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VINYL CATIONS, 16[1]

A 1.2 - Hydride Shift in the Solvolysis of a Vinyl Triflate.

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The intense studies of solvolysis reactions of suitable vinyl derivatives have shown that the vinyl cations formed as intermediates do not differ in principal from saturated (tri-substituted) cations[2]. Reactions, which have been observed with tri-substituted carbenium ions, such as rearrangement, substitution and elimination reactions have also been observed during the solvolysis of vinyl triflates[2] or vinyl nonaflates[3]. With vinyl cations generated by solvolysis reactions two types of rearrangement are known: Rearrangements of groups towards the double-bond and rearrangements of groups across the double-bond[2][4]. In both cases, in which the shifted group can be either an alkyl or an aryl group, the driving force for the rearrangement is the formation of the more stable vinyl cation. Rearrangements of this type have been observed in the solvolyses of acyclic or cyclic vinyl triflates and nonaflates[2][4].

To our knowledge, a 1.2 - hydride shift, which is very common when tri-substituted carbenium ions are generated by solvolysis reactions[5], have not been observed in the solvolysis of a vinyl compound leading to the formation of a vinyl cation[6]. We report here the solvolysis reactions of cis- and trans-3-cyclopropyl-2-propen-2-yl-trifluoromethanesulfonate (Triflate)(1;2) in which, under the stabilizing influence of the β-cyclopropane ring, a 1.2 - hydride shift across the double-bond occurs.

The cis- and trans-triflates 1 and 2 respectively were prepared by treatment of cyclopropyl acetone (8) with trifluoromethanesulfonic acid anhydride in methylene chloride and pyridine for 10 hrs. The resulting mixture of triflates was purified by column chromatography and distillation. The triflates 1, 2 and 3 are obtained in a ratio of 1:2:2.2 and were separated by preparative gas chromatography; the structures and configurations of the triflates were determined by NMR spectroscopy (CCl_4; 60 MHz). Cis-1: τ=5.03 (d, 1H, vinyl proton, J=9.5 Hz), 7.87 (s, 3H, methyl protons); 8.72 (m, 1H, tert.ring proton); 9.10 - 9.58 (2 m, 4H, cyclopropane protons). Trans-2: τ= 5.36 (d, 1H vinyl proton, J=9.5 Hz); 7.94 (s, 3H, methyl protons); 8.31 (m, 1H, tert. ring proton); 8.95-9.60 (2m, 4H, cyclopropane protons). - 3: τ=4.90 (s, 2H, vinyl protons); 7.78 (d, 2H, $-CH_2-$protons, J=6.5Hz); 8.78 (m, 1H, tert. ring proton); 9.28-9.93 (2 m, 4H, cyclopropane protons).

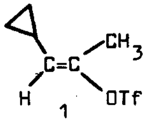
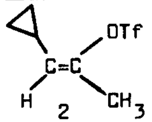
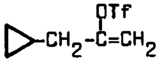
1, 2 and 3 were solvolyzed in 60 and 80% aqueous trifluoroethanol (TFE) buffered with pyridine for 3 days at 80°C. The solvolysis products are shown in the table. The solvolysis products 4 - 8 for each run were separated by preparative gas chromatography and their structures prooven unequivocally by IR, NMR and mass spectrometry or by comparison with authentic samples.

As is shown in the table, the *trans*-2 as well as the *cis*-isomer 1 yield a considerable amount of cyclopropylethyl ketone (7). The formation of 7 can only be explained with the intermediate formation of the vinyl cation 9 generated in the solvolysis of either the triflate 1 or 2, which subsequently rearrange by 1.2 - hydride shift across the double bond to form the cyclopropyl vinyl cation 10 which reacts further to form the cyclopropylethyl ketone (7).(Scheme). The driving force for this particular rearrangement including a 1.2 -hydride shift is the higher stability of the cyclopropyl vinyl cation 10 compared to the vinyl cation 9. The comparatively high stability of cyclopropyl vinyl cations such as 10 has been demonstrated in many of the solvolysis reactions of suitable cyclopropyl vinyl derivatives[7], as well as in the rearrangement reactions of homoallenyl compounds[2]. The relative amounts of the hydride shifted product are not very much different between the *trans*-2 - and the *cis*-triflate 1 . This indicates that the hydride shift $9 \rightarrow 10$ occurs in a vinyl cation which is free of its leaving group and in which the stereochemistry between the *trans*- and *cis*-isomer is already lost. Otherwise one should expect a higher degree of hydride shift in the *trans*-triflate 2. In addition the relative amount of 7 does not change very much going from 60 to 80% TFE.

