THE PREPARATION AND ISOLATION

OF THE GAMMA ISOMER OF

1, 2, 3, 4, 5, 6, HEXACHLOROCYCLOHEXANE

Thesis for the Degree of Ph. D.

MICHIGAN STATE COLLEGE

Roger Leo Saur

1949

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THE PREPARATION AND ISOLATION OF THE GAMMA ISOMER

OF 1,2,3,4,5,6 HEXACHLOROCYCLOHEXANE

By

ROGER LEO SAUR

A THESIS

Submitted to the School of Graduate Studies of Michigan
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INTRODUCTION

1, 2, 3, 4, 5, 6 hexachlorocyclohexane, also known as benzene hexachloride and 666, was first made by Faraday (1), in 1852. It was not until 1887 that Meunier (2), showed the presence of two isomers, the alpha isomer, melting at 157°, and beta isomer, having a much higher melting point. Then in 1912 Van der Linden (8) proved that there were at least four isomers of this compound:

alpha	m.p.	158°
beta	m.p.	over 200°
gamma	m.p.	108°-111°
delta	m.p.	129°-132°

In 1947 the fifth isomer, epsilon, was separated by Kauer, DuVall, and Alquist (9). The melting point is 202-227°C (sublimed).
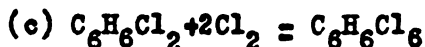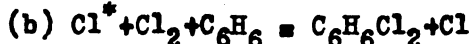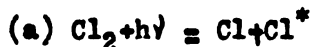
Pure alpha and beta isomer samples were prepared and their toxicity to insects was investigated in 1942 (3). When the gamma isomer was isolated in 1943 and its insecticidal properties estimated (3), it was found to be more toxic to weevils than any substance heretofore tried. It was subsequently verified that the insecticidal property of benzene hexachloride was due almost entirely to the gamma isomer. This isomer has since become a major insecticide.

The purpose of this investigation was to study the effect of wavelengths of light on the formation of the isomers of benzene hexachloride, and to investigate different methods of separation of the isomers. The odor removal from the commercial product was also studied.
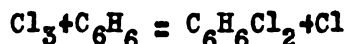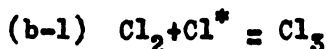
THEORETICAL

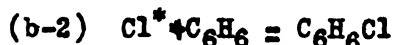## Addition of chlorine to benzene

W. A. Noyes, Jr. and coworkers in studying the photochemical addition of chlorine to benzene (4), have found that the addition rate at the beginning of the reaction was nearly proportional to the square root of the light intensity, and proportional to the pressures of chlorine and benzene. Very small amounts of chlorine substitution products were found at reaction temperatures between 25 and 35°, with a deficiency of chlorine. With an excess of chlorine the reaction gave dodecachlorocyclohexane (C_6Cl_{12}). The addition reaction mechanism postulated by Noyes and coworkers was:

$$\text{(a)} \quad Cl_2 + h\nu = Cl + Cl^*$$

$$\text{(b)} \quad Cl^* + Cl_2 + C_6H_6 = C_6H_6Cl_2 + Cl$$

$$\text{(c)} \quad C_6H_6Cl_2 + 2Cl_2 = C_6H_6Cl_6$$

Activated Cl^* furnished the activation energy for the addition reaction (b). The compound $C_6H_6Cl_2$ was considered to be the first addition compound, and there was some evidence that the chlorine added to this without further activation to give hexachlorocyclohexane. Reaction (b) as it stands means that a three-body collision must take place. However, it is to be remembered that an intermediate must have a definite life-span, so the reaction could also be written:

$$\text{(b-1)} \quad Cl_2 + Cl^* = Cl_3$$

$$Cl_3 + C_6H_6 = C_6H_6Cl_2 + Cl$$

or

$$\text{(b-2)} \quad Cl^* + C_6H_6 = C_6H_6Cl$$

$$C_6H_6Cl + Cl_2 = C_6H_6Cl_2 + Cl,$$

either reaction being the equivalent of reaction (b).

Chromatography

In 1906, Michael Tswett introduced a method with which he studied the green pigments of leaves. Although his experiments did not result in the isolation of the pure substances, Tswett insisted on the great importance of his discovery. Very few paid this important new discovery the attention it warranted, partly because his comprehensive book, "Chromophylls in Plant and Animal World", published in 1910, had only appeared in Russian.

The period from 1906 to 1931 can be regarded as the latent period of chromatography. In 1931 Kuhn and Lederer succeeded in separating alpha and beta carotene, making known tremendous possibilities of chromatography. In the period from 1936 to 1946 over one thousand papers have been published on chromatographic experiments.

The theoretical foundations of chromatography were already recognized by Tswett. Though it can be a function of many separate processes, chromatography is primarily due to selective adsorption of the components on the adsorbent, as contrasted with their difference in solubility in the solvent used.

For simplicity, assume a solution in which there are two components, each soluble to the same degree. If such a solution in an inert solvent is poured into an adsorbent column, the solute will be adsorbed and removed from solution, if the adsorptive attraction between the column and the components is of sufficient magnitude. Should the attraction be weaker than that required to hold one component, that component will

pass through the column with the solvent, leaving the more strongly adsorbed component on the column. It sometimes happens that both components are strongly adsorbed. In this case the difference in attraction of the two solutes toward the column causes them to "band"--that is, the two components are separated, one being above the other on the column. When the mixture first comes in contact with the adsorbent, both solutes are removed from solution. As more solution comes in, the more strongly adsorbed component "desorbs" or displaces the less strongly adsorbed component. It moves down the column to be adsorbed at a place free from solutes. This process continues until all of the stronger component has been adsorbed, thereby displacing the weaker which moves to a place lower on the column.

It must be kept in mind that such systems are not static, but dynamic. The above system was chosen with a neutral solvent--one which is not effectively adsorbed by the column. Actually, this is never the case, for the solvent must "wet" the column in order for the solute to come in contact with it. It is more a matter of degree of adsorption than whether it is adsorbed or not. An equilibrium is set up between the amount of the solvent and solute adsorbed on the column, and the quantity of each remaining in solution. The adsorbent contests with the solvent, and the relative amount of the solute adsorbed depends on its attraction to the solute compared to its solubility, or its attraction to the solvent. That the solvent tends to be adsorbed lessens the attraction of the solute toward the column. It can be at once seen that even a simple adsorption on an inert column becomes a phenomenon

of many separate processes, each with its own characteristics; all of these add up to give the total effect call chromatography.

Just as a solvent will dissolve a limited amount of solute, so an adsorbent will adsorb a given amount of adsorbate. However, adsorption and solution are opposite phenomena. Solution may be regarded as the evaporation of a solute into a solvent until equilibrium is reached between the solute and the undissolved material. Adsorption is the condensation of a solute onto an adsorbent until equilibrium is reached between the dissolved material and condensed solute. The processes in each probably are more or less the same. It is a matter of definition whether the adsorption, or solution for that matter, is physical or chemical. Just as a complex between solvent and solute must form in order that the solute dissolve, so must a complex form between the adsorbent and adsorbate in order that the adsorbate be adsorbed. There are two factors which primarily bring about adsorption and solution; chemical similarity and spatial effects. Each has its separate contribution. Spatial effects mostly concern ionic and molecular size, and dipole moment of molecules. Size is not important in solutions except perhaps for very large differences between solute and solvent molecules. Dipole moments are important, however. Ethanol dissolves in hexane due to chemical similarity, and in water probably because of both similarity and dipole moments. However, hexane and water are nearly immiscible because of dissimilarity of both. For the same reasons, charcoal is an excellent adsorbent of carbon compounds, but not for water, while silica gel is a good adsorbent of water but not very satisfactory for carbon

compounds of low dipole moment. But silica gel adsorbs ethanol, probably due to both dipole moment, and chemical similarity through the hydroxyl group. The relative forces of adsorption and solution largely determine which way and how far the equilibrium for the solute will go.

The relative amount adsorbed depends upon the nature of the complex formed and upon how strongly the substance is adsorbed. The type of complex depends both upon the structure of the adsorbate and upon the force with which it is held. Each is somewhat interdependent. The structure is important in two different ways; if it is a symmetrical structure it will allow the molecules to approach each other more closely, thereby increasing the amount of substance adsorbed. But if the structure of the adsorbate is such that it satisfies the attractive needs of the adsorbent, then the amount adsorbed is less. However, if these needs are not completely satisfied by the same amount of substance, then more material is adsorbed. Probably both primary and secondary forces play a part, the main difference being in the distance through which they act. Thus, an adsorbed substance may be many molecules deep, the inner molecules held by primary valence forces and the ones toward the outside of the adsorbed area held by the secondary valence forces of both the adsorbent and adsorbate. The relative structural symmetries between the adsorbent and adsorbate also assume an important part. The more symmetrically similar they are the closer do their molecules approach each other, thus bringing the primary valence forces into the picture. In turn, this better orders the configuration of the outside of the layer, making it easier for the adsorbate molecules to make use of primary forces. Thus the amount adsorbed is greater.

Molecular dipole forces probably operate through a greater distance than primary valence effects. Their purpose may be to bring about close enough proximity of atoms of different molecules so that primary and secondary valence forces can play an important part. The closeness of approach is still a function of relative symmetry, the dipole force merely increasing the chance of the two molecules coming together. It must still be remembered that adsorption is an equilibrium reaction. Even if both molecules are very dissimilar, the dipole force alone may be of sufficient strength to cause appreciable adsorption, if the solute is not selectively adsorbed, and if the solvent-adsorbate attraction is not too great.

CHEMICALS

Acetone from J. T. Baker or Merck and Co., was used without purification, conforming to A.C.S. standards.

Alumina from Aluminum Company of America, E-20 grade, 80-200 mesh, was used without activating.

Benzene, a Merck and Co. product, Reagent grade, was used without purification.

Benzene Hexachloride, a commercial sample, was furnished by Niagara Chemical Division, Food Machinery and Chemical Corp., Middleport, N. Y.

Carbon Disulfide, Baker's Analyzed, contained 0.0006% non-volatile material, 0.00% sulfides and sulfur, less than 0.002% sulfites and sulfates. B.P. 46-47 C.

Alpha, beta, delta, and gamma isomers of benzene hexachloride was furnished by Niagara Chemical Division, Food Machinery and Chemical Corp., Middleport, N. Y.

Petroleum and Naptha Skelleysolve B, from Skelley Oil Co., was used without purification.

APPARATUS

Beckman Infrared Spectrophotometer, Model IR-2, adjusted to $25 \pm 0.4^\circ$C. by water. It was used with sodium chloride optics and cell. Cell thickness was approximately 0.28 mm.

