

Unusual Cycloaddition Products from the Trapping of an α -Oxo-sulphine (-thioketone S-oxide) with Simple Alkenes

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The reaction of the trimethylsilyl enol ether of 1-thiochroman-4-one 1,1-dioxide with thionyl chloride gives the corresponding α -oxo-sulphine, which has been found to give a new type of [4 + 2] cycloadduct when trapped with simple electron-rich alkenes such as isobutylene and norbornene.

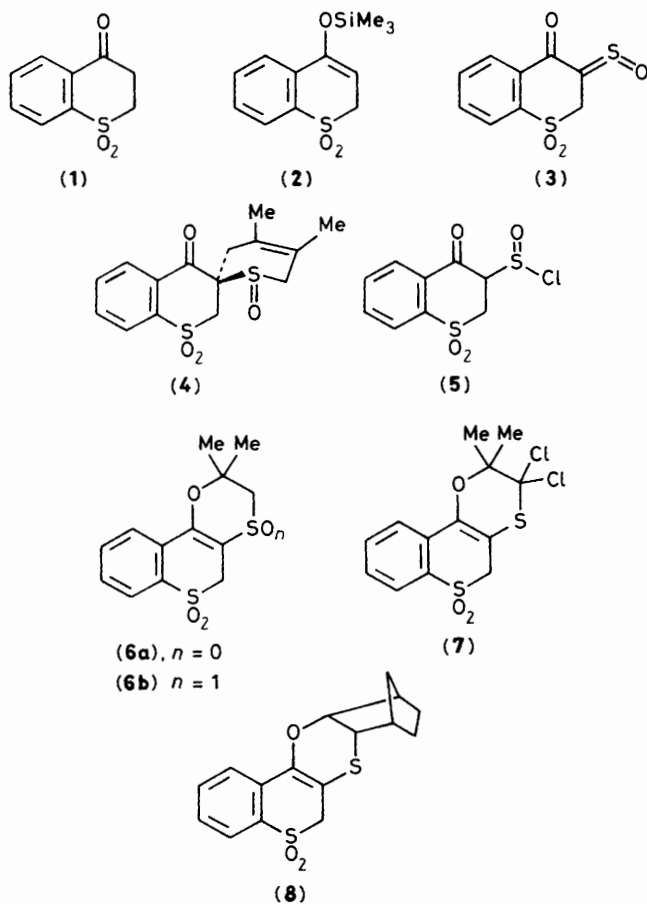
As part of our study of the reactivity of 1-thiochroman-4-one 1,1-dioxide (**1**) towards α -alkyldienation,¹ we have examined the reactivity of the corresponding trimethylsilyl enol ether (**2**) towards various electrophiles. While, to our knowledge, enol ethers such as (**2**) have not previously been caused to react with thionyl chlorides to produce α -oxo-sulphines, the recent communication of Zwanenburg *et al.*² and the earlier report by Faulk and Hull³ have shown that α -sulphinylation can be used to convert suitable ketones directly into α -oxo-sulphines. We report the successful reaction of (**2**) with thionyl chloride to produce (**3**) under very mild conditions, and also the unexpected results of trapping experiments used to verify the formation of (**3**).

When (**2**) was treated with thionyl chloride (CH_2Cl_2 -diethyl ether 1:1, 0 °C, 10 min) the expected sulphine (**3**) was trapped by adding an equimolar amount of 2,3-dimethylbuta-1,3-diene⁴ and allowing the resulting solution to remain at 25 °C for 6 h. The white, crystalline adduct (**4**)[†] (45%) was purified by chromatography on silica gel (CH_2Cl_2 -acetone 99:1) [m.p. 203–204 °C decomp. (from 95% ethyl alcohol); ν_{max} (CHCl_3) 1685 (C=O), 1321 and 1129 (SO_2), 1061 (S=O) cm^{-1} ; ^1H n.m.r. (CDCl_3) δ 1.7 (s, 6H), 2.7–3.2 (m, 2H), 3.6 (d, J 7 Hz, 1H), 3.4–3.9 (m, 2H), 4.3 (dd, J 2, 7 Hz, 1H), 7.7–8.2 (m, 4H); m/z 324(10), 276(34), 261(28), 197(100%)]. Since only one diastereoisomer was detected, and since this

