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VINYL CATIONS 33 [1]: 1-ALKENE-3-YNE-2-YL TRIFLATES, PRECURSORS OF TRIPLE BOND STABILIZED VINYL CATIONS - SYNTHESIS AND FIRST SOLVOLYTIC STUDIES.

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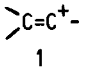
Abstract: The α-alkynyl vinyl triflates (3) are synthesized and the solvolyses reactions studied in different solvents. The solvolysis products and kinetic data indicate, that the hitherto unknown triple bond stabilized vinyl cation 2a ⟷ 2b is formed as an intermediate.

A direct solvolytic generation of vinyl cations 1 in the solvolysis of vinyl derivatives is possible if either very good leaving groups are used (triflates, nonaflates) [2] or if the developing vinyl cation is stabilized by neighboring groups with electron donating ability[3]. All kinds of groups leading to classical and nonclassical stabilization of the vinyl cations have been thouroughly investigated[3] but there still remains a missing link in classical stabilization: an α-alkynyl vinyl cation 2a.

We report here the synthesis of the new class of alkenynyl triflates 3, precursors suitable fo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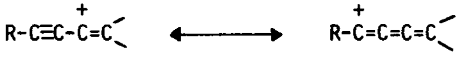
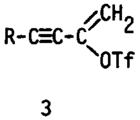

2a 2b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	R =
3a	t.-Bu
3b	Me
3c	H

the solvolytic generation of α-alkynyl vinyl cations 2a which are mesomeric with the trienyl cations 2b.

Synthesis: The various approaches to synthesize alkynylvinyl triflates 3 are given in scheme 1. The first reaction attempted from the silylenolether 5 by successive treatment with methyllithium and trifluoromethanesulfonic acid anhydride (Tf_2O) gave only traces of the triflate 3 (scheme 1, route c). However the acetylenic ketones 4 could be converted in moderate yields with Tf_2O directly into the triflates using sodium carbonate as a base in methylene chloride (scheme 1, route a). The yields of the triflates 3 increase to 70 - 80% if the highly steric hindered 2,6-di-tert.-butyl-4-methylpyridine 6 [4] is used as the base (scheme 1, route b). Use of other bases like triethylamine, tributylamine, pyridine, 2,6-lutidine or dicyclohexylethylamine yielded no required product. The reactive triflates 3 were generally isolated by high-vacuum-destillation. Some physical data of the triflates 3 are given in Table 1.

Scheme 1:

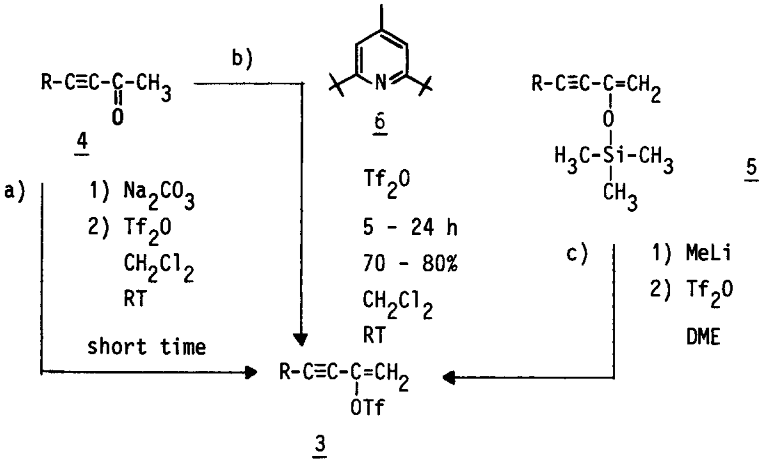
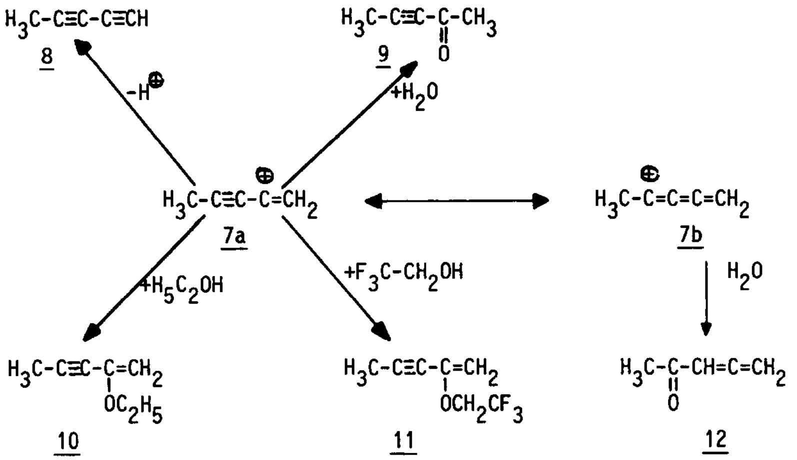


