

A NEW UNUSUAL PHOTOISOMERIZATION OF SYDNONES

Hans Gotthardt* and Friedemann Reiter

FB 9 - Lehrstuhl für Organische Chemie, Gesamthochschule Wuppertal

Gaubstr. 20, D-5600 Wuppertal 1, BRD

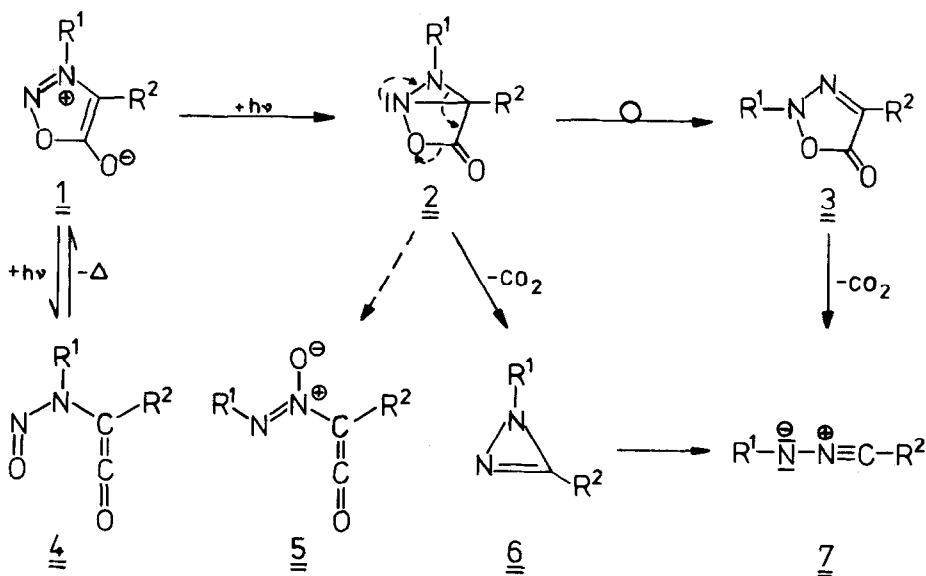
Alfred Gieren and Viktor Lamm

Max-Planck-Institut für Biochemie, Abteilung Strukturforschung I,

Am Klopferspitz, D-8033 Martinsried, BRD

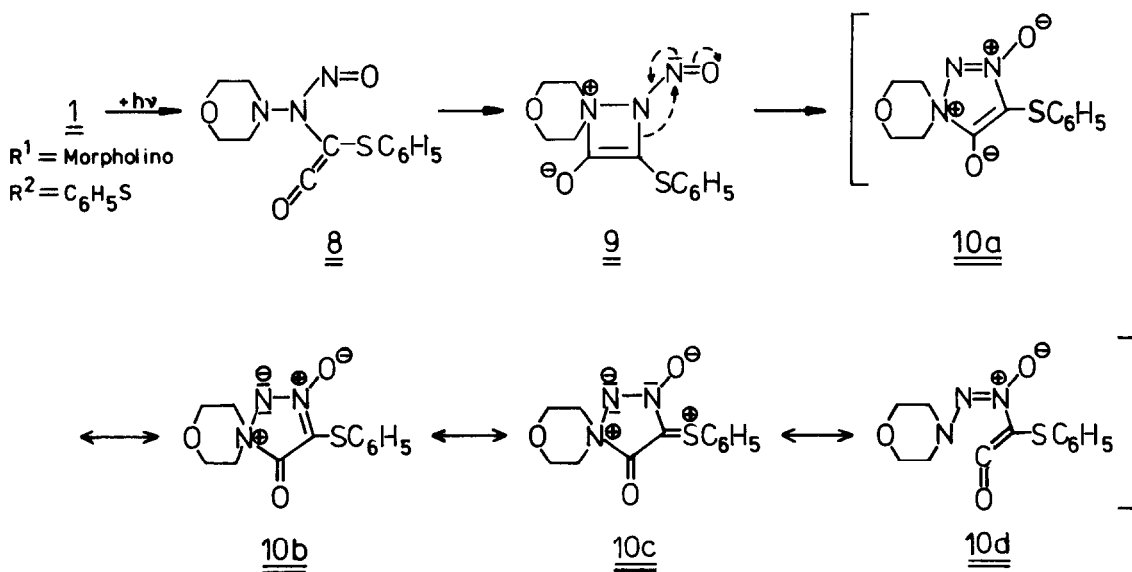
(Received in UK 30 March 1978; accepted for publication 4 May 1978)

After a first report¹, the investigation of the photochemistry of sydnones 1 has been the subject of independent and almost simultaneous study by several groups²⁻⁵. For example, it has been established that the light-induced reaction of several substituted sydnones 1 proceed with formation of non-isolable nitrile imines 7 by way of the postulated intermediates 2¹⁻⁶, 6¹⁻⁵ or 3⁶. In the presence of alkynes or alkenes, the photochemically generated 7 undergo [3+2] cycloaddition reactions leading to pyrazoles or pyrazolines, respectively²⁻⁵.

