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DIALLYL SULFOXIDE: A CONVENIENT SOURCE OF THIOACROLEIN FOR DIELS-ALDER TRAPPING

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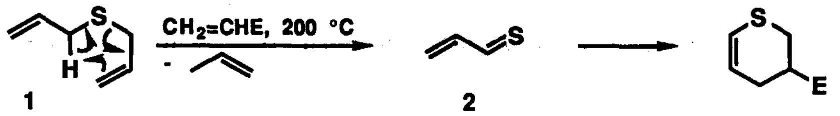
Summary: When diallyl sulfoxide is heated with dienophiles at 90-110 °C, 3,4-dihydro-2*H*-thiopyrans, the thioacrolein Diels-Alder adducts, are formed in good to excellent yield.

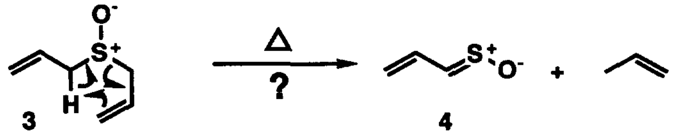
We have noted that diallyl sulfide (**1**) undergoes retro-ene decomposition in solution at 200 °C giving thioacrolein (**2**, 2-propenethial) which can be trapped in modest yields with dienophiles (eq 1).[1] This observation prompted us to examine the thermolysis of diallyl sulfoxide (**3**) which, in view of the known weakness of the C-S(O) bond,[2] might be expected to undergo an analogous but even more facile decomposition affording the presently unknown 2-propenethial S-oxide (**4**, thioacrolein S-oxide, eq 2).[3] We report that in fact diallyl sulfoxide serves as a convenient low-temperature source of ***thioacrolein***, which can be trapped with suitable dienophiles in good to excellent yields, and propose a mechanism to explain our novel observations. Our work illustrates the synthetic utility of Diels-Alder trapping of thioacrolein with added dienophiles as a route to 3,4-dihydro-2*H*-thiopyrans.[4]

Diallyl sulfoxide can be conveniently prepared in 91% yield on a large scale via oxidation of diallyl sulfide with hydrogen peroxide followed by crystallization at 0 °C (see below). The reaction of excess diallyl sulfoxide with norbornene (bicyclo[2.2.1]hept-2-ene) at 90 °C affords *exo*-3-thiatricyclo[6.2.1.0^{2,7}]undec-4-ene **5** in 40% isolated yield in addition to allyl alcohol, indicating that thioacrolein rather than its S-oxide has been generated and trapped (eq 3). Peracetic acid oxidation of **5** yields *exo*-3-thiatricyclo[6.2.1.0^{2,7}]undec-4-ene S,S-dioxide (**6**), identical to the compound previously prepared by Dittmer.[5] Dimethyl fumarate and N-phenyl maleimide react similarly with diallyl sulfoxide at 90-110 °C affording thioacrolein-adducts **7** and **8** in 95% and 91% yield, respectively, and allyl alcohol (see Table I). Reaction of diallyl sulfoxide with excess ethyl acrylate gives a 7.3:1 mixture of 3- and 2-carboethoxy-3,4-dihydro-2*H*-thiopyran (**9** and **10**, respectively; previously characterized by us[1]) in 50% yield; (E)-stilbene gives adduct **11** in 28% yield after 3 h at 150 °C.

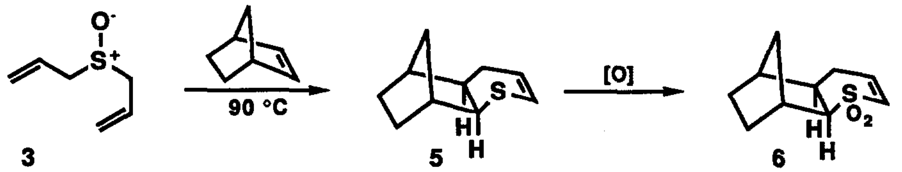
We have sought to determine the mechanism of this unusual reaction. We find that Diels-Alder adduct **12** of 2-methylthioacrolein can be obtained in good yield by heating bis(2-methyl-2-propenyl) sulfoxide with N-phenyl maleimide (Table I, entry 3). In the absence of dienophiles the major products from thermolysis of diallyl sulfoxide are diallyl disulfide, dimers of thioacrolein, and allyl alcohol. We find that the addition does not pro-



