

CARBON-SULPHUR BOND CLEAVAGE IN THE PHOTOCHEMISTRY
of 9-THIABICYCLO[3.3.1]NONANDIONES.

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The mass spectra of diketosulphoxide (2) (M^+/e) 186 and diketosulphone (3) (M^+/e) 202 exhibit a prominent peak at m/e 138 indicating facile C-S bond cleavage under electron impact. In contrast diketosulphide (1)¹ (M^+/e) 170 shows only a low intensity peak at m/e 137 ($(M-S)^+$), the ion $(M-S)^+$ being absent. In the UV spectrum, 1 exhibits² a sulphur-carbonyl charge transfer band at 250 nm, not shown by 2.

Photolysis of cyclic β -ketosulphides yields^{3,4} products of C-S bond fission (C_α -S cleavage) as well as of α -cleavage and β -ketosulphoxides undergo photostereomutation,³ possibly caused by C-S homolysis. 1, 2 and 3 were thus photolysed to investigate how their photochemistry would reflect the above spectroscopic differences and to examine in particular the possibility of two C_α -S cleavages, effectively photochemical desulphurisation, occurring where a thioether (or its oxides) possesses two β -carbonyl groups.

Photolysis under N_2 of 1 in MeOH ($10^{-2}M$) with a medium-pressure Hg lamp gave photoproducts arising from both α - and C_α -S cleavages but all retained sulphur. After 2 hr the reaction mixture contained substrate, 4 (31%) [δ 1.95 (m, 2H; C-7), 2.5 (m, 6H; C-4, C-5, C-8), 2.8 (t, 2H, J = 3 Hz; C-6), 3.53 (t, 1H, J = 6 Hz; C-2) and 3.7 (s, 3H); $\nu_{max}(CCl_4)$ 1740 and 1714 cm^{-1}], 7 (2%) [δ ($CDCl_3$) 1.85 (m, 4H), 2.45 (m, 8H; CH_2S and CH_2CO) and 3.68 (s, 6H)], 8 (5%), m.p. ca. 23° [δ ($CDCl_3$) 1.95 (m, 8H), 2.55 (m, 16H; CH_2S and CH_2CO) and 3.68 (s, 6H); $\nu_{max}(CCl_4)$ 1740 and 1718 cm^{-1}] and a trimeric product. After 16 hr, 7 (4%), 8 (12%) and trimer were accompanied by 9 (26%) [δ ($CDCl_3$) 2.1 (m, 2H; C-6), 2.75 (m, 8H; CH_2S and CH_2CO), 3.4 (m, 1H; CHS) and 3.7 (s, 3H); $\nu_{max}(CCl_4)$ 1740 and 1712 cm^{-1}] but 4 and 1 were absent.

4 is formed (Scheme 1) by methanolysis of ylide (11) which arises through charge transfer (as in 10) and α -cleavage. The charge transfer mechanism is supported by the formation of 5 on photolysis of 1 in MeOD, the absence of 6 precluding a normal Norrish Type-1 process. 4 undergoes a second α -cleavage to give 7; alternatively, C_α -S fission and thiyl radical pairing gives 8. That 4 is a precursor of 7 and 8 is supported by its absence after 16 hr irradiation of 1 and is corroborated by the formation of 7 and 8 on photolysis of 4 itself.

9 Arises by α -cleavage and solvolysis of the β -ketosulphide moiety of 13. Rearrangement⁴ to 13 is achieved (Scheme 2) by C_α -S fission of 1, intramolecular hydrogen transfer and subsequent recyclisation of 12.

2, m.p. 190-193° [δ ($CDCl_3$) 2.6 (m, 8H) and 4.1 (m, 2H; $CHSO$); $\nu_{max}(KBr)$ 1695 and 1059 cm^{-1} ; $\lambda_{max}(EtOH)$ 230 (sh, ϵ^a 610), 298 (115) and 306 (115)] was obtained (80%) by $NaIO_4$ treatment of 1.¹ Jones oxidation of 14 furnished (15%) 3, m.p. 248-250° [δ (d_6 - Me_2CO) 2.4 (m, 4H), 2.8 (m, 4H) and 4.1 (m, 2H; $CHSO_2$); $\nu_{max}(KBr)$ 1705, 1305 and 1112 cm^{-1}].

Photolysis (20 hr) of 2 in MeOH or Me₂CO gave the desulphurised and photo-reduced dione (15)⁵ (15%), m.p. ca. 23° [δ (CDCl₃) 2.2 (m, 4H) and 2.5 (m, 8H)]. 4 Hr irradiation of 3 in MeOH furnished both 15 (8%) and the transannularly coupled dione (18)⁶ (10%) as an oily solid [δ (CDCl₃) 2.23 (m, 8H) and 2.93 (m, 2H)]. Aliquots taken during each reaction showed a concentration-dependent, deuterium-exchangeable signal in the NMR spectrum, ascribed to the OH absorption of the sulphenic (16) and sulphinic (17) acids, indicating sequential, rather than concerted C-S cleavage. Unsuccessful attempts were made to trap 16 and 17 as their methyl acrylate or N-phenylmaleimide adducts.⁷

Thus in the photochemistry of 1, 2 and 3 complete sulphur removal is encountered only where the sulphur bridge is in an oxidised form.

Satisfactory analytical data have been obtained for 2-4, 7-9, 15 and 18.

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References

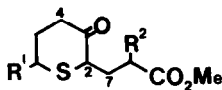
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1 Z = S

2 Z = SO

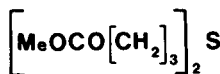
3 Z = SO₂



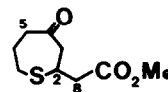
4 R¹ = R² = H

5 R¹ = D, R² = H

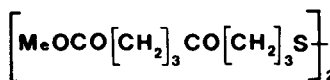
6 R¹ = H, R² = D



7

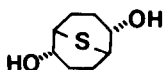
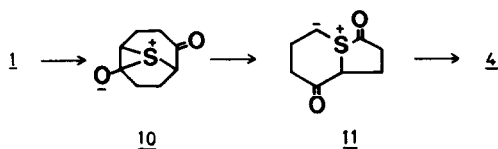


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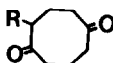


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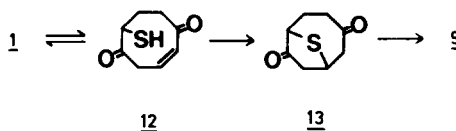
SCHEME 1



14



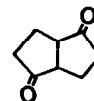
SCHEME 2



15 R = H

16 R = SOH

17 R = SO₂H



18