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On the Yields of Eight Isomers of Benzene Hexachloride

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A simple statistical calculation of the yields of eight isomers of benzene hexachloride(BHC) on an assumed chlorination mechanism has been carried out. Processes of chlorination are proposed and several rate controlling factors and coefficients have been estimated from data on the yields of BHC isomers from benzene tetrachloride(BTC) isomers according to a study by Orloff, *et al.*, and the principle for calculating the yields of products has been applied to all the chlorination processes from benzene to BHC by way of benzene dichloride(BDC) and BTC. The calculated values are in fairly good agreement with observed data. A reason for a rich yield of the α -isomer, a possibility of finding still unknown isomers and a possibility of obtaining a good yield of the γ -isomer are also discussed.

Introduction

The molecular structures of the benzene hexachlorides (BHC) have been widely studied by means of dipole moments, infrared and Raman spectra, electron and X-ray diffractions, and chemical reactions. The more stable form of cyclohexane is the chair form. If one of the two hydrogen atoms combined to each carbon atom of cyclohexane is substituted by chlorine, many BHC isomers are possible, the form of the chair-like ring remaining unchanged. Thirteen structural isomers would appear to be possible, but only six isomers have been discovered. Identifications of the molecular structures of the six isomers have been completely carried out.^{1,2}

The relation between the structures of these six and other unknown isomers and the processes by which they are produced will be discussed. Why the α -isomer is obtained in abundance, and the factors influencing the yield of the γ -isomer (Gammexane) which has an exceptionally strong insecticidal activity, will also be treated.

Chlorination Mechanism.—In preparation of BHC gaseous chlorine is introduced into liquid benzene in a flask under sun light. Benzene dichlorides probably are formed first, then tetrachlorides and finally hexachlorides. We should like to trace these processes in detail.

According to modern views an additive reaction of halogen to a double bond is interpreted in this way: at first a Cl^+ ion combines with the π -electrons of a double bond and a π -complex is formed. The attachment of a Cl^- ion to the complex completes the halogenation. We extend this idea to the chlorination of benzene and remodel it somewhat so that a simple statistical treatment can be made.

Orloff, *et al.*,² synthesized five isomers of benzene tetrachloride (BTC). Bastiansen, *et al.*,³ studied their molecular structures by means of dipole moment determination and electron diffraction. The hexagons of BTC were all in the chair form. Orloff, *et al.*, also photochlorinated each isomer of BTC and obtained BHC isomers. Their two excellent tables are reproduced here in Tables I

(1) See, for example, E. L. Lind, M. E. Hobbs and P. M. Gross, *THIS JOURNAL*, **72**, 4474 (1950); Y. Morino, I. Miyagawa and T. Oiwa, *Botyu-Kagaku*, **15**, 181 (1950).

(2) H. C. Orloff, A. J. Kolka, G. Calingaert, M. E. Griffing and E. R. Kerr, *THIS JOURNAL*, **75**, 4243 (1953); see also G. Calingaert, M. E. Griffing, R. E. Kerr, A. J. Kolka and H. D. Orloff, *ibid.*, **73**, 5224 (1951).

(3) O. Bastiansen and J. Markali, *Acta Chem. Scand.*, **6**, 442 (1952); O. Bastiansen, *ibid.*, **6**, 875 (1952).

and II. (The letter "a" signifying "axial" has been used throughout this paper instead of the letter "p" signifying "polar." Moreover, a misprinted entry in the bottom line of their Table III is corrected here.) Tables I and II show that there is a considerable amount of *cis* addition of chlorine to BTC as well as large amounts of *trans* addition as indicated by Orloff, *et al.* We now propose a simple reaction mechanism in order to interpret the chlorination of BTC to BHC and also of benzene to BTC.

TABLE I

BTC configurations	THEORETICAL RELATIONSHIPS BETWEEN BTC AND BHC			
	BHC isomers expected—		—	
	<i>trans</i> Addition	aa	<i>cis</i> Addition	ea or ae
α , eeaa	α	$1/\alpha^a \rightarrow \alpha$	η	γ
β , aeaa and eaee	ϵ and α	$1/\alpha \rightarrow \alpha$ and $1/\epsilon \rightarrow \epsilon$	η	
γ , eeea	δ	γ	θ	α
δ , eeee	β	α		δ
ϵ , eeae	δ	η	ϵ	θ
ζ , eaea	θ	$1/\theta \rightarrow \theta$	η	ϵ

^a The symbols indicated as reciprocals (e. g., $1/\alpha$) designate the less favored and hence not isolated high energy conformation.

