

between August 27 and 31, and the rice-plants bloomed September 12. The variety of rice plants used was "Kyoto Asahi," the midseason variety. The yield of this year was slightly less than that of the average year, due to low temperature and short of sunshine, during the middle of September to the beginning of October.

The results obtained are as follows:

(1) Between the ears of uninfested culms in the infested rice plants and ones in the uninfested rice plants, any significant difference is not recognized regarding the average number of paddy in a ear and the specific gravity of a rice grain. But with this result, I think it is impossible to conclude that rice plants have no compensative ability against the infestation by the rice-borer.

(2) The reduction of yield increases with the increase of the number of the internodes infested, and with the rise of the height of the internodes infested. When the culms of different degrees of infestation and the culms have the same height of infested internode, the reduction of the mean weight of a grain in a ear resembles one another more closely than when culms with the same degree of infestation and a different height of infested internode.

This fact suggests that the influences of the position of infestation is greater than those of the degree of infestation.

(3) The cumulative frequency curve of the mean weights of a grain arises from a infested culm and the daily increase of the number of the infested culms shows a similar tendency. When the ears having many blasted grains examined the mean value of weight of a grain and the ratio of the number of perfect grain to that of excluding the blasted grains both decreases markedly. Whether the grains are blasted or not is determined at an early period, during the several days after the flowering of rice plants. Therefore, it seems that the reductions of the yield and the ratio of perfect grains are influenced by the earliness of the relative period of borer infestation against the maturation of rice plants.

(4) From these facts it can be concluded that the degree of infestation by the rice-borer affecting the reduction of yield of rice plants are determined by the time and the position of the borer's infestation but the number of infested internodes is negligible.

(5) The ratio of reduction of the yield and the ratio of the reduction of perfect grains were calculated. The former was found to be about 7% and the latter to be about 27% to the control. Accordingly, it seems that the damage of rice caused by the rice-borer is greater in the quality than in the quantity of the rice grain.

Molecular Structure of  $\gamma$ -BHC. Minoru NAKAZIMA and Toshihiko ORWA (Laboratory of Agricultural Chemicals, and Takei Laboratory, Institute for Chemical Research, Kyoto University) Received May 31, 1950, *Botyu-Kagaku* 15, 114, 1950 (with English résumé 116)

20.  $\gamma$ -BHC の分子構造に就て \* 中島稔, 大岩俊彦 (京都大学 農薬化学研究室 及び 化学研究所 武居研究室) 25. 5. 31 受理

Vloten 等<sup>(1)</sup> 及び Bijvoet<sup>(2)</sup> は X 線解析から, 又 Bastiansen 等<sup>(3,4,10)</sup> は電子線廻折法で  $\gamma$ -BHC の構造は pppccc であると報告した。有機化学的方法による構造決定の爲にかねてから中島等<sup>(5,6,7)</sup> は  $\gamma$ -BHC の脱塩酸反応とその反応生成物の塩素化を行い, 又大岩等<sup>(7,8,10)</sup> は  $\gamma$ -BHC の直接の塩素化を行っていたが, 今回両者の得た実験結果を綜合検討することによって  $\gamma$ -BHC 並びにその近縁化合物の原子の立體配置を決定し得たので茲に報告する。

Cristol<sup>(9)</sup> は dioxane 溶液中で  $\alpha$ -BHC に brucine を作用させて光學活性體 (I-form) の分離に成功したが,  $\gamma$ -BHC に同様に brucine を作用させて得た油状

固體は旋光性を持たなかつた。大岩等も亦  $\gamma$ -BHC に種々の條件で brucine を作用させて得た産物がやはり旋光性を持たない事を知つた。このことから  $\gamma$ -BHC は対称構造であろうと考えられる。(実験結果 1)。

又大岩等は先に  $\gamma$ -BHC の塩化物から融点 55~55.5° の heptachlorocyclohexane の一新異性體を得た。<sup>(8)</sup> その後 dioxane 溶液中でこのものに brucine を作用させて融点 54~55° 比旋光度 -21.6° の結晶を得

\* 本研究に対して御指導戴いた武居三吉教授, 大野稔博士, 種々の御指示を戴いた東京大学理学部森野米三教授並びに実験に協力された大久保達雄, 勝村安行, 山田良一の諸氏に感謝する。