ANALYSIS

Many methods of analysis have been advanced for the isomers, some specific for the gamma isomer alone, as the gamma isomer action on mosquito larvae (11), a dechlorination procedure (12), a polarographic method (13), and a cryoscopic method (14). The only methods of estimation of all the isomers are methods of fractional crystallization such as set forth by Slade (3), partition chromatography (10) (17), and infrared analysis (15) (16). The method of Daasch (16) was used by the author. The method was accurate to 0.001 g. isomer in 10 cc. carbon disulfide solution. A single cell was used throughout, the thickness being 0.28 mm. as calculated from cell thickness and extinction values of the isomers given in the work by Daasch.

As there were many solutions to be analyzed, the author set up nomographs for the alpha, delta, and gamma isomers in carbon disulfide solution. Beta isomer was ignored because of its insolubility, and epsilon isomer was ignored because its concentration was low, and because no pure isomer was available.

As each isomer has some absorption at the alpha (12.64), delta (13.22 mu) and gamma (14.53 mu) analytical wavelengths, the equations follow:

A(a) g(a)+D(a) g(d)+G(a) g(g) = E(a) at 12.64 mu

A (d) g(a)+D(d) g(d)+G(d) g(g) = E(d) at 13.22 mu

A (g) g(a)+D(g) g(d)+G(g) g(g) = E(g) at 14.53 mu

where

A(alpha) = A(a) = slope of alpha isomer at 12.64 mu,

A(delta) = A(d) = slope of alpha isomer at 13.22 mu,

A(gamma) = A(g) = " " " at 14.53 mu,

D(alpha) = D(a) = delta at 12.64 mu,

D(delta) = D(d) = " " " at 13.22 mu,

D(gamma) = D(g) = " " " at 14.53 mu,

G(alpha) = G(a) = " gamma " at 12.64 mu,

G(delta) = G(d) = " " " at 13.22 mu,

G(gamma) = G(g) = " " " at 14.53 mu,

g(alpha) = g(a) = weight of alpha isomer in sample,

g(delta) = g(d) = " " delta " " "

g(gamma) = g(g) = " " gamma " " "

E(alpha) = E(a) = extinction at 12.64 mu,

E(delta) = E(d) = " " 13.22 mu,

E(gamma) = E(g) = " " 14.53 mu.

By inspection of the working curves (Figures 1, 2, and 3), A(alpha), A(delta), A(gamma), D(alpha), etc. can be found. So there are three equations which can be used for calculating the weights of the isomers in solution, if the extinctions at the three wavelengths are known. These working curves are useable with only one absorption cell thickness.

Then, solving for g(alpha), g(delta), and g(gamma),

$$g(alpha) = \frac{\begin{vmatrix} E(a) & D(a) & G(a) \\ E(d) & D(d) & G(d) \\ E(g) & D(g) & G(g) \end{vmatrix}}{\Delta}$$
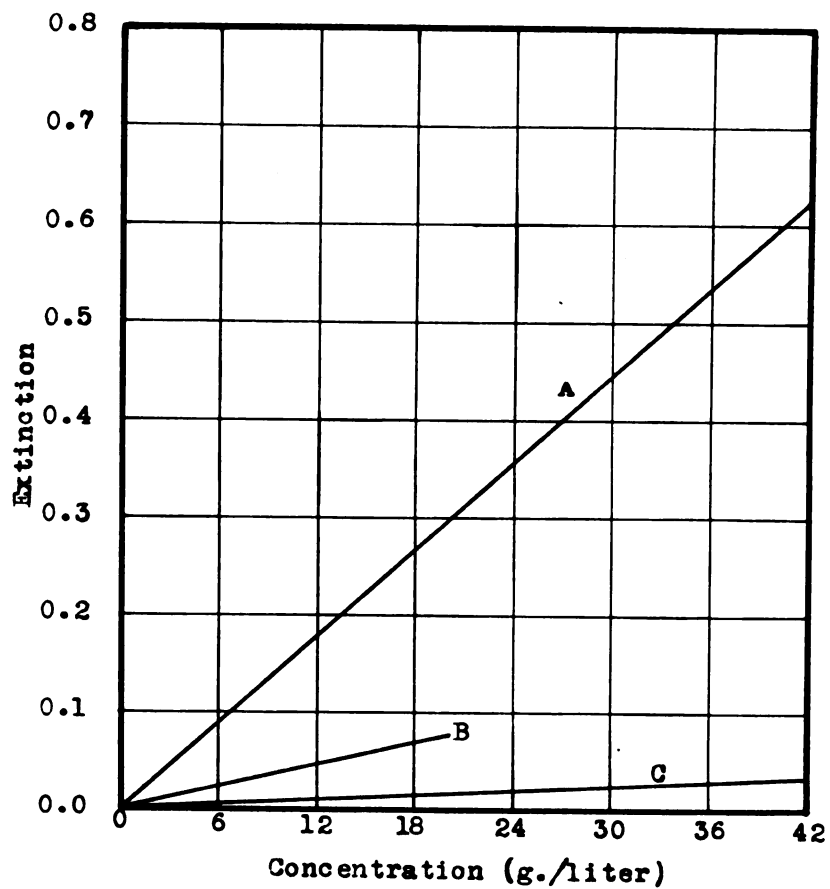
FIGURE 1
Working curve of alpha isomer
12.64 mu. CS_2
0.28 mm. cell
2.08 mm. slit
A- Alpha Isomer
B- Gamma Isomer
C- Delta Isomer
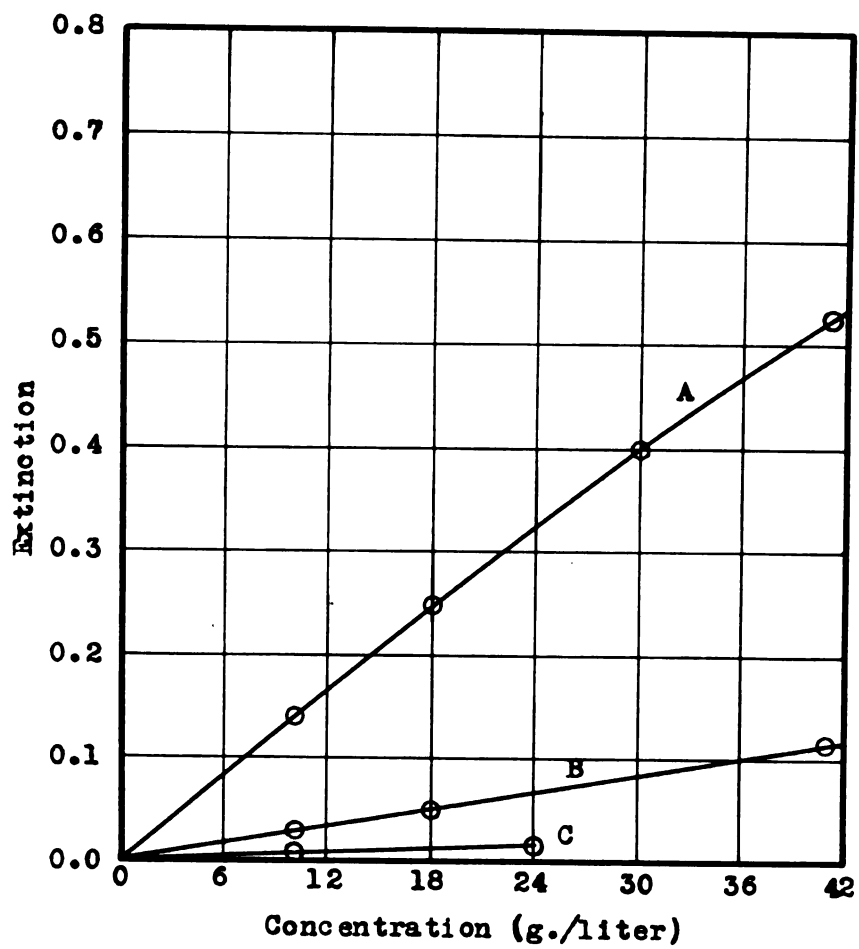
FIGURE 2
Working curve of delta isomer
13.22 mu.   CS$_2$
0.28 mm. cell
2.55 mm. slit
A- Delta Isomer
B- Alpha Isomer
C- Gamma Isomer

FIGURE 3
Working curve of gamma isomer
14.53 mu.   CS$_2$
0.28 mm. cell
1.55 mm. slit
A- Gamma Isomer
B- Delta Isomer
C- Alpha Isomer

FIGURE 4
Working curve of beta isomer
13.46 mu. Acetone
0.28 mm. cell
1.01 mm. slit
A- Beta Isomer
B- Delta Isomer
C- Alpha Isomer
D- Gamma Isomer

$$g(\text{delta}) = \frac{\begin{vmatrix} A(a) & E(a) & G(a) \\ A(d) & E(d) & G(d) \\ A(g) & E(g) & G(g) \end{vmatrix}}{\Delta}$$