TABLE II

BTC isomers	PRODUCT DISTRIBUTION FROM BTC CHLORINATION					
	BHC isomers obtained in photochlorination, %					
	α	β	γ	δ	ϵ	Other
α , eeaa	89		11			
β , aeaa, eaee	81				19	1
γ , eeea	39		40	11		1
δ , eeee	70	13		17		
ϵ , eeae				33	40	27

A chlorine molecule dissociates under irradiation to two chlorine atoms. When a Cl atom approaches an ethylene molecule, the field around the molecule changes and it is chemically excited. The bond strength of its double bond becomes weakened and π -electrons come to occupy p_π -orbitals of both C atoms. A Cl atom approaches a p_π -orbital in a perpendicular direction to the molecular plane. At approximately the same time the other Cl atom approaches a p_π -orbital of the other C atom. The C atoms change their sp^2 hybrid orbitals into sp^3 orbitals and dichloroethane is produced. These two Cl atoms may approach the C atoms from the same side or from the opposite side of the molecular plane. Internuclear distances of C=C, C—C and Cl—Cl bonds are 1.33, 1.54 and 2 Å, respectively. The

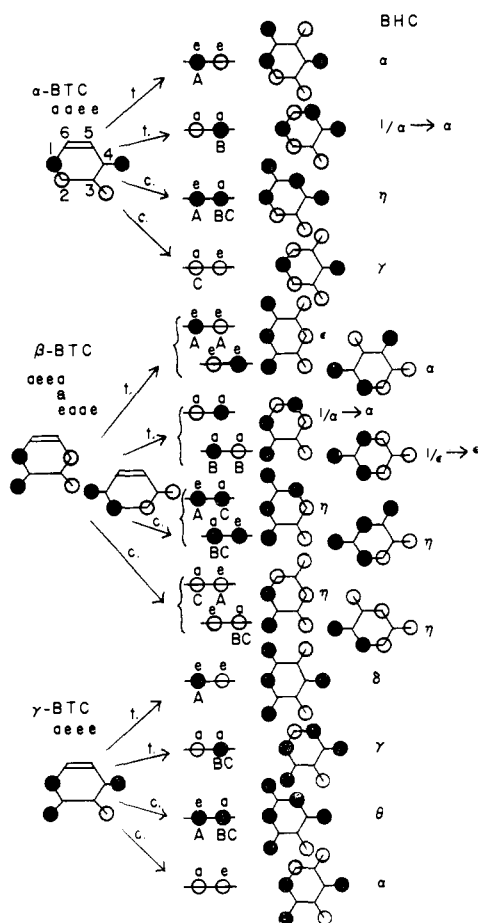


Fig. 1(a).—Chlorination processes from α -, β - and γ -BTC to BHC.

distance 2 Å. is the closest one between two Cl atoms. If two chlorine atoms approach the C atoms from the same side at almost the same time, the additive reaction is unfavorable compared with *trans* addition. We may have a majority of the *trans* addition compound and a minority of the *cis* product. If Cl atoms do not come to the C atoms in the perpendicular direction to the plane, the addition may be slow since the p_π -orbital extends only in that direction.

Chlorination of Benzene Tetrachloride.—Orloff, *et al.*, discussed in detail three factors controlling the rate of chlorination of BTC: namely, (1) the mechanism of addition whether *cis* or *trans*, (2) a so-called "entry factor" resulting from the structures of the BTC isomers and involving steric and/or electrostatic influences, and, finally, (3) the steric strains and thermodynamic stability of the product BHC. Figures 1(a) and 1(b) illustrate the chlorination mechanism of the six isomers of BTC listed in Table I. A Cl atom is represented by a black circle ● or a white circle ○. For BHC isomers a black circle denotes a Cl atom of an axial or an equatorial Cl-C bond above the plane of the hexagon ring which is approximately in the paper surface, while a white circle shows a Cl atom of bonds below the plane of the ring. This manner of expression is analogously applied to BTC isomers. Several symbols, such as ●-○-, are used

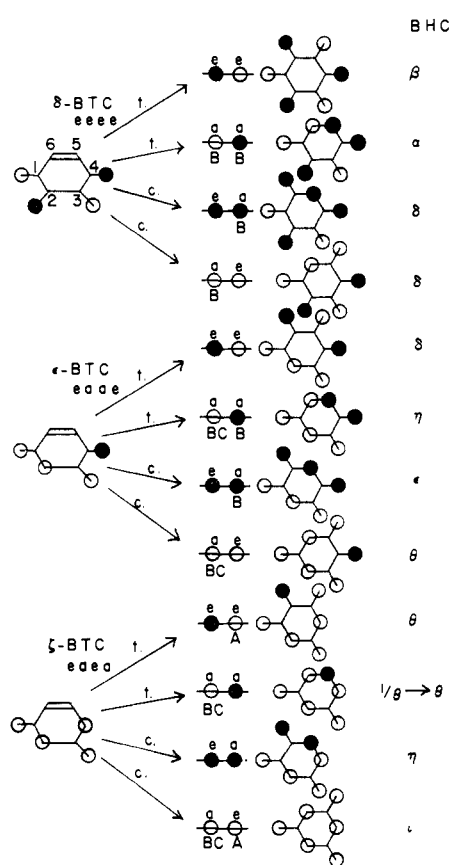


Fig. 1(b).—Chlorination processes from δ -, ϵ - and ζ -BTC to BHC.

