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γ-RADIOLYSIS OF GAMMA-HEXACHLOROCYCLOHEXANE

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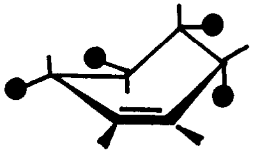
There have been a few studies of the effects of radiation on chlorinated insecticides. Of these compounds, DDT[1,1,1-trichloro-2,2-bis(p-chlorophenyl)-ethane] underwent dechlorination to DDD[1,1-dichloro-2,2-bis(p-chlorophenyl)-ethane] with high G value by the γ-irradiation of the 2-propanol solution.1,2) While, isomers of 1,2,3,4,5,6-hexachlorocyclohexane(BHC) were isomerized and/or dehydrochlorinated by the irradiation with 1 MeV electrons in solid state.3)

When the solutions of 1,2,3,4,5,6-hexachlorocyclohexane(BHC) isomers in 2-propanol were irradiated by Co-60 γ-ray, we found that gamma isomer of BHC undergoes more decomposition than the other isomers. The G value of the decomposition of γ-isomer was 42 under 120 min irradiation at 5 x 10^5R/h, whereas those of α-, β-, δ- and ε-isomers were very small under the same conditions. The gas chromatogram of the irradiated product of γ-isomer indicates the formation of four major compounds except hydrochloric acid and acetone. Separation of these compounds was performed using a preparative liquid chromatograph. The column used was silicic acid (Mallinckrodt Chem.) moistened with nitromethane and the eluting solvent was hexane saturated with nitromethane. The purity of each compound eluted was examined by a gas chromatograph equipped with an ECD detector. The columns employed were OV-17 3% and OV-210 5%. After repetition of the liquid chromatography and recrystallization, four compounds were obtained in pure state.

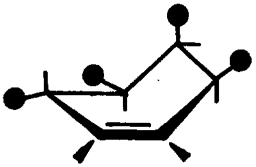
The compound (I) whose relative retention time to γ-BHC on OV-17 column was 0.31 and that on OV-210 was 0.27, showed mp 86-8° and M^+ 218. This compound was concluded to be an isomer of tetrachlorocyclohexene($C_6H_6Cl_4$). From mp4) and ir4) and nmr5) spectra, **I** was identified to be γ-isomer of tetrachlorocyclohexene, and thus its steric configuration is 3α, 4α, 5β, 6α or the conformation of the chlorine atoms is 3a 4e 5e 6e.

The second compound (II) whose relative retention time to γ-BHC on OV-17 column was 0.33 and that on OV-210 was 0.24, showed mp 99-100°, and M^+ 218. This compound is also an isomer of tetrachlorocyclohexene($C_6H_6Cl_4$). The ir spectrum, mp4) and coupling constants of the nmr spectrum5) of II agree with those of ε-isomer of tetrachlorocyclohexene. Therefore, the steric configuration of II, *viz.*, the ε-isomer is 3α, 4α, 5α, 6β or the conformation of the chlorine atom is 3e 4a 5e 6e.

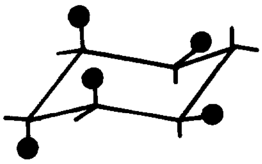
The third compound (III) whose relative retention time to γ-BHC on OV-17 column was 0.57, showed mp 78-78.5° and M^+ 254. This compound was shown to be an isomer of pentachlorocyclohexane($C_6H_7Cl_5$). From mp and nmr spectrum6), III was identified to be meso-pentachlorocyclohexane, whose steric configuration is 1α, 2α, 3β, 4α, 5α or the conformation of the chlorine atoms is 1e 2a 3a 4a 5e.



I (3a 4e 5e 6e)



II (3e 4a 5e 6e)



III (1e 2a 3a 4a 5e)

Finally, the forth compound (IV) whose relative retention time to γ-BHC on OV-17 column was 0.88, was mp 75° and M^+ 254. Anal. Fd: C, 28.23; H, 2.63. Calcd: C, 28.11; H, 2.75. The nmr and ms spectra of this compound are shown in Fig. 1. From these data, this compound is an isomer of pentachlorocyclohexane ($C_6H_7Cl_5$). Two isomers of pentachlorocyclohexane were so far obtained and their configurations were determined. One of them is meso-isomer above mentioned and the other is racemic isomer (1α, 2β, 3α, 4α, 5β)7) whose mp is 108°. However, the compound isolated here is not the racemic isomer from the mp and nmr spectra.6) It is very difficult to elucidate the steric configuration of the compound by the chemical and spectral investigations.