$$g(\text{gamma}) = \frac{\begin{vmatrix} A(a) & D(a) & E(a) \\ A(d) & D(d) & E(d) \\ A(g) & D(g) & E(g) \end{vmatrix}}{\Delta}$$
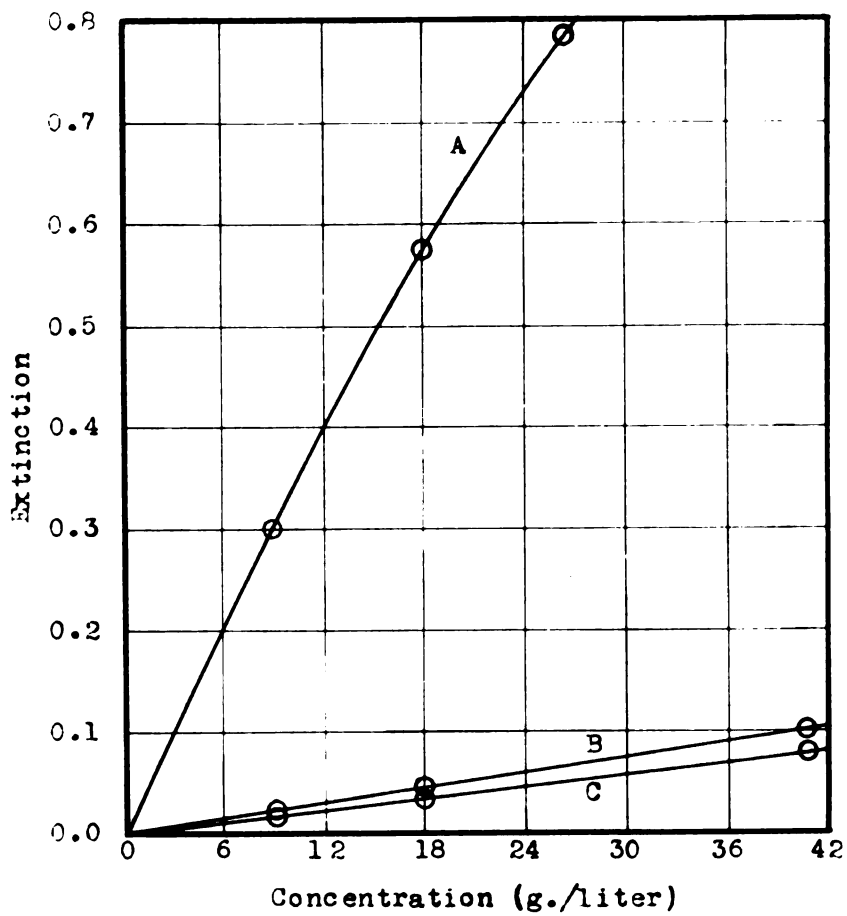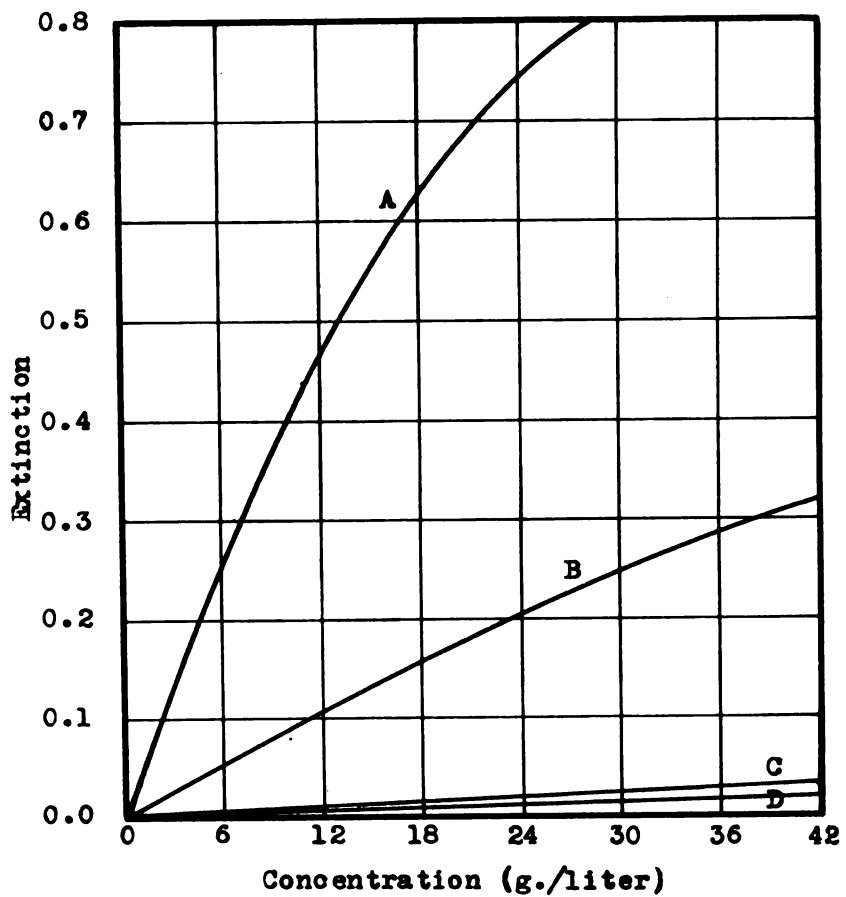
$$\Delta = \begin{vmatrix} A(a) & D(a) & G(a) \\ A(d) & D(d) & G(d) \\ A(g) & D(g) & G(g) \end{vmatrix}$$

Simplifying further,

$$g(a) = \frac{E(a)(\ G(g)D(d)-D(g)G(d))-D(a)(E(d)G(g)-G(d)E(g))+G(a)(E(d)D(g)-D(d)E(g))}{\Delta}$$

$$g(d) = \frac{A(a)(E(d)G(g)-G(d)E(g))-E(a)(A(d)G(g)-G(d)A(g))+G(a)(A(d)E(g)-E(d)A(g))}{\Delta}$$

$$g(g) = \frac{A(a)(D(d)E(g)-E(d)D(g))-D(a)(A(d)E(g)-E(d)A(g))+E(a)(A(d)D(g)-D(d)A(g))}{\Delta}$$

These three equations may be used to solve for the isomer weights in solution. They apply only where Beer's law holds.

In the case of the author's graphs, the values for the slopes were:

$A(\text{alpha}) = 1.514$	$D(\text{alpha}) = 0.275$	$G(\text{alpha}) = 0.205$
$A(\text{delta}) = 0.0825$	$D(\text{delta}) = 1.375$	$G(\text{delta}) = 0.225$
$A(\text{gamma}) = 0.345$	$D(\text{gamma}) = 0.030$	$G(\text{gamma}) = 3.255$

from whence $\Delta = 6.619$

Then,

I.
$$g(a) = 0.675 \quad E(a) - 0.0290 \quad E(d) - 0.0712 \quad E(g)$$

$$g(d) = -0.1313 \quad E(a) + 0.7339 \quad E(d) - 0.0075 \quad E(g)$$

$$g(g) = -0.0320 \quad E(a) - 0.0557 \quad E(d) + 0.3112 \quad E(g)$$

Each equation may be set up as a graph so that, knowing E(alpha), E(delta), and E(gamma), the isomer weights may be calculated. The procedure for doing this can be found in almost any book on nomography (18).

As an example for preparing a nomograph, the equation —

$$g(g) = -0.0320 \quad E(a) - 0.0557 \quad E(d) + 0.3112 \quad E(g)$$

may be set up in the determinant form.

$$\begin{vmatrix} mq & -0.0557\ m & E(d) & 1 \\ -nq & -0.0320\ n & E(a) & 1 \\ 0 & \dfrac{mn}{m+n} & h & 1 \end{vmatrix} = 0$$

for the equation --

$$(0.0557 \quad E(d) = -h - 0.0320 \quad E(a).)$$

The quantities m and n are scalars, q is a scalar used to adjust the proportions of the nomograph, and E(alpha) and E(delta) are unit vectors of the variables in the y direction. The variable h is also a vector in the y direction, but it has a value dependent on the other variables.

$$\text{Letting } 0.0557\ m = 1, \quad m = 17.95$$

$$0.0320\ n = 0.5, \quad n = 15.63$$

$$\frac{mn}{m+n} = 8.355$$

So the above determinant becomes,

II.
$$
\begin{vmatrix}
17.95 - E(d) & 1 \\
-15.63 - 0.5\,E(a) & 1 \\
0 \quad + 8.355h & 1
\end{vmatrix} = 0
$$

Then, for the equation --

$$g(g) = 0.3112 \ E(g) + h$$

$$
\begin{vmatrix}
mq & mg(g) & 1 \\
-nq & -0.3112\,n\,E(g) & 1 \\
0 & \dfrac{mn}{m+n}\ h & 1
\end{vmatrix} = 0
$$

Let $0.5\,m = 8,\quad m = 16$

$$\frac{mn}{m+n} = 8.355$$

$$+0.3112n = +5.443,\quad n = 17.49$$

The quotient $\dfrac{mn}{m+h}$ of the first determinant must equal the quotient $\dfrac{mn}{m+n}$ of the second, because the factor of $\underline{h}$ must be the same in both determinants. So the above determinant now becomes:

III.
$$
\begin{vmatrix}
16 & 8g(g) & 1 \\
-17.49 & -5.443\,E(g) & 1 \\
0 & +8.355\ h & 1
\end{vmatrix} = 0
$$

Using determinants II and III a nomograph can be set up. Considering the two determinants by the row: the third row in each is the same, so the $\underline{h}$ - line may be used as a base, with its $\underline{y}$ intercept equal to zero. Then, $g(g)$ lies 16 units in the $\underline{x}$ direction, and extends 8 units in the $\underline{y}$ direction; it is to be marked off in units up to 0.5 g. in the 8 units of length. $E(g)$ is 17.49 units in $-\underline{x}$ direction, and extends

-13-

5.443 units in -y direction; within the 5.443 units of length it is

calibrated up to 1.0. The E(a) line lies 17.95 in the -x direction,

is one unit in length in the -y direction, and is marked up to one

unit. The E(d) line is 15.63 units in the -x direction, is 0.5 unit

long in -y direction, and is marked up to one unit. The h line is not

marked, as the value is not required. The values of m and n may be

varied at will so that the accuracy of the nomograph may be at an opti-

mum.

The nomograph is operated through h- line; a straight-edge is

placed on the E(d) and E(a) values, and the intersection on the h- line

is noted. Then the straight-edge is placed across this h- line inter-

section and E(g) measurement, and the g(g) value is read at the inter-

section of the straight-edge and g(g) line. Values in full agreement

with the working curve calculations may be obtained at ease with a

properly constructed nomograph.

g(g)