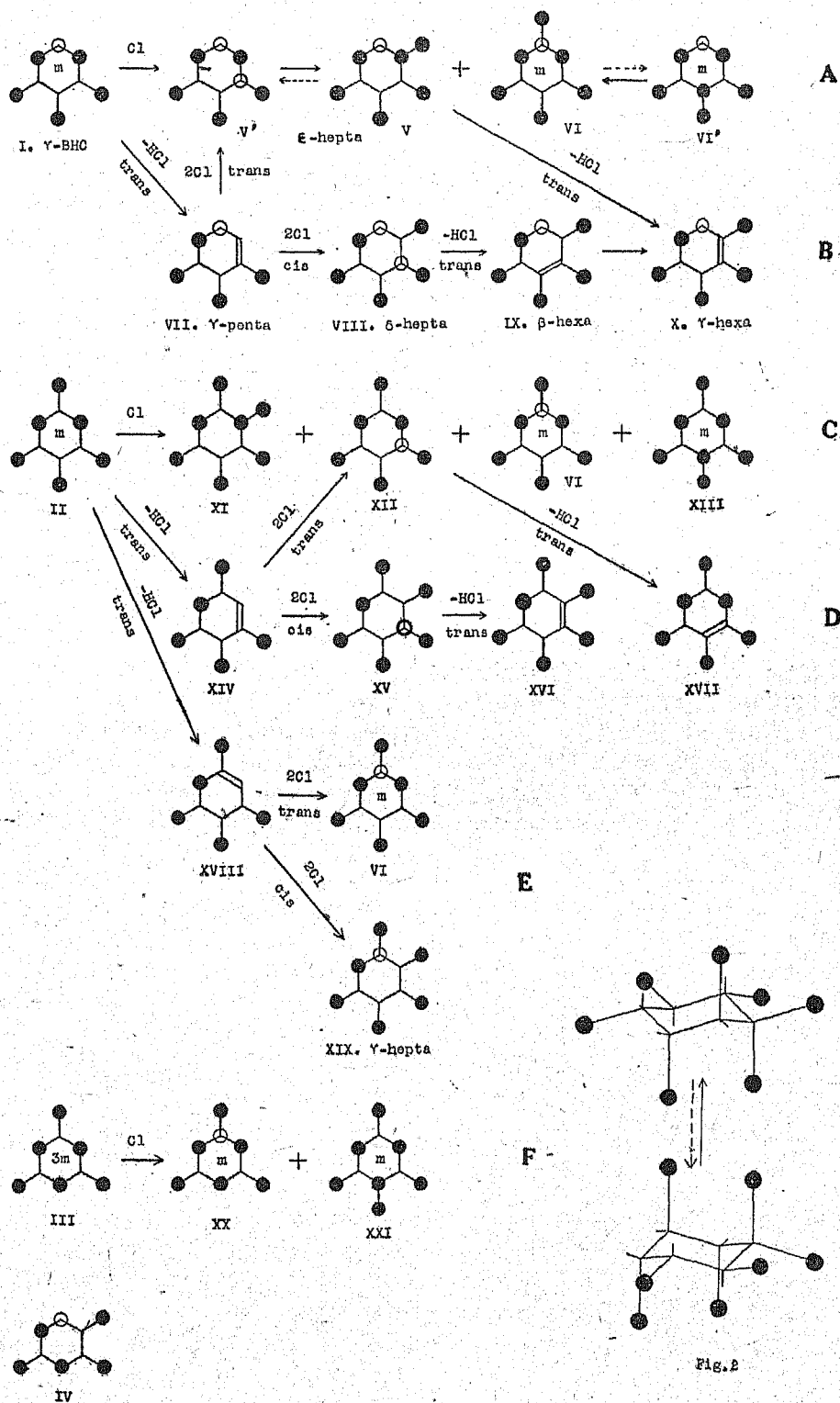


Fig.1 The reactions of  $\gamma$ -BHC and its related compounds

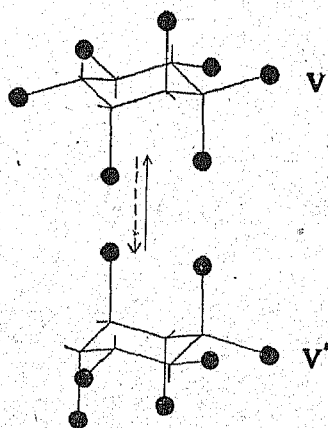


Fig.2

Fig.2 The "inversion" of  $\epsilon$ -Hepta

た。このものの塩素の定量値は $C_6H_5Cl_7$ 計の算値と一致し、原試料と混融しても融点の降下を示さない。従つてこのものは非対称の構造である(実験結果2)。次でこのもののアルカリによる脱塩酸を行つて、融点 $160\sim 101^\circ$ の柱状の結晶を得た。この結晶の塩素の分析値は $C_6H_4Cl_6$ と一致し、hexachlorocyclohexeneと考えられる。

