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VINYL CATIONS, 22[1)]

A 1.2-HYDRIDE SHIFT IN THE SOLVOLYSIS OF 3-METHYL-1-BUTEN-2-YL TRIFLATE

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Recently we reported about the first example of a 1.2-hydride shift during the generation of a vinyl cation, a process well known for trisubstituted carbenium ions[2)]: This was observed during the solvolysis of cis-and trans-3-cyclopropyl-2-propen-2-yl-trifluoromethanesulfonate (triflate)[3)]. The 1.2-hydride shift was found to be across the double bond.

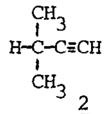
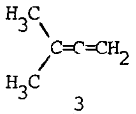
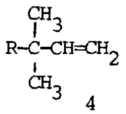
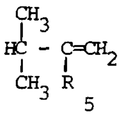
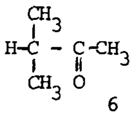
As the first example of a 1.2-hydride shift towards the double bond we report here on the solvolysis of 3-methyl-1-buten-2-yl triflate (1)[1)]

The triflate 1 was prepared by the addition of trifluoromethanesulfonic acid to isopropylacetylene (2) in absolute methylene chloride at -40 to -50°C[1)4)5)], and purified by vacuum transfer. NMR (CCl_4, 60 MHz): τ=4.90 (d, 1H, vinyl proton cis to the triflate group, J = 3.8 Hz); 5.04 (dd, 1H, vinyl proton trans to the triflate group, J = 3.8 Hz, J = 1 Hz); 7.18 - 7.64 (sept., 1H, tertiary proton, J = 6.5 Hz); 8.81 (d, 6H, methyl protons, J = 6.5 Hz).

1 was solvolyzed for 2 d at 80°C in absolute trifluoroethanol (TFE), 80% and 60% aqueous TFE respectively. All solutions were buffered with 1.1 M pyridine. The solvolysis products 2-6 (see Table) were separated by preparative vpc and identified unequivocally either by NMR, IR and mass spectrometry or by comparison with authentic samples.

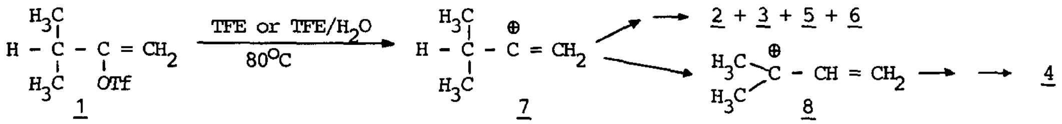
Table

Solvolysis products in % of 3-methyl-1-buten-2-yl triflate (1). T = 80°C, buffered with 1.1 M pyridine, reaction time 2 d, R = $-O-CH_2-CF_3$

Solvent % TFE/Water	 $\mathrm{H-\overset{CH_3}{\underset{CH_3}{C}}-C\equiv CH}$ 2	 $\mathrm{(H_3C)_2C=C=CH_2}$ 3	 $\mathrm{R-\overset{CH_3}{\underset{CH_3}{C}}-CH=CH_2}$ 4	 $\mathrm{H\overset{CH_3}{\underset{CH_3}{C}}-\underset{R}{C}=CH_2}$ 5	 $\mathrm{H-\overset{CH_3}{\underset{CH_3}{C}}-\underset{O}{\overset{\|}{C}}-CH_3}$ 6
100	15.7	8.8	16.8	51.6	7.1
80	9.2	34.3	13.0	29.3	14.2
60	22.8	30.3	6.8	26.3	13.8

The formation of 3-[2.2.2-trifluoroethoxy]-3-methyl-butene-1 (4) (6.8-16.8%; see Table) can be explained by the intermediate formation of the carbenium ion 8 which is itself formed from the primarily generated vinyl cation 7 by a 1.2-hydride shift towards the double bond (see Scheme). The driving force for the 1.2-hydride shift in the solvolysis of 1 is provided by the formation of the more stable tertiary cation 8. 2-Methyl-3-buten-2-ol, which could also be formed from 8

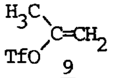
Scheme



was not found. It was shown that this alcohol decomposes under the reaction conditions with the formation of the solvolysis products 2 and 3.

The main solvolysis products of 1 are isopropylacetylene (2) and 1.1-dimethylallene (3), both of which could be formed either from the intermediate vinyl cation 7 or by a synchronous β-elimination. A small dependence of the solvolysis rate on the pH-value (cf. $k=2.74 \pm 0.06\times10^{-4}s^{-1}$, 1.03 M pyridine, $k=3.68 \pm 0.19\times10^{-4}s^{-1}$, 2.06 M pyridine in 60% aqueous TFE at 80.35°C) suggests the participation of a synchronous β-elimination. A 1.2-methyl migration towards the double bond, such as is found in the solvolysis of 1-tert.butyl vinyltriflate[4] was not observed in the solvolysis of 1. The secondary carbenium ion which would be formed in such a step would be less stable than the tertiary cation 8.

The solvolysis rates of 1 were measured at 80.35°C in absolute, 80% and 60% aqueous TFE all buffered with 1.03 M pyridine, using a gas chromatographic method: $k=4.25 \pm 0.09\times10^{-5}s^{-1}$ (100% TFE), $k=1.47 \pm 0.05\times10^{-4}s^{-1}$ (80% TFE), $k=2.74 \pm 0.06\times10^{-4}s^{-1}$ (60% TFE). The solvolysis of 1 in 60% aqueous TFE is 6 times, and in 80% aqueous TFE about 3 times faster than in absolute TFE under similar conditions. Since the ionizing power of TFE, in contrast to ethanol[6], decreases on addition of water, it might be expected that the rate would decrease and not increase for a pure k_c-process on going to solutions of higher water content. This again indicates the participation of a synchronous β-elimination reaction.



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A comparison of the solvolysis rate of propene-2-yl-triflate (9)[5] with that of 1 in absolute TFE at 80.35°C shows that 1 reacts 6 times faster. In 50% aqueous ethanol 1 reacts 2-3 times faster than 9[5]. The slightly higher solvolysis rate of 1 indicates a hydrogen participation in the rate determining step.

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