0.50

h

0.25   8 units

17.49 units   16 units

5.443 0.5
units
       1.0

h

E(g)

g(g)
.15
h
.10
.05

1
E(a)
.2
1.
E(d)
.4

h

E(g)
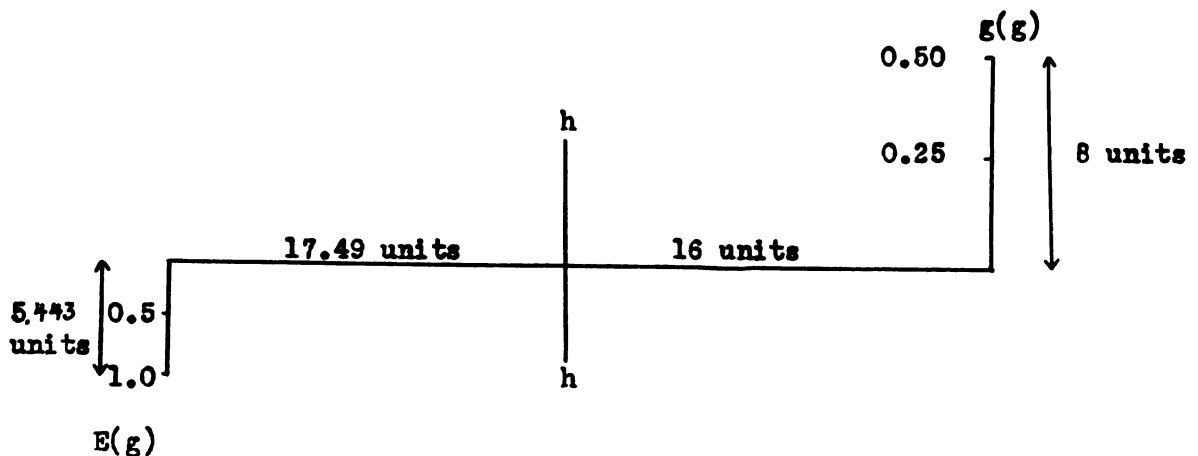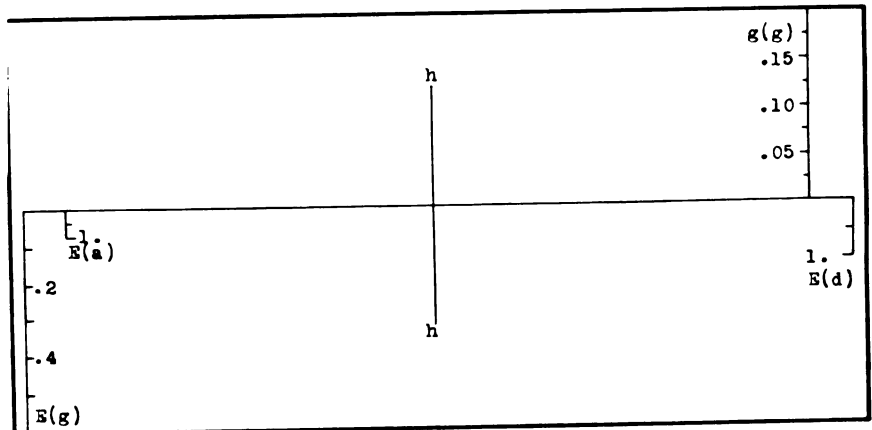
FIGURE 5-Nomograph of gamma isomer

g(d)

.2
h
.1

1
E(g)
.1
.2
1.0
E(a)
h
.3
E(d)
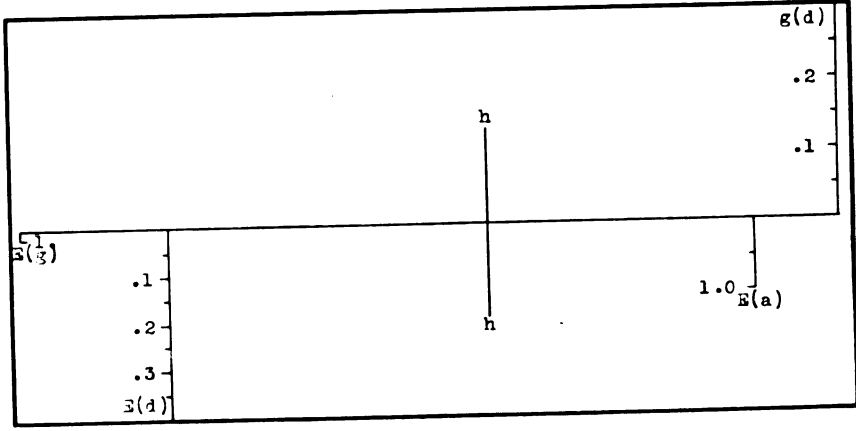
FIGURE 6-Nomograph of delta isomer

In a similar manner, working from the equations I, from the equations for g(d), the determinants were:

$$\begin{vmatrix} 7.446 & -E(a) & 1 \\ -13.33 & -0.1\ E(g) & 1 \\ 0 & 4.777h & 1 \end{vmatrix} = 0 \text{ for } 0.1313\ E(a) = -0.0075\ E(g) - h$$

$$\begin{vmatrix} 10 & +5\ g(d) & 1 \\ -9.148 & -6.712\ E(d) & 1 \\ 0 & 4.777\ h & 1 \end{vmatrix} = 0 \text{ for } g(d) = h + 0.7339\ E(d)$$

The delta isomer nomograph was not very accurate, possibly to an incorrect value for the slope of a line on the working curve. The alpha isomer nomograph that the author calculated was poorly designed and therefore not satisfactory. However, not much research was put into the delta and alpha isomer nomographs, as the gamma isomer nomograph was the only one needed. With proper selection of m and n and careful determination of slopes of lines, a nomograph could be constructed for all three isomers. Such a nomograph would give isomer weights in exact agreement with those obtained from the working curves by the customary lengthy procedure.

DISCUSSION

Removal of odor

Attempts were made to remove the pungent mold-like odor* of the commercial isomer mixtures. Neither the fractional sublimation procedure, the steam distillation, nor the chromatographic separation of the isomers on alumina operating on the prepared benzene hexachloride effected this. Chromatographing through activated silica gel, litharge, Superfiltrol, Bentonite, Florisil, magnesium silicate and Permutit was also unsuccessfully tried, using Skelleysolve B as solvent.

The removing of the odor chemically was also unsuccessful. The chemicals tried were: concentrated nitric acid, concentrated mixture of nitric and sulfuric acids, concentrated mixture of nitric and hydrochloric acids, sodium chromate in concentrated sodium hydroxide, zinc with hydrochloric acid, and zinc with sodium hydroxide. These were mixed with the benzene hexachloride and let stand at room temperature over a five day period. Chlorine in sodium hydroxide, chlorine in water solution, and warm concentrated nitric acid were also used over a period of six hours, with no appreciable results.

Chromatographic attempts to purify C.P. grade benzene before irradiation with silica gel, litharge, Superfiltrol, aluminum oxide, Bentonite, Florisil, magnesium silicate and Permutit also met with failure.

*Mr. Ernest Crocker's opinion of the odors of the pure isomer
samples purified by a crystallization methods were: alpha
isomer stung the eyes, but the odor was not strong--more of
a smart than an odor; beta isomer had a slight moldy odor
with slight eyesting; gamma isomer had a sweet fragrant odor;
delta isomer had very little odor. The commercial benzene
hexachloride odor compared to the odor of none of the purified isomers.

The benzene was partially chlorinated, distilled in a two-foot packed column, then the chlorination completed, with no success.

The crude insecticide was also placed in a dessicator under vacuum alongside a dish of activated charcoal. Adsorption methods were also used. The adsorbant was mixed dry in a pestle with the benzene hexachloride and let stand in the air over a long period afterwards. The unsuccessful adsorbants used were Superfiltrol, aluminum oxide, silica gel, Permutit, Florisil, and Bentonite.

The only two partially successful deodorizations were by adsorption with charcoal--one with Norite A, and the other with 20 mesh Cenco activated charcoal. With Norite, the odor returned after a two week period of exposure to air. An attempt to remove the benzene hexachloride with n-hexane and leave the odor with the Norite was unsuccessful. With Cenco activated charcoal, best results were obtained by shaking the powdered hexachloride with the charcoal and allowing to stand covered over a two day period. The charcoal and the hexachloride were then separated by screening. No appreciable odor increase was noticed in the screened insecticide over a three month period in air, as judged by the author's associates. Quantitative analysis of the separated benzene hexachloride showed either that the delta and gamma isomers were adsorbed to a greater extent than the alpha isomer, or that part of both isomers (delta and gamma) were converted to alpha isomer. No further tests were made; the results of the analyses have been shown in Table (I).

TABLE I

Analysis of deodorized samples of benzene

hexachlorocyclohexane

	Sample No. 1		Sample No. 2	
Isomer	Original	Deodorized	Original	Deodorized
Alpha	72%	77%	72%	86%
Delta	12%	9%	13%	9%
Gamma	16%	14%	15%	5%

Each sample was mixed with two separate samples of Cenco activated charcoal (20 mesh), and separated from each by screening. Each charcoal sample was about one third the weight of the benzene hexachloride. Percentages were taken on sum of alpha, delta, and gamma weights.

Preparation of hexachlorocyclohexane

A quartz receptacle and quartz mercury vapor lamp were used below 4000 $\overset{o}{A}$ incident light. Above 4000 $\overset{o}{A}$, a tungsten lamp with pyrex containers were used. Wherever filters were used, except in one case (the irridiation with 2537 $\overset{o}{A}$ light (7)), the pyrex filters were made by Corning. The reaction was not kept entirely free of stray light. Immediately prior to irradiation the benzene was boiled to remove dissolved oxygen. (5). During the reaction chlorine was bubbled through the liquid benzene while being irradiated with light. The benzene hexachloride formed as a white crystalline precipitate. After allowing

the reaction to go nearly to completion, the remaining benzene was removed. The samples were then analyzed for alpha, delta, and gamma isomer content by infrared analysis. The isomers are generally formed in the approximate percentages: alpha, 60-70%; beta, 5%; gamma, 12-15%; delta 10%; epsilon, less than 5%.

The differences in structure arise at the time of preparation of the hexachloride, as the isomers are fairly stable. Considering the photoactivation of chlorine (4),

$$Cl_2 + h\nu = Cl + Cl^*$$
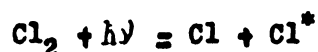
the incident radiant energy must be of such a frequency that it is absorbed. It also must possess adequate energy to activate the chlorine atom sufficiently to add. The addition of the first chlorine starts the reaction. The resulting molecule is unstable, and chlorine adds without further activation. By automatically ruling out all strained forms of benzene hexachloride, the differences in the remaining five isomers may arise from either statistical or energy considerations, or both. Obviously, the spatial arrangements of the hydrogen on the benzene ring, when the chlorine atoms add, give rise to the different isomers. Data has so far shown that each isomer is formed in a definite percentage of the total. Assuming that all irradiations were performed with light of adequate energy to form all isomers, this definite proportion is the result of the molecule, before chlorine addition, possessing a definite probability of any one structure. That this definite proportion may be effected by the energy of the incident light, as shown by the trend of Table II, seems to indicate that the activation energies of the various

TABLE II

Sample	Alpha Isomer	Delta Isomer	Gamma Isomer	Wavelength Å
No.	%	%	%	
1	64.5	9.5	12.5	Mercury Arc
2	70.8	6.0	9.0	3660
3	62.0	5.8	7.8	3660
4	79.3	3.3	3.8	2537*
6	56.3	10.5	13.8	4358
7	75.8	6.5	9.8	4900
8	69.1	9.4	14.5	5250
9	60.2	11.4	11.9	4358
10	62.4	10.0	15.2	5250
11	71.0	7.0	10.4	tungsten
12	65.8	8.5	8.7	diffuse daylight
13	58.7	10.5	13.6	5250
14	60.7	12.0	16.0	5900
15	58.8	10.6	14.9	6000
16	55.9	10.4	13.5	6400
17	52.7	12.7	15.2	6000
18	52.6	12.4	14.4	5250
19	58.7	10.5	16.7	4900
20	60.2	11.3	14.8	4200

*See reference (7).