in the figures. A black circle in these means that a Cl atom approaches a p_π -orbital of one carbon atom of a double bond in a direction from above the double bond down to the carbon, while a white one signifies that a Cl atom comes to a p_π -orbital of one of the carbon atoms of a double bond in the opposite direction to that of a black circle. A black circle on the left of a symbol ●-○- means that a Cl atom attacks the left carbon of a double bond of a BTC isomer in the figures from above the ring, while a white circle on the right of the symbol means an attack against the right carbon from below the ring. We introduce three rate-controlling factors A, B and C. The 1-carbon of α -BTC has an axial Cl-C bond in an upward direction whose Cl atom obstructs a Cl atom represented by a black circle in a symbol ●-○- from approaching the 6-carbon from above. These steric and/or electrostatic factors are designated "A." A letter "e" means that a Cl atom comes to an equatorial position when it attaches itself to one of carbon atoms of a double bond, while a letter "a" means that a Cl atom comes to an axial position when it combines with one of carbon atoms of a double bond. If a Cl atom comes to the 5-carbon of α -BTC from above, a Cl atom in an equatorial Cl-C bond belonging to the 4-carbon obstructs its approach a little. The blocking factor is represented as "B." When two Cl atoms add *cis* to α -BTC, two 1,3-axial Cl-C bonds appear in γ - and η -

BHC. They repel each other. This repulsion decreases the yields of both isomers. The decreasing factor is expressed as "C." Each factor is written under a symbolized Cl atom ● or ○, which the factor concerns, in a symbol -●-○- and others. When a reciprocal form, such as 1/α, appears, it is assumed that the form easily goes over to a normal form. No rate factor is introduced in the inversion process. For β-BTC two conformations aeea and eaea exist. The chlorination is traced for both forms.

Now we calculate yields of BHC isomers as results of chlorination of each BTC isomer according to the reaction schemes shown in Figs. 1(a) and 1(b). The yields of the products from α-BTC can be calculated as follows: We assume there is 100% of α-BTC at the beginning of the reaction; of this 80% is subject to *trans* addition and the remaining 20% is subject to *cis* addition. The possibility of *trans* addition is divided in two categories, *i.e.*, ee and aa additions. The ee addition is regarded as less favorable than the aa addition. We assign 10% to the ee addition and

70% to the aa. The factors A, B and C are assumed to be 0.5, 0.9 and 0.5, respectively. We give a factor BC a value $0.9 \times 0.5 \times 0.6$, which includes an additional coefficient 0.6, necessary since reaction is expected to be much slower when two blocking factors appear at the same time. For the same reason an additional coefficient 0.2 is introduced in calculation when two Cl atoms in a symbol -●-○- and others have any of the factors simultaneously. However, in the case of the *trans* aa addition the coefficient 0.2 is omitted since this reaction is presumed to be carried out most smoothly. These values for the factors and coefficients are estimated by a trial-and-error method so that calculated yields of BHC isomers can be adjusted to the observed data as closely as possible. Of course, these estimates are only tentative and a much better set of values could be assigned to them. In this calculation every effort was exercised in order to obtain calculated results nearest to the observed data with the smallest number of parameters and the simplest values.

$$\begin{array}{l} \alpha\text{-BTC} \\ 100 \end{array} \begin{array}{l} \nearrow \text{trans} \\ \searrow \text{cis} \end{array} \begin{array}{l} 80 \\ 20 \end{array} \left\{ \begin{array}{l} \text{ee } 10 \\ \text{aa } 70 \end{array} \right. \left. \begin{array}{l} 10 \times 0.5(A) = 5 \\ 70 \times 0.9(B) = 63 \end{array} \right] 68 \quad \begin{array}{l} \text{BHC} \\ \alpha, 92.8\% \end{array}$$

$$\left\{ \begin{array}{l} \text{ea } 10 \\ \text{ae } 10 \end{array} \right. \left. \begin{array}{l} 10 \times 0.5(A) 0.9(B) \times \\ 0.5(C) \times 0.6 \times 0.2 = 0.3 \\ 10 \times 0.5(C) = 5 \end{array} \right] 0.8 \quad \begin{array}{l} \eta, 0.4\% \\ \gamma, 6.8\% \end{array}$$

