

## The Photolysis of Tetraphenylethylene Episulfide

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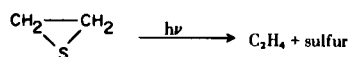
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The major process in the photolytic decomposition of oxirane (1) and cyclopropane (2) is photorearrangement with double bond formation which is accompanied by secondary fragmentations. In contrast, thiirane (3) undergoes primarily desulfurization, while very little isomerization to thioacetaldehyde occurs. The difference in



behavior observed for the three-membered carbocyclic and oxoheterocyclic compounds, on the one hand, and the sulfur analog on the other, has been attributed (4) to the much larger enthalpy changes which accompany transformations of C-O and C-C single bonds to double bonds compared to that for the C-S→C=S transformations. The reduction in driving force probably accounts for the striking differences observed. Similar arguments involving the relative magnitudes of enthalpy changes have been advanced to explain the differences in the behavior between ground state CH<sub>2</sub>, O, and S atoms in cycloadditions to ethylene (5) and acetylene (4).

*vic*-Aryl substitution alters the photochemical behavior of oxiranes (6) and cyclopropanes (7). Photolysis of tetraphenylethylene oxide, for example, gives mainly diphenylmethylene and benzophenone, and similarly 1,1,2,2-tetraphenylcyclopropane yields primarily diphenylmethylene and 1,1-diphenylethylene. The photolytic fate of tetraphenylethylene episulfide (I) in contrast had not yet been examined and a study of the primary mode(s) of photodecomposition was obviously of interest.

The long wavelength tail of the uv spectrum (6) of the episulfide I extends above 280 nm and photolysis is feasible with Pyrex-filtered light. Four identical samples, each consisting of four ml. of a 0.1 M solution of I in cyclopentene sealed in evacuated Pyrex tubes, were irradiated with a 450 watt Hanovia medium pressure mercury lamp until decomposition of I was complete

(24 hours). The products were identified by comparison of their properties with the glc retention times, nmr, and mass spectra of synthetic samples. The reaction products retrieved, and the observed yields were: 9,10-diphenylphenanthrene (II) (100%), bi-3-cyclopenten-1-yl (III) (~40%), cyclopentene episulfide (IV) (25%), hydrogen sulfide (5%), hydrogen, traces of cyclopentylmercaptan, and a yellow solid, probably elemental sulfur. The quantitative conversion of I to II clearly shows that sulfur extrusion is the principal primary process and carbon-carbon bond cleavage is negligible. Since cyclopentene is an excellent scavenger of the SH radical and of H atoms, hydrogen sulfide and hydrogen must be formed by molecular processes, and cyclopentene episulfide through intervention of ground state S atoms or a direct transfer of sulfur from excited I to cyclopentene. It is also noteworthy that diphenylmethylene could not be detected among the photoproducts of episulfide I by epr measurements at 77° K, (8), although epr studies earlier had shown that diphenylmethylene is formed in the low-temperature photolysis of tetraphenylloxirane. In addition, luminescence studies of the photolytic products of I indicate that the phenanthrene II is formed, but the luminescence of diphenylmethylene could not be detected (6). The following steps are believed to be implicated in the overall mechanism for the photodecomposition of I.

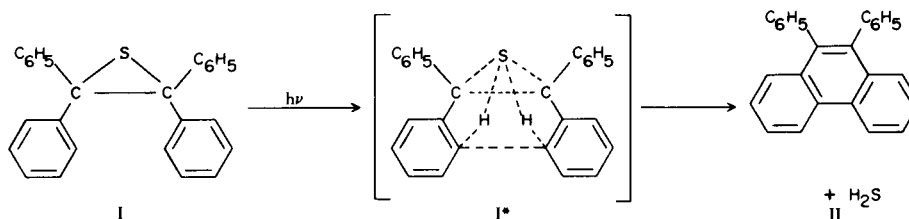
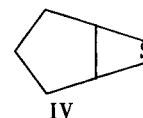
See Table

It is reasonable to assume that hydrogen sulfide elimination occurs from the first excited singlet state of I reached upon photon absorption. A possible transition state for the conversion of I to II is depicted below.

