

VINYL CATIONS 23¹⁾

TRIPLE BOND PARTICIPATION IN THE SOLVOLYSIS OF A VINYL TRIFLATE

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Participation of multiple bonds with a developing saturated carbenium ion center in solvolysis reactions is well documented in the literature^{2,3)}. It has recently been shown that remote double bonds can also participate with vinyl cations in solvolysis reactions⁴⁾. The study of the possible participation of a triple bond with a vinyl cation would be highly interesting in that two vinyl cations 4 and 5/6 will be involved in the total spectrum of the reaction.

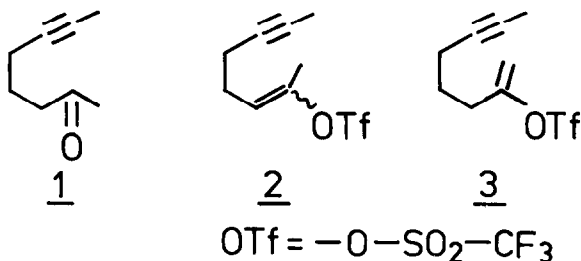
We report here the first account of such a participation by a triple bond, leading to cyclic products in the solvolysis of 6-octyn-2-en-2-yltrifluoromethanesulfonate (2).

All attempts to prepare the triflate 2 by the direct reaction of trifluoromethanesulfonic acid-anhydride with 6-octyn-2-one (1) in the presence of various bases under different conditions failed⁵⁾. Attempted conversions of the ketone 1 to the trimethylsilylenolether with subsequent conversion to 2, also did not work well⁶⁾. Finally potassium hydride was used in the synthesis of the triflate 2⁷⁾. The ketone 1 was treated with potassium hydride in absol. tetrahydrofuran at 20°C and the resulting potassium enolate on treatment with trifluoromethanesulfonic imidazolide⁸⁾ at -78°C gave a mixture of triflates 2 and 3. These were separated, as far as possible, by column chromatography on silica gel (eluent, petroleum ether 30-50°C). The triflate 2 was finally purified by preparative gaschromatography (ethyleneglycol succinate 10%, 2 m, 150°C) and the structure confirmed by its NMR, IR and mass spectra. 2 consisted of the Z- and E-isomer as was shown by gaschromatographic analysis. Since they differed only very little in their retention times, they were not separated.

NMR (CCl₄): τ = 8.23 (s, CH₃ at C=C); 7.9 (CH₃ at C=C); 7.4-8.05 (m, 4H), 4.5-5.1 (1H, vinylproton).

IR (film): $\nu_{C=C}$ 1615, 1415, 1245, 1215, 1140 (-O-SO₂-CF₃).

The solvolysis of triflate 2 in 50% aq. ethanol at 145°C was found to be very slow, the reaction occurring only to an extent of 12%. The product was mainly 1 and traces of the cyclic ketone 5b. In 70% TFE as solvent, at 145°C, the solvolysis was practically complete after 10 days. 13% of the product was a mixture



of the cyclic ketones 5b and 6b. These were formed from the primary cyclization products 5a and 6a by rearrangement under the reaction conditions. The extent of triple bond participation giving cyclic products was still higher in 99.5% TFE. The exact product composition is shown in the Table.

Table
Solvolysis of 6-octyn-2-en-2-yltrifluoromethanesulfonate (2) buffered with 2 equiv. of 2,6-lutidine

Solvent	Temp. in °C	Time in days	Percentage reacted	Products ^{a)b)}			
				acyclic		cyclic	
				<u>1</u>	<u>5a</u>	<u>5b</u>	<u>6b</u>
50% ethanol	145	10	12	98	-	1.5	-
70% TFE ^{c)}	145 ^{d)}	10	100	78	-	9	4
98% TFE	120	12	85.4	60.3	traces	19	5.9
99.5% TFE ^{e)}	120	10	75	53.2	traces	28	7.4

a) Product percentages were determined by g.c., assuming 100% reaction.

b) In addition to the products given here, an unidentified product was formed in every case.

c) TFE = 2,2,2-trifluoroethanol.

d) At this temperature, a tarry product, insoluble in ether was also obtained.