In order to calculate the yields of the products from β-BTC it is necessary to know the concentration ratio of the two conformations aeea and eaea. Bastiansen³ calculated the ratio and gave a value 87:13 from the results of the dipole moment determination. We use this value in the calculation as:

$$\begin{array}{l} \beta\text{-BTC} \\ 100 \end{array} \begin{array}{l} \nearrow \text{trans} \\ \searrow \text{cis} \end{array} \begin{array}{l} 80 \\ 20 \end{array} \left\{ \begin{array}{l} \text{ee } 10 \\ \text{aa } 70 \end{array} \right. \left. \begin{array}{l} 10 \times 0.87 \times 0.5 \times 0.5 \times 0.2 = 0.4 \\ 10 \times 0.13 = 1.3 \end{array} \right] 1.7 \quad \begin{array}{l} \text{BHC} \\ \alpha, 86.6\% \end{array}$$

$$\left\{ \begin{array}{l} \text{ea } 10 \\ \text{ae } 20 \end{array} \right. \left. \begin{array}{l} 70 \times 0.87 = 60.9 \\ 70 \times 0.13 \times 0.9 \times 0.9 = 7.4 \end{array} \right] 8.7 \quad \begin{array}{l} \epsilon, 12.3\% \end{array}$$

$$\left\{ \begin{array}{l} \text{ea } 10 \\ \text{ae } 20 \end{array} \right. \left. \begin{array}{l} 10 \times 0.87 \times 0.5 \times 0.5 \times 0.2 = 0.4 \\ 10 \times 0.13 \times 0.9 \times 0.5 \times 0.6 = 0.4 \end{array} \right] 0.8 \quad \begin{array}{l} \eta, 1.1\% \end{array}$$

The calculations of yields of products from other BTC isomers can easily be done as:

$$\begin{array}{l} \gamma\text{-BTC} \\ 100 \end{array} \begin{array}{l} \nearrow \text{trans} \\ \searrow \text{cis} \end{array} \begin{array}{l} 80 \\ 20 \end{array} \left\{ \begin{array}{l} \text{ee } 10 \\ \text{aa } 70 \end{array} \right. \left. \begin{array}{l} 10 \times 0.5 = 5 \\ 70 \times 0.9 \times 0.5 \times 0.6 = 18.9 \end{array} \right] 23.9 \quad \begin{array}{l} \text{BHC} \\ \delta, 12.4\% \\ \gamma, 47.0\% \end{array}$$

$$\left\{ \begin{array}{l} \text{ea } 10 \\ \text{ae } 10 \end{array} \right. \left. \begin{array}{l} 10 \times 0.5 \times 0.9 \times 0.5 \times 0.6 \times 0.2 = 0.3 \\ 10 \end{array} \right] 10.3 \quad \begin{array}{l} \theta, 0.8\% \\ \alpha, 39.8\% \end{array}$$

$$\begin{array}{l} \delta\text{-BTC} \\ 100 \end{array} \begin{array}{l} \nearrow \text{trans} \\ \searrow \text{cis} \end{array} \begin{array}{l} 80 \\ 20 \end{array} \left\{ \begin{array}{l} \text{ee } 10 \\ \text{aa } 70 \end{array} \right. \left. \begin{array}{l} 10 \\ 70 \times 0.9 \times 0.9 = 56.7 \end{array} \right] 66.7 \quad \begin{array}{l} \text{BHC} \\ \beta, 11.8\% \\ \alpha, 66.9\% \end{array}$$

$$\left\{ \begin{array}{l} \text{ea } 10 \\ \text{ae } 10 \end{array} \right. \left. \begin{array}{l} 10 \times 0.9 = 9 \\ 10 \times 0.9 = 9 \end{array} \right] 18 \quad \begin{array}{l} \delta, 21.3\% \end{array}$$

$$\begin{array}{l} \epsilon\text{-BTC} \\ 100 \end{array} \begin{array}{l} \nearrow \text{trans} \\ \searrow \text{cis} \end{array} \begin{array}{l} 80 \\ 20 \end{array} \left\{ \begin{array}{l} \text{ee } 10 \\ \text{aa } 70 \end{array} \right. \left. \begin{array}{l} 10 \\ 70 \times 0.9 \times 0.9 \times 0.5 \times 0.6 = 17 \end{array} \right] 27 \quad \begin{array}{l} \text{BHC} \\ \delta, 25.8\% \\ \eta, 43.9\% \end{array}$$

$$\left\{ \begin{array}{l} \text{ea } 10 \\ \text{ae } 10 \end{array} \right. \left. \begin{array}{l} 10 \times 0.9 = 9 \\ 10 \times 0.9 \times 0.5 \times 0.6 = 2.7 \end{array} \right] 11.7 \quad \begin{array}{l} \epsilon, 23.3\% \\ \theta, 7.0\% \end{array}$$

$$\begin{array}{l} \zeta\text{-BTC} \\ 100 \end{array} \begin{array}{l} \nearrow \text{trans} \\ \searrow \text{cis} \end{array} \begin{array}{l} 80 \\ 20 \end{array} \left\{ \begin{array}{l} \text{ee } 10 \\ \text{aa } 70 \end{array} \right. \left. \begin{array}{l} 10 \times 0.5 = 5 \\ 70 \times 0.9 \times 0.5 \times 0.6 = 18.9 \end{array} \right] 23.9 \quad \begin{array}{l} \text{BHC} \\ \theta, 69.9\% \end{array}$$

$$\left\{ \begin{array}{l} \text{ea } 10 \\ \text{ae } 10 \end{array} \right. \left. \begin{array}{l} 10 \\ 10 \times 0.9 \times 0.5 \times 0.5 \times 0.6 \times 0.2 = 0.3 \end{array} \right] 10.3 \quad \begin{array}{l} \eta, 29.2\% \\ \iota, 0.9\% \end{array}$$