(Sample No. 5 did not pertain to this experiment)

benzene configurations are different. This means that, if the light activates the chlorine atom below a certain minimum energy, it will not bring about addition to a certain configuration of the benzene molecule. However, it may add to one of a different configuration of lower addition energy. If so, the fact that the wavelength of light has any effect on the isomer proportions indicates that the further addition of chlorine is very rapid. Otherwise, the statistical rearrangement of the activated "di-chloro benzene" atom would nullify any favored addition of a certain structure. As seen in Table II, with increase in wavelength, the alpha isomer tends to decrease, and the delta and gamma isomers formed tend to increase. This shows that the alpha isomer configuration of the benzene molecule possesses greater activation energy than either the delta or gamma isomer configurations. Nothing quantitative can be said, as the author's data of Table II are not sufficiently accurate. As the rearrangement of the "di-chloro benzene" molecule is apparently slow compared to the further additions of chlorine, the factors bringing about a greater percentage formation of delta and gamma isomers should therefore be: (a) lowered temperature, thereby decreasing thermal agitation of the molecule, and (b) increased chlorine pressure, increasing the number of "di-chloro benzene"-chlorine collisions. Both of these bring about increased yields (19).

There is also, apparently, an equilibrium between at least three of the isomers, alpha, delta, and gamma, in the solid state. Infrared analyses made of the gamma isomer show that what was originally pure gamma isomer rearranged into alpha (4%) and delta (1%), leaving 95%

gamma isomer. The tests were made three years apart, on the same
sample, kept at room temperature in darkness over that period, so no
photochemical or mechanical reactions due to light or excessive heat
took place. One is led to believe that the decomposition was either
statistically brought about, or was due to thermodynamic instability.
It was shown not to be photochemically unstable. If the alpha con-
figuration of the benzene molecule is more difficult to add chlorine
to, it may be that this benzene configuration, and consequently the
alpha isomer, is in a lower energy state than the delta and the gamma
isomers. If this is so, then the statistical weight of the alpha iso-
mer configuration operates in conjunction with the energy differences
between the isomers. These energy differences are probably very small,
however.

Separation of the isomers

In the following separations, only attempts at separating the
alpha, delta, and gamma isomers were made, as they were more diffi-
cult to separate. The beta isomer may be almost quantitatively sepa-
rated by differential solubility in carbon disulfide, the beta being
nearly insoluble (16). The epsilon isomer was ignored, as the author
had none pure with which to construct working curves for infrared
analysis.

Distillation methods of separation

A fractional distillation procedure was attempted. A two liter
plastics reactor containing about 20 g. of crude insecticide was placed

in an oil bath. The reactor was exhausted and the oil bath heated. The distillate collected as a white film on the cover of the reactor, and was washed into a flask with acetone. When the acetone was evaporated, carbon disulfide was added prior to analysis with an infrared spectrograph. The residue was also analyzed by the same method.

Another method of separation tried was steam distillation. Steam was passed into a water suspension of the isomers. The steam emerging from the flask containing the suspension was condensed in a water condenser and collected in a flask. The isomer which remained in the condenser was washed out with acetone. The acetone solution was collected, evaporated, and carbon disulfide added to the residue prior to infrared analysis. The isomer remaining in the filtrate was separated by filtration through a Gooch crucible with a sintered-glass bottom. The isomer mixture was then dissolved with acetone, which was collected and and evaporated. Carbon disulfide was added to the solid for infrared analysis. The residue was not analyzed.

The results have been shown in Tables III and IV. Though the results were not accurate, it is evident that gamma-enriched distillates were brought about in each distillation. It can be seen that the vapor pressure of the alpha isomer is appreciably lower than that of either the delta or the gamma. The gamma tends to be lower than the delta vapor pressure also. However, the greatest differences in vapor pressure given in Slade's article fell in the neighborhood of 40°. The fractional distillation results contradict this, the temperature being probably closer to 100°. The results of both distillation tables may

TABLE III

Fractional distillation of benzene hexachloride

Sample	Oil bath temp.	Pressure	Temp. inside reactor	Isomer	%Isomer
Distillate No. 1	65°	1 mm.	about 44°	alpha	40.0
				delta	30.0
				gamma	30.0
Distillate No. 2	140°	1 mm.	about 70°	alpha	4.3
				delta	46.1
				gamma	49.5
Distillate No. 3	175°	60 mm.	about 103°	alpha	46.2
				delta	27.4
				gamma	26.5
Residue after run				alpha	69.8
				delta	17.7
				gamma	11.5
Original				alpha	70.*
				delta	12.*
				gamma	15.*

* Isomer percents are accurate to 1%.

TABLE IV

Steam distillation of benzene hexachloride

Sample	isomer	% isomer[*]
Portion of distillate remaining in condenser	alpha	44.
	delta	18.
	gamma	32.
Portion of distillate passing through condenser	alpha	41.
	delta	4.
	gamma	49.
Total distillate	alpha	45.
	delta	20.
	gamma	30.
Original	alpha	70.
	delta	12.
	gamma	15.

* Isomer percents are accurate to 1%.

be approximate, as each was the third and last attempted. The temperatures listed for the fractional distillation probably lie somewhere between the oil bath temperature and the temperature inside the reactor. Therefore, it is assumed that No. 1 was collected in the neighborhood of 55°, distillate No. 2 about 100°, etc.

In the steam distillation, a portion of the residue collected in the condenser while the rest remained suspended in the water and was collected in the distillate. Analyses made of each were noticeably different, as seen in Table IV. The main difference between them is in the percentage of delta isomer, which was larger in the condenser residue than in the distillate. The percentage of gamma was less in the condenser by about the same amount, the alpha remaining nearly constant. An accurate graph of the Clausius-Clapeyron equation of the isomers, in conjunction with their relative molecular polarity, would clarify this somewhat. The vapor pressures listed in Slade's article are probably not accurate enough for this purpose, as small amounts of impurities, perhaps in the form of lower-boiling azeotopes, would give incorrect results.

Comparing the results of the two distillates, the only point at which they can be compared is at the distillate No. 2 of the fractional distillation, which took place near 100°. Comparison of the data of the fractional distillate No. 2 with that of the steam distillation shows that the alpha mostly remained in the residue in the fractional distillation. Again, investigation of the Clausius-Clapeyron graph in conjunction with the relative isomer polarites would help to explain this.

Rough calculations made on the basis of the Clausius-Clapeyron equation using Slade's vapor pressures of the isomers indicate that the molar heat of vaporization of the alpha, delta, and gamma isomers is of the order of 12 kcal, while that of the beta isomer is about 19 kcal. The beta structure is known by x-ray analysis to be the symmetrical 1,3,5 form. Its higher heat of vaporization could be explained by postulating that the greater molecular symmetry allows closer approach of the molecules, and therefore, greater attraction of the molecules, thereby requiring more energy to separate them. That the heat of vaporization of the other three isomers is nearly the same is an indication of similarity in structure, the similarity arising from the supposition that their molecules must all be less symmetrical, for there is only one molecule theoretically possible that gives an isometric crystal structure (16).

Chromatography

About 35 g. of crude isomer mixture were shaken with 250 cc. of Skellysolve B and allowed to stand overnight. The mixture was filtered and washed once with a small amount of Skellysolve B. The mixture was retained until use. Then the sample was prepared for the column by taking a definite amount and evaporating the Skellysolve B. The residue was taken up in the desired amount of the solvent used for the chromatograph. In every case but one, the solvent volume was the same as the volume of solvent evaporated.

All chromatographs used an alumina column. They were packed by vacuum applied at the bottom. The tube was tapped while the vacuum

was applied to settle the alumina. The benzene hexachloride was added to the top of the column dissolved in a given solvent used for that chromatograph. The percolate was caught in fractions of a given volume, from which the solvent was evaporated by reduced pressure. The residue was taken up in carbon disulfide for infra-red analysis.

For the study of the action of benzene hexachloride on alumina, the chromatographic method used by the author would be classed as partition chromatography. The mobile solvent was Skelleysolve B, the immobile solvent carbon disulfide. It was not strictly true in this case that carbon disulfide was immobile, because the two solvents were both adsorbed to some extent. However, the carbon disulfide was probably adsorbed more, as predicted by a slightly higher dielectric constant than Skelleysolve B, and as shown by the fact that at the start of a chromatogram, the odor of Skelleysolve B always appeared in the percolate before that of carbon disulfide.

Alumina is a very active adsorbent. There are many examples of chemical reactions which take place on an alumina column. The fact that carbon disulfide-Skelleysolve B mixtures and even acetone would not remove all the adsorbed isomer may be ascribed to this high activity. The amount retained was roughly proportional to the quantity of alpha and gamma isomers added, as seen in Table V, amounting to around 50.% in most cases. According to the data in Table VII, the amount retained was independent of column length. It may have been due to deterioration of a certain percentage of the isomer. The amount retained was nearly constant between ratios of 1:1 and 2:1

TABLE V

Skelleysolve B / Carbon Disulfide	Milligrams alpha isomer added				
	57	114	170	228	342
1:1	27	42	85		
	23	46	87	97	
3:2				116	
2:1			83		
			85	101	180

Alpha isomer retained on six inch by one-half inch alumina column eluted with solvent of ratio shown.

Skelleysolve B / Carbon Disulfide	Milligrams gamma isomer added				
	27	53	80	106	159
1:1	11	7	37		
	10	31	26	62	
3:2				56	
2:1			29		
			24	37	74

Gamma isomer retained on six inch by one-half inch alumina column eluted with solvent of ratio shown.

Skellysolve B to carbon disulfide, as shown by Table V. Most variations in Table V can be accounted for as errors in analysis, variations in column packing, etc. However, the two discrepancies for the gamma isomer retained when 53 and 106 mg. were added could not have been due to experimental errors. Their cause was not known, but they may have been due to atmospheric humidity differences. Alumina has a great affinity for water vapor, which would tend to prevent as much gamma from being adsorbed.

Certain structural predictions may be made from a study of the relative adsorbability of the isomers. The structure of the beta isomer has been found by x-ray analysis (20) to be the symmetrical 1,3,5 form. The structures of the other isomers have not been proved. However, it has been shown statistically (2) that the 1,2,4 form has the greatest probability of formation, and this has been called the alpha isomer. The one chair form has been called the epsilon configuration. Of the remaining two, the 1,3 and the 1,2,3 forms, not many predictions have been made. However, relative adsorption of the 1,3 and 1,2,3 forms, as well as the 1,2,4 alpha form, give indication as to their structure.

