Tetrahedron Letters,Vol.25,No.23,pp 2455-2458,1984 0040-4039/84 $3.00 + .00
Printed in Great Britain

TRANSFORMATION OF cis-ENYNE-SUBSTITUTED OXIRANES TO 2-VINYLFURANS
SEVEN-MEMBERED CYCLOALLENES AS INTERMEDIATES ?

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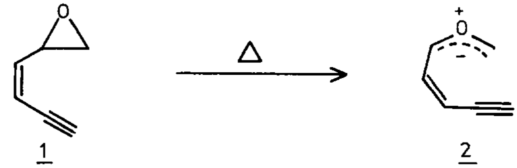
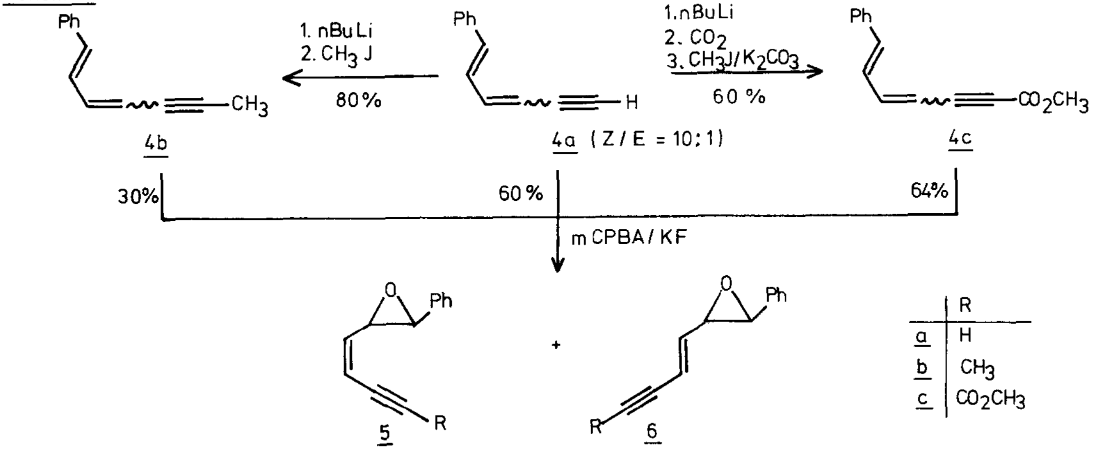
Summary. Upon thermal activation the 1,2-epoxy-(Z)-3-hexen-5-ynes 5a-c are transformed predominately into the 2-vinylfurans 9a-c/10a-c. A reaction mechanism is proposed which involves the formation of 7-membered cycloallenes (structure 3) as central intermediates.

Intramolecular participation of acetylenic bonds in pericyclic reactions often gives rise to the formation of highly unsaturated ring systems containing one or two allene moieties [1]. These transformations take place with surprising ease despite the substantial strain energy content of the cyclic products. In connection with our continuous interest in the intramolecular reactivity of 1,3-dipoles we investigated the thermal behavior of some derivatives of 1,2-epoxy-(Z)-3-hexen-5-yne (1) [2]. Assuming a reaction pathway analogous to the well studied butadienyloxirane-dihydrooxepin isomerisation [3], the 8e-electrocyclisation of the expected dipolar intermediate 2 then should lead to the oxacyclohepta-1,2,4-triene 3, a new representative within the class of 7-membered cycloallenes [4].



Indeed, evidence for a reaction sequence 1 ⟶ 2 ⟶ 3 was born out during our studies with the substituted epoxy-enynes 5a-c. For the synthesis of these compounds the hexadienyne 4a, prepared in 75% yield by the known Wittig route from cinnamaldehyde and propargyl phosphonium bromide [5], was the common intermediate (Z/E-ratio = 10 : 1). Introduction of the methyl- and ester-functions, respectively, at the terminal alkyne position was achieved by reacting the Li-salt of 4a with either methyliodide (to give 4b), or with carbon dioxide (affording the acid of 4c), followed by esterification (see Scheme I). The final epoxidation of 4a-c has been performed in methylenechloride using m-CPBA as 1 : 1-complex with KF [6]. Compared to the procedure without KF this method turned out to give about 20% higher yields of the desired oxiranes. No indications for the formation of other regioisomers have been obtained. Of course the ratio 5/6 is still 10 : 1, reflecting the distribution of the stereoisomers 4a after the olefination reaction [7].

Scheme I



Since a clean separation of the oxiranes could be effected only in low yield by repeated chromatography operations, the thermolysis experiments have been carried out with the mixture of diastereomers containing 5 as the major component (90%).

