

S-Vinyl Thio-oximes from Thioketenes and Benzylnitrene

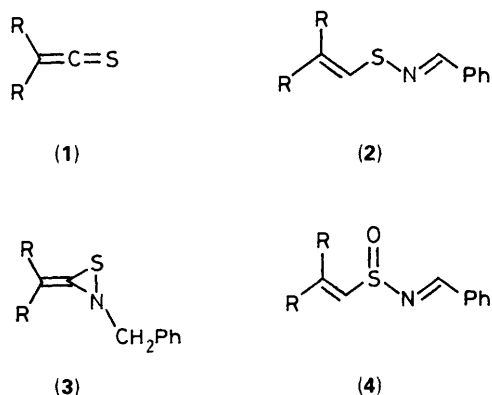
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Sterically hindered thioketenes when heated with benzyl azide gave S-vinyl thio-oximes in a sequence involving nitrene formation, [2 + 1] cycloaddition, and rearrangement.

Cycloadditions of thioketenes to various π bond systems have been shown to provide a wealth of heterocycles.¹ Among 1,3-dipolar cycloadditions, aryl azides have been successfully employed in the reaction with bis(trifluoromethyl) thioketene.² With the same conditions or higher temperatures, we found that the kinetically stabilized thioketenes (**1a,b**) are unreactive toward phenyl, methyl, tosyl, or trimethylsilyl azide. However, the thioketenes (**1a,b**) when heated at >135 °C with benzyl azide gave adducts with a molecular composition corresponding to the two reactants minus nitrogen (yields of isolated products 73 and 60%, respectively). On the basis of spectroscopic evidence, the constitution (**2**), *N*-(alk-1-enylthio)imines [*S*-(alk-1-enyl)thio-oximes], is assigned to the products. To account for the formation of (**2**), we exclude a 1,3-dipolar cycloaddition as the initial step since the azide is known to decompose above 138 °C.³ Instead, we assume thermal nitrene formation from the azide and subsequent [2 + 1] cycloaddition to the C=S bond of (**1**). Then, in the resulting 3-alkylideneethiaziridines (**3**) the C(3)–N bond is cleaved and eventually a 1,4-H shift involving the benzyl methylene hydrogens yields products (**2**), probably in a free-radical process.

In an alternative mechanism, the nitrene may first rearrange to benzyldieneamine^{2a} which then adds to the thioketene (**1**) to give the products (**2**). However, nitrogen nucleophiles usually attack the central carbon in (**1**) rather than the sulphur, *i.e.* show



a ; R = Bu^t
b ; 2 R = Me₂C(CH₂)₃CMe₂

the opposite regioselectivity.¹ Moreover, a control experiment in which diphenylmethylenamine and (**1b**) were kept at 130 °C for 15 h gave only a trace of a blue material. This could not be fully characterized, but the colour and the lack of stability are in

accord with the structure of a *N*-thioacylimine⁵ rather than a regioisomeric thio-oxime of type (2).

Since *S*-arylthio-oximes are known to give a series of remarkable oxidation products,⁶ we looked at the reaction of (2) with 3-chloroperbenzoic acid. Clean conversion of (2a,b) into the corresponding *S*-oxides (4) in 95% yield each was observed. However, further oxidation of (4) with the peracid failed to give identifiable products.

Experimental

Synthesis of the Thio-oximes (2a,b).—The thioetene (1a) or (1b) (2.7 mmol) dissolved in benzyl azide (5 ml, 40 mmol) was kept at 135 °C for 20 h. The contents of the flask often solidified in which case they were extracted with dichloromethane–light petroleum (1:1). Chromatography of the reaction mixtures through a short column of silica gel using ethyl acetate–light petroleum (1:20) removed decomposition products of the azide. After evaporation, excess of azide was distilled off at 0.1 mmHg/40 °C. The residue was recrystallized from methanol–light petroleum (5:2) to give (2a), m.p. 92 °C (Found: C, 74.3; H, 9.2; N, 5.05; S, 11.75. C₁₇H₂₅NS requires C, 74.13; H, 9.15; N, 5.08; S, 11.64%); $\nu_{\max}(\text{KBr})$ 1 590 cm⁻¹ (C=C, C=N); $\delta_{\text{H}}(\text{CDCl}_3)$ 6.78 (s, C=CH) and 8.53 (s, N=CH); $\delta_{\text{C}}(\text{CDCl}_3)$ 123.45 (tert, C=CH), 149.07 (quart, C=CH), 155.92 (tert, CH=N) or (2b), m.p. 94–96 °C (Found: C, 75.2; H, 8.55; N, 4.9; S, 11.25. C₁₈H₂₅NS requires C, 75.21; H, 8.77; N, 4.87; S, 11.15%); $\nu_{\max}(\text{KBr})$ 1 590 cm⁻¹ (C=C, C=N); $\delta_{\text{H}}(\text{CDCl}_3)$ 6.72 (s, C=CH) and 8.49 (s, N=CH); $\delta_{\text{C}}(\text{CDCl}_3)$ 122.16 (tert, C=CH), 148.04 (quart, C=CH), and 155.67 (tert, CH=N).

Oxidation of (2a,b) to (4a,b).—3-Chloroperbenzoic acid (0.52 g, 3 mmol) dissolved in dichloromethane (10 ml) was added dropwise to a solution of the thio-oxime (2a) or (2b) (2.9 mmol) in pentane (10 ml) at 20 °C. After 5 min, the mixture was

extracted with NaOH. The organic layer was dried (Na₂SO₄) and evaporated and the residue was recrystallized from pentane to give (4a), m.p. 85 °C (Found: C, 70.0; H, 8.55; N, 4.7; S, 11.0. C₁₇H₂₅NOS requires C, 70.06; H, 8.65; N, 4.81; S, 11.00%); $\nu_{\max}(\text{KBr})$ 1 603 (C=C), 1 570 (C=N), and 1 075 (S=O); $\delta_{\text{H}}(\text{CDCl}_3)$ 5.58 (s, C=CH) and 8.53 (s, N=CH); or (4b), m.p. 95 °C (Found: C, 70.65; H, 8.45; N, 4.55; S, 10.65. C₁₈H₂₅NOS requires C, 71.24; H, 8.30; N, 4.62; S, 10.57%); $\nu_{\max}(\text{KBr})$ 1 603 (C=C), 1 570 (C=N), and 1 078 (S=O); $\delta_{\text{H}}(\text{CDCl}_3)$ 5.68 (s, C=CH) and 8.62 (s, N=CH).

Acknowledgements

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