The Dehydrochlorination of Isomeric Hexachlorocyclohexanes (Benzene Hexachlorides).

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The mixtures obtained by the partial alkaline dehydrochlorination of four stereoisomeric hexachloro*cyclo*hexanes have been examined by chromatography on paper and on cellulose. In the dehydrochlorination of the α- and the β-isomer intermediate pentachloro- or tetrachloro-compounds were not detected, and this was in agreement with conclusions arrived at from kinetic studies by Hughes, Ingold, and Pasternak (*J.*, 1953, 3832). With the γ- and the δ-isomer, only pentachloro-intermediates accumulated and this too was consistent with the kinetic conclusions.

When the known isomers of hexachloro*cyclo*hexane (benzene hexachloride) are treated with an excess of alkali, each loses 3 moles of hydrogen chloride and forms a mixture of the three trichlorobenzenes. From kinetic and other evidence Hughes, Ingold, and Pasternak (*J.*, 1953, 3832) made deductions concerning the dehydrochlorination processes in each isomer. The chromatographic techniques developed for the analysis of chlorinated organic insecticides (Moynihan and O'Colla, *Chem. and Ind.*, 1951, 406; O'Colla, *J. Sci. Food Agric.*, 1952, 130) provided a sensitive method for the detection and isolation of any intermediate penta- or tetra-chloro-compounds in the reactions. Hence the products of the partial dehydrochlorination of four hexachloro*cyclo*hexane isomers were examined chromatographically to see if the results were in agreement with the deductions from kinetic data. Hughes *et al.* (*loc. cit.*) deduced that, for the α- and the β-isomer one, and for the γ- and the δ-isomer two rate-controlling steps were involved in the dehydrochlorination. Where two steps were involved the intervening pentachloro*cyclo*hexene was isolated, but they did not prove conclusively that other intermediate tetra- and penta-chloro-compounds were not present in smaller quantities.

In the present investigation the hexachloro*cyclo*hexanes were dehydrochlorinated in ethanol, by addition of known fractions of the theoretical quantity of sodium hydroxide required to bring about complete dehydrochlorination. Drops from the solution were examined by paper chromatography. When developed, sprayed, and heated, the chromatograms containing the products from the α- and the β-isomer each showed only one spot corresponding to the unchanged isomer. The methods used were capable of detecting 30—50 μg. of the possible intermediates. Spots containing up to 1 mg. of starting material were examined: hence no appreciable quantities of such intermediates were present. The chromatograms containing the products from the γ- and the δ-isomers showed two spots in each, corresponding to the unchanged isomers and the derived pentachloro*cyclo*hexenes. The three trichlorobenzenes were present in all cases, as shown later in column chromatography, but they were not detectable by the sprays used. These findings were confirmed by fractionation of the partially dehydrochlorinated β-, γ-, and δ-isomers on hydrocellulose columns, the same solvent system being employed as in the paper chromatography.

The column fractionation of the products from the β-isomer yielded only the unchanged isomer and three trichlorobenzenes. According to the hypothesis developed by Hughes *et al.* (*loc. cit.*) the pentachloro-intermediate from the β-isomer should be the same as that from the δ-isomer, and hence should be capable of isolation. However, it is evidently decomposed rapidly at the higher temperature necessary for the dehydrochlorination of the β-isomer. The column chromatography of the partially dehydrochlorinated γ- and δ-isomers yielded the intermediate pentachloro*cyclo*hexenes, together with the unchanged isomers and trichlorobenzenes. The chromatographically pure pentachloro-compound from the γ-isomer was a viscous liquid, whereas that from the δ-isomer had m. p. 69°. The latter compound also moved more slowly on a chromatogram, thus confirming previous evidence (*idem, loc. cit.*) that the compounds were quite different. In each fractionation the solvent was evaporated from the eluate fractions and residues were examined on paper chromatograms, since any hitherto undetected intermediates would be obtained in greater concentration by the procedure. No compound other than those already described was detected. Hence, the results obtained by the comparatively sensitive chromatographic examination were in agreement with the deductions from kinetic data concerning the elimination reactions.

In the course of the work it was found that the solvent system used by Ramsay and Patterson (*J. Assoc. Off. Agric. Chem.*, 1946, **29**, 337) for the separation of hexachloro*cyclo*hexanes on silicic acid columns also gave excellent separations when used on paper. The isomers separated in the same order as that obtained with the acetic anhydride–light petroleum system mainly used in the present investigation.

EXPERIMENTAL

The four hexachloro*cyclo*hexanes were kindly presented by Imperial Chemicals Limited. Examination by paper chromatography indicated traces of other isomers in each; *e.g.*, the γ- and the δ-isomer contained traces of α- and β-isomer, respectively. The isomers were purified by recrystallisation—the β-isomer from acetone and the others from chloroform. Two recrystallisations sufficed to produce chromatographically pure compounds.