On heating a solution of 5/6 in bromobenzene or isooctane up to 220 °C, a complex mixture of so far unidentified material is produced, which is probably the result of catalyzed C/O-ring opening reactions; however, under short-time pyrolysis conditions [8] at 350 °C/10-15 s a transformation into two types of products has been observed, namely the 3-alkinyl-2,3-dihydrofurans 7/8 and the 2-vinylfurans 9/10, the latter ones predominating by a factor of about 3.5 (see table 1).

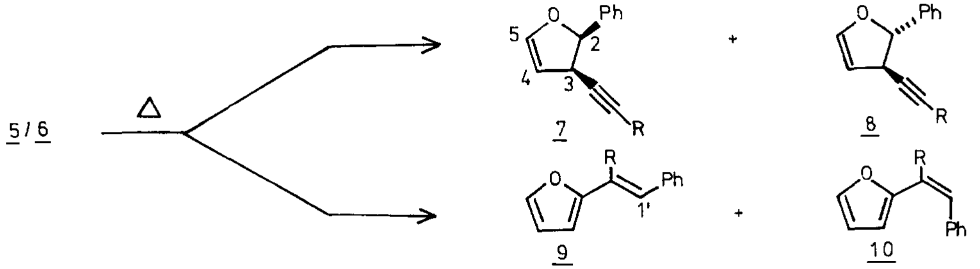


Table 1. Product Distribution after Thermolysis of the 10 : 1-mixture of 5/6 [a)]

Oxiranes	Yield of 7 - 10 (%)	Dihydrofurans [b)]		Vinylfurans [b)]	
		7	8	9	10
5a/6a	88	12	8	60	8
5b/6b	72	9	6	42	15
5c/6c	79	11	7	26	35

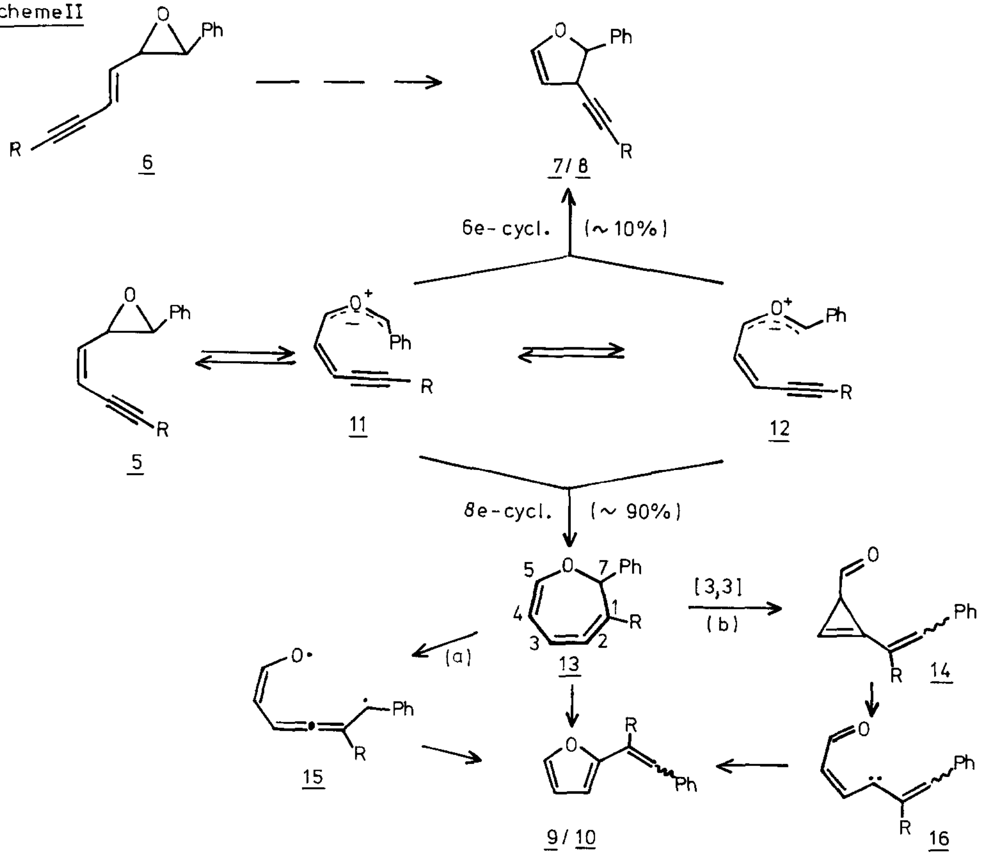
[a)] Reaction conditions: 350 °C/10-15 s [8)]; 100% conversion.- [b)] Numbers in %.

