BRIEF COMMUNICATIONS

A CASE OF ADDITION OF CHLORINE TO A PHENOLIC ETHER

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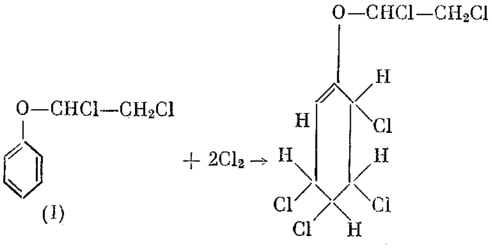
It is known [1] that alkyl ethers of phenol usually react with chlorine without irradiation to form substitution products. As shown by Rosen and Stallings [2], a decrease in the electron-donor properties of the oxygen atom in ethers increases the capacity of the aromatic ring to add on chlorine. These authors [2] established that phenyl trichloroacetate gives a high yield of an addition product with six chlorine atoms, whereas phenyl acetate does not give such products, even with UV irradiation.

It was found that when elementary chlorine acts on α,β-dichloroethylphenyl ether (I) at room temperature in absence of irradiation and catalysts, we obtain not only the usual products of electrophilic substitution of the aromatic ring (I), but also highly chlorinated products. The product of addition of four chlorine atoms to the benzene ring of (I), α,β-dichloroethyl-2,3,4,5-tetrachlorocyclohexene-1-yl ether (II), was obtained in crystalline form. The scheme of formation of (II) is as follows:

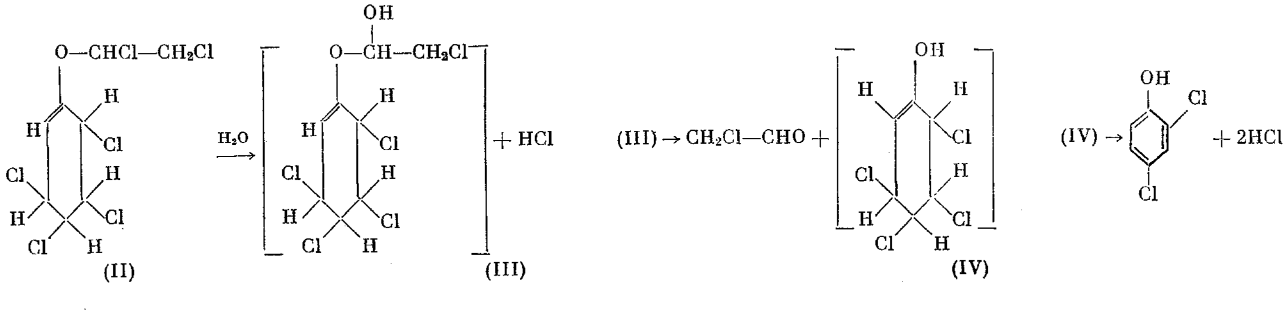


(I)

(II)

This case agrees with the conclusions of Rosen and Stallings [2], but the fact that the reaction occurred without irradiation was somewhat unexpected.

The structure of (II) follows from the ultimate analysis data, the molecular weight, and the infrared spectrum. This spectrum has a strong line characteristic of the C = C bond (1668 cm^{-1}). No bands at 1600-1500 cm^{-1}, characteristic of the benzene ring, are observed. The C = C bond remaining in the ring of (II) is very inert. It resists the action of chlorine, does not add on hydrogen in the presence of Raney nickel, and is not determined by the bromine-bromate method. According to the first-order kinetic equation, in an aqueous alcoholic medium (II) liberates three HCl equivalents simultaneously, while other α,β-dichloroethers liberate only one equivalent [3]. This indicates that the first, slowest stage of the reaction is replacement of the α-chlorine atom. The polyacetal of chloroacetaldehyde (III) thus obtained is unstable and decomposes to form chloroacetaldehyde and a cyclic enol (IV), which is stabilized as 2,4-dichlorophenol, splitting off two HCl equivalents. The hydrolysis scheme of (II) is as follows:



(II) (III) (IV)

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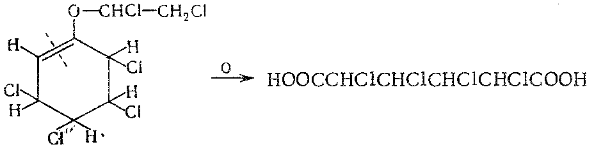
The second and third stages are much faster than the first stage.

Among the hydrolysis products we identified chloroacetaldehyde as the 2,4-dinitrophenylhydrazone [4]; 2,4-dichlorophenol was identified by gas-liquid chromatography (no isomeric dichlorophenols were observed). We can assume that the C=C bond in the ring is located next to the alkoxy group because it is particularly inert. This was confirmed by the fact that oxidation of (II) with potassium permanganate in aqueous H_2SO_4 gave tetrachloroadipic acid:



If the double bond were located in any other position, we would get an acid of different structure.

EXPERIMENTAL

Preparation of α,β-Dichloroethyl-2,3,4,5-tetrachlorocyclohexene-1-yl Ether (II). Chlorine was passed into a flask containing 48.6 g of (I) at 20°C until the weight reached 67.6 g. Vacuum distillation of 54.0 g of the reaction products gave (allowing for the intermediate fractions) 6.4 g (12 mole %) of (I), 19.5 g (42.5 mole %) of (II), and 1 g of the α,β-dichloroethyl ether of 2,4-dichlorophenol (2 mole%).* The residue was a thick oil which crystallized almost completely when left to cool in the condenser. After recrystallization from a mixture of n-hexane and ether, the mp of (II) was 64-65°C and the mol. wt. 320 (from benzene). Found %: C 28.61, 28.62; H 2.26, 2.59; Cl 63.46, 63.64. $C_8H_8OCl_6$. Calculated %: C 28.81; H 2.40; Cl 63.98.

Compound (II) was not hydrogenated at room temperature at atmospheric pressure in dioxane in the presence of Raney nickel. The dynamics of HCl accumulation during solvolysis of (II) were studied in 80% aqueous ethanol at 62.5° by the method in [3]; $k = 0.040\ \text{min}^{-1}$. Titration of 0.1856 g of (II) took 16.50 ml of 0.1 N NaOH.

Oxidation of (II) by potassium permanganate was performed by the method in [5]. The tetrachloroadipic acid thus obtained melted with decomposition at 300°. Found %: Cl 49.42, 49.86. $C_6H_6Cl_4O_4$. Calculated %: Cl 49.95. Titration of 0.12 g of (II) took 8.46 ml of 0.1 N NaOH.

CONCLUSIONS

1. The authors have established that chlorine adds on to α,β-dichloroethylphenyl ether at the benzene ring in absence of irradiation and catalysts, with formation of a stable product.

2. Hydrogenation, hydrolysis, and oxidation reactions confirmed the structure of the product, α,β-dichloroethyl-2,3,4,5-tetrahexene-1-yl ether.

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*For the identification of these compounds, see [4].

LITERATURE CITED

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