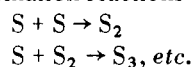
Intersystem crossing of excited I to the lowest triplet state is an efficient (95%) process. The triplet state must be invoked since cyclopentenyl mercaptans, which can only be formed from metastable S (<sup>1</sup>D) atoms (9), could not be found among the reaction products. The I (T<sub>1</sub>)\*

Table

$I(S_0) + h\nu$	$\longrightarrow$	$I(S_1)^*$	[1]
$I(S_1)^*$	$\xrightarrow{5\%}$	$II + H_2S$	[2]
$I(S_1)^*$	$\xrightarrow{95\%}$	$I(T_1)^*$	[3]
$I(T_1)^*$	$\xrightarrow{>37\%}$	$(C_6H_5)_2C=C(C_6H_5)_2 + S(^3P)$	[4]
$I(T_1)^* + C_5H_8$	$\xrightarrow{<58\%}$	$(C_6H_5)_2C=C(C_6H_5)_2 +$	[5]
$I(T_1)^* + C_6H_6$	$\longrightarrow$	$I(S_0) + C_5H_8$	[6]
$S(^3P) + I$	$\longrightarrow$	$(C_6H_5)_2C=C(C_6H_5)_2 + S_2$	[7]
$S(^3P) + C_5H_8S$	$\longrightarrow$	$C_5H_8 + S_2$	[8]
$S(^3P) + C_5H_8$	$\longrightarrow$	$C_5H_8S$	[9]
$(C_6H_5)_2C=C(C_6H_5)_2$	$\xrightarrow{<60\%}$	$II + H_2$	[10]
$(C_6H_5)_2C=C(C_6H_5)_2$	$\xrightarrow{>40\%}$	$II + H + H$	[11]
$H + C_5H_8$	$\longrightarrow$	$C_5H_9^{\cdot}$	[12]
$C_5H_9^{\cdot} + C_5H_8$	$\longrightarrow$	$C_5H_{10} + C_5H_7^{\cdot}$	[13]
$2C_5H_7^{\cdot}$	$\longrightarrow$	$III + C_5H_8 + C_5H_6$	[14]



molecules can suffer collisional deactivation by solvent molecules, transfer a sulfur atom to the olefinic bonds of cyclopentene, or decompose unimolecularly to tetraphenylethylene and a triplet ground state sulfur atom. If the only reaction mode leading to loss of sulfur from I is direct transfer then the photolysis should not take place in paraffinic solvents. Upon repeating the photolysis of I in cyclopentane solution under conditions otherwise identical, the reaction products included phenanthrene II (98%), hydrogen sulfide, hydrogen, and a yellow solid, probably sulfur. While the decomposition of I takes place readily under these conditions the rate of decomposition was found to be slightly lower than in cyclopentene; during the time required for the complete photolysis of I in cyclopentene (24 hours), only 75% decomposition occurred in cyclopentane. Thus, the extent of decomposition of step 4 is at least one-half of this, *viz.*, 37%, which is then followed by the abstraction step 7 and the combination reactions



The occurrence of these processes has been shown in

earlier gas phase studies from which the relative importance of steps 7 and 8 can be estimated as being at least 10%, as compared to step 9, but probably much higher. These reactions explain the low yield of cyclopentene episulfide (IV) and the formation of elemental sulfur.

The photolysis of tetraphenylethylene (steps 10 and 11) was examined in an auxiliary experiment. Under identical conditions 80% conversion to II occurred during a 24 hour irradiation period. Based on the yield of bi-3-cyclopenten-1-yl, the molecular mode of hydrogen elimination is less than 60%. It should be noted that the analogous cyclization process, the formation of phenanthrene in the photolysis of *cis*-stilbene sulfide (11) and other stilbene derivatives (12) has been reported in the literature. The reaction reportedly requires the presence of a suitable oxidant such as oxygen, iodine or sulfur; however, no such oxidants are required in the photolytic conversion of I to II possibly because sulfur is formed in the reaction. Other examples of photoextrusion have been reported by Padwa and co-workers (13). The driving force for the desulfurization of carbonyl substituted episulfides reported by these investigators is attributed

to the tendency of the excited state having the  $n, \pi^*$  (CO) configuration to eliminate  $\alpha$ -substituents as odd-electron species. Since photoextrusion is an efficient process for other episulfides not bearing carbonyl substituents the role of the  $n, \pi^*$  excited state in the desulfurization process may not be crucial.

The hydrogen atoms produced in the reaction II add readily to the cyclopentene solvent molecules to give the cyclopentyl radical which can abstract an allylic hydrogen from a second solvent molecule to give cyclopentane and a cyclopentenyl radical. The observed dimer III arises from a combination of two such radicals (step 14). No attempt was made, however, to detect the expected cyclopentane or cyclopentadiene.

Thus, it is concluded from the present study that tetraphenyl substitution in thiirane does not alter the photolytic behavior of thiirane; the decomposition is characterized by sulfur elimination in the absence of any detectable products arising from carbon-carbon bond cleavage. This conforms to the general behavior of organosulfur compounds which exhibit a marked reluctance to undergo transformations in which the carbon-sulfur single bond is converted to a double bond (4).

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