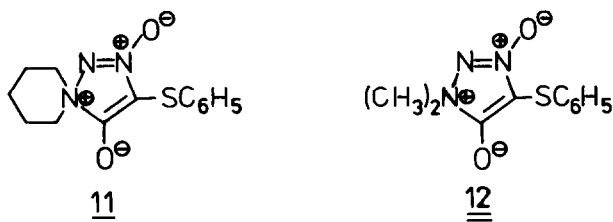


Now we have evidence for another photochemical process which probably involves the ketene derivatives 4 or 5 as intermediates. In this communication we wish to report on the synthesis, reaction pathway, and crystal structure analysis of new unusual photoisomers derived from sydnones.

When a benzene solution of 3-morpholino-4-phenylthio-sydnone 1 ($R^1 = \text{morpholino}$, $R^2 = \text{C}_6\text{H}_5\text{S}$)⁷ is irradiated ($\lambda \approx 300 \text{ nm}$, or $\geq 400 \text{ nm}$) in a quartz tube, colorless crystals of a new sydnone photoisomer 10 (15% yield, mp 179–181°C dec, from ethyl acetate) and diphenyldisulfide (22% yield) as well as some unreacted sydnone are obtained after thin layer chromatography on silica gel. 10 shows the following spectroscopic data: ir (KBr), 1780, 1769 (C=O), 1327 cm^{-1} (N-O); uv (CH_2Cl_2), λ_{max} (lg ϵ) = 235 (4.24), 329 nm (3.75); ¹H-NMR (60 MHz, [D_6]DMSO), $\tau = 6.10\text{--}6.68$ (m, 2 NCH₂), 5.70–6.10 (m, 2 OCH₂), 2.78 (s, C₆H₅); ms (70 eV), $m/e = 279$ (93%, M⁺), 135 (46, C₆H₅SCN⁺), 128 (100, C₅H₈N₂O₂⁺).



The analogous photoreaction of 1 ($R^1 = \text{piperidino}$, $R^2 = \text{C}_6\text{H}_5\text{S}$)⁷ in benzene, acetone or methylene chloride afford the isomer 11 (mp 190–191.5°C dec) in 14–27% yield and 24% diphenyldisulfide (11: ir, 1778, 1763 (C=O), 1332 cm^{-1} (N-O); uv (CH_2Cl_2), λ_{max} (lg ϵ) = 236 (4.26), 328 nm (3.77); ¹H-NMR (CDCl_3), $\tau = 7.48\text{--}8.47$ (m, 3 CH₂), 7.08–5.97 (m, 2 NCH₂), 2.78 (s, C₆H₅); ms, $m/e = 277$ (80%, M⁺)).



Similarly, the light-induced reaction of 1 ($R^1 = \text{N}(\text{CH}_3)_2$, $R^2 = \text{C}_6\text{H}_5\text{S}$)⁷ in benzene produces 12 (mp 154.5–155.5°C dec) in 18–22% yield and diphenyldisulfide (20%) (12: ir, 1776

(C=O), 1342 cm^{-1} (N-O); $^1\text{H-NMR}$ (CDCl_3), $\tau = 6.75$ (s, $\text{N}(\text{CH}_3)_2$), 2.73 (s, C_6H_5); ms, $m/e = 237$ (100% , M^+), 135 (53 , $\text{C}_6\text{H}_5\text{SCN}^+$), 86 (89 , $\text{C}_3\text{H}_6\text{N}_2\text{O}^+$).

Since several possible structures for the photoisomers did not give full agreement with the spectroscopic data, an X-ray structure analysis of 10 was performed which showed unexpectedly the spirane 10.

10 crystallizes from a mixture of methanol/ethyl acetate (95:5) in the monoclinic space group $P2_1/b$ with $a=12.743$, $b=23.106$, $c=9.555\text{ \AA}$, $\gamma=112.40^\circ$ and eight molecules per unit cell. The crystal structure contains two independent molecules. On an automatic single crystal diffractometer, 4754 independent reflexions were measured with Cu K_α -radiation. The structure was solved by direct methods and refined by least-squares methods. All hydrogen atoms were found by difference Fourier syntheses and were included into the refinement. The R-value converged to 5.8% (3681 observed reflexions). Except for the twofold coordinated N atom, the classification (C or N) of the atoms in the heterocyclic five-membered ring was not straightforward. It was unambiguously performed and proved by temperature factor comparison, by parallel least-squares refinements, Fourier syntheses, and difference maps of the six alternative models⁸. 11 was also investigated by X-ray methods. It crystallizes from ethyl acetate isomorphously with 10: $a=13.12$, $b=23.10$, $c=9.56\text{ \AA}$, $\gamma=112.40^\circ$. Therefore the conclusion can be drawn, that its molecular structure is the same as 10, except of the change of the oxygen atom in the morpholine ring in 10 by a CH_2 group in the piperidine ring in 11.

