

Four-membered Ring Adducts from $2\pi + 2\pi$ Cycloaddition of Ketenimines to Sulphur Dioxide. Isolation of 1,2-Thiazetid-3-one 1-Oxides

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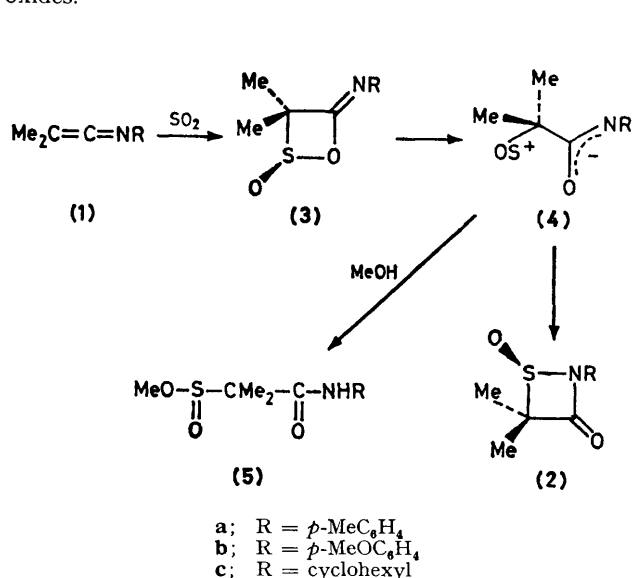
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Summary The 1:1 adducts obtained from the reaction of dimethylketenimines with liquid sulphur dioxide have been identified, by spectral data and X-ray crystallography, as 1,2-thiazetid-3-one 1-oxides.

RING-FORMING reactions involving sulphur dioxide are gaining their due place in synthetic organic chemistry.

Cheletropic reactions and 1,2-cycloadditions of SO_2 to dienes ($4 + 2$ processes),¹ as well as cyclisations between imines and heterocumulenes with keten- SO_2 dipolar adducts generated *in situ*,² have been reported. On the other hand, $2\pi + 2\pi$ cycloadditions of SO_2 are limited to a few examples, namely the reactions with fluoroalkenes,³ ketens,⁴ and phosphorus ylides,⁵ to give highly unstable cyclic sulphinic

esters. We report here the reaction between ketenimines and sulphur dioxide for which evidence supports an initial 2 + 2 mode of cycloaddition to give the unstable four-membered ring adducts oxathietanimine *S*-oxides (β -sultinimines) which rearrange to stable thiazetidinone *S*-oxides.



Solutions of dimethylketenimines⁶ (**1**) (ca. 1 g) in liquid sulphur dioxide (ca. 15 ml) for 1 h at -78°C followed by warm-up at room temperature and evaporation of the excess of sulphur dioxide, gave the corresponding 1,2-thiazetidin-3-one 1-oxides† (**2a**) m.p. $49\text{--}54^\circ\text{C}$ (from *n*-pentane), (**2b**) oil, and (**2c**) m.p. $63\text{--}65^\circ\text{C}$ (from *n*-pentane) in ca. 90% yield whose relevant spectroscopic characteristics were two n.m.r. signals (¹H δ ca. 1.6 and ¹³C δ 16–18 p.p.m.) for the diastereotopic methyls at C-4, ¹³C n.m.r. peak at δ ca. 167 p.p.m. and a strong i.r. absorption at ca. 1770 cm^{-1} for the amide function in the four-membered ring. The latter signals are in the region of n.m.r.⁷ and i.r.⁸ absorptions of β -lactams and 1,2-thiazetidinone oxides.⁹ The mass spectra of (**2**) exhibited, in addition to M^+ , the peaks corresponding to m/e ($M^+ - \text{SO}$) and to isocyanate RNCO. Unequivocal proof for the structure of adducts (**2**) was provided by *X*-ray diffraction analysis of (**2a**).

