Distinctive Thermal Behaviour of Geometrically Isomeric Oxetans

By NOBUJIRO SHIMIZU* and SHINYA NISHIDA

(Department of Chemistry, Faculty of Science, Hokkaido University, Sapporo, Hokkaido, Japan)

Summary *trans*-2-Phenyl-3-n-propyloxetan thermolysed at 250—300° to give *trans*-1-phenylpent-1-ene stereospecifically, whereas the *cis*-isomer decomposed more slowly (by a factor of *ca.* 2) to produce a mixture of *cis*- and *trans*-olefin.

DURING the course of investigations on the Paterno–Büchi reaction, it was noted that *trans*-3-cyclopropyl-2-phenyloxetan decomposed at 200° to give *trans*-2-cyclopropylstyrene quantitatively, while the *cis*-isomer was unchanged under the same conditions.[1] This contradicts the expectation that steric congestion will make the *cis*-isomer more reactive than the *trans*-isomer, which is the case in the thermolysis of 1,2-dimethylcyclobutanes.[2] We report the distinctive thermal behaviour of isomeric 2-phenyl-3-n-propyloxetans (**1**), which is in accord with the previous observations.[1]

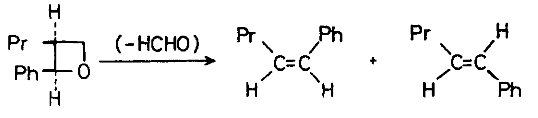
Isomeric oxetans were prepared by photoreaction of benzaldehyde with pent-1-ene. Practically pure *cis*-(**1**)

TABLE. Rates and product ratio of oxetan thermolysis in n-decane[a]

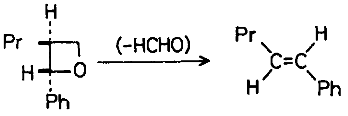
Oxetan	Temp./°C	$10^5 \cdot k_1/s^{-1}$	*cis*-(**2**)/*trans*-(**2**)[b]
cis-(**1**)	242	0·25	8·1
,,	260	1·1	6·7
,,	280	3·5	4·6
,,	290	6·6	1·9
trans-(**1**)	242	0·78	(0·01)[c]
,,	260	2·5	(0·01)[c]
,,	280	6·9	(0·01)[c]
,,	290	12·7	(0·01)[c]

[a] As a 4·0 vol. % solution. [b] The ratio did not change at various % conversions; the ratio of an equilibrated mixture at 290° is estimated to be 0·3. [c] Small contamination of *cis*-(**2**) is due to the limited purity of *trans*-(**1**) (98·5 % pure).

(99·8%) and *trans*-(**1**) (98·5%)† were obtained by g.l.c. The stereochemical assignment was based on the magnitudes of the n.m.r. coupling constant between the two tertiary protons (J_{trans} 6·5 Hz, J_{cis} 8·5 Hz).[3] Thermolyses were carried out in n-decane (not degassed) in sealed ampoules and the rates and products were examined by g.l.c. The thermolysis followed first-order kinetics to give 1-phenylpent-1-ene (**2**) quantitatively and paraformaldehyde. Reversion to benzaldehyde and pent-1-ene was not observed.[4] The product olefins were characterized by comparisons with authentic specimens.[5] Results are summarized in the Table. Control experiments indicated that isomerization of oxetans and olefins did not take place under the experimental conditions.



cis – (1) *cis*–(2) *trans*– (2)



trans – (1) *trans* – (2)

As shown in the Table, *trans*-(**1**) decomposed more rapidly than *cis*-(**1**) by a factor of *ca.* 2. The only olefin produced in the thermolysis of *trans*-(**1**) was *trans*-(**2**), in marked contrast to *cis*-(**1**) which gave a mixture of *cis*-(**2**) and *trans*-(**2**). The presence of a trace of CCl_3Br however, accelerated the thermolysis and resulted in loss of stereospecificity in the thermolysis of *trans*-(**1**); the ratio *cis*-(**2**)/*trans*-(**2**) was 0·27 at 290°. Similarly, *cis*-(**1**) yielded an olefinic mixture in a ratio of 0·32 in the presence of CCl_3Br. Hydrogen chloride and trifluoroacetic acid, on the other hand, did not show significant catalytic activity. t-Butyl peroxide resulted in the formation of polymeric material, in addition to some minor products other than (**2**).

These results may be explained by an assumption that *trans*-(**1**) fragments through a concerted $2s + 2a$ pathway,[6] while *cis*-(**1**) decomposes to olefin and formaldehyde, at least in part, *via* a diradical intermediate. In the $2s + 2a$ transition state, the four-membered ring is twisted[6] in such a way that considerable destabilization by non-bonded repulsions occurs in the *cis*-isomer.

(*Received*, 11*th June* 1974; *Com.* 682.)

---

† Samples exhibited satisfactory elemental and spectroscopic analyses.

[1] N. Shimizu, M. Ishikawa, K. Ishikura, and S. Nishida, *J. Amer. Chem. Soc.*, in the press.

[2] H. R. Gerberich and W. D. Walter, *J. Amer. Chem. Soc.*, 1965, **83**, 3935.

[3] J. A. Barltrop and H. A. J. Carless, *J. Amer. Chem. Soc.*, 1972, **94**, 1951.

[4] For the regioselectivity of oxetan thermolysis, see: G. Jones, II, S. R. Schwartz, and M. T. Marton, *J.C.S. Chem. Comm.*, 1973, 374.

[5] M. Schlosers and K. F. Christmann, *Annalen*, 1967, **708**, 1.

[6] R. B. Woodward and R. Hoffmann, 'The Conservation of Orbital Symmetry,' Academic Press, New York, 1970.