

ANHYDROUS FERRIC CHLORIDE AS A REARRANGEMENT
CATALYST FOR SOME CHLORINATED
DIPHENYLETHANES

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During the course of the investigation of the catalytic dehydrochlorination of DDT and related compounds (1), it was noted that 1,1-dichloro-2,2-bis(*p*-chlorophenyl)ethane (I), known as TDE or DDD, behaved abnormally when heated with anhydrous ferric chloride. By analogy with DDT, (I) should lose a mole of hydrogen chloride to form 1-chloro-2,2-bis(*p*-chlorophenyl)ethylene (II). It was found that when (I) was heated at 115–120° with small amounts of anhydrous ferric chloride from 0.1 to 1.0 mole of hydrogen chloride was evolved. Further investigation showed that, when the heating was carried out at the melting point of (I) in the presence of about 6% of catalyst, a minimum of hydrogen chloride was evolved, and rearrangement took place to form a compound which melted at 227–228°, and which proved to be isomeric with the starting material.

The rearrangement product was found to be identical with a tetrachlorobibenzyl, which was prepared by the addition of chlorine to 4,4'-dichlorostilbene. This shows that the rearrangement involves the shifting of a chlorine atom and a chlorophenyl group, and establishes III or IV as the structure of the rearrangement product.

Rearrangements of this general type, involving a shift of the phenyl group to change an unsymmetrical diphenylethane into a symmetrical one, have been observed by Elbs (2). He showed that with zinc dust and ammonium hydroxide, as well as by distillation with zinc dust, α -diphenyltrichloroethane derivatives were rearranged and simultaneously dehydrochlorinated to form substituted stilbenes. Recently Forrest *et al.* (3) demonstrated a similar migration of the phenyl group when DDT was reduced in boiling alcohol with zinc and concentrated hydrochloric acid. In these examples some of I was obtained in the products of the reduction of DDT, indicating that the formation of the stilbenes may proceed through this intermediate compound.

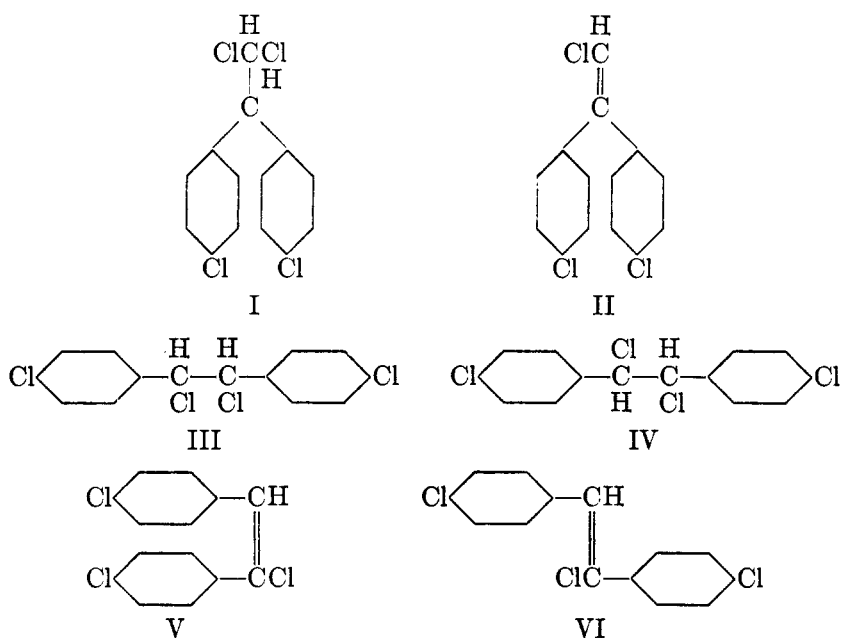
When the tetrachlorobibenzyl, obtained by rearrangement, was refluxed with alcoholic caustic, 1 mole of hydrogen chloride was eliminated and a trichlorostilbene of melting point 59–60° was obtained. The same compound was prepared by this process, starting with the synthetic tetrachlorobibenzyl.

An isomeric trichlorostilbene of melting point 95–96° was obtained by heating III at 200° with a small amount of anhydrous ferric chloride. Both of these trichlorostilbenes gave a strong unsaturation test with tetranitromethane, and the melting point was depressed when the two were mixed. These compounds may be represented by formulas V and VI, to which, on the basis of melting points,

the low-melting form may be assigned the *cis* form (V) and the high-melting form the *trans* form (VI) (4).

Both of these trichlorostilbenes were oxidized with chromic acid to 4,4'-dichlorobenzil. The identity of this compound was established by determination of the mixed melting point with authentic material, and by preparation of 2-(4-chlorophenyl)-3-(4-chlorophenyl)quinoxaline, melting point 187–188°, by reaction with *o*-phenylenediamine.