(1)



(2)



(3)

ceed well under conditions where the diallyl sulfoxide concentration is substantially diluted by solvent or a large excess of dienophile or when the reaction mixture is rigorously dried and a drying agent (CaH_2) is present during the reaction. Higher temperatures are required for decomposition of allyl methyl sulfoxide and allyl benzyl sulfoxide; neither gives clean decomposition products. Finally, we find no evidence for formation of **6** when diallyl sulfone is heated with excess norbornene at temperatures up to 210 °C. It has already been reported that thioacrolein S,S-dioxide, generated from thiete 1,1-dioxide at 180-190 °C, can be trapped with norbornene giving **6** in good yield[5]).

Allylic sulfoxides are known to undergo reversible [2,3]-sigmatropic interconversion to alloxysulfenates, a synthetically useful reaction.[6] We suggest that the sulfur atom of reversibly formed allyl alloxysulfenate **13** functions as a nucleophile toward the sulfur in a second molecule forming an ionic intermediate (Scheme 1), behavior commonly seen with sulfenyl derivatives.[7] Attack of water on the latter intermediate in S_N2' fashion releases allyl propenethiosulfinate **14** (allicin), a known low temperature source of **2**[1] which then reacts with ECH=CHE giving adduct **15**. Since water is generated by decomposition of **14**, it is required only in catalytic quantities. Cage disproportionation of the radical pair ($CH_2=CHCH_2S\cdot\ \cdot OCH_2CH=CH_2$) formed by homolysis of **13** could also yield **2** and allyl alcohol. However Scheme 1 is more consistent with the above observations regarding the influence of concentration and water.

Diallyl Sulfoxide (3): Diallyl sulfide (100 g, 0.87 mol) in acetone (200 mL) is treated at 0 °C with H_2O_2 (30%, 100 g, 0.88 mol; added slowly). The mixture is stirred at 0 °C for 2 h, warmed to 25 °C overnight, extracted with CH_2Cl_2 and the extract washed with brine/1N NaOH, dried ($MgSO_4$) and concentrated. The crude product was dissolved at 25 °C in 5:1 pentane:ether, cooled to 0 °C for 1 h and then kept overnight at -22 °C. The solid was subjected to rapid filtration at room temperature and was then kept under vacuum for several hours giving a colorless oil (103 g, 91% yield) solidifying at 5 °C, MS m/e 130 (M^+, 1.5%), 100 (3.3%), 81 (20%), 68 (7%), 41 (100%); ^{1}H NMR δ 5.89 (m, 1 H), 5.42 (m, 2 H), 3.55 (m, 1 H), 3.40 (m, 1 H); ^{13}C NMR δ 125.7 (CH), 123.5 (CH_2), 54.1 (CH_2).

trans-2,3-Bis(carbomethoxy)-3,4-dihydro-2*H*-thiopyran (7): Diallyl sulfoxide (13 g, 1 mol) and dimethyl fumarate (1.44 g, 0.1 mol[8]) are heated at 107 °C under argon for 4.5 h. The product is then placed under vacuum with slight warming to remove volatile sulfides, filtered through a short column of silica gel with CH_2Cl_2 and then purified by flash chromatography (silica gel, 6:1 c-C_6H_{12}:EtOAc) to give the title compound as a viscous colorless liquid (2.06 g, 95% yield); ^{1}H NMR ($CDCl_3$) δ 5.95 (dd, 1 H, J = 10.0, 2.0 Hz), 5.75 (ddd, 1 H, J = 10.5, 5.6, 3.0 Hz), 4.10 (d, 1 H, J = 9.1 Hz), 3.69 (s, 3 H), 3.66 (s, 3 H), 3.08 (ddd, 1 H, J_{cis} = 4.8, J_{trans} = 8.9 Hz), 2.49 (ddt, 1 H, J = 18, 5, 2 Hz), 2.30 (dddd, 1 H, J = 18, 9, 4, 2 Hz); ^{13}C NMR ($CDCl_3$) δ 173.6 (C), 170.8 (C), 119.6 (CH), 117.9 (CH), 52.8 (CH_3), 52.4 (CH_3), 42.0 (CH), 40.3 (CH), 25.7 (CH_2); MS m/e 216 (M^+); Anal. Calcd for $C_9H_{12}O_4S$: C, 50.00; H, 5.60. Found: C, 49.99; H, 5.60.