The main solvolysis product of the *trans*-triflate 2 is 1-cyclopropyl-propyne-1 (6) which can be easily formed from the intermediate vinyl cation 9 but also by a synchronous β-elimination. That a high degree of vinyl cation mechanism is involved in the solvolysis of the *trans*-isomer 2 shows in a comparison of its product analysis with the solvolysis products of *trans*-3-buten-2-yl-triflate (80% aqueous ethanol)[8]. While in the latter case the only solvolysis product was the corresponding acetylene (2-butyne), 2 in addition to the hydride shifted product 7 solvolyzes with formation of 1.5 to 2% cyclopropyl-

Table

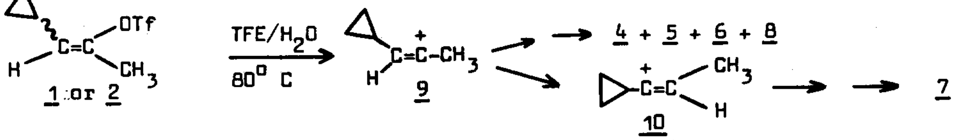
Solvolysis products of cis- and trans-3-cyclopropyl-2-propen-2-yl-triflate (1 and 2) and 3-cyclopropyl-1-propen-2-yl-triflate (3); T = 80°C buffered with 1.2 mol pyridine, reaction time 3 days.

Compounds	Solvent	Solvolysis Products (%)				
		▷-CH$_2$-C≡CH 4	▷-CH=C=CH$_2$ 5	▷-C≡C-CH$_3$ 6	▷-$\overset{O}{\overset{\Vert}{C}}$-C$_2H_5$ 7	▷-CH$_2$-$\overset{O}{\overset{\Vert}{C}}$-CH$_3$ 8
 1	60% TFE	-	14.7	55.0	13.0	17.3
	80% TFE	-	12.1	56.9	16.9	14.1
 2	60% TFE	2.7	1.6	81.0	12.7	2.0
	80% TFE	2.3	1.6	83.5	11.1	1.5
 ▷-CH$_2$-$\overset{OTf}{C}$=CH$_2$ 3	60% TFE	53.8	27.2	-	-	19.0
	80% TFE	57.0	25.8	-	-	17.2

acetone (8) formed via the vinyl cation 9 by direct substitution (Scheme).

An even higher degree of vinyl cation mechanism is found in the cis-isomer 1. This is shown by the fact that 1 in additon to the hydride shifted ketone 7 forms, depending upon the solvent mixture, between 14 and 17% cyclopropylacetone (8). This is formed by reaction of the unrearranged intermediate vinyl cation 9 with the solvent. In addition around 14% 1-cyclopropylallene (5) is formed, which arises from the intermediate vinyl cation 9 through elimination of a proton, while the corresponding trans-triflate 2 yields only 1.6% of this allene (See table).

Scheme



The solvolysis rates of the triflates 1, 2 and 3 were measured in 60 and 80% TFE at 80.6°C by gas chromatography: 1: $k=5.61 \pm 0.09 \cdot 10^{-5} sec^{-1}$(60% TFE), $k=2.74 \pm 0.06 \cdot 10^{-5} sec^{-1}$ (80% TFE); 2: $k= 4.26 \pm 0.03 \cdot 10^{-4} sec^{-1}$ (60% TFE), $k=1.56 \pm 0.05 \cdot 10^{-4} sec^{-1}$ (80% TFE); 3: $k=1.50 \pm 0.02 \cdot 10^{-4} sec^{-1}$(60% TFE), $k=4.2 \pm 0.1 \cdot 10^{-5} sec^{-1}$ (80% TFE).

The trans-isomer 2 reacts 6 to 7 times faster than the cis-isomer 1. The higher rate of 2 also is an indication for a partly synchronous mechanism in which the trans-hydrogen participates in the rate determining step of the solvolysis. On the other hand, the rate difference of 2 and 1 is not as large as the rate difference between the trans- and cis-butenyl triflates ($k_{trans}/k_{cis} = 40$)[8] and in which the trans isomer was considered to react completely via a synchronous elimination mechanism. In respect to the triflates 2 and 1 the lower trans/cis rate ratio is in agreement with a high degree of vinyl cation formation also in case of the trans-isomer 2.

3-Cyclopropyl-1-propen-2-yl-triflate (3) which was also formed when 1 and 2 were synthesized from the ketone 8 was also solvolyzed under the same conditions. The formation of 17 to 19% of the ketone 8 and 25 to 27% of the allene 5 point to the formation of an intermediate vinyl cation in the solvolysis reaction. On the other hand, no product is found which originates from a hydride shift towards the double bond and which could transform the initially formed vinyl cation 11 into the cyclopropylcarbinyl cation 12.

The absence of the rearrangement reaction 11 → 12 shows, that there is no participation of the hydrogen on the saturated carbon atom next to the intermediate vinyl cation.

LITERATURE and FOOTNOTES

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