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1,4-C,H Insertion of Vinyl Vinylidene to Intermediate Cyclobutadiene does not occur during Flash Vacuum Pyrolysis of 1-Buten-3-yne

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Abstract: 1-Buten-3-yne (**1**) and [4-D]1-buten-3-yne (**1a**) have been treated between 800 and 1000 °C under flash vacuum pyrolysis as well as under gas phase pyrolysis in nitrogen and the effluents thoroughly analyzed by GC, GC/MS, GC/FTIR, ^{1}H- and ^{2}H-NMR spectroscopy. Since no evidence for a D-shift in **1a** from the acetylenic to the olefinic position could be detected, the formation of cyclobutadiene as a highly reactive species from the intermediately generated vinyl vinylidene has to be excluded.

At high temperatures, alkynes are known to undergo an acetylene-vinylidene rearrangement[1] in the course of which vinylidene species are formed via 1,2-R-shift reactions. If R stands for hydrogen or deuterium the driving force of this migration is proved to have a maximum, while alkyl substituents at the acetylenic C atoms hardly show such a reaction event.[2]

Recently we have demonstrated a 1,2-styryl migration if vinyl substituted alkynes are exposed to temperatures above 550 °C.[3] Whenever alkylidene and alkenylidene carbenes are qualified to stabilize by intramolecular 1,x-C,H insertion, such cycloisomerizations compete with the back reaction to the parent alkynes. This is basically the case whenever the prerequisites for a 1,5- or a 1,6-C,H insertion are given.[2,4] Not yet finally decided, however, is the question whether, at high temperatures, vinyl substituted vinylidenes are able to undergo 1,4-C,H insertion[2] forming cyclobutadiene as a highly reactive intermediate (see Scheme 1). If this were the case [4-D]1-buten-3-yne (**1a**) should isomerize by retro-insertion into its isomers **1b** and **1c** having the D atom in the olefinic part of the molecule. In order to examine experimentally these important questions[5] we synthesized **1** from 3-butyn-1-yl toluene-p-sulfonate as already reported in ref.,[6] and **1a** by decomposition of the Grignard compound of **1** with D_2O, and used both as starting compounds for pyrolysis studies.

When **1** is pyrolysed at 800 °C (0.3 s reaction time) in a tubular quartz reactor (for set up see ref.[7]) in twenty-five-fold molar excess of nitrogen, its conversion degree amounts to 30 % and the products listed in table 1 are formed, obviously by radical processes. When **1** is exposed, however, to the same temperature or even at 1000 °C under flash vacuum pyrolysis conditions (0.1 to 1.0 mbar), the degree of conversion is reduced to values < 1 % and synthesis reactions can be neglected.

The 1-buten-3-yne fractions recovered from the analogous pyrolysis runs of **1a**, were thoroughly analyzed by

Scheme 1

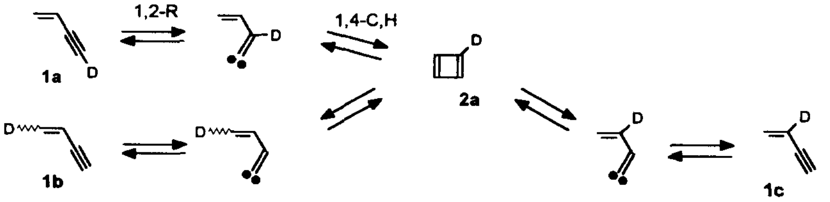

Table 1 Composition of the product of the pyrolysis of **1** in nitrogen at 800 °C

product	S	product	S	product	S
ethyne	0.5	styrene [a]	36.0	1-methylene-1H-indene	tr.
butadiyne [b]	0.5	1,5-dihydropentalene [a]	4.0	naphthalene	3.0
benzene [a]	0.5	5 compounds (C_8H_8)	2.0	9-methylenefluorene	tr.
toluene	tr.	indene	0.5	phenanthrene	tr.
ethynylbenzene [b]	1.0	4-phenyl-1-buten-3-yne	tr.		

conditions: reaction time: 0.3 s, conversion degree: 30 %, data given in selectivity units (S), S = moles formed per 100 moles of **1** converted.

a) already described in ref.[8], b) already described in ref.[9]

GC/MS and demonstrate that the D-depletion only took place to an extent below one percent, and that dideuterated **1** could not be detected. The FTIR spectra of the 1-buten-3-yne fraction recovered from FVP runs of **1a** do not show the characteristic stretch vibrations of olefinic C-D bonds. This statement is thought to be certain because olefinic as well as acetylenic C-H and C-D stretch vibrations are clearly separated in the FTIR spectra (see table 2). These findings are also supported by the ^{1}H- and ^{2}H-NMR data (for coupling constants see note[10]): the corresponding data of **1a** before and after the pyrolysis runs in question do not show any significant change and, because of that, the formation of cyclobutadiene (**2a**) as a reaction intermediate by 1,4-C,H insertion of the precedingly formed vinylidene (see scheme 1) has to be considered as an unimportant pathway under conditions where 1,5- and 1,6-C,H insertions are well proved.

Table 2 C-H- and C-D- stretch vibrations in the FTIR spectra of 1-buten-3-yne

vibration	wave number [cm^{-1}]	vibration	wave number [cm^{-1}]
acetyl. C-H	3319	acetyl. C-D	2590
olefin. C-H	3100	olefin. C-D	2330
olefin. C-H	3039	olefin. C-D	2285

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10. ^{1}H-NMR (400 MHz, CD_3COCD_3, Varian UNITY 400): $\delta = 3.38$ (m, $^4J_{HH} = 2.2$ Hz, $^5J_{HH} = 0.5$ Hz, $^5J_{HH} = 0.8$ Hz), 5.58 (o, $^2J_{HH} = 2.3$ Hz, $^3J_{HH} = 11.1$ Hz, $^5J_{HH} = 0.8$ Hz), 5.69 (o, $^2J_{HH} = 2.3$ Hz, $^3J_{HH} = 17.6$ Hz, $^5J_{HH} = 0.5$ Hz), 5.85 (o, $^3J_{HH} = 11.1$ Hz, $^3J_{HH} = 17.6$ Hz, $^4J_{HH} = 2.2$ Hz);
    ^{2}D-NMR (61 MHz, CH_3COCH_3, Varian UNITY 400) $\delta = 3.38, 5.58, 5.69, 5.85$

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