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Abstract

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ADDITION OF HYDROGEN CHLORIDE AND ACETIC ACID TO ISOMERIC CYCLODODECATRIENES-1,5,9

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In the present work we have investigated the addition of hydrogen chloride and acetic acid to trans,trans,trans-cyclododecatriene-1,5,9 (I) and cis,trans,trans-cyclododecatriene-1,5,9 (II). As it turned out, in these reactions the two hydrocarbons behave differently. The addition of acetic acid to I and II proceeds in the presence of boron trifluoride etherate with formation, as the principal reaction products, of monoacetoxy derivatives. In the case of I the addition proceeds in the normal manner, leading only to 1-acetoxy-trans,trans-cyclododecadiene-5,9:

$$(\mathrm{I}) + \mathrm{CH_3COOH} \xrightarrow{\mathrm{BF_3 \cdot (C_2H_5)_2O}} \text{1-acetoxy-trans,trans-cyclododecadiene-5,9}$$

On hydrogenation it absorbs exactly 2 moles of hydrogen with formation of the previously known acetoxycyclododecane. Saponification of 1-acetoxycyclododecadiene-5,9 with alcoholic alkali gave 1-hydroxy-trans,trans-cyclododecadiene-5,9 (^{1}). The addition of acetic acid to II leads to a mixture of monoacetoxy derivatives, inseparable by distillation. Gas-chromatographic analysis of this mixture showed that it consists of no fewer than four components, with one of them predominating (about 50%). On quantitative hydrogenation of the mixture, only 1.4 moles of hydrogen are absorbed per mole of monoacetoxy derivatives, which indicates the presence in the mixture, along with acetoxycyclododecadiene, of bicyclic and possibly tricyclic compounds. This is also indicated by the higher specific gravity of the hydrogenation products in comparison with the specific gravity of the known acetoxycyclododecane and by the difference in the IR spectra. The IR spectrum of the mixture of acetoxy derivatives shows that, calculated per molecule, it contains approximately one trans bond and 0.4 cis bond, which is in good agreement with the hydrogenation data. Upon hydrolysis of the mixture of acetoxy derivatives a mixture of alcohols was obtained; treatment of this mixture with phenyl isocyanate gave, in about 50% yield, the phenylurethane of 1-hydroxy-trans,trans-cyclododecadiene-5,9. Cyclododecanol was isolated in the same yield upon hydrogenation of the mixture of alcohols. This indicates that, probably, all the trans bonds determined from the IR spectrum in the mixture of acetoxy derivatives are accounted for by 1-acetoxy-trans,trans-cyclododecadiene-5,9, formed upon addition of acetic acid to the cis double bond of II. The structure of the bicyclic product, which has not yet been isolated by us in individual form, has not yet been established. The most probable bicyclic compounds with a cis double bond that can be formed from II are derivatives of bicyclo-(4,0,6)-dodecane (III) and bicyclo-(3,0,7)-dodecane (IV).

$$\text{(II)} + \mathrm{CH_3COOH} \xrightarrow{\mathrm{BF_3{\cdot}(OC_2H_5)_2}} \text{acetate product} + [\text{(III)} + \text{(IV)}]$$

The addition of hydrogen chloride to I and II proceeds smoothly in the presence of ferric chloride in methylene chloride solution at low temperature. In the case of I, a mixture of mono- and dichloro derivatives is formed, the ratio of which depends on the reaction time. The monochloro derivative is 1-chloro-trans,trans-cyclododecadiene-5,9, and the dichloro derivative is 1,5- (or 6-)dichloro-trans-cyclododecene-9:

$$\text{I} + \mathrm{HCl} \xrightarrow{\mathrm{FeCl_3}} \text{1-chloro-trans,trans-cyclododecadiene-5,9} + \text{1,5- (or 6-)dichloro-trans-cyclododecene-9}$$

On hydrogenation of the monochloro derivative, 2 moles of hydrogen are absorbed and chlorocyclododecane is formed; on hydrogenation of the dichloro derivative, 1 mole of hydrogen is absorbed and 1,5- (or 6-)dichlorocyclododecane is formed. Addition of hydrogen chloride to II gives a mixture of monocyclic and bicyclic (possibly also tricyclic) monochloro derivatives. Gas-chromatographic analysis of the mixture shows the presence of two components (possibly more), present in approximately equal amounts. On hydrogenation, about 1.1 moles of hydrogen are absorbed per mole of the mixture of monochloro derivatives, which indicates the presence in the mixture, along with chlorocyclododecadiene, of bicyclic compounds.

