

PHOTO-INDUCED DESULFURIZATION OF STILBENE TRITHIOCARBONATE

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The chemistry of dithiocarbenes has been an area of continuing interest in the chemical literature.^{1,2} Corey and coworkers^{3,2,b} have converted trithiocarbonates to olefins by treatment with trialkyl phosphites at elevated temperatures, *via* a transient carbene. Schöllkopf⁽⁴⁾ and Lemal⁽⁵⁾ decomposed *p*-toluenesulfonyl hydrazone salts, thermally, leading ultimately to a tetrathioethylenes *via* a dithiocarbene intermediate.

Remarkable by its absence is a photochemical route to dithiocarbenes. Such a pathway would, perhaps, allow isolation or trapping of the carbene at very low temperature. The report by Blackman⁶ that photolysis of 1,2,4-triazoline-3-thione produces 1,2,4-triazole (and that this reaction is "unaffected by O₂") tempts one to surmise that a carbene is an intermediate and that it inserts into the neighboring N-H bond to give product.

An investigation of the photochemistry of a number of cyclic trithiocarbonates was undertaken to determine if a photochemical route to dithiocarbenes were feasible. In every instance tried, irradiation of absolute ethanol solutions of the trithiocarbonates (Hanovia 450 watt Hg arc, Pyrex filter), under N₂, caused the absorption band of the trithiocarbonate group at 320 nm gradually to disappear. Only when *cis*- or *trans*-stilbene trithiocarbonate⁷ was irradiated was a new absorbance observed (a complex series of bands with λ_{max} at 250 nm) to increase as the trithiocarbonate band decreased. Regardless of which isomer was chosen (*cis* or *trans*) the same fluorescent, white solid, mp. 100°, was isolated by preparative tlc on silica gel (sulfur-free, Na-fusion). The infrared, mass and nmr spectra are identical with the data obtained from an authentic sample of phenanthrene. (Absorptions (uv, ir, nmr) characteristic of stilbene or stilbene-like products are evident in the impure samples of the

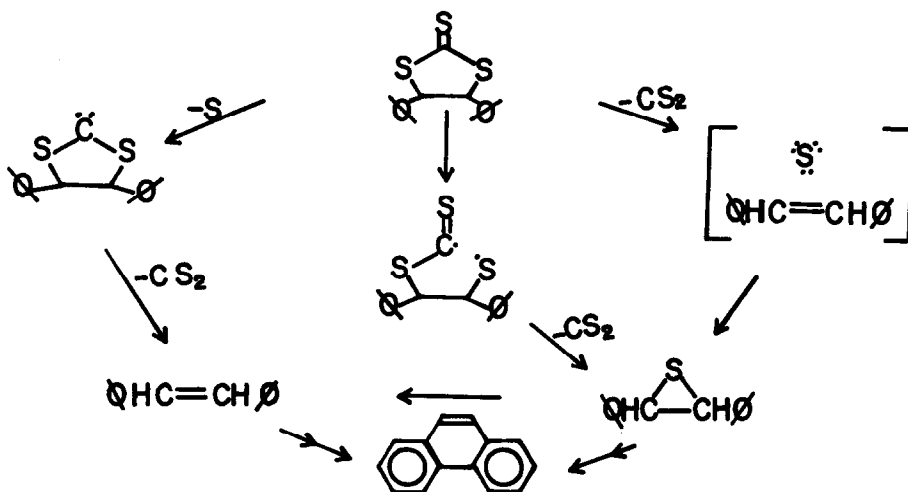
photoproduct obtained from preparative-scale photolyses.)