Structures of the greatest symmetry tend to have greater heats of vaporization, indicating greater intermolecular attraction. The structure of the isomer with the greatest symmetry would therefore tend to be adsorbed more, due to this same symmetry. On a silicic acid column (10) the order of elution is alpha first, then gamma. The beta traces and delta can be removed by acetone, which is both

a better solvent and is probably adsorbed more on the column. The author's work with alumina adsorbent substantially confirmed this; though beta was not investigated. This adsorption sequence indicates that the beta and the delta isomers have the greatest symmetry. X-ray analysis of the beta has confirmed this (20); the other configuration of highest symmetry is the 1,2,3 form, which is therefore probably the delta isomer. The remaining two, the 1,2,4 form (probably alpha) and 1,3 form may be the alpha and the gamma structures, as their symmetries are least. If the alpha form is the 1,2,4 configuration, as it may be on the basis of statistical calculations (3), this leaves the gamma form as the 1,3 configuration. They are eluted very close together from an adsorbent column, also evidence of their similarity of molecular properties.

It is known that there is one isometric form of hexachlorocyclohexane, the other four isomers belonging to either the orthorhombic or monoclinic crystal classes (16). The chromatographic adsorption and crystal symmetry can be made into a table:

Isomer	Order of elution	Probable crystal system	Probable configuration
alpha	1	monoclinic	1,2,4
gamma	2	monoclinic	1,3
delta	3 or 4	orthorhombic	1,2,3
beta	4 or 3	isometric (by x-ray analysis)	1,3,5

No adsorption studies of the epsilon isomer have been made, but on the symmetry basis, it should act on an adsorbent column similarly

to the alpha isomer as it belongs to the monoclinic class.

Chromatographs of mixtures of the alpha, delta and gamma isomers were made on alumina to determine the effect of variations in percolation rate, column length, change in ratio of Skelleysolve B to carbon disulfide, and amount of isomers added. The results have been shown in Figures 7 through 17. The number of the 25 ml. sample containing benzene hexachloride has been shown along the absissa. The alpha isomer first appeared between the 100-125 cc and 150-175 cc fraction in every case with a 6 inch column. The amount of prerun was not measured accurately. Along the ordinate have been shown the weights of the isomers in each fraction. It can be seen that in every case the alpha isomer was eluted first, followed by the gamma isomer. In every case the delta isomer was retained on the column, which could be partially eluted with acetone. This has been discussed later.

The effect of differences in percolation rate can be seen by comparing Figures 7 and 8.

Both columns were 6" x $\frac{1}{2}$". The 15 cc. sample contained 170 mg. alpha, 52 mg. delta and 80 mg. gamma isomer. The solvent ratio was a 1:1 mixture of Skelleysolve B-carbon disulfide. Figure 7 showed the result of a percolation rate of 25 cc./6 min, Figure 8 the result of a percolation rate of 25 cc./12 min. 70 mg. alpha and 23 mg. gamma were elated pure; 18 mg. alpha and 20 mg. gamma were in the mixed portion in Figure 7. In Figure 8, 68 mg. alpha and 37 mg. gamma appeared pure, while 17 mg. alpha and 17 mg. gamma were elated mixed. The slower elution rate caused the isomers to define a sharper band. This
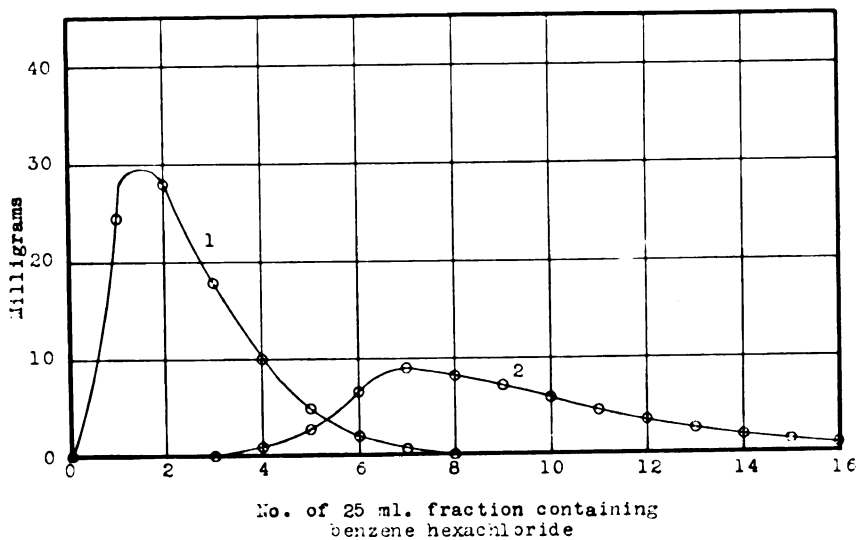
No. of 25 ml. fraction containing
benzene hexachloride

FIGURE 7 (1) Alpha isomer (2) Gamma isomer

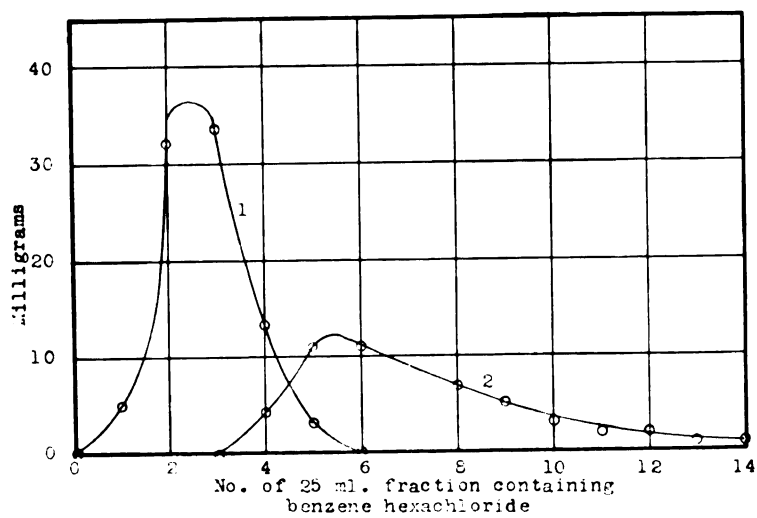No. of 25 ml. fraction containing
benzene hexachloride

FIGURE 8 (1) Alpha isomer (2) Gamma isomer

was because the components as they flowed down the column were probably in concentrations closer to those of equilibrium. The further away from equilibrium, or the faster the rate, the less distinct the band became. When the two components were introduced into the column, the solute flow was so rapid for the faster column, that the alumina particles had no chance to remove from solution as many as they were able. Naturally all were removed later, but the efficiency of initial separation was impaired. As this took place during the entire run for the faster rate, the bands were spread out. Too slow a rate is possible also, though there are no examples of it here. If the rate of flow is of the order of diffusion velocities, then the components tend to come to equilibrium throughout the whole column, and less efficient separations can again be expected. No run with less than the 2 cc. per minute was performed. An example of too fast elution has been shown in Figure 7, as compared to Figure 8. It can also be seen by comparing these two graphs that the faster elution rate required more solvent. This was also because the solvent flow was so rapid that the solute did not have time to come to equilibrium between the solvent and adsorbent. Consequently, the solvent did not remove all the solute it was able; thus more solvent was required. A difference could also be noticed between the first and last part of each band. The first part had a steeper slope in every case, and the differences were greater as the elution velocity increased, as seen also by the three previously mentioned graphs. Non-attainment of equilibrium explained this by the same reasoning. It follows that the sharper is the band, the higher is the maximum for the same amount eluted.

Also studied was the effect of varying the amounts of solute introduced into the column. The solute was made up to a nearly saturated solution which varied from 5 to 30 cc. in volume. The results can be seen by comparing Figures 7 and 9, and Figures 10, 11 and 12.

TABLE VI

The effect of varying amount of sample on a 6 inch alumina column.

Figure	Elution Rate	Skelly-solve B carbon di-sulfide	Isomer	mg. Sample	mg. Eluted pure	mg. Eluted mixed	mg. retained on column
7	25cc/6min.	1:1	alpha	170	70	18	82
			delta	52	0	0	52
			gamma	80	23	20	37
9	25cc/5min.	1:1	alpha	57	32	2	23
			delta	18	0	0	18
			gamma	27	15	2	10
10	25cc/8min.	2:1	alpha	170	73	12	85
			delta	52	0	0	52
			gamma	80	46	10	24
11	25cc/6min.	2:1	alpha	228	88	39	101
			delta	70	0	0	70
			gamma	106	42	27	37
12	25cc/3min.	2:1	alpha	342	160	20	162
			delta	104	0	0	104
			gamma	159	55	19	85

It was found that the efficiency of separation on a six inch column was not greatly altered with variations of 100 to 300 mg. solids in a carbon disulfide-skelleysolve B ration of 1:1, or with variations of 300 to 600 milligrams solids in a solvent of a 2:1 ratio. That is, the area of the sections where the isomers overlapped varied directly with the weight of the sample. The solvent volume separating the
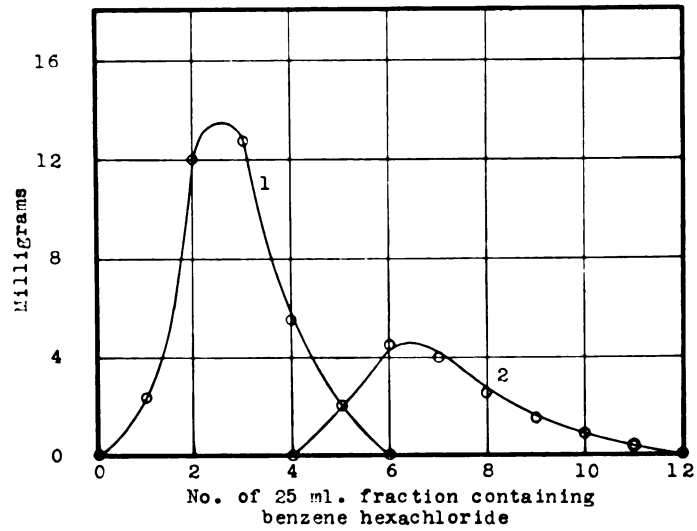
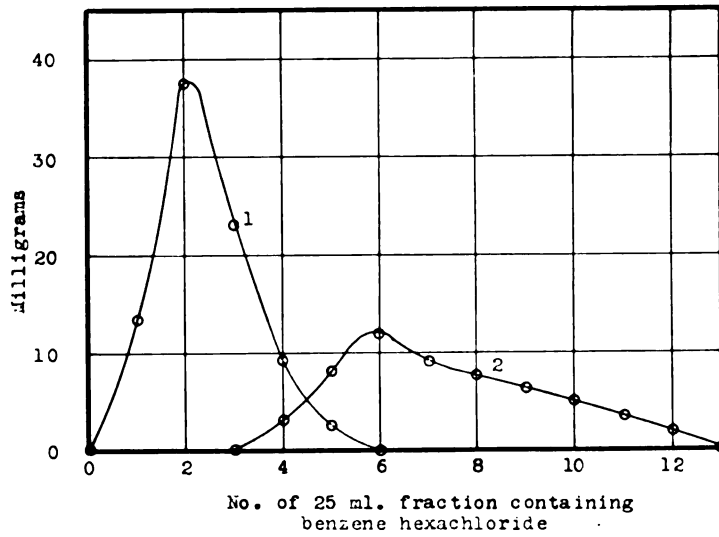FIGURE 9 (1) Alpha isomer (2) Gamma isomer

