Tetrahedron Letters,Vol.30,No.26,pp 3443-3444,1989 0040-4039/89 $3.00 + .00
Printed in Great Britain Maxwell Pergamon Macmillan plc

HIGHLY STEREOSPECIFIC THERMOLYSIS OF SPIROOXETANES CONTAINING TETRAHALOGENATED 1,4-BENZOQUINONE MOIETIES

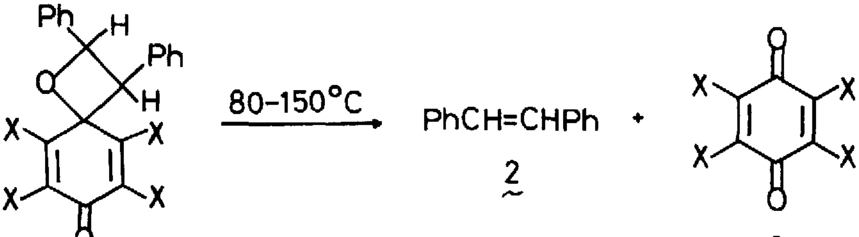
Takumi Oshima* and Toshikazu Nagai
Institute of Chemistry, College of General Education,
Osaka University, Toyonaka, Osaka 560, Japan

Summary: Thermolysis of *cis*- and *trans*-spirooxetanes(**1**) proceeded with 94-100% retention of stereochemistry to give stilbene(**2**) and quinones(**3**). Important role of a concerted pathway was assumed.

Thermal decomposition of oxetanes, which usually gives two different sets of alkenes and carbonyl compounds, due to two modes of cleavage, is generally argued to occur by a 1,4-diradical intermediate rather than by a concerted process.[1] One of the most definitive evidences comes from the considerable loss of stereochemical configuration in the alkenes.[1a,2,3]

We want to report here that thermolysis of *cis*- and *trans*-spirooxetanes(**1**)[4] was cleanly regiospecific and highly stereospecific to provide stilbene(**2**) and quinones(**3**) at relatively low temperature. The data in Table apparently show that neither solvent nor temperature excerted essential effects on the stereochemical course of this thermolysis. The stereoretention for *cis*-**1a** was appreciably lower than that for *trans*-**1a** probably because of steric repulsion between the *cis*-phenyl groups. However, as far as we know, the cis to trans ratios are the highest in the thermal decomposition of *cis*-arranged oxetanes yet examined.

The observed high degree of stereospecificity leads to the ideas that a concerted fragmentation should be dominant over the diradical process.[5] Such a concerted pathway can be rationalized as an allowed $\sigma 2_s + \sigma 2_a$ cycloreversion by analogy with the concerted nature of the thermal conversion



1 (a) X=F; (b) X=Cl; (c) X=Br

2

3

of 2-oxetanones into olefins and carbon dioxide.[6] Accordingly, the high stereoretention of olefinic moiety is indicative of the important participation of HOMO-LUMO interaction between the nascent stilbene and quinones in the orthogonal transition state. Thus, the unusual thermolysis of present oxetanes may be ascribed to the especially low-lying LUMO level of tetrahalogenated quinones, by which the enhanced orbital mixing will partly recover the cost of antarafaciality of quinone function.

Table. Thermolysis of Spirooxetanes(**1a-c**)

Oxetane[a]	Temp(°C)	Reaction time	Solvent	Conversion(%)[b]	Stilbene(**2**) (*cis*:*trans*)[b]
cis-**1a**	80	12 h	Propionitrile	64	94.8 : 5.2
	80	12 h	Ethyl acetate	60	95.1 : 4.9
	80	15 h	Dioxane[c]	60	94.2 : 5.8
	150	5 min	Without solvent	89	95.5 : 4.5
trans-**1a**	80	126 h	Dioxane	69	0.2 : 99.8
	150	5 min	Without solvent	76	0.3 : 99.7
trans-**1b**	80	7 h	Dioxane[c]	94	0.2 : 99.8
trans-**1c**	80	3 h	Dioxane	84	0 : 100

[a] Oxetanes used were geometrically pure and no epimerization was observed during the thermolysis(by HPLC). [b] Determined by HPLC using naphthalene as an internal standard. [c] Presence of 10% volume of pyridine caused no appreciable change in the cis:trans ratios; 94.4 : 5.6 for *cis*-**1a** and 0.2 : 99.8 for *trans*-**1b**. This observation excludes the possible participation of some acidic impurities in the stereochemical course of reaction.

REFERENCES

1. a) K. A. Holbrook and R. A. Scott, *J. Chem. Soc. Faraday Trans. 1*, **70**, 43 (1974); b) *Idem*, *ibid*., **71**, 849 (1975); c) A. D. Clements, H. M. Frey, and J. G. Frey, *ibid*., **71**, 2485 (1975); d) M. J. Clark and K. A. Holbrook, *ibid*., **73**, 890 (1977).
2. H. A. J. Carless, *Tetrahedron Lett*., 3425 (1974).
3. G. Jones, II and J. C. Staires, *Tetrahedron Lett*., 2099 (1974).
4. For **1b**; see T. Oshima and T. Nagai, *Bull. Chem. Soc. Jpn*., **53**, 726 (1980). Physical properties for other oxetanes will be reported elsewhere.
5. Nishida *et al*. have proposed that a concerted fragmentation occurs concurrently with a stepwise-diradical fission in the thermolysis of 3-alkyl-2-phenyloxetanes; *J. C. S. Chem. Comm*., 735 (1974); *Chem. Lett*., 41 (1980); *Can. J. Chem*. **59**, 2503 (1981).
6. a) S. Mageswaran and M. U. S. Sultanba, *J. Chem. Soc. Perkin Trans. 1*, 884 (1976); b) T. Imai and S. Nishida, *J. Org. Chem*. **45**, 2354 (1980).

(Received in Japan 13 April 1989)