Table 1:

Triflate	bp/Torr	^{1}H-NMR (CCl_4), δ [ppm]	IR, ν [cm^{-1}]
3a	23/0.3	5.40 (d,1H), 5.33 (d,1H), 1.27 (s,9H)	2230 (C≡C); 1645 (C=C); 1435,1255,1225,1145 (OSO_2CF_3)
3b	25/2	5.42 (d,1H), 5.36 (d,1H), 2.02 (s,3H)	2260,2230 (C≡C); 1640 (C=C); 1430,1260,1215,1140 (OSO_2CF_3)
3c	24/10	5.58 (s,2H), 3.26 (s,1H)	3330 (≡C-H); 2120 (C≡C); 1640 (C=C); 1440,1260,1225,1145 (OSO_2CF_3)

Solvolysis: Product studies were carried out with triflate 3b in 80% aqueous ethanol (EtOH) and 80% trifluoroethanol (TFE). Scheme 2 shows the possible products deriving from 3b via the first formed vinyl cations 7a ⟷ 7b.

Scheme 2:



The solvolysis products formed in 80% aqueous EtOH and in 80% aqueous TFE are given in Table 2.

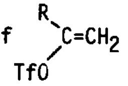
Table 2: Solvolysis products of 3b in 80% aqueous EtOH and 80% aqueous TFE at 40°C.

Solvent	Buffer (1,1 fold excess)	Products [a] (%) 8	9	10	11	12	Polymers (%)
80% aq.EtOH	$N(C_2H_5)_3$	30	4	15	-	3	48
80% aq.TFE	2,6-lutidine	24	20	-	28	0	28

a) Average values from five runs. Internal standard: n-octane. Product analysis was carried out by capillary GC using two columns with different coatings by comparing with authentic samples and/or GC/MS.

The solvolysis products in Table 2 show that 3b solvolyze via the vinyl cation 7a. This is proved by the formation of the enolethers 10 and 11. Only in case of solvolysis in 80% aqueous ethanol small amounts of 12 were found, which is formed by substitution of the mesomeric cation 7b. The comparatively high amounts of polymers are probably formed from other substitution products of 7b, which are not stable under the reaction conditions.

Kinetic measurements were carried out for the triflates 3b and 3c and also for 1-propene-2-yl triflate (13a) and 1-pentene-2-yl triflate (13b) for comparison (Table 3).

Table 3: Solvolysis rates of  $\mathrm{R(TfO)C{=}CH_2}$ in 50% aqueous EtOH a).

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Triflate No.	R =	T [^{o}C]	k_1 [s^{-1}]
13a	CH_3	40	0,96 ± 0,04 x 10^{-5}
13b	C_3H_7	40	1,97 ± 0,02 x 10^{-5}
3b	$H_3C-C{\equiv}C$	40	7,20 ± 0,07 x 10^{-4}
3c	$H-C{\equiv}C$	60	1,88 ± 0,09 x 10^{-5}

a) Measurements done by potentiometric titration

By comparison of the solvolysis rates listed in Table 3 it becomes evident that 3b solvolyses 70 times faster than vinyltriflate 13a and 35 times faster than the C_5-analogue 13b. The higher rate of 3b is undoubtedly due to the stabilizing effect of the triple bond on the intermediate vinyl cation 7a which in its mesomeric form 7b is also a secondary vinyl cation5). Our results are consistent with the early work of Buroway and Spinner6) on the solvolysis of differently substituted tertiary propargylic chlorides. The much lower rate of triflate 3c, the representative with an unsubstituted triple bond, does not contradict a stabilizing effect, since one has to make allowance for the sum of inductive and mesomeric effects of the triple bond which are opposite to each other. For that reason our kinetic data are also in good agreement with the recent calculations of Apeloig, Schleyer and Pople7). According to them the low stabilization of an α-ethynyl-group is probably due to cancellation between a stabilizing π-conjugation and a destabilizing withdrawal by the acetylenic group. The failure of the unsubstituted triple bond to provide an higher stabilization does not arise from ineffective charge delocalization as the charge in the empty orbital on C_2 is almost the same as in the case of an α-ethenyl-group, but probably due to the inductive effect of the triple bond7). Calculation of the stabilization of a 1-propynyl-group are intended to be carried out to confirm our results8).

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