X-ray crystal structure analysis was undertaken to clarily the molecular conformation. Crystals are formed in the monoclinic space group $P2_1/c$: a=8.061 (1), b=7.992(1), c=16.554(3) Å, β=110.43(1)°, z=4, D_x=1.70, D_m=168g/cm^3. Three dimensional intensity data were collected on a Hilger and Watts Y-290 diffractometer using Zr-filtered Mo Kα radiation. The structure was solved by the program MULTAN[9)] with local modifications on a FACOM 270-30 computer, and refined by a block diagonal least squares method. Anisotropic refinement on the non hydrogen atoms gave an R value, where $R=\Sigma|\Delta F|/\Sigma|F_0|$, of 0.042 for 1516 reflexions ($\theta \leqq 25.0°$).

Fig.1 Nmr and ms spectra of compound IV

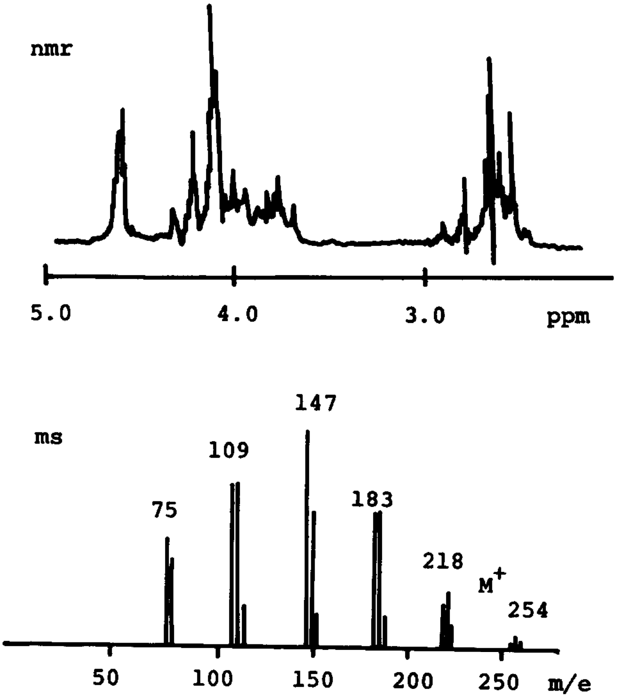
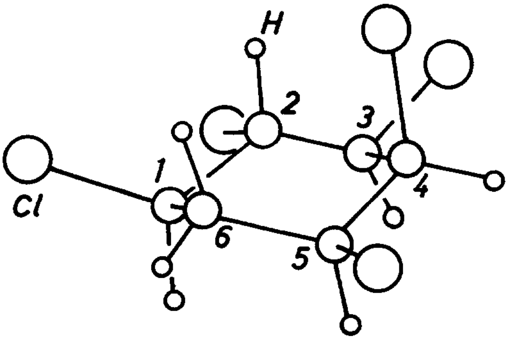


Fig.2 Perspective view of compound IV



The molecular structure shown in Fig. 2, indicates 1α, 2β, 3α, 4α, 5α configuration or 1e 2e 3e 4a 5e conformation of chlorine atoms. Mean bond length is 1.520 Å (ranging from 1.510 to 1.528) for C-C, and 1.792 Å (1.786-1.796) for C-Cl. Mean bond angle is 110.5° (106.8-112.8) for C-C-C, and 109.7° (108.6-110.9) for C-C-Cl. The cyclohexane ring is little distorted; the absolute values of torsion angles range from 54 to 60°.

The G values of the formation of the four compounds were 5.2, 3.4, 5.4 and 7.4 in the order above mentioned under 120 min irradiation at 5 x 10^5R/h. The former two compounds are produced by the elimination of two chlorine atoms of γ-BHC and the latter two by the dechlorination of γ-BHC through the radical reaction initiated by radiation.

Full details of the chemical and the X ray investigation will be published in separate papers.

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