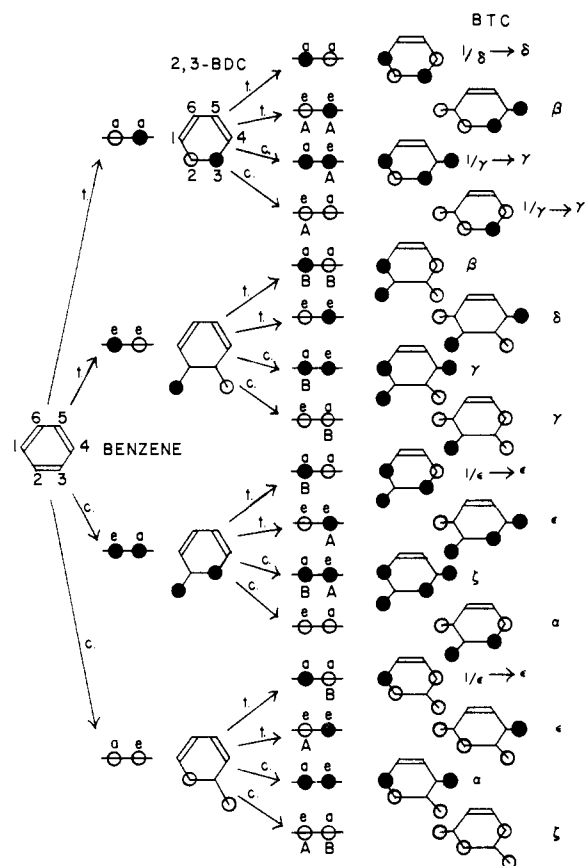


Fig. 2(a).—Chlorination processes from benzene to 2,3-BDC and finally to BTC.

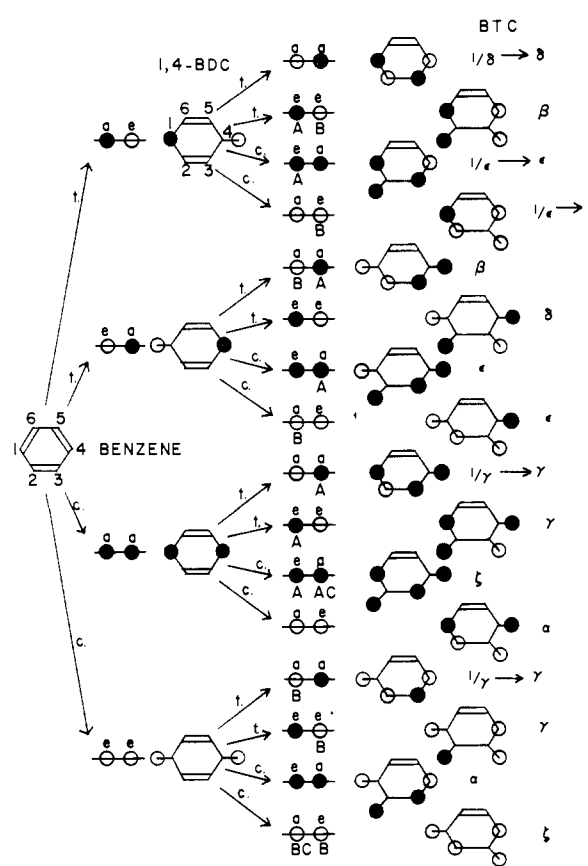


Fig. 2(b).—Chlorination processes from benzene to 1,4-BDC and finally to BTC.

The calculated values for the yields of the BHC isomers are seen to be in fairly good agreement with the observed data listed in Table II. The yields of the products from the unknown ζ -isomer of BTC also may be calculated by the same principle as that applied to the five known BTC isomers.

Now, if we knew the relative concentrations of the BTC isomers in the course of the chlorination of benzene, the yield ratio of eight BHC isomers might be calculated very easily. The chlorination mechanism of benzene to BTC will be discussed.

Chlorination of Benzene to Benzene Tetrachloride.—When benzene is chlorinated, benzene dichloride (BDC) presumably is obtained first and then benzene tetrachloride (BTC). The reaction processes are illustrated in Figs. 2(a) and 2(b), in which the conventions used are essentially the same as those in Figs. 1(a) and 1(b).