中島等<sup>(6)</sup>は $\gamma$ -BHCを適当な条件でアルカリ分解すると $\gamma$ -pentachlorocyclohexene (bp  $123\sim 124^\circ/11\text{mm}$ ,  $\gamma$ -Penta)が生成する事を報告した。その後 $\gamma$ -Pentaの塩素添加を行つて融点 $139\sim 140^\circ$ の heptachlorocyclohexane の一新異性体( $\delta$ -Hepta)と融点 $55\sim 56^\circ$ の heptachlorocyclohexane ( $\epsilon$ -Hepta)を得、収量は後者の方がはるかに多いことを知つた。<sup>(6)</sup>混融の結果 $\epsilon$ -Heptaは大岩等が先に得ていた上記の $55\sim 55.5^\circ$ の Heptachlorocyclohexane と同一物質であることを知つた(実験結果3)。

又中島等<sup>(6)</sup>は $\delta$ -heptaをアルカリで脱塩酸して融点 $127\sim 128^\circ$ の heptachlorocyclohexene の一新異性体( $\beta$ -Hexa)を得、このものは或る条件で、融点 $100\sim 101^\circ$ の hexachlorocyclohexene の一新異性体に轉位することを知り、混融の結果( $\gamma$ -Hexa)は上述した大岩等が得た $100\sim 101^\circ$ の hexachlorocyclohexene と同一物であることが明かになった(実験結果4)。

以上4つの実験結果に中島等<sup>(6)</sup>が先に $\delta$ -BHCの脱塩酸反応及びその産物の塩素化の階段的検討によつて立證した考え即ちアルカリによる脱塩酸は $trans$ の位置のHとClによつて起り易いこと( $trans$  elimination),更に又炭素原子に2つの塩素原子が結合している場合この $trans$  eliminationはより一層行はれ易いと言ふことを考え合せて $\gamma$ -BHCとその近縁化合物5種の原子の立体配置を次の様にして決めた。

BHCの16の理論異性体中既知の $\alpha$ -,  $\beta$ -,  $\delta$ -及び $\epsilon$ -異性体の構造<sup>(6,7,10)</sup>を除き、塩素原子間の斥力を考慮すると $\gamma$ -BHCの構造はFig.1のI, II, III及びIVの中の何れかであると考えられる。その中IVは非対称構造であるから実験結果Iと矛盾するので除く。次にI, II及びIIIを塩素化して得られる異性体はFig.1のA, C及びF系列に示すとおりである。その中IIIから生成する heptachlorocyclohexane は共に面対称を有する構造である。このことは実験結果2と矛盾する。従つて $\epsilon$ -Heptaの構造はV, V', XI及びXIIの何れかであり、 $\gamma$ -BHCの構造はI及びIIの何れかである。I及びIIが1 molの $trans$ 脱塩酸して生じ得る pentachlorocyclohexene 及びそれに塩素添加して生じ得る heptachlorocyclohexane を示したのがB, D及びE系列である。AとB, CとD及びE系列を比較して

実験結果3と矛盾しない構造はV'とXIIである。従つて $\epsilon$ -HeptaはV'かXIIと云ふことになり、E列は考慮しなくとも良いことになる。而して実験結果4を満足するためにはA及びB列に於てFig.2に示す様にV'が反轉してVとなつてから1 molの $trans$ 脱塩酸した場合のみである。かくして $\gamma$ -HexaはX,  $\beta$ -HexaはIX,  $\epsilon$ -HeptaはV(V')となり $\delta$ -HeptaはXIIIの構造となり $\gamma$ -BHCの構造はIであることが明かになった。更に実験結果3及び4を満足する構造は16の異性体中I及びIVの両構造に限られるのでこの事からも $\gamma$ -BHCの構造はIと考えられる。尚VとV'に熱平衡が成立していると考えるのが妥当である。又本議論に於て cyclohexene 環を椅子型の立体構造と考えても充分である。

以上吾々は $\gamma$ -BHC及びその近縁化合物5種の原子の立体配置を有機化学的に決めると共に多塩化cyclohexaneに於てFig.2に示す様な反轉が行はれると云ふ一例を示した。

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## Résumé

It was already reported that the molecular configuration of  $\gamma$ -BHC was p p p e e e by Vloten et al<sup>(1)</sup> and Bijvoet<sup>(2)</sup> on the basis of X-ray analysis, and Bastiansen et al<sup>(3,4)</sup> on the basis of electron diffraction methode. In order to determine the molecular configuration of  $\gamma$ -BHC, Nakazima et al<sup>(5,6)</sup> have been studying on the dehydrochlorination of BHC and its related compounds and Oiwa et al<sup>(7,8,10)</sup> also investigating the direct chlorination of BHC and its related compounds. The molecular configurations of  $\gamma$ -BHC and its five

related compounds were determined by these both experimental results.

