939); P. C. Henriquez, *Proc. Acad. Sci. Amsterdam*, **37**, 532 (1934).

[24] This assumption is strongly supported by dehydrochlorination[12] and physico-chemical[13] studies which indicate that β-BTC exists predominantly in the peep form. In the case of the BHC isomers, Bijvoet[9] suggested that "in the gaseous state or in solution, the conversion of the ring will give rise to a chemical equilibrium more or less one-sided in position. In a crystalline modification, on the contrary, in general, only one form will be present."

TABLE V

PARTITION CHROMATOGRAPHY OF CHLOROCYCLOÖLEFIN DISTILLATE

Fraction no.[a]	Composite wt., g.	Appearance	Isomer composition (spectrophotometric)	Recrystallized isomer Yield, g.	Recrystallized isomer M.p., °C.	Isomer designation of purified crystals
1–29	0.09	Trace oil				
30–37	0.10	Needle-like crystals	Pentachlorobenzene[b]		80–82	
38–63	20.44	Yellow oil	γ-$C_6H_5Cl_5$			
64–73	2.52	Yellow solid, slow to crystallize	α-BTC			
74–75	0.07	Yellow oil + solid				
76–96	2.71	Yellow solid	α-$C_6H_5Cl_5$	0.68	58.2–58.8	α-$C_6H_5Cl_5$
97–113	1.77	Yellow solid	α-, δ-$C_6H_5Cl_5$, δ-BTC			
114–134	2.00	Striated crystalline mass	δ-BTC	0.38	47.8–48.9	δ-BTC
135–144	1.28	White solid	β-, δ-BTC	5.48	75.2–78.1	β-BTC
145–154	2.72	White solid	β-BTC			
155–164	3.49	White solid	β-BTC			
165–174	3.72	White solid	β-, ε-BTC			
175–184	2.52	White solid	ε-BTC, trace γ-BTC	1.23	96.1–98.6	ε-BTC
185–194	3.18	White solid	γ-, ε-BTC			
195–204	3.32	White solid	γ-, trace ε-BTC	3.90	86.9–88.0	γ-BTC
205–215	2.03	White solid	γ-BTC			
216–280	0.29	Yellow oil				
Acetone extract of packing	0.27	Brown tar				
	52.50					

[a] Each fraction represents 50 ml. of eluate solution. [b] Confirmed by mixed m.p. with authentic material, m.p. 85–86°.

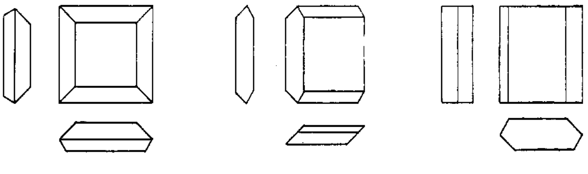
After one week in a refrigerator, 15–20% of each of the ten highest boiling cuts separated as crystals which were removed by filtration. The infrared spectra of these crystals were identical. Recrystallization of a portion of this material yielded a product melting at 67–68° (uncor.) which was shown by chlorine analysis to be a pentachlorocyclohexene.[25] *Anal.* Calcd. for $C_6H_5Cl_5$: Cl, 69.69. Found: Cl, 69.28.

No further attempts were made to separate the chlorocycloölefins by rectification. All subsequent work, which resulted in the separation of the isomeric components, was effected by partition chromatography, using a modification of the procedure described by Ramsay and Patterson[26] for the isomers of BHC. The column packing (silicic acid, C.P., J. T. Baker Co., *ca.* 24.5% water) was prepared in 500-g. batches by slurrying in 1500 ml. of *n*-hexane and adding 250 ml. of nitromethane over a 5–10 minute period. In the separation of liquid isomer mixtures, the material charged to the column was diluted with an equal volume of *n*-hexane saturated with nitromethane; for solids, slightly more than the quantity of the *n*-hexane–nitromethane reagent required for solution was employed.

Table V records the data obtained for the partition chromatography, on a 5.1 × 195-cm. column packed with 1500 g. of silicic acid, of 53.86 g. of distillate boiling in the middle of the chlorocycloölefin range (b.p. 128°, 8.0 mm., $n^{20}D$ 1.5600). The material balance was good; 97.5% of the material charged was accounted for. Those fractions which were shown by infrared spectrophotometry to be essentially a single isomer or predominantly one isomer were composited and recrystallized from a small quantity of hexane. Melting points and microchlorine analyses made it possible to identify the components of the chromatogram as BTC or pentachlorocyclohexene. Those which were found to be BTC were assigned Greek letter symbols in the order of their characterization.