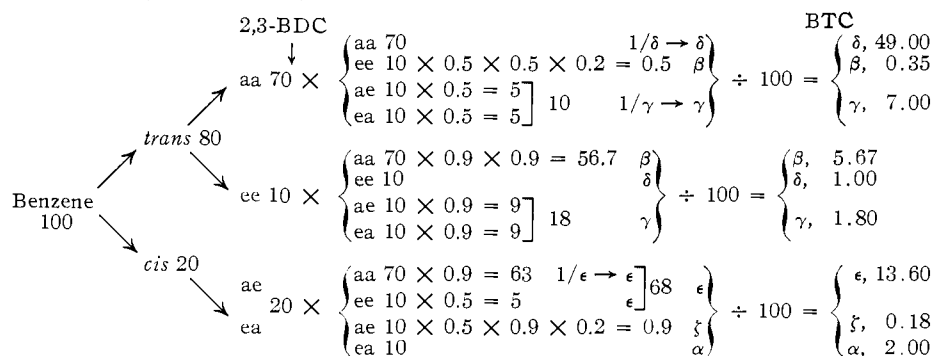
Although benzene dichloride has not yet been isolated, we can expect to obtain benzene 2,3-dichloride (2,3-BDC) and benzene 1,4-dichloride (1,4-BDC). For the former the name benzene 1,2-dichloride (1,2-BDC) is correct, but we have used the alternate name here so that the numbers will conform with those in the figures. The cyclohexadiene ring of 2,3-BDC is not coplanar but has a shallow chair-like form. For 2,3-BDC there are two isomers derived through *trans* *aa* and *ee* additions and one isomer through *cis* *ea* or *ae* addition. All three isomers have optical antipodes.

When 2,3-BDC is chlorinated to BTC, two Cl atoms attach themselves to the 1- and 4-carbon atoms. Since the 1-, 6-, 5- and 4-carbon atoms have sp^2 -hybridization and one p_π -electron with each, it is highly probable that the free valence values of the 1- and 4-carbon atoms are greater than those of the 5- and 6-carbon atoms although the resonance energy due to conjugation of two double bonds may be very small. We obtain, therefore, 1,2,3,4-BTC as shown in Fig. 2(a). On the other hand, it is also probable that two Cl atoms attack the 1- and 4-carbon atoms in the initial chlorination of benzene. We obtain one isomer through *trans* *ae* and *ea* additions and two isomers through *cis* *aa* and *ee* additions. The cyclohexadiene ring of 1,4-BDC has a boat form. The next chlorination occurs at the 2- and 3-carbon atoms. We obtain 1,2,3,4-BTC, as shown in Fig. 2(b). Subsequently, we obtain β -, γ - and δ -BTC from 2,3-BDC which is derived through *trans* *aa* and *ee* additions to benzene, and α -, ϵ - and ζ -isomers from 2,3-BDC derived through *cis* *ea* and *ae* additions to benzene. Isomers β , δ and ϵ of BTC are obtained from 1,4-BDC derived through *trans* *ae* and *ea* additions to benzene and the α -, γ - and ζ -isomers from 1,4-BDC derived through *cis* *aa* and *ee* additions to benzene.

In this connection special attention must be given to the circumstance that *trans* and *cis* additions can occur with the same probability in chlorinations at the 1- and 4-carbon atoms from

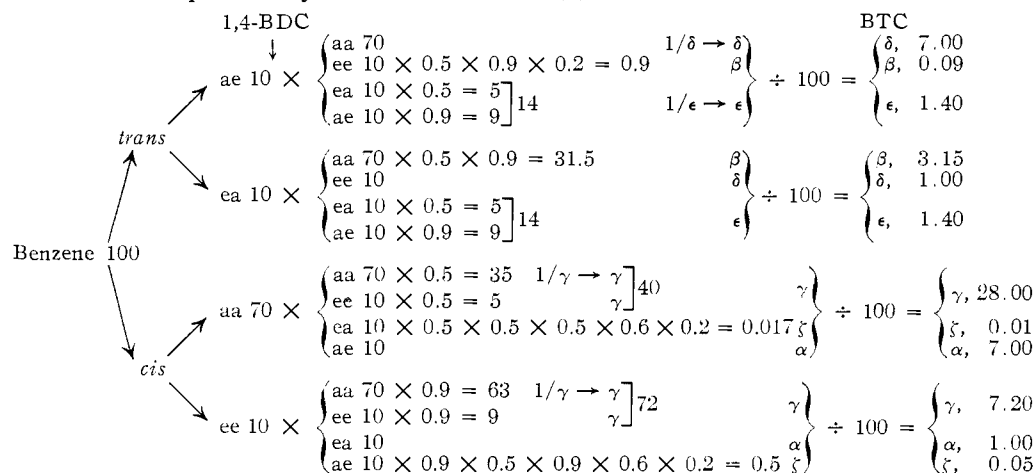
benzene to 1,4-BDC and from 2,3-BDC to 1,2,3,4-BTC, since the internuclear distance between the 1- and 4-carbon atoms is at least 2.74 Å, and two Cl atoms can easily approach them from the same side of the hexagon. Moreover, the same values are assigned to ae, ea, aa and ee terms in the 1,4-additions as those assigned in the 2,3-additions from benzene to 2,3-BDC and in the 5,6-additions from BTC to BHC. In other words, a rate-controlling factor dependent on the mechanism of addition whether *trans* or *cis* as discussed by Orloff, *et al.*, has no significance but, instead of it, the ae, ea, aa and ee terms have more basic functions in all the chlorination processes from benzene to BHC. We can, therefore, eliminate the words *trans* and *cis*, but they are written in the figures and calculations as conventional terminologies.