Chromatographic Methods.—The paper chromatograms were prepared as described by O'Colla (*loc. cit.*). Acetic anhydride was the fixed phase with *n*-pentane, *n*-hexane, or light petroleum (b. p. 60—80°) as the mobile phase. When the solvent system devised by Ramsay *et al.* (*loc. cit.*) was used on filter-paper, this was impregnated with nitromethane, and *n*-hexane saturated with nitromethane was the mobile phase used. Hydrocellulose columns were prepared as previously described (O'Colla, *loc. cit.*), acetic anhydride being used as fixed phase with light petroleum (b. p. 60—80°) as mobile phase.

Location of Isomers.—The " visualiser " usually used was devised by Winteringham and Harrison (personal communication). The chromatograms were sprayed with monoethanolamine solution, heated to 100° for 30 min., and then sprayed with 1% silver nitrate solution containing nitric acid. When the strips were washed four times with distilled water and exposed to light, blue spots appeared.. The limit of detection was 20 μg. of hexachloro*cyclo*hexane. The ferrous sulphate–acetic acid spray (O'Colla, *loc. cit.*) produced brown spots with any compound which was readily dehydrochlorinated, but it was necessary to heat the sprayed strips until the paper began to char. The limit of detection was 25 μg. of hexachloro- or 35 μg. of pentachloro-*cyclo*hexene.

Partial Dehydrochlorination of the Isomers.—Three solutions of each isomer were treated, respectively, with $\frac{1}{3}$, $\frac{1}{2}$, and $\frac{2}{3}$ of the quantity of alkali necessary for complete dehydrochlorination. The following preparation of one-third dehydrochlorinated α-, γ-, or δ-isomers is typical: The isomer (0·2 g.) in ethanol (5 ml.) was cooled to 0°, and sodium hydroxide (1·5 ml.; 0·5N) added during 30 min. After 24 hr. the neutral solution was concentrated to 2 ml. The dehydrochlorination of the β-isomer was conducted at 60°.

Paper Chromatography.—Drops from the 12 solutions were examined on paper chromatograms. When sprayed and heated after 16-hr. runs, the strips containing the products from the α- and the β-isomer showed only one spot corresponding to the unchanged isomer. The remaining chromatograms showed two spots in each, corresponding to the γ- and the δ-isomer and the pentachloro*cyclo*hexenes derived from them. The pentachloro-compound from the δ-isomer was prepared according to Cristol (*J. Amer. Chem. Soc.*, 1947, **69**, 338) and was chromatographically identical with that appearing on the δ-chromatograms. In a 16-hr. run, the distances in cm. moved by the detected compounds were: β- (25), δ- (31), γ-hexachloro*cyclo*hexene (40), δ- (43), α- (46), γ-pentachloro*cyclo*hexene (52).

Fractionation on Hydrocellulose Columns.—*γ-Isomer.* The γ-isomer (0·4 g.) was two-thirds dehydrochlorinated. The ethanolic solution was evaporated to dryness and the residue was extracted with light petroleum (b. p. 60—80°) saturated with acetic anhydride. The extract (10 ml.) was chromatographed on the column, and the eluate collected in fractions (15 ml.). Every fifth fraction was concentrated and examined on a paper chromatogram. The fractions which left residues when the solvent was evaporated were then amalgamated and examined as in the following Table.

δ-Isomer. The fractionation of the two-thirds dehydrochlorinated δ-isomer was similarly carried out, and the compounds isolated were δ-pentachloro*cyclo*hexene which, when recrystallised from light petroleum (b. p. 40—60°), had m. p. 69° (Found: Cl, 69·5%), unchanged δ-isomer, and a mixture of trichlorobenzenes.

Fractions	Description	Identified as		Cl, %: Found	Cl, %: Calc.
55— 90	Viscous liquid	$C_6H_6Cl_5$	B. p. 132°/12 mm.	69·5	69·7
130—150	Crystals	γ-Isomer	M. p. 113°	—	—
205—215	Crystals	1 : 3 : 5-Trichlorobenzene	M. p. 62°	58·3	58·7
215—220	Solid	Trichlorobenzene	M. p. 50—60°	57·8	—
220—240	Liquid	Mainly 1 : 2 : 4-trichlorobenzene	B. p. 214°/758 mm.	58·1	—

β-*Isomer.* A similar fractionation of two-thirds dehydrochlorinated β-isomer yielded only the unchanged β-isomer and a mixture of trichlorobenzenes. The β-isomer was found in fractions 180—190 of the eluate and the trichlorobenzenes were found in fractions 210—240.

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