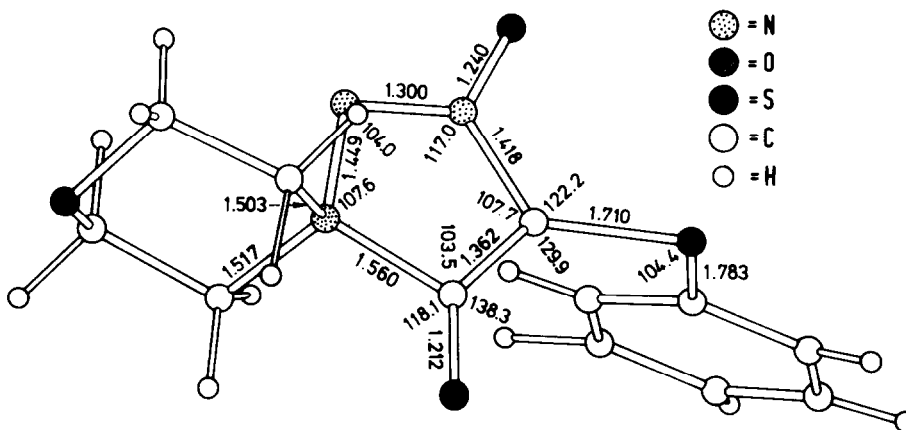


FIGURE 1. Molecular structure of 10. The distances and angles given are averaged values of the two molecules in the asymmetric unit.

The molecular structure of 10 is shown in the FIGURE 1. The five-membered heterocyclic ring and its oxygen and sulphur atom substituents are coplanar. The S-phenyl substituted C-atom of this heterocyclic ring and the S-phenyl group are also almost coplanar. These planes are nearly perpendicular to each other. The bond distances and angles lead to a bonding

discription via the resonance formulae 10a-d. Accordingly, the compound can be regarded as a *frozen transition state* of a nucleophilic addition of the amino nitrogen of the morpholine ring on the carbonyl-carbon of a ketene group. The significantly elongated single bond distance between these two atoms and the short C-O distance as well as the deformation of the angles at the C-O group show the participation of formula 10d.

Since, this surprising formation of 10 was neither sensitized, using acetone as triplet sensitizer, nor quenched in the presence of 1.7 m piperylene, we assume that the first step of the isomerization of 1 to 10 proceeds via the $^1(\pi, \pi^*)$ state of 1. Two possible alternative reaction pathways can be discussed. The first involves the formation of the valence tautomer 8 by way of an electrocyclic ring-opening of the sydnone 1. Intramolecular nucleophilic attack of the amino nitrogen on the carbonyl carbon of the ketene 8 converts 8 to the four-membered ring 9, which undergoes ring-expansion to the spiro compound 10. A second and more direct way includes the previously postulated bicyclic intermediate 2 followed by ring-opening to the ketene derivative 5 which collapses to 10. The observed formation of diphenyl-disulfide is a result of secondary photolysis of the C-S bond followed by recombination of the generated phenylthio radicals.

All new described compounds gave satisfactory analytical results.

Acknowledgement: This work was supported by the *Fonds der Chemischen Industrie*.

REFERENCES

1. C.H.Krauch, J.Kuhls, and H.-J.Piek, *Tetrahedron Lett.* 1966, 4043.
2. H.Gotthardt and F.Reiter, *Tetrahedron Lett.* 1971, 2749.
3. M.Märky, H.-J.Hansen, and H.Schmid, *Helv.Chim.Acta* 54, 1275 (1971).
4. C.S.Angadiyavar and M.V.George, *J.Org.Chem.* 36, 1589 (1971).
5. Y.Husaya, A.Chinone, and M.Ohta, *Bull.Chem.Soc.Jpn.* 44, 1667 (1971); 45, 3202 (1972).
6. H.Kato, T.Shiba, E.Kitajima, T.Kiyosawa, F.Yamada, and T.Nishiyama, *J.Chem.Soc., Perkin Trans. 1*, 1976, 863.
7. The sydnones were prepared according to the procedure described by K.Masuda and T.Okutani, *Jap.Pat.* 7020902 (1970); *Chem.Abstr.* 73, 87927m (1970); *Tetrahedron* 30, 409 (1974).
8. A.Gieren and V.Lamm, *Acta Crystallogr.*, manuscript in preparation.