PHOTOLYSIS OF ALKENYL DISULFIDE

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Several alkenyl disulfides were prepared and the products of the photolysis were determined. The main products in this reaction were not thiacycloalkanes but unexpected 3-thiacycloalkanylalkenyl sulfides.

The photochemical behavior of the alkenyl thiols has been reported by many workers.$^{1)}$ In this case, the main products obtained were the mixture of two possible products, anti-Markovnikov type addition compound(2) and Markovnikov type addition compound(3), in 30 - 100% yields. A typical result$^{1c)}$ is shown below.

(1) (2) (3)

The initial step of the photolysis of this alkenethiol gives undoubtedly the alkenethiyl radical(1) which then attacks the double bond intramolecularily to form the products(2) and (3), of which product ratio is controlled by the thermodynamic stabilities of the two sulfides.

We have studied the photochemistry of a few alkenyl disulfides hoping to obtain similar results via the initial formation of alkenethiyl radicals and to study the difference of the photochemical behaviors between alkenyl disulfides and corresponding thiols. The photolysis of the disulfides(concentration : 0.1 mol. lit^{-1}, solvent : i-PrOH) was carried out under irradiation with low pressure mercury lamp for 15 hr. at room temperature. The structure of the products was determined by nmr spectroscopy, elemental analyses and comparison with the authentic samples. In the photolysis of allyl disulfide, the expected products, such as, methylthiirane and 2,5-dimethyldithiane, which would be produced via the dimerization of allylthiyl radical initially formed, were not obtained, while practically no polymeric material was formed.

In the case of 4-pentenyl disulfide, the main product was unexpected 3-thiacyclohexyl 4-pentenyl sulfide(8): bp 91-2°/2mmHg, Elemental anal., Calcd., C%; 59.35, H%; 8.97, Found, C%; 59.82, H%; 9.03, besides a trace of thiacyclohexane(6).

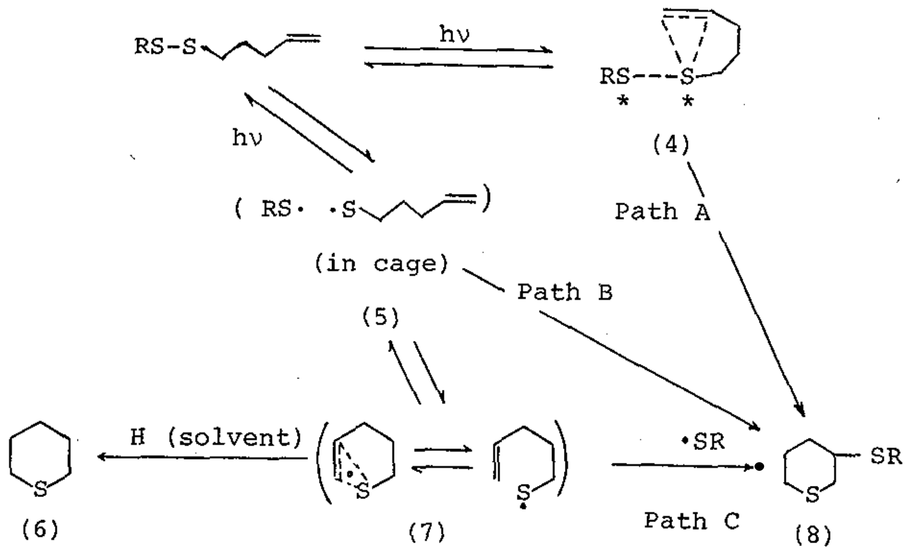
The uv spectral data, newly measured, are summarized at Table 1.

Table 1. UV Spectral Data of Some Alkenyl Disulfide.

(in EtOH)

Compound	λ_{max}	log ε
Allyl disulfide	213	2.8
4-Pentenyl disulfide	250	2.6
trans-4-Hexenyl disulfide	253	2.8
n-Pentenyl disulfide	264	2.8

Meanwhile, 3-thiacyclohexyl 4-pentenyl sulfide(8) has no significant absorption band in the uv spectrum. Thus, these observations seem to suggest that the photolysis of 4-pentenyl disulfide proceeds as shown below. (Scheme I)



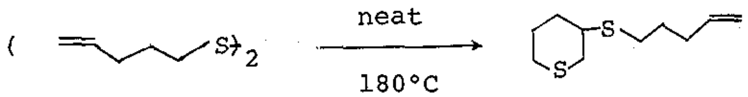
R= 4-pentenyl-

Scheme I.

Two probalble routes are conceivable for the formation of 3-thiacyclohexyl 4-pentenyl sulfide(8). One Path, ie., Path A, involves the excited stat(4) (this may be the $n - \sigma^*$ transition state of the disulfide group in view of the rather small value of $\log \varepsilon$ as shown in Table 1.) in which the double bond participates in the excited state, and the other, ie., Path B, which involves the thiyl radical pair in cage(5). The other path, ie., Path C, is quite inconceivable in view of the negligible amount of thiacyclohexane(6) and the lack of 2,5-dimethyldithiane in the photolysis of allyl disulfide. Evidence for the lack of the mixed compound(8, (R=Ph-) in the cross-over experiment of 4-pentenyl disulfide with diphenyl disulfide would also suggest strongly the unimportance of Path C. The lack of (6) would be also rationalized in terms of the weak hydrogen abstracting ability of the thiyl radical(7) and its marked affinity to the double bond in the addition.$^{2)}$

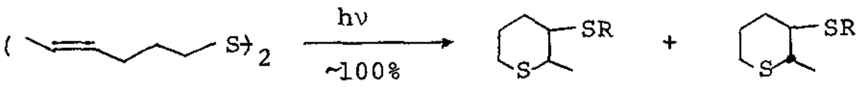
The thermal reaction of alkenyl disulfide is also interesting and may lead to the same products, since thiyl radicals are known to be formed by the thermolysis of disulfide.$^{3)}$

Indeed the thermal reaction of 4-pentenyl disulfide using no solvent, the product obtained in nearly quantitative yield at 180°C was also 3-thiacyclohexyl 4-pentenylsulfide(8) (reaction rate is about 2.6×10^{-5} sec^{-1}, which is ten times slower than that of the photolysis).



(8)

Apparently this result also would suggest that there are definite interactions between the sulfur atoms and the double bond both in the ground state and also in the excited state of thiyl radical pair in cage(6) in Path B of Scheme I. In the reaction of trans-4-hexenyl disulfide the product obtained was a mixture of cis- and trans-2-methyl-3-thiacyclohexyl 4-hexenyl sulfide, (9) and (10).



R= 4-hexenyl-

(9) (10)

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