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Matrix Isolation Study of the Vacuum Ultraviolet Photolysis of Methyl Mercaptan. Spectroscopic Evidence for Thioformaldehyde

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H_2CS has been trapped in argon and nitrogen matrices at 14 K as a product of the ultraviolet or vacuum ultraviolet photolysis of CH_3SH . A small concentration of H_2CS has also been observed upon vacuum ultra-violet photolysis of a mixture of CH_4 and H_2S in an argon matrix. The isotopic data support the assignment of absorptions at 993 and at 1063 cm^{-1} to the out-of-plane deformation and the $\text{C}=\text{S}$ stretching fundamentals of H_2CS in an earlier gas-phase study [1] were confirmed in the matrix experiments. The formation of substantial concentrations of both HDCS and D_2CS on vacuum ultraviolet photolysis of CD_3SH suggests that photolytic rupture of a $\text{C}-\text{D}$ bond followed by rapid intramolecular rearrangement of CD_2SH to CHD_2S may occur on exposure of the sample to radiation of wavelength shorter than 2500 \AA . Subsequent photolysis of this intermediate by vacuum ultraviolet or ultraviolet radiation leads to the formation of thioformaldehyde.

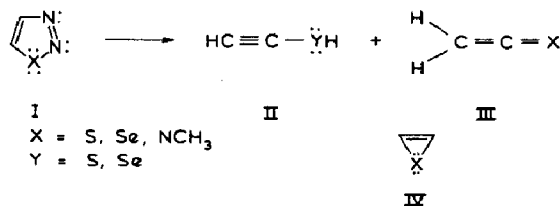
1 J. W. C. Johns and W. B. Olson, *J. Mol. Spectrosc.*, **39** (1971) 479.

S3

Photolysis of Matrix-isolated 5-Membered Heterocycles

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The photodecomposition of 1,2,3-thiadiazole I ($\text{X} = \text{S}$) in inert gas matrices at 8 K using Pyrex filtered light leads to thioketene and ethynyl mercaptan. The photodecomposition of 1,2,3-selenadiazole I ($\text{X} = \text{Se}$) under the same conditions produces selenaketene and ethynyl selenol as well as acetylene. Photolysis of the



N-methyltriazole I ($\text{X} = \text{N}-\text{CH}_3$) gives the hetero *N*-methyl ketenimine, apparently free of ethynyl amine. Labeling experiments designed to detect potential anti-aromatic intermediates IV will be described.

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Radiative and Radiationless Processes Involving the Second Excited Singlet State of Thiocarbonyl Compounds

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Recent evidence [1, 2, 3] indicates that both fluorescence and photochemical processes may originate from the second excited singlet state of thiocarbonyl compounds. In the present paper experimental evidence that fluorescence is obtained in high yield from S_2 of thiophosgene, Cl_2CS , and other thiocarbonyl compounds is presented and discussed.

The S_2-S_0 adsorption, emission and excitation spectra of thiophosgene vapour have been measured and the observed single vibronic transitions assigned. Comparison of the absorption and excitation spectra reveals that emission is excited only when transitions to the upper state terminate in $3^m 4^n$ [4], m or $n = 0$ or 1, and that the upper state is depopulated by rapid radiationless processes when higher vibrational levels are populated. The most prominent bands in the emission spectrum are those in which the transitions terminate in $1_p 3_q 4_r$ [4] with $1 < p < 10$, $1 < q < 5$ and $1 < r < 4$. All three types of spectra are consistent with a pyramidal excited state in which equilibrium internuclear distances are substantially greater than those of the ground state. The implications of this fluorescence anomaly with respect to the nature of radiationless

processes in thiophosgene and other thiocarbonyl compounds will be discussed.

- 1 S. Levine, A. R. Knight and R. P. Steer, *Chem. Phys. Letters*, 29 (1974) 73.
- 2 J. R. Huber and M. Mahoney, *Chem. Phys. Letters*, 30 (1975) 410.
- 3 P. de Mayo and H. Shizuka, *Mol. Photochem.*, 5 (1973) 339.
- 4 Modes 1, 3 and 4 are the C-S stretch, CCl_2 scissor and out-of-plane bend, respectively.

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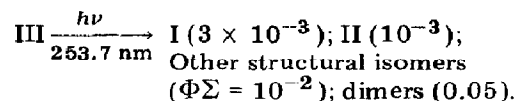
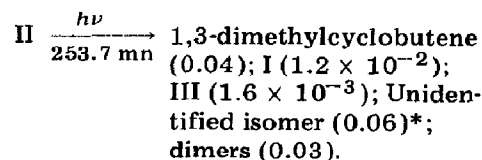
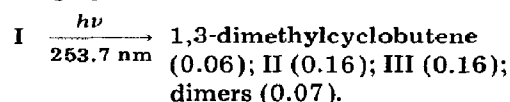
Photochemical Behavior of Acyclic 1,3 Dienes: Mechanistic Implications of 1,5-Hydrogen Shifts in the S_1 State[†]

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The present knowledge of the photochemical behavior of acyclic conjugated dienes and the properties of the S_1 state which were subsequently deduced are largely based on quantitative studies carried out on the 1,3-pentadienes and to a smaller extent on the 2,4-hexadienes [1]. Thus it has been proposed that the S_1 dienes first relax by a twist of one p_π orbital, yielding an allylmethylene entity which then internally converts into the corresponding geometry of S_0 [1], unless the possibility exists (for the *s-cis* conformers) that a concerted 1,4 overlap leads to a cyclobutene, this last process being then preferred [2]. The alternative hypothesis has been put forward that prior to internal conversion the S_1 state relaxes by acquiring a "bicyclobutane-like" conformation via a double twist of p_π orbitals [3]. Thus far the 1,5 shift of hydrogen has not been envisioned as a possibly efficient way for deactivating the S_1 state of dienes, presumably because it was considered as arising exclusively from a *cis-s-cis* configuration whose population is generally negligible at room temperature. However, since most quantitative anal-

[†] A full paper on this work has been submitted for publication in the *J.C.S. Perkin II*.

yses have dealt with the pentadienes, should a 1,5 shift have taken place it would not have been observed for it corresponds to an identity reaction. Therefore we looked at the three photochemically interconvertible dienes *cis*-2-methylpenta-1,3-diene(I), *trans*-2-methylpenta-1,3-diene(II) and 4-methylpenta-1,3-diene(III) which constitute a well suited system for studying photochemical competitive processes and in particular the efficiency of 1,5 hydrogen migrations relative to the 1,4 cyclomerization and to the geometrical isomerization [4]. The data are summarized hereunder, the initial Φ being given in parentheses for a starting concentration ranging around 10^{-1} mol l^{-1} .



The kinetic study shows that in opposition to former conclusions [4], 1,3-dimethylcyclobutene directly arises from the singlet excited state of I, indicating that this diene largely assumes a *s-cis* ground state conformation as was suggested by its UV spectrum. The results emphasize that both the isomerization to cyclobutenes and the 1,5 shift of a hydrogen may play an important role in the $S_1 \rightarrow S_0$ decay of a *s-cis* diene while *s-trans* conformers mainly return to their ground state by internal conversion. It was shown however unambiguously that *trans* configurations do undergo, though with a low quantum yield, the 1,5 sigmatropic shift (II \rightarrow III and III \rightarrow II); this definitely rules out the allylmethylene structure for at

*This compound proved photochemically labile and it was not possible, in a preparative run, to accumulate enough of it for spectroscopic analyses.