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THE REACTION OF o-QUINODIMETHANE WITH SULFUR DIOXIDE COMPETITION BETWEEN THE $\pi + \pi\pi$ and n + $\pi\pi$ CYCLOADDITIONS

Tony Durst and Lorraine Tétreault-Ryan
Department of Chemistry, University of Ottawa
Ottawa, Canada, K1N 9B4

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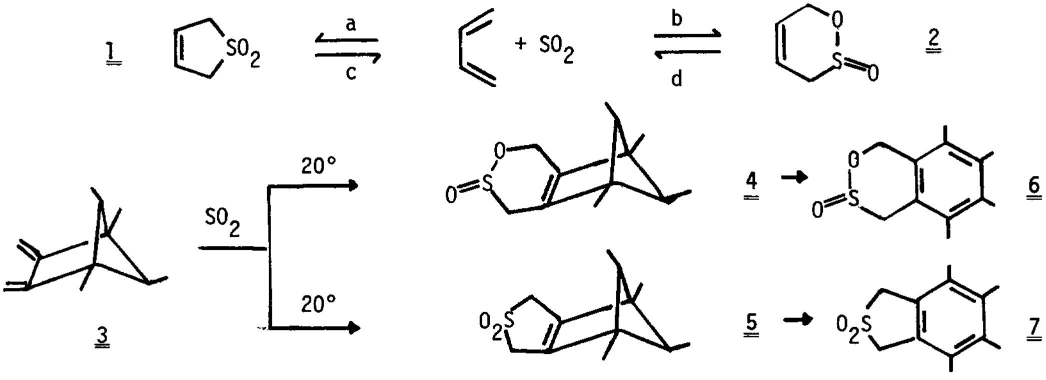
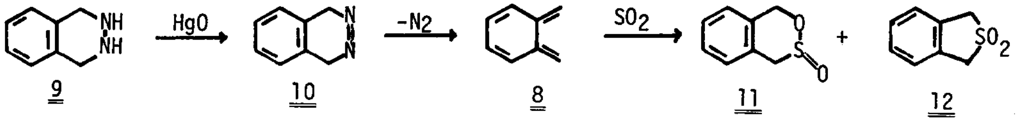
The reaction of sulfur dioxide with 1,3-dienes can, in principle, yield either a 2,5-dihydrothiophehe, 1,1-dioxide 1 (reaction a) or 3,6-dihydro-1,2-oxathiin-2-oxide 2 (reaction b). Both the formation of 1, the result of a 2 + 4 (n + $\pi\pi$)[1] cycloaddition reaction and the corresponding cycloreversion (c) have been well known for over 60 years.[2,3] Several years ago, we described several examples of the 2 + 4 ($\pi + \pi\pi$) cycloreversion of 2 (reaction d) and the benz-fused analogue 11.[4] More recently, Heldeweg and Hogeveen[5] reported the first example of a 2 + 4 ($\pi + \pi\pi$) cycloaddition between the strained diene 3 and SO_2, which yielded the sulfinate ester 4 if the reaction was carried out below 20° and the sulfone 5, the result of a 2 + 4 ($\pi + \pi\pi$) cycloaddition above that temperature. Both products were isolated as the rearranged materials 6 and 7.



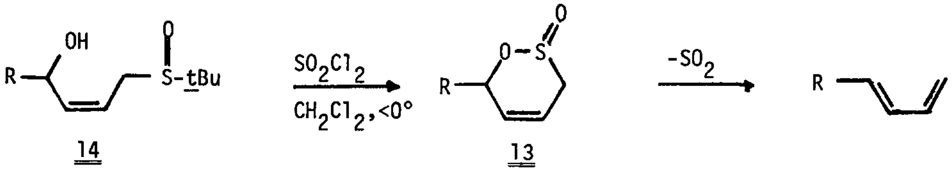
We would like to report a second example of the 2 + 4 ($\pi + \pi\pi$) 1,3-diene-SO_2 cycloaddition reaction and a measure of the competitiveness between the processes leading to the 6 and 5-membered ring compounds.[6]

We had chosen to investigate the reaction between SO_2 and o-quinodimethane 8, generated below room temperature. Thus oxidation of 1,2,3,4-tetrahydrophthalazine 9 with HgO[7] at -20° to +20° in the presence of SO_2[8] afforded, via 10 and 8, the sulfinate ester 11 and the sulfone 12 in an 90 ± 4:10 ratio,[9] (45% yield based on the hydrochloride of 9). The nmr spectrum of the crude reaction mixture showed only the presence of 11 and 12. Their identity was clearly established by comparison with the spectra of both pure 11 and 12, and 11 partly isomerized to 12 which were available from our earlier studies. Investigation of the reaction mixture at various times during the reaction revealed the presence of both isomers, thus showing that 12 was not formed due to isomerization during workup.[10]

The 90:10 ratio of 11:12 can therefore be taken to reflect the ratio of the two cycloaddition reactions and translated into a $\Delta\Delta G^{\ddagger}$ of approximately 12 Kcal/mole in favor of the $\pi + \pi\pi$ vs. $n + \pi\pi$ cycloaddition between SO_2 and 9.



4 + 2 ($\pi + \pi\pi$) type cycloadditions are commonly observed between 1,3-dienes and several structural analogues of SO_2 such as N-sulfinyl amines (RN=S=O)[11] and sulfines (R_2C=S=O)[12]; selenium dioxide also reacts with dienes to give 6-membered ring seleninic esters.[13] In contrast, in the case of simple 1,3-dienes and SO_2, the formation of sulfinate esters has not been observed probably due to their instability. For example, 3,6-dihydro-1,2-oxathiin-2-oxide 13 and its 6-phenyl analogue, generated from 14 and SO_2Cl_2 both decomposed within seconds at 0°. Thus, under the usual conditions of the SO_2-1,3-diene reaction (25°) only the stable 2,5-dihydrothiophene 1,1-dioxides are obtained.[2,14]



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6. The instability of the two products, 4 and 5, makes it somewhat difficult to examine the competitiveness of the two cycloaddition pathways with respect to 3.
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8. The oxidation was complicated by the reversible reaction between SO_2 and the diamine 9, and thus required a variable period. For example, compound 9, obtained from 260 mg of its hydrochloride by treatment with excess KOH was taken up in CH_2Cl_2 and cooled to -20°. SO_2 was added (∼ 10-fold excess), followed by 336 mg of freshly prepared HgO. The solution was then stirred at 20° overnight, filtered and evaporated, yielding 115 mg of a mixture of 10 and 12.
9. The ratio was determined by comparing the integration due to the CH_2 groups of 12 at δ = 4.37 with that of the two CH_2 groups of 11 (AB's at δ = 3.51, 4.37, 4.91 and 4.27).[4]
10. We had earlier shown[4] that 11 was stable at room temperature for several days.
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14. The financial assistance of the National Research Council is Canada is greatly appreciated.