The propensity of stilbene to cyclize to phenanthrene is well documented.⁸ However, the instance at hand differs from the general case in that the oxidizing agent needed to convert the dihydrophenanthrene intermediate to the final product is not added to the reaction vessel (usually, the combination of I_2 and O_2 is used) but is generated during the photolysis, i.e., atomic sulfur.⁹

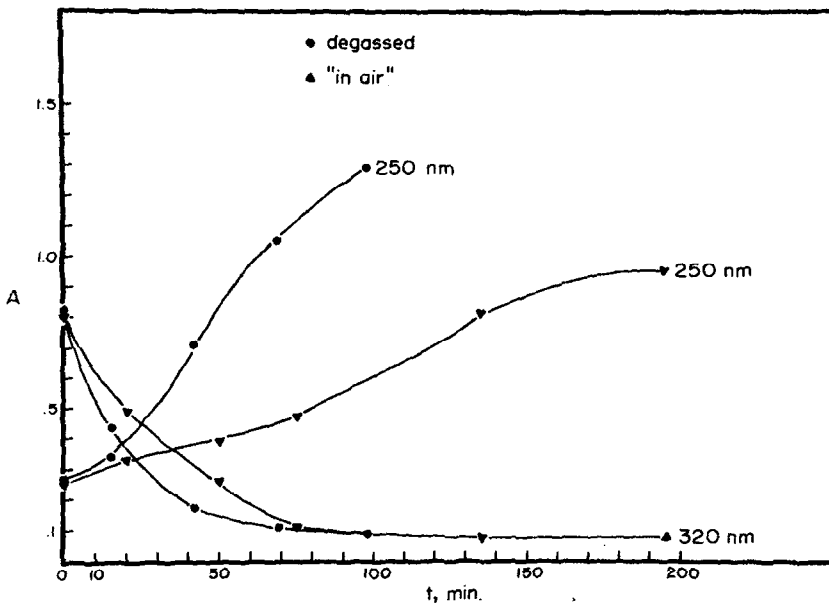
Kinetic measurements were made by monitoring the disappearance and appearance of trithiocarbonate and phenanthrene, respectively, in the presence of air and in degassed cells, *in vacuo*. The data do not allow meaningful comparisons of reaction rates between the *cis* or *trans* isomers (because of contributions to the absorption spectrum from other products) but, in both instances, the rate of formation of phenanthrene is much slower in the presence of air than in its substantial absence, while the rate of disappearance of starting material is essentially unchanged.

A possible explanation of these results is that the agent causing the dehydrogenation of the intermediate is atomic sulfur in the triplet state ($S(^3P)$) and that oxygen functions as a radical scavenger, decreasing the rate at which the phenanthrene is formed.¹⁰

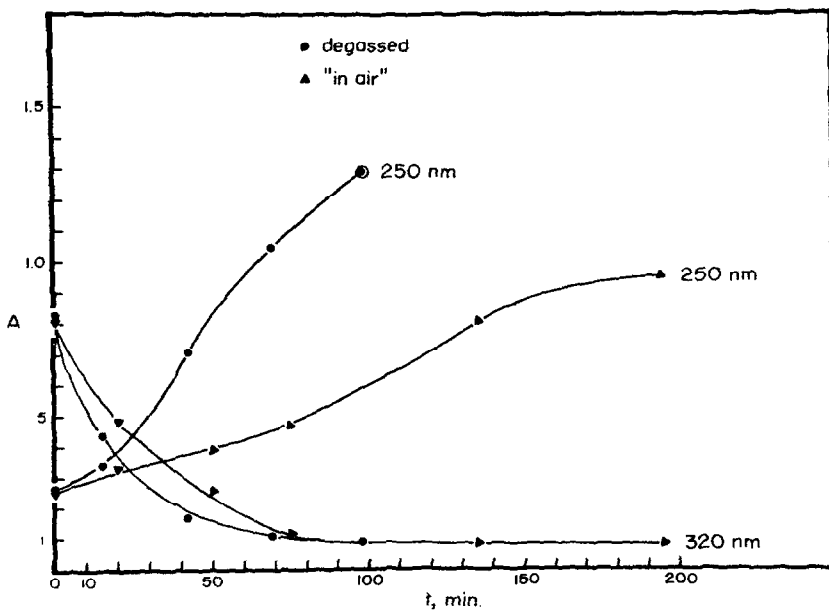
An overview of the possible mechanistic paths operative in this system is given below.



Photolysis of trans-stilbenetrithiocarbonate



Photolysis of cis-stilbenetrithiocarbonate



We are currently investigating the scope and stereochemical nature of this reaction in systems of the type $X-\overset{\text{S}}{\text{C}}-Y$ where X and Y may be O, N, S, etc.

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