From the IR spectrum it follows that, calculated per one molecule, there are approximately 0.5 trans- and 0.4 cis-double bonds. The presence of chlorocyclododecadiene (apparently 1-chloro-trans,trans-cyclododecadiene-5,9) in the mixture was shown in the following way. When the mixture of monochloro derivatives is heated with methylamine, hydrogen chloride is eliminated with formation of a mixture of unsaturated hydrocarbons; after hydrogenation of this mixture, cyclododecane and a mixture of other hydrocarbons were obtained. The amount of cyclododecane is about 30%.

The specific gravity of the mixture of hydrocarbons after removal of cyclododecane is greater than the specific gravity of cyclododecene. The IR spectrum of this mixture indicates the presence of bicyclic structures not containing strained rings. The structure of the bicyclic compounds has not yet been established. Addition of hydrogen chloride to II proceeds as follows:

$$\mathrm{II} + \mathrm{HCl} \xrightarrow{\mathrm{FeCl_3}} \text{chlorocyclododecadiene} + \text{bicyclic compounds } \mathrm{C_{12}H_{19}Cl}$$

The differences we have found in the addition of acetic acid and hydrogen chloride to I and II are apparently due to the different conformations of the molecules of these hydrocarbons. In II the trans double bonds are probably closer together than in I, which accounts for the possibility of formation of bicyclic structures.

Experimental Part

Addition of acetic acid to trans,trans,trans-cyclododecatriene-1,5,9. A solution of 50 g of trans,trans,trans-cyclododecatriene-1,5,9 in 200 ml of glacial acetic acid

in the presence of 2.5 g of boron trifluoride etherate was heated for 30 h at 100°. Distillation gave 20 g of 1-acetoxy-trans,trans-cyclododecadiene-5,9 with b.p. 110–113° at 2.5 mm, n_D^{20} 1.4877, d_4^{20} 0.9902.

Found, %: C 75.39; 75.44; H 9.78; 9.74
$C_{14}H_{22}O_2$. Calculated, %: C 75.67; H 9.91

1-Acetoxy-trans,trans-cyclododecadiene-5,9 was saponified with alcoholic alkali, and 1-hydroxy-trans,trans-cyclododecadiene-5,9 was obtained, m.p. 66.5–67° (from petroleum ether).

Found, %: C 80.11; 79.88; H 11.21; 11.06
$C_{12}H_{20}O$. Calculated, %: C 79.98; H 11.12

The phenylurethane of 1-hydroxy-trans,trans-cyclododecadiene-5,9 had m.p. 131–132°.

On hydrogenation of 6 g of 1-hydroxy-trans,trans-cyclododecatriene-5,9 over Raney nickel in 25 ml of ethyl alcohol, 5.8 g of cyclodecanol was obtained, m.p. 79–80° (from petroleum ether). Literature data ([2]): m.p. 80°.

Addition of acetic acid to cis,trans,trans-cyclododecatriene-1,5,9. A solution of 60 g of cis,trans,trans-cyclododecatriene-1,5,9 in 200 ml of glacial acetic acid in the presence of 2.5 g of boron trifluoride etherate was heated for 30 h at 100°. The acetic acid was distilled off in vacuo, the residue was diluted with water and extracted with ether. The ethereal solution was washed with soda solution and dried over sodium sulfate. The ether was distilled off, and the residue was distilled in vacuo. This gave 24.2 g of the starting triene and 28.3 g of a mixture of monoacetoxy derivatives with b.p. 101–105° at 1 mm.

Found, %: C 75.47; 75.24; H 9.87; 10.00
$C_{14}H_{22}O_2$. Calculated, %: C 75.67; H 9.91

1.0037 g of the mixture of monoacetoxy derivatives was hydrogenated over 0.2 g of Pd/$BaSO_4$ in 15 ml of glacial acetic acid. 130.8 ml of hydrogen was absorbed; 218.9 ml of hydrogen is required for two double bonds.

A solution of 18 g of monoacetoxy derivatives and 20 g of caustic potash in 120 ml of ethyl alcohol was heated at boiling for 10 h. After cooling, the solution was diluted with water; the oily layer was extracted with ether and dried over sodium sulfate. This gave 11 g of a mixture of hydroxy derivatives with b.p. 107–110° at 2 mm; after heating with phenyl isocyanate, the phenylurethane of 1-hydroxy-trans,trans-cyclododecadiene-5,9 was isolated, m.p. 131–132°.