Crystal data: C₁₁H₁₃NO₂S, prisms (from *n*-pentane), monoclinic, space group $P2_1/a$, $a = 12.052(7)$, $b = 9.651(5)$, $c = 9.967(5)$ Å, $\beta = 97.11(3)$, $Z = 4$. Least-squares anisotropic refinement using 1012 observed reflections gave $R = 0.057$ and indicated the structure depicted in the Figure.‡

† Adducts (**2**) gave satisfactory microanalytical data. Spectral data for (**2a**): e.g. i.r. (CCl₄) ν_{max} 1770 cm^{-1} (N-CO); ¹H n.m.r. (CDCl₃) δ 1.66 (s, 3H, CMe), 1.68 (s, 3H, CMe), 2.34 (s, 3H, R-Me), and 7.33 (A₂B₂, 4H, arom.); ¹³C n.m.r. (CDCl₃) δ 15.7 (q, Me), 18.5 (q, Me), 20.9 (q, Me), 78.3 (s, CMe₂), and 166.9 (s, N-CO). While in solution (CDCl₃, CCl₄, xylene), the adduct (**2a**) was indefinitely stable, but, as a solid, decomposed within 2–3 days.

‡ The atomic co-ordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.

§ From (**1a**) (0.3 g) and 20 ml of SO₂ and 3 ml of MeOH, oil, i.r. (CCl₄) ν_{max} 1678, 3310, and 3430 cm^{-1} ; ¹H n.m.r. (CDCl₃) δ 1.50 (s, 3H, Me), 1.58 (s, 3H, Me), 2.33 (s, 3H, Me), 3.84 (s, 3H, OMe), 7.29 (A₂B₂, 4H, arom.), and 8.5–8.75 (br, 1H, NH); mass spectrum, m/e 255 (M^+), 176, 148, and 107.

The thiazetidinone ring is planar within experimental error and makes a dihedral angle of 22.9° with the aryl ring. Crystal packing is consistent with van der Waals interactions.

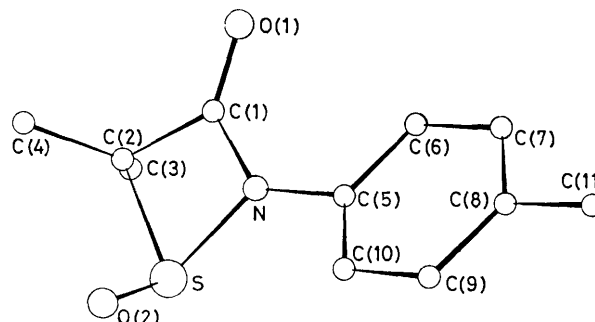


FIGURE. Structure of (**2a**). Relevant geometrical parameters of the heterocyclic ring are: S–N 1.741(6), S–C(2) 1.863(8), N–C(1) 1.353(97), and C(1)–C(2) 1.519(11) Å, N–S–C(2) 75.7(3), S–N–C(1) 97.1(5), N–C(1)–C(2) 100.9(6), S–C(2)–C(1) 86.4(4), O(2)–S–C(2) 110.0(3), and O(2)–S–N 110.9(3) $^\circ$.

Thiazetidinone *S*-oxides (**2**) can be viewed as 2 + 2 cycloadducts between heterocumulenes, viz. the couple sulphine–isocyanate or keten–sulphinylamine. With respect to the cycloaddition of the latter couple which has been in fact employed for the preparation of aryl-substituted terms,⁹ the ketenimine–SO₂ reaction presented here offers several advantages such as high yields and rates, ready availability of the reactants and simplicity of the operative conditions.

Cleavage of one of the S–O bonds of SO₂ must occur along the reaction pathway from reactants (**1**) plus SO₂ to adducts (**2**). This may be achieved by an initial $2\pi + 2\pi$ cycloaddition between the S=O bond of SO₂ and the cumulene C=C bond of ketenimine to give a four-membered ring adduct, 1,2-oxathietan-4-imine 1-oxide¹⁰ (β -sultinimine) (**3**) which rapidly rearranges to product (**2**) through the open-chain intermediate (**4**). To rule out other possibilities, such as the 2 + 2 cycloaddition of SO₂ across the cumulene C=N bond of (**1**), intermediate (**4a**) was trapped by methanol as the sulphinic ester (**5a**).§ On the other hand, the direct detection of adduct (**3a**) from low temperature (-78°C) n.m.r. spectra of the reaction mixture between (**1a**) and SO₂, was unsuccessful.

Unlike other four-membered ring sulphinic esters^{4,5,11} which undergo retrocycloaddition to open-chain components β -sultinimines (**3**) rearrange into more stable four-membered ring compounds (**2**) by fission of the S–O bond only. This

different behaviour may be ascribed to the exocyclic C=N function which stabilises through conjugation the open-chain intermediate (4) long enough to allow rotation about the C-C bond before its cleavage, and provides an alternative centre, *viz.* nitrogen, for the attack by sulphur.

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