Cristol<sup>(9)</sup> has isolated the optical active  $\alpha$ -BHC by the action of brucine but not isolated from  $\gamma$ -BHC. We, also, did not isolated any optical active substance from  $\gamma$ -BHC and we assumed that the molecular structure of  $\gamma$ -BHC had the symmetrical form. (Exp. Result No. 1)

In the previous<sup>(8)</sup> reports, we obtained a new isomer of heptachlorocyclohexane ( $\epsilon$ -Hepta), melted at  $55\sim55.5^\circ$ , by the direct chlorination of  $\gamma$ -BHC.  $\epsilon$ -Hepta was treated with brucine in the dioxane and the crystal of which the melting point was  $54\sim55^\circ$  and the specific rotation was  $-21.6^\circ$ , was obtained. The analytical value of the chlorine of this compound was identical with the theoretical value of  $C_6H_5Cl_7$  and this compound did not show the depression of the melting point mixing with  $\epsilon$ -Hepta, so the structure of  $\epsilon$ -Hepta must be unsymmetrical form (Exp. Result No. 2). From the partial dehydrochlorination of  $\epsilon$ -Hepta, the columnar crystal, melted at  $103\sim101^\circ$ , was obtained and the analytical value of the chlorine of this compound was identical with the theoretical value of  $C_6H_4Cl_6$  and so this was regarded to be a new isomer of hexachlorocyclohexene ( $\gamma$ -Hexa).

It was already reported<sup>(6)</sup> that the  $\gamma$ -BHC was decomposed to the  $\gamma$ -pentachlorocyclohexene (bp  $123\sim124^\circ/11\text{mm}$ ,  $\gamma$ -Penta) by the alkaline dehydrochlorination. When the  $\gamma$ -Penta was chlorinated, two isomers of heptachlorocyclohexane were obtained and the melting point of them were respectively  $130\sim140^\circ$  ( $\delta$ -Hexa) and  $55\sim55.5^\circ$ . The latter was the same as the  $\epsilon$ -Hepta described above by the mixed melting point method (Exp. Result No. 3)

And a new isomer of hexachlorocyclohexene ( $\beta$ -Hexa), melted at  $127\sim128^\circ$ , was obtained by the partial dehydrochlorination of  $\delta$ -Hepta and  $\beta$ -Hexa was converted to the other new isomer of hexachlorocyclohexene melted at  $100\sim101^\circ$ .

This compound was the same as  $\gamma$ -Hexa described above by the mixed melting point method (Exp. Result No. 4)

From the rule of the *trans* elimination of hydrogen chloride<sup>(6)</sup> and by the above four experimental results, we determined the molecular configuration of  $\gamma$ -BHC and its related compounds as follows; in 16 possible isomers of BHC, by excepting the structures of  $\alpha$ -,  $\beta$ -,  $\delta$ -, and  $\epsilon$ -isomer and considering the Cl-Cl repulsion the possible structure of  $\gamma$ -BHC was any one of I, II, III, and IV in Fig. 1. But IV was the unsymmetrical form and was omitted by the experimental result No. 1. The possible isomers of heptachlorocyclohexane produced by the direct chlorination of I, II, and III, were shown in A, C and F in Fig. 1, but III was omitted because all of the isomers of heptachlorocyclohexane derived from III had the symmetrical form and this was in conflict with Exp. Result No. 2. Consequently, the structure of  $\gamma$ -BHC should be I or II and that of  $\epsilon$ -Hepta any one of V, V', XI and XII.

The possible isomers of pentachlorocyclohexene derived from I and II in accordance with the rule of *trans* elimination and those of the Hepta synthesized by the chlorine addition to the Penta were shown in B, D and E in Fig. 1. In the reaction of A and B or C, D and E, the structures which could satisfy the Exp. Result No. 3, were only V' and XII and it became evident that the reaction of E did not occur. The dehydrochlorination of V and VIII, or XII and XV were shown in B and D in Fig. 1, and the same hexachlorocyclohexene was produced only when V' was rearranged to V as shown in Fig. 2. From this fact and the Exp. Result No. 4, the structure of  $\gamma$ -BHC was determined to be I, that is p p p e e e. Moreover, the structure of  $\gamma$ -BHC (I) is reasonable, because in 16 possible isomers, only (I) and (IV) could satisfy Exp. Result No. 3 and 4. And in this case, the structure V and V' are at the thermal equilibrium.