Evidence for the Formation of Unscavengeable Diradical Intermediates in the Photolysis of *cis*- and *trans*-3-Ethyl-2-propylthietan

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Summary The gas-phase photolysis of either *cis*- or *trans*-3-ethyl-2-propylthietan produces but-1-ene, *cis*- and *trans*-hept-3-ene, and isomerized substrate, the yields of which are unaffected by adding NO or CO_2; a short-lived diradical intermediate is indicated.

Insight into the detailed mechanisms of the photolysis and thermolysis of pyrazolines, cyclic ketones, and cyclic sulphides has been obtained from an analysis of product stereochemistry,[1] by emission and e.s.r. spectroscopy,[2] and by diradical trapping experiments.[3,4] We have shown previously[4] that in the photolysis of thietan vapour, the addition of common radical and diradical trapping agents (NO, O_2, and labile hydrogen donors) has no measureable effect on the yields of the primary products, C_2H_4 and CH_2S. However, it was impossible to distinguish unequivocally between the formation of the primary decomposition products *via* a molecular pathway or *via* initial single bond cleavage yielding a short-lived diradical. We present evidence here that in the thietan photolysis system the latter possibility is most likely correct.

cis- and *trans*-3-Ethyl-2-propylthietan were prepared by the method of Searles, Hays, and Lutz[5] and were separated and purified by preparative gas chromatography. Photolysis of the two isomers at 200 °C and 313 nm for 24 h gave the products shown in the Table. The addition of 10 Torr NO as a radical and diradical scavenger or 760 Torr CO_2 as an inert deactivating agent had no measureable effect on the yields. Dark reactions carried out under similar conditions produced no decomposition or isomerization of either isomer.

TABLE

Isomer	Pressure of substrate (Torr)[a]	Yields (mol × 10^6) A	B	C	D
cis	5·90	1·66	1·19	0·59	2·52[b]
	9·85	2·44	1·91	0·98	—
trans	5·90	1·37	0·28	1·87	1·29
	9·00	1·83	0·42	2·97	—

A ≡ but-1-ene, B ≡ *cis*-hept-3-ene, C ≡ *trans*-hept-3-ene, D ≡ isomerized substrate.

[a] At 85 °C. [b] Corrected for a small amount of isomeric impurity in the starting material.

The fact that both *cis*- and *trans*-hept-3-ene isomers together with isomerized substrate are obtained on photolysis of either thietan isomer is indicative of initial C–S cleavage to form a diradical in which C–C bond rotation can occur. However, the magnitudes of the *trans*- to *cis*-hept-3-ene product ratios observed (0·506 from the *cis*-isomer and 6·88 from the *trans*-isomer) reflect a tendency for the olefin to retain the configuration of the substrate. This observation, together with the lack of effect of NO or CO_2, indicates that the diradical formed initially is very short-lived and decomposes to olefin and thioaldehyde before complete isomerization is effected and before scavenging can occur. This tendency to retain configuration is apparently greater in the photolysis of the *trans*-isomer and is possibly a consequence of the presence of greater steric compression in the initially formed *cis*-diradical than in the corresponding *trans*-diradical. Although the possibility that part of the products are formed *via* a concerted cleavage cannot be totally eliminated, the evidence presented here indicates that such a process should be of secondary importance.

Within experimental error, photolysis of the *cis*-isomer yields equal amounts of butene and heptene, indicating that cleavage of either C–S bond occurs with equal probability. There does appear to be some preference for C-2–S cleavage on photolysis of the *trans*-isomer, however, as the ratio of heptene to butene products is **1·71 ± 0·14**.

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