Found, %: C 76.35; 76.40; H 8.48; 8.25
$C_{19}H_{25}O_2$. Calculated, %: C 76.35; H 8.37

It gives no depression of the melting point with an authentic sample of the phenylurethane obtained from 1-hydroxy-trans,trans-cyclododecadiene-5,9.

0.4521 g of the phenylurethane was hydrogenated over 0.2 g of Pd/$BaSO_4$ in ethyl alcohol. The phenylurethane of oxycyclododecane was obtained, m.p. 128–129°. Literature data (^{2}): m.p. 128–129°.

Found, %: C 75.30; 75.32; H 9.60; 9.72
$C_{19}H_{29}O_2$. Calculated, %: C 75.25; H 9.56

It gives no depression of the melting point with an authentic sample of the phenylurethane obtained from cyclododecanol.

5 g of the mixture of hydroxy derivatives was hydrogenated over 4 g of Pd/$BaSO_4$ in 15 ml of ethyl alcohol. The product was distilled, b.p. 115–130° at 8 mm. On standing, 2.5 g of cyclododecanol separated, which was filtered off and recrystallized from petroleum ether. M.p. 79–80°; it gives no depression of the melting point with an authentic sample of cyclododecanol.

Addition of hydrogen chloride to trans,trans,trans-cyclododecatriene-1,5,9. To a solution of 20 g

trans,trans,trans-cyclododecatriene-1,5,9 in 150 ml of methylene chloride, in the presence of 0.5 g of anhydrous ferric chloride, a stream of dry hydrogen chloride was passed at $-40°$ to an increase in weight of 15 g. The solution was left overnight at $-60°$. It was then washed with water and dried over calcium chloride. This gave 2.4 g of 1-chloro-trans,trans-cyclododecadiene-5,9, b.p. 101–103° at 1 mm, n_D^{20} 1.5130, d_4^{20} 1.0118.

Found, %: C 74.58; 74.76; H 9.53; 9.68; Cl 17.91; 18.16
$C_{12}H_{19}Cl$. Calculated, %: C 72.55; H 9.57; Cl 17.88

Also obtained were 5.7 g of 1,5(or 6)-dichloro-trans-cyclododecene-9, with b.p. 113–114° at 1.5 mm, n_D^{20} 4 1.5188, d_4^{20} 1.1117.

Found, %: C 61.29; 61.40; H 8.63; 8.57; Cl 29.90; 29.83
$C_{12}H_{20}Cl_2$. Calculated, %: C 61.45; H 8.54; Cl 30.01

On hydrogenation of 1-chloro-trans,trans-cyclododecadiene-5,9 over 0.3 g of Pd/$BaSO_4$ in acetic acid, 2 moles of hydrogen were absorbed. On hydrogenation of 1,5(or 6)-dichloro-trans-cyclododecene-9, 1 mole of hydrogen was absorbed.

Addition of hydrogen chloride to cis,trans,trans-cyclododecatriene-1,5,9. Into a solution of 40 g of cis,trans,trans-cyclododecatriene-1,5,9 in 100 ml of methylene chloride, in the presence of 0.5 g of anhydrous ferric chloride, a stream of dry hydrogen chloride was passed at −40° in an amount of 17 g, and the mixture was left overnight at −60°. This gave 18.9 g of a mixture of monochloro derivatives, b.p. 105–110°/2.5 mm.

Found, %: C 72.87; 72.57; H 9.61; 9.59; Cl 17.39; 17.56
$C_{12}H_{19}Cl$. Calculated, %: C 72.55; H 9.57; Cl 17.88

0.6263 g of the mixture of monochloro derivatives was hydrogenated over 0.2 g of Pd/$BaSO_4$ in acetic acid solution. 89 ml of hydrogen was absorbed; 155 ml of hydrogen is required for two double bonds. A solution of 15 g of the mixture of monochloro derivatives and 15 g of dimethylamine in 80 ml of ethyl alcohol was heated in an autoclave for 18 h at 200°. The alcohol was distilled off, and the residue was treated with HCl solution and extracted with ether. Distillation gave 6.5 g of a mixture of cyclic and bicyclic products, b.p. 90–94° at 10 mm.

16.5 g of this mixture was reduced in ethyl alcohol over Raney nickel. After the usual work-up and cooling of the hydrogenation products, 4 g of cyclododecane was isolated, m.p. 60–61°; it gives no depression of the melting point with an authentic sample.

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