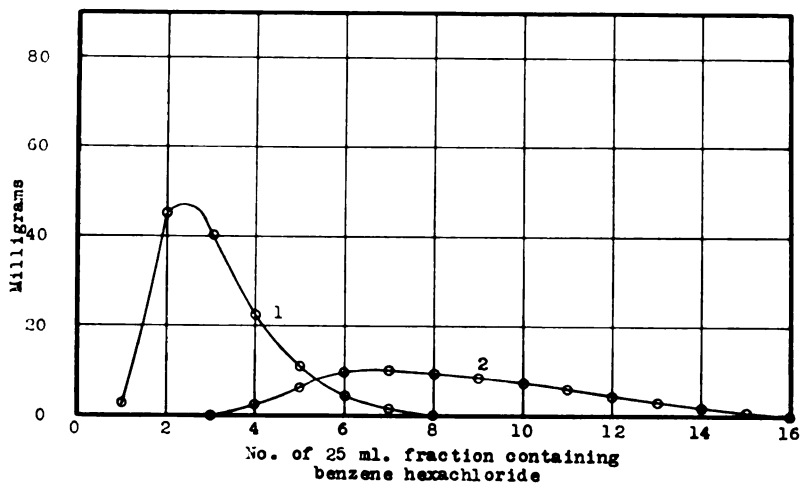FIGURE 10 (1) Alpha isomer (2) Gamma isomer
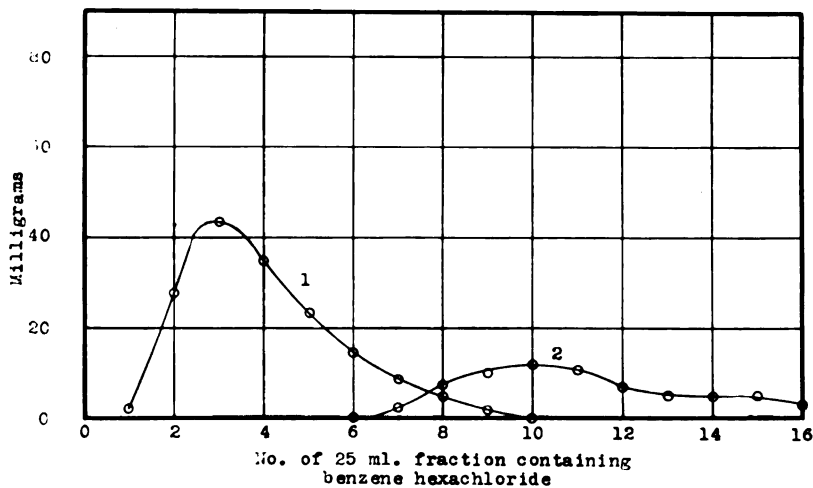
FIGURE 11 (1) Alpha isomer (2) Gamma isomer

FIGURE 12 (1) Alpha isomer (2) Gamma isomer

elution heads of the isomers tended to become more separated with greater solute samples. No measurements were made on the comparative volume of pre-run; this would tell whether the alpha isomer came through sooner or the gamma came through later. Probably, the alpha isomer came through sooner and also the gamma later, due to the fact the gamma tended to desorb the alpha, but also because there was an equilibrium set up. That is, alpha tended to desorb gamma also, but this reaction was not dominant. The eluent volume increase as seen in Figures 10, 11 and 12 was also partly due to increase in percolation rate.

The volumes of the original solutions prior to introducing them into the column were also investigated, as seen in Figures 9 and 13. Each figure is the plotted result of a sample of 57 mg. alpha, 18 mg. delta and 27 mg. gamma chromatographed through a 6" x $\frac{1}{2}$" alumina column using a solvent consisting of a 1:1 ratio of Skelleysolve B-carbon disulfide. Percolation rates were 25 cc./5 min. for Figure 9, and 25 cc./6 min. for Figure 13. In Figure 9, 32 mg. alpha and 15 mg. gamma were eluted pure, with 2 mg. alpha and 2 mg. gamma mixed, with 23 mg. alpha, 18 mg. delta and 10 mg. gamma retained. For Figure 13, 27 mg. alpha, and 16 mg. gamma were eluted pure, 3 mg. alpha and 2 mg. gamma mixed, and 27 mg. alpha, 18 mg. delta and 11 mg. gamma retained on the column.

The solution volume was varied ten-fold, from 5 cc in Figure 9 to 50 cc. in Figure 13, with little noticeable effect on the eluate. The difference in eluate volume required to completely elute each isomer was probably due to the difference in percolation rate.
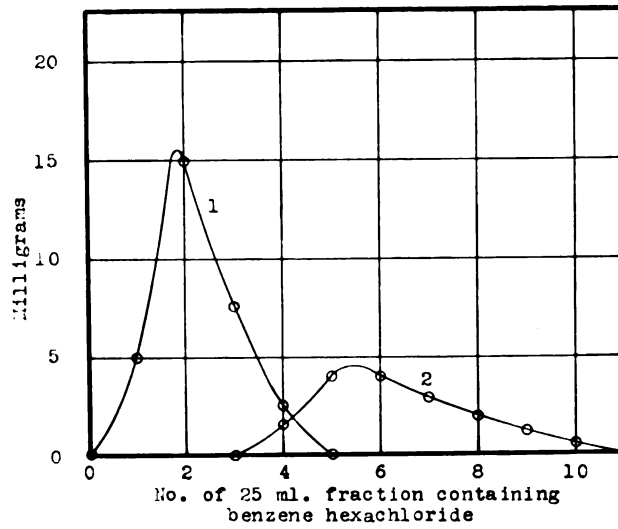
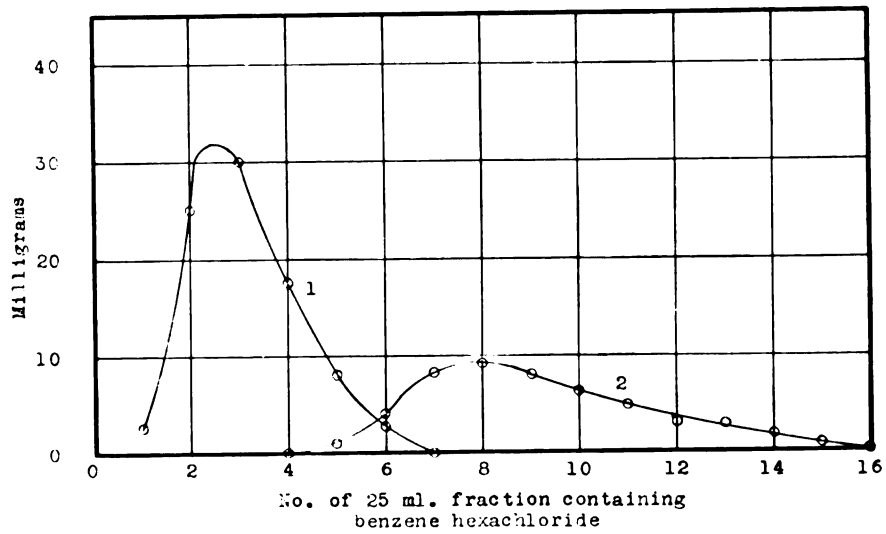FIGURE 13 (1) Alpha isomer (2) Gamma isomer

FIGURE 14 (1) Alpha isomer (2) Gamma isomer

The ratios of Skelleysolve B to carbon disulfide affected the percolate somewhat. The higher the proportion of Skelleysolve B, the less eluting power of the solvent, as seen by comparing the graphs in Figures 7 and 14. Both were from 6" x ½" alumina columns, with a flow rate of 25 cc./6 min. in Figure 7 and 25 cc./7 min. in Figure 14. The samples were 170 mg. alpha, 52 mg. delta and 80 mg. gamma isomer. ~~That~~ *The data represented in* ~~of~~ Figure 7 ~~had~~ *was the result of* a Skelleysolve B-carbon disulfide solvent ratio of 1:1; that of Figure 14 had 2:1. Little difference was found between the elution curves themselves. The difference was in the prerun, which was 50 cc. greater in Figure 14. This was due to both the lower adsorbability of the Skelleysolve B, and to the lower solubilities of the isomers in Skelleysolve B. (See Table VIII on solubilities.) For Figure 14, 76 mg. alpha and 46 mg. gamma were eluted pure, 11 mg. alpha and 5 mg. gamma mixed, and 83 mg. alpha and 29 mg. gamma were retained on the column.

