THE EPOXYHEXENYNE - VINYLFURAN TRANSFORMATION : EVIDENCE FOR CARBENE INTERMEDIATES 1

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Abstract. The thermal conversion of the (Z)-epoxyhexenynes 3a/3b into three pairs of isomeric vinylfuran derivatives is explained on the basis of a multistep mechanism with butenynyl carbonyl ylides, cycloallenes and vinyl carbenes as intermediates.

Among the numerous known furan syntheses the thermally induced conversion of epoxyhexenynes into 2-vinylfurans represents a useful and versatile new route (type $I \rightarrow II$).² In connection with investigations on the application of such furan systems for preparative purposes, derivatives of II were needed which bear a terminal ketone functionality at the vinyl unit (group A in II).



In this communication we report on our findings with two carbonyl compounds, 3a and 3b, which have been prepared by aldol condensation of (Z)pentenynal $(\underline{1})$ and subsequent regio- and stereoselective epoxidation of 2 with hydrogen peroxide in alkaline solution. 4



Under short-time thermolysis conditions 2 at 350 $^{\circ}$ C/10 s both derivatives were converted to products in 70-80% yield. However, careful analysis of the reaction mixture revealed that in addition to the expected 2-vinylfurans (E/Z)-4 two further pairs of isomers have been formed in each case, namely the aldehydes (E/Z)-5 and (E/Z)-6 (see Table 1).

The structural proof for the compounds 4-6 has been carried out by extensive H-NMR investigations (Table 2) in combination with ¹³C-NMR data of (E/Z)-5b and 6b (Table 3).





Table 1. Thermolysis Products of 3a and $3b^{a}$

	<u>4</u> (E/Z)	<u>5</u> (E/Z)	<u>6</u> (E/Z)
<u>3a</u>	62 (11 : 1)	28 (2:3)	10 (1:2)
<u>3b</u>	49 (15 : 1)	15 (3 : 2)	36 (1:1)

a) Relative yields in %. Total yield 70 - 80%

The unexpected results of the thermal reactions are explained on the basis of the following mechanistic considerations (as illustrated in the Scheme): 1,3-dipolar cycloreversion of $\underline{3a}, \underline{b}$ leads to the conjugated carbonyl ylides $\underline{7}$ which react by 1,7-electrocyclization affording the highly strained sevenmembered cycloallenes 8.⁵ Although the formation of the furans 4 and 5 might take place by simple recombination of the subsequently formed bis-oxapentadienyl radicals <u>10</u> (between the positions 5/1 or 5/9, respectively) the carbenes 11 represent other possible precursors. Depending on which oxygen participates in the oxadienyl-carbene cyclization ⁶ (i.e. the former r i n g or carbonyl oxygen) either 4 or 5 are produced, the ratio being determined by the favored conformation of 11. In view of this alternative the question arises if diradicals like 10 are involved at all in the reaction process, because not only a direct transition $8 \rightarrow 11$ is conceivable but also a route via the Oxa-Cope products $\frac{9}{2}$ ⁷ which then undergo the well known cyclopropene-vinylcarbene rearrangement ⁸ leading to the bis-oxabutadienyl carbenes <u>11a,b</u>.

Convincing evidence for the intermediacy of structures like 9 and 11 has been obtained by the occurence of furans 6 as the third thermolysis products. The specific substitution pattern can be satisfactoryly explained by assuming (i) cyclization of 11 to the cyclopropenes 12, (ii) reopening of 12 with formation of the isomeric vinylcarbenes 13 which (iii) finally undergo 6e ring closure affording the furans 6.



<u>Summary</u>. The results with <u>3a,b</u> support the general mechanistic concept proposed earlier for the transformation of epoxyhexenynes into vinylfurans.² However, with regard to the deactivation pathway of the intermediate heterocycloallenes the involvement of carbene spezies, instead of or in competition to diradicals, has to be considered in the above examples.⁹