The structure and configuration of the new products have been assigned unambiguously on the basis of the NMR- (see table 2) as well as IR- and MS data (for 9/10). In addition, the furans 9a/10a proved to be identical with authentic material [7].

Whereas the conversion of the (E)-epoxyhexenynes 6 to 2,3-dihydrofurans 7/8 has ample precedent and was the subject of detailed investigations [9], the rearrangement of the (Z)-isomers 5 to vinylfurans 9/10 is unique and deserves special comment. A reasonable mechanism is outlined in Scheme II and includes the following steps: (i) 4e-electrocyclic ring opening to the conjugated carbonyl ylide 11, which possibly undergoes , at least partially, C/O-bond rotation to 12; (ii) 1,7-dipolar cyclisation of the 8e-system 11 (or 12) affording the 7-membered cycloallene 13; (iii) the concluding transformation to 9/10 (a formal [1.3]-O-shift) might proceed either by cleavage of the O/C-7 bond of 13 and subsequent rebonding between C-2 and the oxygen (path (a)), or by a sequence of allowed pericyclic reactions involving a [3.3]-sigmatropic shift (13 ⟶ 14), a cyclopropene-vinylcarbene rearrangement (14 ⟶ 16) [10], and the electrocyclisation of the resulting carbonylvinylcarbene (16 ⟶ 9/10; see path (b)) [11]. The pronounced dependence of the ratio of 9/10 on the kind of substituent R (see table 1) is compatible with either route.

As indicated in Scheme II there is a competition between the 1,5- and 1,7-cyclisation processes of the extended dipoles 11/12 with a high preference

Scheme II



in favor of the 8e-reaction (about 90%12)). This observation is in line with results obtained in the case of the butadienyloxirane-dihydrooxepin rearrangement 3) and can be explained by assuming a helical geometry of 11/12 which is specially suitable for a bonding overlap between the terminal atoms.

The preparative aspects of this novel entry to 2-vinylfurans as well as further experiments directed to a confirmation of the intermediacy of cyclohepta-1,2,4-trienes like 13 are currently under active investigation 13).

Table 2. ^{1}H NMR Data of the Dihydrofurans 7a-c/8a-c and Furans 9a-c/10a-c

	δ-Values a)							J (Hz)				
	1'-H	2-H	3-H	4-H	5-H	R b)	Ph-H	$J_{2,3}$	$J_{3,4}$	$J_{4,5}$	$J_{3,R}$	$J_{1',R}$ b)
7a		5.53	3.97	5.08	6.54	1.91	7.1-7.5	10.5	2.6	2.6	2.6	
7b		5.49	3.92	5.06	6.52	1.46	7.1-7.5	10.2	2.6	2.6	2.8	
7c		5.63	4.12	5.10	6.61	3.61	7.3-7.6	10.5	2.5	2.5	2.5	
8a		5.46	3.67	4.98	6.48	2.25	7.1-7.5	8.8	2.6	2.6	2.6	
8b		5.40	3.66	4.98	6.46	1.80	7.1-7.5	8.1	2.6	2.6	2.8	
8c		5.55	3.81	5.02	6.59	3.77	7.3-7.6	8.2	2.5	2.5	2.5	
9a	7.02		6.29	6.37	7.34	6.85	7.1-7.5		3.4	1.8		16.0
9b	7.14		6.34	6.39	c)	2.16	7.2-7.4		3.2	1.7		1.5
9c	7.23		6.40	6.44	7.43	3.78	7.3-7.4		3.6	1.7		
10a	6.44		6.21	6.27	7.24	6.29	7.1-7.5		3.4	1.8		12.0
10b	6.42		6.09	6.26	c)	2.15	7.2-7.4		3.2	1.7		1.5
10c	7.85		6.47	6.47	7.40	3.84	7.1-7.4		3.4	1.7		

a) 250 MHz, $CDCl_3$.- b) a : R= H; b : R= CH_3; c : R = CO_2CH_3.- c) Signals covered

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12) Based on the assumption that the (E)-isomers 6 are transformed mainly to 7 8,9).

13) Financial support of this work by the DEUTSCHE FORSCHUNGSGEMEINSCHAFT and the FONDS DER CHEMISCHEN INDUSTRIE is gratefully acknowledged.

(Received in Germany 13 February 1984)