The two column lengths studied were 6 and 27 inches long. The isomers eluted were just resolved from the 27 inch column, whereas they were not resolved on the 6 inch column. Comparing Figures 15 and 16 with those of a six inch column, it can be seen that the solvent volume containing benzene hexachloride for the 27 inch column was roughly twice that required by the 6 inch column. The solutions were therefore about twice as concentrated from the 6 inch column. Roughly 2½ times the solvent was required to elute the alpha and gamma isomers from a 27 inch column as from a 6 inch column, about 1200 cc. being required by the 27 inch column.
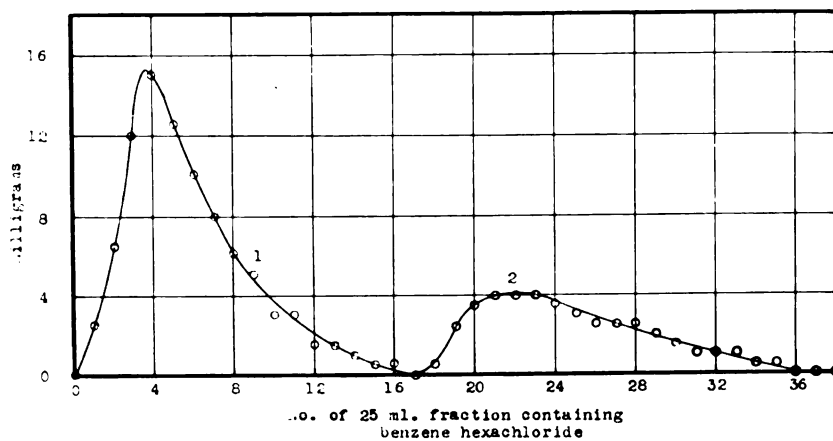
No. of 25 ml. fraction containing
benzene hexachloride

FIGURE 15 (1) Alpha isomer (2) Gamma isomer

No. of 25 ml. fraction containing
benzene hexachloride
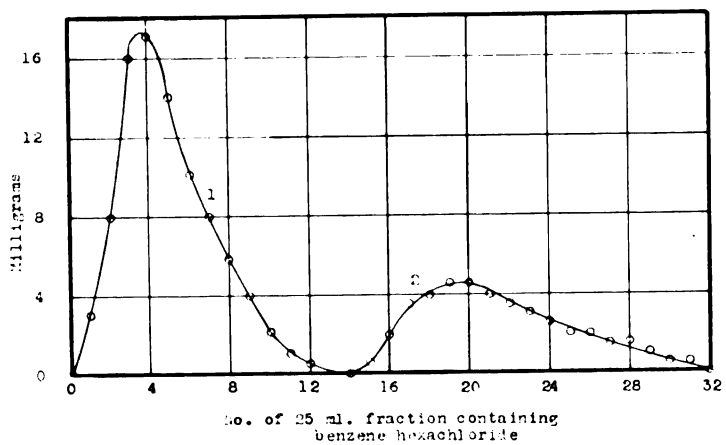
FIGURE 16 (1) Alpha isomer (2) Gamma isomer

The conditions for the chromatograph of Figure 15 were: column, 27" x ½" alumina; Skelleysolve B-carbon disulfide solvent ratio, 1:1; sample, 170 mg. alpha, 52 mg. delta, 80 mg. gamma, and percolation rate 25 cc./6 min. The conditions of Figure 16 were the same as for Figure 15, except that the percolation rate was 25 cc./7 min. A comparison of these two graphs also shows the effect of changing the percolation rate. These two chromatographs were the only ones made on a 27" column with this sample of alumina. The isomers have been just resolved, with 89 mg. alpha and 41 mg. gamma recovered in Figure 15, and 83 mg. alpha and 39 mg. gamma recovered in Figure 16. 81 mg. alpha and 39 mg. gamma were retained on the column for Figure 15, and 87 mg. alpha and 41 mg. gamma were retained for Figure 16. The alpha isomer started to be eluted with the 450-475 cc. fraction in each case.

Figure 17 is the result of a chromatograph through a 27" x ½" alumina column also, but the alumina was from a newer sample. The sample was made up of pure isomers, 153 mg. alpha, 53 mg. delta and 76 mg. gamma isomer. 91 mg. alpha and 29 mg. gamma were eluted pure, while 62 mg. alpha, 55 mg. delta and 47 mg. gamma were retained on the column. The pure gamma eluted was low because the elution was stopped before all the gamma was eluted that was possible to elute. The percolation rate was 25 cc./5½ min., and the Skelleysolve B-carbon disulfide ratio was 1:1. It can be seen that the alpha and gamma isomers were again just resolved. The abscissa has been labeled "cc. eluted" instead of "no. of 25 cc. sample containing benzene hexachloride". The greater volume of solvent containing benzene hexachloride was probably due to
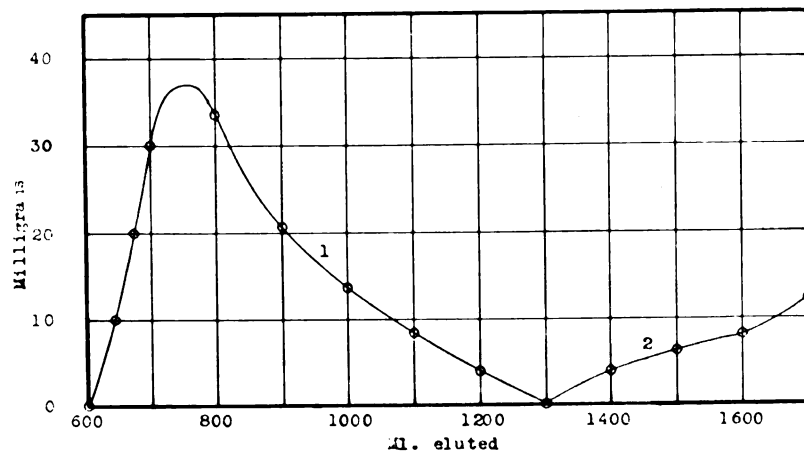
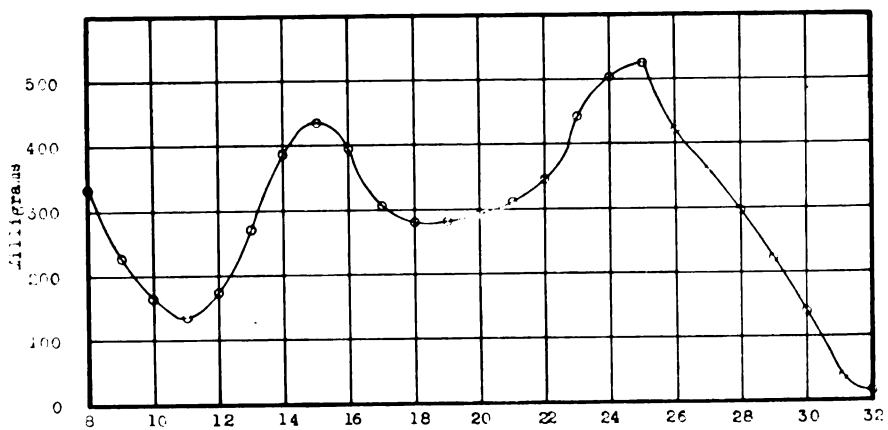FIGURE 17 (1) Alpha isomer (2) Gamma isomer

FIGURE 18-No. of 25 ml. fraction

the greater activation state of the alumina. That the activation state of the alumina caused no relatively greater separation demonstrated that the ratio of the strength of adsorption of the alpha and gamma isomers on alumina was the same in each case.

The results of the four experiments made eluting the column with acetone are shown in Table VII. The amount of delta recovered was independent of column length, and approximately 70% of the original delta added. The amounts of alpha and gamma varied between zero and 12%. This variation may have been due to instability, as many reactions are known to take place on alumina. It could also have been due to humidity changes, though this is doubtful.

Ramsay and Patterson published their findings of a chromatographic separation of the alpha, delta, and gamma isomers of benzene hexachloride (10), the results of which were graphed in Figure 18. The beta traces and delta remained on the column, and were removed with acetone. Samples prepared from crude hexachlorocyclohexane did not give clearcut separation between the alpha and gamma isomers. The column material used was silicic acid, with n-hexane the mobile solvent and nitromethane the immobile solvent. No figures could be given concerning the per cent recovery from a chromatogram of a commercial sample, as the original analysis was not available. Calculations of the author of the thesis made by assuming that the eluent between two bands consisted of only those two constituents indicate that total gamma contained 6% impurity and alpha 33%. Tests run using pure isomers gave recovery of 93% alpha, 84% delta and 98% gamma which were separated well on the column.

TABLE VII

Weights of isomers eluted from column after chromatographing

Column length	Figure No.	Isomer	Mg. into column	Mg. eluted by acetone	% isomer eluted
27	17*	alpha	153	19	12
		delta	55	40	73
		gamma	76	18	24
27	16	alpha	170	6	4
		delta	52	37	71
		gamma	80	5	6
6	**	alpha	114	0	0
		delta	35	26	74
		gamma	53	5	10
6	7	alpha	170	13	8
		delta	52	37	69
		gamma	80	3	4

* The concentration of the gamma isomer in this sample was high because the carbon disulfide-Skelley-solve B elution was not continued to the point where no gamma appeared in the eluent.

** The graph for the eluent of this column has not been included.

TABLE VIII

Solubilities of alpha, gamma and delta isomers

Isomer	pentane*	Solvent carbon-disulfide**	acetone*
alpha	0.9	5.90	13.9
beta	0.1	0.07	10.3
gamma	2.2	19.95	43.5
delta	1.6	9.50	71.1

Solubilities given in g./100 cc.

*Solubilities taken from Slade's (3) work.

**Solubilities taken Daasch's (16) work.

The author used an alumina column, with Skelleysolve B as the mobile solvent and carbon disulfide as the immobile solvent. Yields of 50% alpha, 50% gamma and 70% delta were obtained. The alpha and gamma fractions were pure of each other and of delta. The delta contained traces up to around 43% of combines alpha and gamma impurities.

SUMMARY

Investigation of the effect of wavelength of light between wavelengths of 2500 and 6500 Å on the preparation of benzene hexachloride revealed that relatively more alpha tended to be formed at lower wavelengths with corresponding decrease in gamma and delta formed. At higher wavelengths the gamma and delta isomers tended to be formed in greater quantities with corresponding decrease in the alpha isomer. Applying this to the mechanism of the addition of chlorine to benzene, it was deduced that the second and third chlorine molecule additions were relatively fast.

The disagreeable odor of crude benzene hexachloride was partially removed by mixing it dry with activated charcoal. The odor did not return over a three month period whether the charcoal and benzene hexachloride were separated or not. Infrared analysis indicates that relatively more gamma and delta isomers were adsorbed by the charcoal.

Chromatographic separation on alumina using carbon disulfide-Skelleysolve B mixtures as solvent, resulted in pure alpha and gamma isomers being separated, each in 50% of the original isomers entered into the column. By eluting the column with acetone, 75% of the delta isomer was recovered, about 60% pure. The effects of elution rate, amount of sample, column length, and solvent ratio were discussed.

On the basis of the order of chromatographic adsorption, the delta isomer was assigned the 1,2,3 structure and the gamma the 1,3 structure. The dissymetry of the 1,3 (gamma) and 1,2,4 (alpha) isomer configurations was also evident from chromatographic adsorption. Nomographs were constructed for the analysis of the gamma and delta isomers.

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