In connection with the chlorination of 4,4'-dichlorostilbene to obtain the tetrachlorobibenzyl, melting at 227–228°, a second isomer, melting at 95–96°, was isolated by concentration of the mother liquors. By analogy with the dichlorostilbenes, prepared by the chlorination of stilbene (8), the high-melting isomer



has been designated *meso*- $\alpha, \alpha', 4, 4'$ -tetrachlorobibenzyl (III) and the low-melting isomer *dl*- $\alpha, \alpha', 4, 4'$ -tetrachlorobibenzyl (IV). This *dl*-isomer was converted into the *meso*-isomer by melting the former in contact with a small amount of anhydrous ferric chloride.

The same type of catalytic isomerization was found to occur when *dl*-dichlorostilbene was isomerized into *meso*-dichlorostilbene by the same process. This isomerization is known to be partially effected by heating the *dl*-isomer at 200° (5), but with the catalyst the transformation occurred at 105–115° during the course of ten minutes.

The action of anhydrous ferric chloride in isomerizing the *dl*-isomers into *meso*-isomers undoubtedly accounts for the fact that only the *meso*-isomer could be isolated from the rearrangement products of I.

Since anhydrous ferric chloride is known to remove 1 mole of hydrogen chloride from DDT at 110° to form 1,1-dichloro-2,2'-bis(*p*-chlorophenyl)ethylene, an attempt was made to isomerize the latter compound with anhydrous ferric chloride. The fact that no rearrangement product could be isolated opens up the possibility of using this technique to detect I in the presence of DDT.

EXPERIMENTAL

Rearrangement of 1,1-dichloro-2,2-bis(p-chlorophenyl)ethane. An intimate mixture of 5 g. of I, m.p. 109–110°, and 0.3 g. of sublimed anhydrous ferric chloride (E&A, C.P.) was placed in a test tube and heated in an oil-bath at 110 ± 2° for one hour. A small amount of hydrogen chloride was evolved, and after about fifteen minutes of heating the mass set solid with crystals. The cooled material was transferred to a mortar with 50 ml. of glacial acetic acid and triturated at room temperature. The mixture was filtered and washed with a small amount of acetic acid and then with water. The yield of the crude product, after drying in a vacuum at room temperature was 2.9 g. of material that melted with decomposition at 185°. Repeated recrystallizations from acetic acid, following hot filtration, yielded a colorless product that separated in diamond-shaped crystals which melted at 227–228°. No yellow color was given with tetranitromethane.

Anal. Calc'd for C₁₄H₁₀Cl₄: C, 52.53; H, 3.15; Cl, 44.32; mol. wt., 320.06.

Found: C, 52.45, 52.67; H, 3.22, 3.20; Cl, 44.33; mol. wt., 317 (Rast).

When this rearrangement was carried out in a U-tube connected to an absorption bottle containing water to absorb the liberated hydrogen chloride, the amount obtained ranged from 0.1 to 0.5 mole with individual runs.

Trans-α,4,4'-trichlorostilbene. One gram of the tetrachlorobibenzyl, prepared by rearrangement, was heated in an oil-bath at 210°. A small amount of crude rearrangement product or a trace of anhydrous ferric chloride may have to be added to start the decomposition at this temperature. The dehydrochlorination had finished at the end of five minutes' heating. The residue crystallized when cooled, and when recrystallized from alcohol yielded light yellow needles that melted at 95–96°. It was necessary to remove a red amorphous powder by hot filtration of the alcoholic solution. This powder probably represents a polymerization product. With tetranitromethane a deep yellow-orange color was obtained.

Anal. Calc'd for C₁₄H₉Cl₃: C, 59.29; H, 3.20; Cl, 37.51.

Found: C, 59.15; H, 3.14; Cl, 36.75.

When this decomposition was carried out in a U-tube and the evolved gases were drawn through an absorption bottle containing water, 1.01 mole of hydrogen chloride was obtained.

Cis-α,4,4'-trichlorostilbene. One gram of the tetrachlorobibenzyl, prepared by rearrangement, was refluxed for one hour in 50 ml. of alcohol and 2 g. of potassium hydroxide. The cooled solution was diluted with water and extracted with ether. The ether solution was washed with water and then evaporated to dryness on the steam-bath. The residue crystallized as needles from alcohol. After drying in a vacuum at room temperature, the product melted at 59–60° and gave a deep yellow color with tetranitromethane. When this product was mixed with *trans-α,4,4'-trichlorostilbene*, the melting point was 50–70°.

Anal. Calc'd for C₁₄H₉Cl₃: C, 59.29; H, 3.20; Cl, 37.51.

Found: C, 59.55; H, 3.40; Cl, 37.98.

Oxidation of cis-α,4,4'-trichlorostilbene with chromic oxide. A solution of 0.4 g. of *cis-α,4,4'-trichlorostilbene* (m.p. 59–60°) in 2 ml. of refluxing acetic acid was oxidized by the slow addition of 0.2 g. of chromic oxide. Vigorous reaction occurred with each addition of chromic oxide. Refluxing was continued for one hour. Crystals separated from the cooled solution. Water was added to complete the crystallization. The product separated from acetone as light yellow needles and melted at 196–197°. No depression of melting point occurred when mixed with 4,4'-dichlorobenzil (6).

