

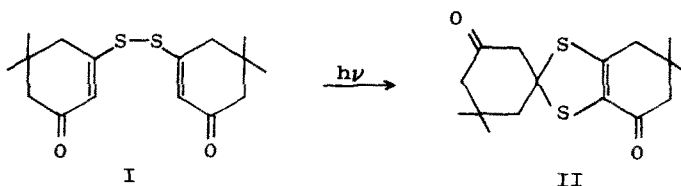
A NEW PHOTO-REARRANGEMENT OF A DIVINYLDISULPHIDE¹

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Although the photochemistry of disulphides has been investigated,² the behaviour of α,β -unsaturated disulphides upon irradiation, to our knowledge, is quite unknown. As part of a study of the thermal and photochemical behaviour of enethiols and their derivatives,^{3,4} the vinyl disulphide⁵ I (m.p. 91°) was irradiated at 2537 Å, giving II in 79% yield (m.p. 167-9°).

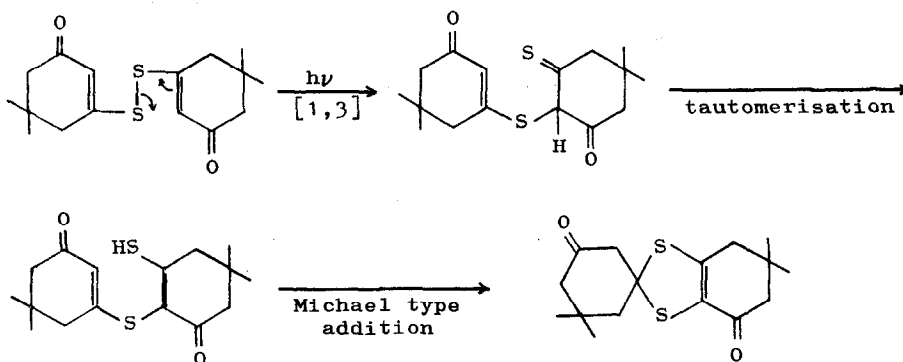


The procedure was that 5.00 g (0.016 mole) of I were dissolved in 200 ml 96% EtOH and irradiated with a low-pressure mercury arc (Rayonet, RS) for 18 hs. Part of II (1.22 g = 24%) solidified in the quartz reaction vessel while 2.73 g (55%) were obtained by evaporating most of the solvent. An amount of 0.26 g (5%) of I was recovered.

Spectroscopic data: **I:** NMR(CCl₄), 1.06(12H, s); 2.19(4H, s); 2.39(4H, d, 1.3); 6.03(2H, t, 1.3). IR ν_{\max}^{KBr} (cm⁻¹), 1650(s); 1580(s). UV(EtOH), 208 nm (log ϵ 3.96); 277 nm (log ϵ 4.26). MS, 310(26%); 277(100%); 155(33%). Anal., C, 61.95; H, 7.16; S, 20.21; C₁₆H₂₂O₂S₂ requires, C, 61.92; H, 7.15; S, 20.6%. **II:** NMR(CDCl₃), 1.05-1.15(12H, 3 singlets); 2.25-2.48(8H, broad singlets and AB splittings); 3.02(2H, br. s). IR $\nu_{\max}^{\text{CHCl}_3}$ (cm⁻¹), 1710(m-s); 1660(s); 1560(m). UV(CHCl₃), 250 nm (log ϵ 3.71); 350 nm (log ϵ 3.71). MS, 310(33%); 253(100%). Anal., C, 61.90; H, 7.12; S, 20.63; C₁₆H₂₂O₂S₂ requires, C, 61.92; H, 7.15; S, 20.6%.

The structure assigned to the photo-product is the most plausible of several possibilities, considering the spectroscopic data. A definite proof was provided by the ^{13}C off-resonance decoupled NMR spectrum of II. The residual splittings revealed the presence of 4 methyl-, 5 methylene-, and 7 quaternary carbon atoms, which appeared as quartets, triplets, and singlets, respectively.

The following mechanism is suggested for this novel reaction in which the first step might be a concerted suprafacial 1,3-sigmatropic rearrangement, allowed in the excited state.⁶ A radical mechanism could not be verified, because attempts to trap the expected thiyl radical with 1,1-dimethyl-1-nitroso-ethane failed.



The scope, versatility and mechanism of this rearrangement are currently being studied.

References and comments

1. A grant from Statens Naturvidenskabelige Forskningsråd is greatly acknowledged.
2. P.S.H.Bolman, I.Safarik, D.A.Stiles, W.J.R.Tyerman, and O.P.Strausz, Can.J. Chem. **48**, 3872 (1970) and refs. cited therein.
3. L.Dalgaard and S.-O.Lawesson, Tetrahedron **28**, 2051 (1972).
4. idem. *ibid.* (to be published).
5. Prepared from 3-chloro-5,5-dimethyl-2-cyclohexen-1-on and $\text{Na}_2\text{S}\cdot 9\text{H}_2\text{O}$ followed by oxidation with iodine.⁴
6. R.B.Woodward and R.Hoffmann, J. Am. Chem. Soc. **87**, 2511 (1965).