Now we calculate the yield ratio of α -, β -, γ -, δ -, ϵ - and ζ -isomers of BTC according to the schemes illustrated in Figs. 2(a) and 2(b) as:



we obtain α , 2.00; β , 6.02; γ , 8.80; δ , 50.00; ϵ , 13.60; ζ , 0.18, as the first total.

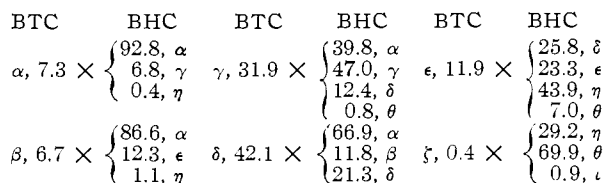
We assume that 2,3-BDC and 1,4-BDC are produced with the same probability.



We obtain α , 8.00; β , 3.24; γ , 35.20; δ , 8.00; ϵ , 2.80; ζ , 0.06 as the second total. Therefore, we obtain the final total with the first and second results, α , 10.00; β , 9.26; γ , 44.00; δ , 58.00; ϵ , 16.40; ζ , 0.24, corresponding to percentages, α , 7.3%; β , 6.7%; γ , 31.9%; δ , 42.1%; ϵ , 11.9%; ζ , 0.4%, respectively.

Yields of BHC Isomers.—We can now calculate the concentrations of BHC isomers from the relative concentrations of BTC isomers and the per-

centages of BHC isomers from each BTC isomer as:



Finally we obtain the yields of the eight BHC isomers as listed in Table III.

The calculated yields of the BHC isomers are in fairly good agreement with the observed data listed in Table IV, if we consider that our data depend exclusively on the reaction conditions of Orloff, *et al.*, and in view of the simplicity of the assumed chlorination mechanism. Our result is only an example of the calculation, but it is still valuable to discuss the chlorination reaction involved.

The preponderance of α -isomer of BHC is easily understood. According to Table II, α -BHC is obtained in large amounts with BTC α -, β - and δ -isomers. However, a main source of

α -BHC comes from the δ - and γ -BTC according to Table III. If we arrange the BTC isomers according to yields from the chlorination of benzene, they are δ , 42.1%; γ , 31.9%; ϵ , 11.9%; α , 7.3%; β , 6.7%; ζ , 0.4%. It must be remembered that the δ -isomer (eeee) which comes first in this order has no axial C-Cl bond, and the γ (eeea)- and ϵ (eeae)-isomers which come next have one axial C-Cl bond each, and finally the α (eeaa)-, β (aeaa and eaae)- and ζ (eaea)-isomers have two axial

TABLE III
 CALCULATED YIELDS OF BHC ISOMERS

BTC	BHC							
	α	β	γ	δ	ϵ	η	θ	ι
α	6.77		0.50			0.03		
β	5.80				0.82	0.07		
γ	12.70		14.99	3.93			0.26	
δ	28.16	4.97		8.97				
ϵ				3.07	2.77	5.22	0.83	
ζ						0.12	0.28	0.004
Total	53.43	4.97	15.49	16.00	3.59	5.44	1.37	.004
%	53.3	5.0	15.4	16.0	3.6	5.4	1.4	.004

 TABLE IV
 YIELDS OF BHC ISOMERS

α	β	γ	δ	ϵ	
70	5	10-12	13-15	..	Slade ^a
70	5	15	10	1.5	Daasch ^b
55	14	12	8	3-4	Kauer, <i>et al.</i> ^c
57	11	18	17		Kato, ^d sun light, 0-10°
70	0	16	15		Kato, sun light, 25-35°
64	4	19	19		Kato, sun light and alkali, 25-30°
54	9	21	16		Kato, alkali, 5-10°
70	5	12	13		Suarez, ^e alkali
58	7.5	16.9	13.5	4.1	Britton, <i>et al.</i> , ^f 5-40°, with halohydrocarbons and organic peroxide