2-(4-Chlorophenyl)-3-(4-chlorophenyl)quinoxaline. A solution of 28 mg. of the 4,4'-dichlorobenzil, obtained from the above oxidation, and 11 mg. of *o*-phenylenediamine in 1 ml. of acetic acid was refluxed for one hour. When the reactants were cooled to room temperature, 25 mg. of colorless needles separated. When recrystallized from acetic acid, they melted at 187-188°. They showed no depression of melting point when mixed with a quinoxaline prepared by the same procedure from authentic 4,4'-dichlorobenzil.

Anal. Calc'd for $C_{20}H_{12}Cl_2N_2$: C, 68.39; H, 3.44.

Found: C, 68.48; H, 3.53.

Oxidation of trans- α ,4,4'-trichlorostilbene with chromic oxide. A solution of 0.4 g. of *trans- α ,4,4'*-trichlorostilbene (m.p. 95-96°) in 2 ml. of acetic acid was oxidized by the procedure used for *cis- α ,4,4'*-trichlorostilbene. The product separated as colorless needles, which melted at 196-197° and did not depress the melting point when mixed with authentic 4,4'-dichlorobenzil (6).

The 2-(4-chlorophenyl)-3-(4-chlorophenyl)quinoxaline prepared from this material, as outlined above, melted at 187-188°, and no depression of melting point was observed when the product was mixed with quinoxaline prepared from authentic material.

Chlorination of 4,4'-dichlorostilbene. Chlorine was passed through a solution of 1.0 g. of 4,4'-dichlorostilbene (7) in 60 ml. of carbon tetrachloride at room temperature for one hour. Crystals began to separate from solution after a half hour. At the end of the reaction period the crystalline material was collected and dried in a vacuum. A yield of 0.55 g. of product was obtained which melted at 217-219°. After recrystallization from acetic acid the melting point was 227-228°. No depression of melting point could be detected when this material was mixed with the rearrangement product of I.

Hydrolysis of this synthetic *meso- α , α' ,4,4'*-tetrachlorobibenzyl with alcoholic potassium hydroxide yielded *cis- α ,4,4'*-trichlorostilbene, m.p. 59-60°. No depression of melting point could be observed when this material was mixed with similar material obtained from the hydrolysis of the product from the rearrangement of I.

The mother liquor from the chlorination procedure was evaporated at room temperature to a volume of about 2 ml. A second crop of *meso- α , α' ,4,4'*-tetrachlorobibenzyl was removed by filtration. The filtrate was evaporated to dryness, and the residue recrystallized from alcohol, yielded prisms which melted at 95-96°.

Isomerization of dl- α , α' ,4,4'-tetrachlorobibenzyl with anhydrous ferric chloride. An intimate mixture of 0.1 g. of *dl- α , α' ,4,4'*-tetrachlorobibenzyl (m.p. 95-96°) with 1-2 mg. of anhydrous ferric chloride was heated in a bath at 110°. The product melted and then immediately set solid. Heating was discontinued after five minutes. The product melted at 227-228° after repeated recrystallizations from acetic acid, and showed no depression of melting point when mixed with *meso- α , α' ,4,4'*-tetrachlorobibenzyl.

Isomerization of dl-dichlorostilbene with anhydrous ferric chloride. An intimate mixture of 0.3 g. of *dl*-dichlorostilbene (8) with 1-2 mg. of anhydrous ferric chloride was placed in an oil-bath at 105-115°. The material melted and then set solid during the course of ten minutes' heating. The product, recrystallized from alcohol, decomposed at 167°. When recrystallized from acetic acid it melted at 193-194°. No depression of melting point could be observed when the product was mixed with *meso*-dichlorostilbene (8). When the experiment was repeated without the addition of anhydrous ferric chloride, only *dl*-dichlorostilbene could be isolated from the heated material.

The carbon and hydrogen determinations were made by W. F. Barthel and S. B. Soloway.

SUMMARY

Anhydrous ferric chloride has been shown to rearrange catalytically 1,1-dichloro-2,2-bis(*p*-chlorophenyl)ethane into *meso- α , α' ,4,4'*-tetrachlorobibenzyl.

The latter compound was dehydrochlorinated by alcoholic caustic and also by heat to give two isomeric $\alpha,4,4'$ -trichlorostilbenes. Both these compounds were oxidized to $4,4'$ -dichlorobenzil and converted into the same quinoxaline derivative.

meso- $\alpha, \alpha', 4, 4'$ -Tetrachlorobibenzyl and *dl*- $\alpha, \alpha', 4, 4'$ -tetrachlorobibenzyl have been prepared by the chlorination of $4, 4'$ -dichlorostilbene.

Anhydrous ferric chloride has been shown to catalyze the rearrangement of *dl*- $\alpha, \alpha', 4, 4'$ -tetrachlorobibenzyl and *dl*-dichlorostilbene into the corresponding *meso*-isomers.

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