The separation of a sufficient quantity of the BTC isomers for purification and chlorination studies involved the partition chromatography of six cuts (299.7 g.) of cycloölefin distillate, b.p. 124–129° (8.0 mm.). Chromatographic separation and spectrophotometric examination of higher boiling cuts failed to reveal the existence of any isomer of BTC other than those recovered from the 299.7 g.

Whereas infrared examination of the chromatograms indicated that at least two-thirds of the β- and δ-BTC isomers present were separated satisfactorily in the preliminary runs, the eluted γ- and ε-isomers appeared to overlap considerably. Pure γ-BTC fractions were obtained from the tailings, but no pure ε-BTC residue was found. To effect maximum possible recovery and purification, the chromatograms obtained from the six rectification distillates were divided into three groups, namely, composites predominant in (a) β-BTC, (b)



β-BTC γ-BTC ε-BTC

Fig. 2.—Diagrammatic representation of crystals of β-, γ- and ε-BTC (from *n*-hexane at room temperature).

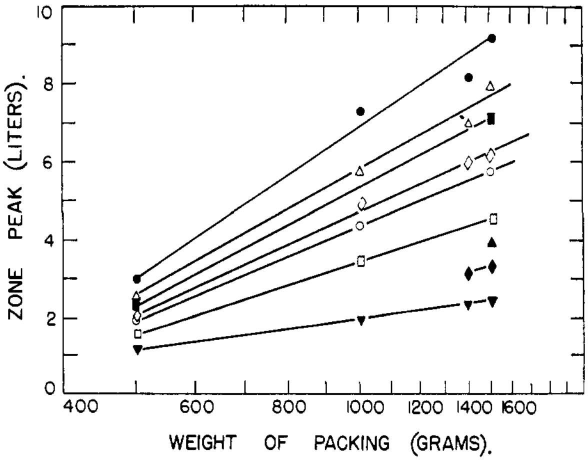


Fig. 3.—Relation of zone peaks of BTC and pentachlorocyclohexene isomers to weight of silicic acid in partition chromatography: ●, γ-BTC; △, ε-BTC; ■, β-$C_6H_5Cl_5$; ◇, β-BTC; ○, δ-BTC; □, α-$C_6H_5Cl_5$; ▲, γ-$C_6H_5Cl_5$; ◆, α-BTC; ▼, β-$C_6H_5Cl_5$.

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[25] Paper III of this series, THIS JOURNAL, to be published.

[26] L. L. Ramsay and W. I. Patterson, *J. Assoc. Offic. Agr. Chemists*, **29**, 337 (1946).