cycloaddition is known to be a stereospecific process,^{2,4} the most likely configuration for the α -oxo-sulphine (**3**) is that of the *Z*-isomer shown, by analogy with Zwanenburg's² findings. Since (**3**) is presumably formed from the sulphinyl chloride (**5**) by elimination of HCl, we were surprised to discover that the presence of a base such as triethylamine consistently *lowered* the yield of cycloadduct obtained, not only in this experiment but in the trapping experiments described below. It appears that the presence of a base is not only unnecessary for the success of the reaction of (**2**) with thionyl chloride but that base may be destructive towards one or more of the reaction intermediates. The formation of the parent sulphone (**1**), (45–60%) was observed to accompany the formation of the cycloadduct in all the trapping experiments. Zwanenburg² has noted the ready hydrolysis of sulphines with various adjacent electron-withdrawing groups to the corresponding methylene analogues.

Since the α -oxo-sulphine system could conceivably act as a *diene component* in [4 + 2] cycloaddition reactions with simple alkenes or alkynes, although this behaviour has apparently not so far been noted, we carried out similar trapping experiments to the one described above using dimethyl acetylenedicarboxylate, isobutylene, and norbornene, respectively. No reaction was observed between (**3**) and the electron-deficient alkyne, but with excess of isobutylene the adduct (**6a**)[†] (37%) was obtained as tan needles after purification by chromatography on silica gel (CCl_4 - CH_2Cl_2 1:3) [m.p. 133–134.5 °C (from light petroleum-ethyl acetate

[†] All new compounds gave satisfactory analytical data.



1:1); ν_{\max} . (CHCl_3) 1619 (C=C), 1315 and 1135 (SO_2) cm^{-1} ; ^1H n.m.r. (CDCl_3) δ 1.5 (s, 6H), 2.9 (s, 2H), 3.85 (s, 2H), 7.3–8.0 (m, 4H); m/z 282(100), 194(15), 185(14), 169(17), 163(52), 162(54%). Compound (6a), is, as far as we are aware, the first example of this heterocyclic system reported. Tentatively, the most reasonable explanation for the forma-

tion of (6a) involves deoxygenation of the initially formed vinyl sulphoxide (6b) by either chlorotrimethylsilane⁵ or thionyl chloride⁶ present in the reaction mixture. Since Cl_2 must be produced by the mode of action of either of the two suspected deoxygenating agents, it is gratifying that a significant amount (10%) of the product of (bis) chlorination of (6a), the dichloride (7),[†] has been isolated as a by-product from the trapping experiment with isobutylene.

The yellow, crystalline cycloadduct (8)[†] could be isolated in 17% yield when an analogous trapping experiment was carried out using an equimolar amount of norbornene. Compound (8) [m.p. 193–194.5 °C (from light petroleum–ethyl acetate 1:1)], is very similar to (6a) in its major spectroscopic characteristics.

These results show for the first time that the sulphoxide moiety can function in cycloaddition reactions as part of a diene unit, as well as in its more familiar rôle as a dienophile.⁷ The reactions of an α -oxo-sulphine with simple alkenes described here also appear to offer a promising route to potentially interesting 2*H*-3-thiapyran-fused heterocyclic compounds.

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References

- 1 I. W. J. Still and F. J. Ablenas, *Can. J. Chem.*, 1984, **62**, 2535.
- 2 B. G. Lenz, R. C. Haltiwanger, and B. Zwanenburg, *J. Chem. Soc., Chem. Commun.*, 1984, 502.
- 3 A. W. Faull and R. Hull, *J. Chem. Soc., Perkin Trans. 1*, 1981, 1078.
- 4 B. Zwanenburg, *Recl. Trav. Chim. Pays-Bas*, 1982, **101**, 1.
- 5 G. A. Olah, B. G. B. Gupta, and S. C. Narang, *Synthesis*, 1977, 583.
- 6 'Synthetic Reagents,' ed. J. S. Pizey, Ellis Horwood, Chichester, U.K., 1974, vol. 1, p. 321.
- 7 Another example of such an inverse-demand [4 + 2] cycloaddition, again involving norbornene, has been reported very recently: M. V. Lakshmikantham, P. Carroll, G. Furst, M. I. Levinson, and M. P. Cava, *J. Am. Chem. Soc.*, 1984, **106**, 6084.