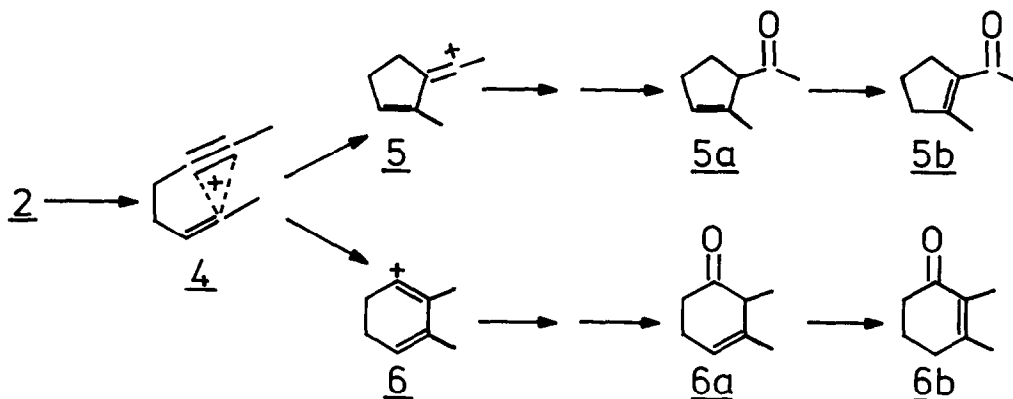
e) The percentage of ketones given, was calculated after the hydrolysis of the enolethers by treatment with dil. HCl.

The very slow reaction of 2 in comparison with (Z)- and (E)-3-methyl-2,6-heptadien-2-yltriflate⁴⁾ is attributed to the inductive effect of the triple bond. The ketones 1 and 5b were separated by preparative gas chromatography (carbowax 20 M, 10%, 3 m, 150°) and identified by comparing their IR spectra with those of authentic samples. 6b was identified by comparing its retention time with that of the authentic sample.

According to the product composition shown in the Table, the solvolysis of the yne-ene-triflate 2 occurs with formation of cyclic products, which indicates

participation of the triple bond in 2 during the formation of the vinyl cation 4. As is evident from the Table, the extent of triple bond participation and thereby the amount of cyclic products, is dependent upon the nucleophilicity and ionizing power of the solvent. The lesser the nucleophilicity of the solvent, the greater is the extent of cyclization. More than 35% cyclization was observed in 99.5% TFE which has the highest ionizing power and lowest nucleophilicity⁹⁾ among the solvents used in the solvolysis of 2. The marked dependence of the product composition on the nucleophilicity and ionizing power of the solvent is indicative of the direct participation of the triple bond in the rate determining step of the solvolysis of 2.

Accordingly, the initially formed vinyl cation 4 or its ion pair (see Scheme) rearranges to the vinyl cations 5 and 6, which are captured by the nucleophile forming the ketones 5a and 6a or the corresponding enolethers. The ketones 5a and 6a are not stable under the reaction conditions and rearrange to the more stable conjugated ketones 5b and 6b, as was shown by control experiments.



The cyclization reaction of 2 leads to the preferential formation of the five-membered ring ketone 5b, which in turn is formed from 5a. This indicates, as was already shown with other examples, the higher stability of the linear vinyl cation 5 compared with the strained cyclohexadienyl cation 6¹⁰⁾. In fact the amount of cyclohexenones 6a (\rightleftharpoons 6b) formed, was comparatively small (see Table) in all runs. The amount of cyclized products in the solvolysis of 2 is comparable to that of the Z- and E-3-methyl-2,6-heptadien-2-yltriflate⁴⁾ showing that, as in the case of saturated cations³⁾, the nucleophilic activity of the triple bond and double bond towards vinyl cations is almost similar.

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