^a R. E. Slade, *Chemistry & Industry*, **40**, 314 (1945).
^b L. W. Daasch, *Anal. Chem.*, **19**, 779 (1947). ^c K. C. Kauer, R. S. Duvall and F. N. Alquist, *Ind. Eng. Chem.*, **39**, 1335 (1947). ^d S. Kato, *Yuki-Gosei-Kagaku Kyokai-Shi*, **7**, 163 (1949). ^e D. V. Suarez, *Rev. facultad farm. y bioquím. Univ. nacl. mayor San Marco (Lima, Peru)* **10**, 323 (1948); *C. A.*, **44**, 1426e (1950). ^f E. C. Britton, F. N. Alquist and K. C. Kauer, U. S. Patent 2,628,260, Feb. 10, 1953; *C. A.*, **48**, 2270h (1954).

C-Cl bonds each. The order is not disturbed even if we assign different values to the factors A, B and C and also other additional coefficients from those used in this calculation. The γ - and δ -isomers of BTC total 74.0%, and we may therefore expect that the yields of products derived from γ - and δ -BTC are of great importance in the yields of all the BHC isomers. It is interesting to sum the BHC yields from γ - and δ -BTC entered in the third and the second lines from bottom of Table II. We obtain α , 39 + 70; β , 13; γ , 40; δ , 11 + 17, corresponding to α , 57.5%; β , 6.8%; γ , 21.1%; δ 14.8%, respectively. These data are also seen to agree well with the observed data in Table IV.

Riemschneider, *et al.*,⁴ obtained an isomer by chromatography which corresponds to the η -isomer in our system from a sample rich in δ -BHC. According to Table III the η -isomer is obtainable from the α -, β -, ϵ - and ζ -isomers of BTC, especially from the ϵ . The unknown θ -isomer should be obtained from γ -, ϵ - and ζ -BTC. Unless the ζ -isomer of BTC is synthesized, it is hopeless to search for

(4) R. Riemschneider, M. Spät, W. Rausch and E. Bötter, *Monatsh.*, **84**, 1068 (1953); see also R. G. Schneider and H. Heuer, *Z. Naturforsch.*, **8b**, 695 (1953).

the final unknown ι -isomer of BHC whose probability of occurrence is very small, *i. e.*, 0.004% according to Table III.

In order to obtain the γ -isomer of BHC (Gammexane) in high yield attention must be given to γ -BTC. This compound is obtainable by chlorination of benzene to 1,4-BDC through *cis* aa and ee additions and further chlorination through *trans* aa and ee additions. A less important process is from benzene to 2,3-BDC through *trans* aa and ee additions and further chlorination through *cis* ae or ea addition. If 1,4-BDC arose exclusively through the *cis* aa and ee additions, the yield ratio of the BTC isomers would be γ , 35.20 (28.00 + 7.20): α , 8.00 (7.00 + 1.00): ζ , 0.06 (0.01 + 0.05), and thus a large proportion of the yield would be γ -BTC. If we can find a suitable catalyst that induces only *cis* aa and ee additions to benzene and thus obtain a good yield of γ -BTC, a high yield of γ -BHC can be expected. Orloff, *et al.*, synthesized γ -BTC and other BTC isomers with iodine as a catalyst. Iodine forms a complex with benzene in which the molecular axis of the iodine lies parallel to the plane of the benzene ring. Therefore, *cis* chlorination occurs with the benzene-I₂ complex more easily than *trans* chlorination. Actually, they found that α -BTC was the predominant isomer in their iodine-catalyzed photochlorination process. According to Figs. 2(a) and 2(b) α -BTC can be obtained by chlorination of benzene to 2,3-BDC through *cis* ea and ae additions and by further chlorination of the 2,3-BDC through *cis* ea or ae addition. The other chlorination processes are from benzene to 1,4-BDC through *cis* aa and ee additions and further from the 1,4-BDC to α -BTC through *cis* ae or ea addition. In other words, α -BTC can be obtained exclusively by *cis* chlorinations. Thus the iodine catalyst used by Orloff, *et al.*, in the preparation of the BTC isomers induced *cis* chlorination and produced a good yield of α -BTC. As for γ -BTC, it is necessary to perform *trans* aa and ee additions to 1,4-BDC obtained from benzene through *cis* aa and ee additions. In other words, we need a suitable catalyst that induces *cis* chlorination of benzene to 1,4-BDC. After the 1,4-BDC is formed the catalyst is no longer necessary. If a suitable catalyst could be found on which benzene could be adsorbed in a monomolecular layer so that the molecular plane of benzene was parallel to the surface and from which, after the 1,4-*cis* chlorination of benzene, 1,4-BDC came off before further chlorination, a high yield of γ -BTC and, in consequence, a high yield of Gammexane could be obtained.

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