ſ	8-values (CDCl ₃ , 250 MHz)								J _{H,H} (Hz)		
}	2-н	3-H(R)	4H	5-H(R)	1'-H(R)	2'-H	СНО	COCH3/COPh	3,4	4,5	1',2'
(E)-4a	-	(2.17)	6,35	7.41	7.34	6.57	-	2.32	-	1.7	16.0
(Z)-4a	-	(2.10)	6.31	7.39	6.46	5.93	-	2.37	-	1.7	12.5
(E)-4b	1 -	(2.16)	6.34	7.41	7.69	7.40	-	8.0-7.4	-	1.7	15.0
(Z)-4b	-	(2.18)	6.28	7.34	6.76	5.92	-	8.1-7.2	-	1.7	12.0
(E)- <u>5a</u> •	_	6.73	6.14	(2.39)	(2.35)	6.48	10.01	-	3.4	-	~
(Z)-5a *	-	6.63	6.14	(2.41)	(2.19)	5.82	10.43	-	3.4	-	-
(E)-5b •	-	6.77	6.88	(7.5-7.2)	(2.45)	6.64	10.12	-	3.5	-	-
(Z)- <u>5b</u> •	-	6.77	6.79	(7.5-7.2)	(2.25)	5.91	10.61	-	3.5	-	-
(E)-6a •	7.31	-	6.68	(2.05)	(2.35)	6.48	10.09	-	-	-	-
(Z)-6a •	7.36	-	6.58	(2.07)	(2.20)	5.84	10.38	-	-	~	-
(E)-6b •	7.78	-	7.08	(7.5-7.2)	(2.48)	6.58	10.14	-	-	-	-
(Z)- <u>6b</u> *	7.84	-	6.98	(7.5-7.2)	(2.29)	5.95	10.43	-		-	

Table 2. ¹H-NMR Data of (E/Z)-<u>4a,b</u>, <u>5a,b</u> and <u>6a,b</u>

 $J_{2',CHO} = 8.0, J_{2',CH_3} = 1 Hz.$

	C-2	C-3	C-4	C-5	C-1'	C-2'	СНО	СНЗ	s-Ph	o-Ph	m-Ph	p-Ph
(E)- <u>5b</u>	•	115.6	107.9	156.5	143.7	122.0	190.6	13.3	•	124.3	128.8	128.6
(Z)- <u>5b</u>	•	117.1	107.2	154.2	143.6	127.7	193.5	22.1	٠	124.4	128.8	128.5
(E)- <u>6b</u>	140.9	٠	111.7	154.3	143.8	122.8	190.8	13.5	131.3	125.8	129.0	127.7
(Z)- <u>6b</u>	141.0	٠	113.4	153.8	142.6	127.6	193.5	22.2	131.2	125.9	129.0	127.8

Table 3. ¹³C-NMR Data of (E/Z)- $\frac{5b}{2}$ and $\frac{6b}{2}$ (δ -values, CDCl₃, 100 MHz)

Signals not identified.

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REFERENCES

- ¹ Taken in part from the forthcoming dissertation of J.Roser, Universität Freiburg.
- ² W.Eberbach and J.Roser, Tetrahedron <u>42</u>, 2221 (1986), and references.
- ³ J.Ojima, T.Katakami, G.Nakaminami and M.Nakawaga, Bull.Chem.Soc.Jpn. <u>49</u>, 292 (1976); T.Katakami, K.Fukui, T.Okamoto and M.Nakagawa, ibid. <u>49</u>, 297 (1976).
- ⁴ <u>3a</u>: 55% yield; IR (film): 3280 (=C-H), 1720 (C=O), 1630 (C=C) cm⁻¹; ¹H-NMR (CDCl₃, 250 MHz): δ 5.38 (3-H), 4.00 (2-H), 3.40 (1-H), 3.34 (6-H), 2.13 (COCH₃), 1.94 (CH₃); J_{1,2}= 2.0, J_{2,3}= 9.0, J_{3,CH₃}= 1.5 Hz. <u>3b</u>: 77% yield; mp 65 °C (pentane/ether); IR (KBr): 3240 (=CH), 1680 (C=O), 1630 (C=C) cm⁻¹; ¹H-NMR (CDCl₃, 250 MHz): δ 8.0-7.4 (Ph-H), 5.55 (3-H), 4.24 (1-H), 4.08 (2-H), 3.22 (6-H), 1.98 (CH₃); J_{1,2}= 2.0, J_{2,3}= 9.0, 5 J_{3,CH₃}= 1.5 Hz.
- ⁵ For a recent review on cyclic cumulenes, see: R.P.Johnson in 'Molecular Structure and Energetics', Vol.3, p. 85, VCH Publishers, Weinheim, 1986.
- ⁶ J.A.Pincock and N.C.Mathur, J.Org.Chem. <u>47</u>, 3699 (1982); J.A.Pincock and A.A.Moutsokapas, Can.J.Chem. <u>55</u>, 979 (1977).
- ⁷ A similar rearrangement has been proposed in the case of an isomeric cycloallene: N.Manisse and J.Chuche, J.Am.Chem.Soc. <u>99</u>, 1272 (1977).
- ⁸ E.N.Marvell in 'Thermal Electrocyclic Reactions', p. 83, Academic Press, New York, 1980.
- 9 The same conclusion has been drawn from results obtained with butenynyl nitrones 10 .
- ¹⁰ W.Eberbach and J.Roser, Tetrahedron Lett., following communication. (Received in Germany 1 March 1987)