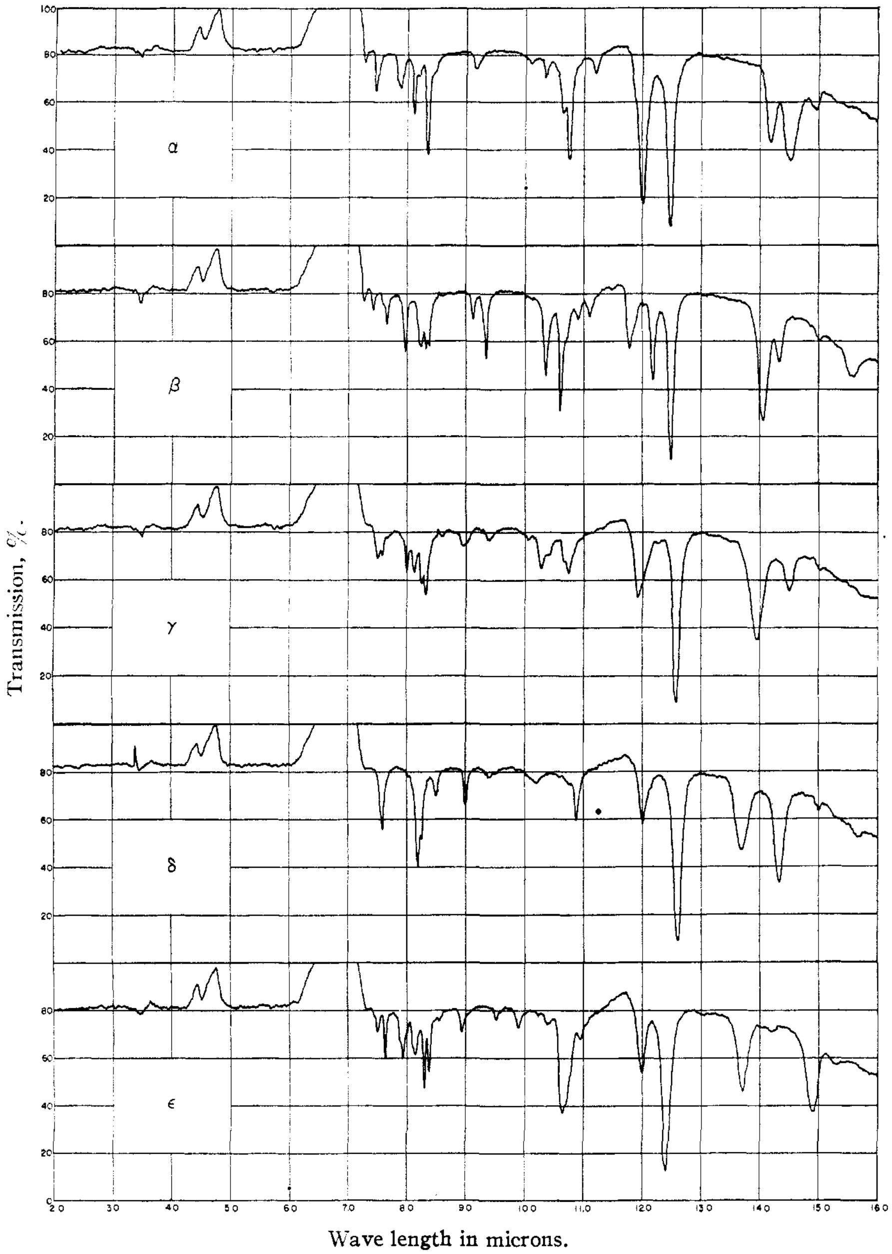

Fig. 4.—Infrared absorption spectra of BTC isomers. Concentrations, g. per liter of carbon disulfide, as follows: α, 15.39; β, 15.32; γ, 13.80; δ, 12.41; ε, 14.41.

δ-BTC, and (c) γ- and ε-BTC. These composites, usually 12–36 g., were rerun in a 4.5 × 185-cm. column. Excellent separations were obtained with β- and δ-BTC; the amounts recovered were 21.8 and 13.6 g., respectively. The mixtures of γ- and ε-BTC were purified somewhat by removal of traces of β-BTC and by the concentration of a small quantity of pure γ-isomer in the tailings from the column. The majority of the material could not be separated, however, except insofar as the ε-isomer predominated in the first fractions of eluate and the γ-isomer in the later fractions. Attempts to isolate ε-BTC by the use of a 4.5 × 240-cm. column were partially successful. To favor the separation, as little as 6–12 g. of the crude ε-isomer, contaminated with small quantities of β- and γ-BTC, was employed. The recovery of purified ε-BTC was low, amounting to little better than one gram per run.

Relatively rapid crystallization from a concentrated solution of the γ- and ε-isomers gave a mixture which could not be resolved. However, by preparing a dilute solution of the mixture, unsaturated with respect to both components, and allowing the solvent to evaporate slowly, it was possible to grow separate crystals which could be distinguished, usually without the aid of a hand lens, and separated manually. Approximately 3–4 g. of a mixture of the two isomers was dissolved in 100 ml. of hexane in a 125-ml. erlenmeyer flask and allowed to stand at room temperature. Only ε-BTC separated initially from a mixture predominant in that isomer. Seeding with pure crystals was helpful although not essential. In this fashion, approximately 1 g. of the ε-isomer was recovered in a 24-hour period. From 1:1 mixtures or from mixtures predominating in γ-BTC, both isomers crystallized together but were readily separable. γ-BTC forms thin rectangular plates which may grow separately or in clusters; ε-BTC forms long rods which are readily distinguished (Fig. 2). Melting point determinations were employed to check the identity of crystal growths which deviated somewhat from the normal form. It was necessary to decant the mother liquor daily during the crystallization process since prolonged standing resulted in contamination from cluster formation. Agglomerates and crystals of uncertain identity were redissolved in the decanted mother liquor and the process of evaporation repeated.

Four columns of different capacity were utilized for the isomer separations. It is possible to summarize the data and, on the basis of infrared spectrophotometry, present some generalizations pertaining to partition chromatography. Since the nature of the work was preparative, the columns were charged with random quantities (based on available materials) of BTC-pentachlorocyclohexene mixtures, thereby minimizing to some extent the effect of the ratio of charge:packing weight. Table VI summarizes pertinent operating data. Although no correlation of zone peak with packed height could be observed, a straight line correlation between the zone peaks (liters ±5%) and the logarithm of the packing weight was found (Fig. 3).

