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EVIDENCE FOR A DUAL MECHANISM IN THE ISOMERIZATION OF A VINYL CATION TO AN ALLYLIC-TYPE CATION.

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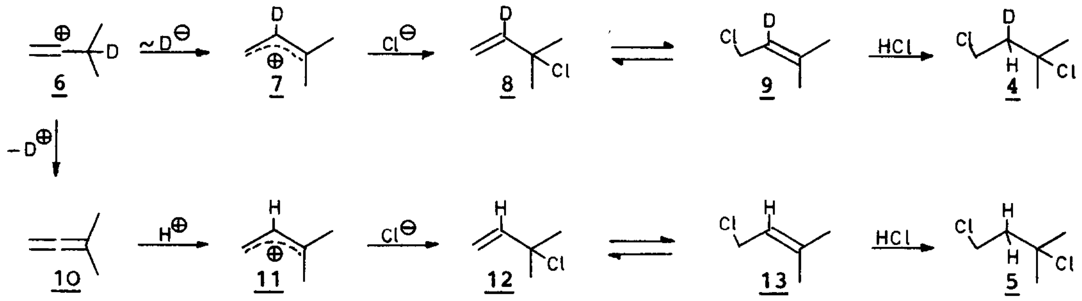
Liquid phase reactions of 1 (1) with excess anhydrous hydrogen chloride (molar ratio 1:3.4) in diethyl ether have been carried out at ambient temperatures in sealed glass ampoules. After complete conversion of 1 (ca. 10 d), g.l.c. analysis showed three product peaks in a ratio of 9:1:1 (column 0.3 x 500 cm, 5 % Carbowax 20 M on Chromosorb G; 60 - 160 °C at 2 °C/min). The products were isolated by preparative g.l.c. and shown to be 2 (major), 3 and a mixture of 4 and 5 (column 0.8 x 500 cm, 12 % Carbowax 20 M on Chromosorb G; 60 °C for 15 min, then 60 - 160 °C at 2 °C/min).

$HC{\equiv}CCD(CH_3)_2$	$CH_3CCl_2CD(CH_3)_2$	$CH_3CHClCCl(CH_3)_2$	$ClCH_2CHXCCl(CH_3)_2$
1	2	3	4 (X=D) 5 (X=H)

The structure of 2 was assigned on the basis of its pmr- and ms-data: δ 1.10, t, 1 cps, 6H; δ 2.03, s, 3H; CCl_4/C_6D_6, TMS; m/e 106, 108, $(M - Cl)^+$; 97, 99, 101, $(CH_3CCl_2)^+$; 44, $(CH_3CDCH_3)^+$. Compound 3 was identified by comparision of its pmr-data with those of an authentic sample (2): δ 1.60, d, 6.7 cps, δ 1.56, s; δ 1.66, s; together 9H; δ 4.03, q, 1H; CCl_4/C_6D_6, TMS. For the identification of 4 and of 5 authentic samples have been prepared by the liquid phase reaction of 12 and/or 13 (3) with DCl and with HCl, respectively. 4: δ 1.57, s, 6H; δ 2.00-2.37, m, 1H; δ 3.53-3.81, m, 2H; CCl_4/C_6D_6, TMS; m/e 106, 108 (relat. intensities 25:10) $(C_5H_9DCl)^+$; 105, 107 (13:7) $(C_5H_8DCl)^+$; 70 (100) $(C_5H_8D)^+$. 5: δ 1.61, s, 6H; δ 2.07-2.39, m, 2H; δ 3.56-3.85, m, 2H; CCl_4/C_6D_6, TMS; m/e 105, 107 (21:9) $(C_5H_{10}Cl)^+$; 104, 106 (9:5) $(C_5H_9Cl)^+$; 69 (100) $(C_5H_9)^+$. The product ratio in the isolated mixture of 4 and 5 was determined by the differences of the intensities of the $ClCH_2$- and the CHX-signals in the pmr-spectrum, as well as by the differences in the intensities of the C_5H_8D- and the C_5H_9-fragment ions in the mass spectrum. The ratio of 4:5 was found to be 45:55 by pmr- and 43:57 by ms-analysis.

The formation of 4 is explained by a 1,2-deuteride shift to the incipient vinylic cation 6 to form the allylic-type cation 7, followed by the sequence $7 \rightarrow 8/9 \rightarrow 4$. The formation of 5 is explained by elimination of D^+ from the



vinylic cation 6 and subsequent HCl-addition to the intermediate dimethyl allene 10 (4). Conceivable alternatives for the formation of 4 would be addition of D^+, which is formed in step 6 → 10, to either 10 or 13. This can be largely ruled out, however, since no deuterium incorporation could be detected in the CH_3CCl_2-group of 2. A conceivable alternate mode of formation of 5 would be a H-D-exchange during the addition of HCl to 8/9. This can be also ruled out, since reaction of excess DCl with either 12 or 13 in diethyl ether afforded 4 as the sole product.

From the above data we conclude that under the prevailing conditions the conversion of the vinylic cation 6 into an allylic-type cation occurs in approximately equal parts by a 1,2-deuteride shift and by an elimination-addition scheme. We assume a similar dual mechanism for the formation of 5 during the addition of HCl to non-deuterated 1 (2). For previously observed conversions of the corresponding non-deuterated vinylic cation 6-H into 11, only 1,2-hydride shifts have been considered (5,6).

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