TABLE VI

PARTITION CHROMATOGRAPHY OF CHLOROCYCLOHEXENE MIXTURES

Column, o.d. × ht., cm.	4.1 × 115	4.5 × 185	4.5 × 240	5.1 × 195
Packed height, cm. ± 2%	98	160	220	180
Diam., i.d., cm.	3.8	4.2	4.2	4.8
Cross-sec., sq. cm.	11.6	13.9	13.9	18.1
Silicic acid, g.	500	1000	1400	1500
Av. flow, cc./min.	3.8	4.6	4.6	6.7
Av. flow, cc./min./sq. cm.	0.33	0.33	0.33	0.37
Number of runs	5	7	6	5

Because of the lack of quantitative techniques, the isomer ratio formed under the conditions of iodine-catalyzed photochlorination could not be determined reliably. Estimates based on the results of chromatographic separation can only be considered rough approximations because of the fact that relatively few of the distillate cuts were subjected to that operation. In view of the appreciable difference in volatility between the α and the other isomers, however, the amount of α-BTC formed is believed to amount to as much as 50% of the total tetrachloride product. The abundance of the remaining isomers with respect to alpha may be summarized as: $\alpha \gg \gamma \gg \beta, \delta, \epsilon$.

Purification of BTC Isomers.—The β-, γ-, δ- and ε-isomers of BTC[27] employed for the determination of melting points and absorption spectra and for the photochlorinations described in this paper were purified by repeated crystallization from *n*-hexane, at 0–5°, of essentially pure material obtained in the chromatographic and manual separations. Two criteria of purity were employed: (1) absence of absorption bands attributable to other isomers in the spectra of the purified material; (2) constancy of melting point and infrared spectrum on repeated recrystallization.

To ensure further that trace quantities of isomeric contaminants were absent, a substantial sacrifice of material was made in the recrystallization procedures. Melting points, determined with a calibrated Anschütz thermometer and with a temperature rise of 0.1°/min., are recorded in Table I.

Boiling Points.—Micro boiling points were determined[28] by Siwoloboff's[29] method, and the average of two readings was taken. The results, recorded in Table I, represent a precision of ±1.5°. The value for the the α-isomer is in excellent agreement with that determined by a macro method.[3]

Chlorination.—The photochlorinations of the BTC isomers in carbon tetrachloride were carried out by the procedure described in the first paper[3] of this series, but with the following modifications: (1) both a 15-watt daylight fluorescent lamp and a 275-watt RS Reflector Sunlamp (General Electric Co.) were used as sources of illumination; and (2) the isomers were dissolved in a small volume of solvent before the addition of the chlorine solution. All reactions reported in this section were carried out with 110% of theory of chlorine. The experimental data and results are recorded in Table IV. To ascertain the effect of non-photocatalyzed thermal chlorination on the ratio of α- and γ-BHC, α-BTC was chlorinated in the absence of light at 98–100°. The cycloölefin and the reagent solution of chlorine in carbon tetrachloride were placed in a 135-ml. Carius tube. After cooling in Dry Ice, the tube was sealed and placed in a thermocouple-equipped length of capped 1.5-inch iron pipe filled with mineral oil as a heat transfer medium. The iron pipe was heated by a thermostatically controlled bath. At the end of the reaction period, the Carius tube was removed, cooled to −70° and cautiously opened. The product was removed and prepared for analysis by the usual procedure. α- and γ-BHC (15:1 ratio) were detected.

Infrared Data.—The infrared spectra were recorded on a Baird Double Beam Spectrophotometer equipped with rock salt optics. These are shown in Fig. 4. Each sample was prepared as a carbon disulfide solution containing 12–15 g. of BTC per liter of solution. Cells with a thickness of 0.4 mm. were used and carbon disulfide was placed in the compensating beam. The distortions, noted in the spectra between 4.3 and 4.8 μ and between 6.3 and 7.3 μ, resulted from overcompensation of the carbon disulfide. The BTC isomers show no absorption bands in these regions as demonstrated by measurements made in other solvents.

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[27] Purification and solubility data for α-BTC have been reported previously.[3] Quantitative solubilities of the four remaining isomers, however, have not been determined. The relative order of solubility of the benzene tetrachlorides in *n*-hexane was found to be: $\alpha > \delta > \gamma > \beta > \epsilon$.

[28] We are indebted to Mrs. Mary L. McCoy for the micro boiling point determinations.

[29] A. Siwoloboff, *Ber.*, **19**, 795 (1886); A. A. Morton, "Laboratory Technique in Organic Chemistry," McGraw-Hill Book Co., New York, N. Y., 1938, p. 51.