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Scheme 1

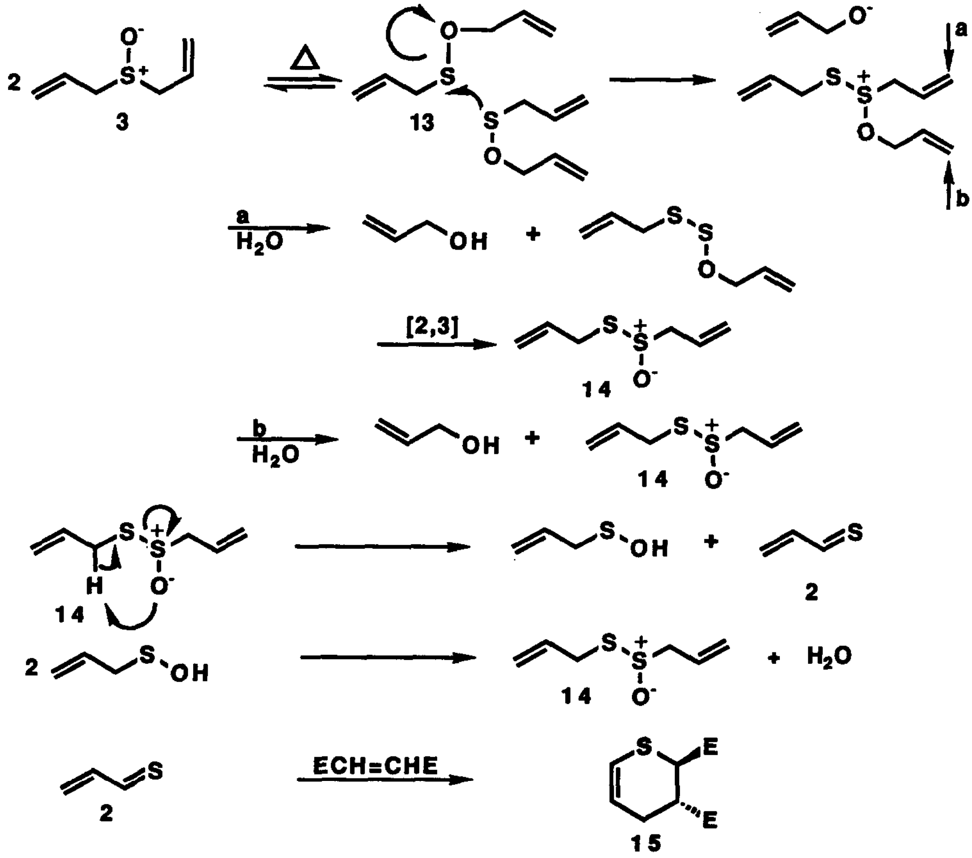
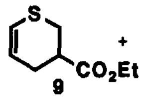
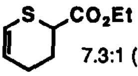
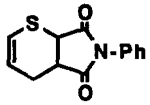
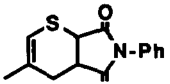
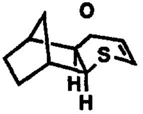
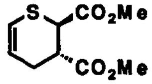
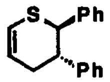


Table I. 3,4-Dihydro-2*H*-thiopyrans from Allyl Sulfoxides

Entry	Sulfoxide	Dienophile	Conditions	3,4-Dihydro-2*H*-thiopyran (Yield)
1	$(CH_2{=}CHCH_2)_2SO$	$CH_2{=}CHCO_2Et$	103 °C, 5 d	 9 +  10 7.3:1 (50%)
2	$(CH_2{=}CHCH_2)_2SO$	N-Phenyl maleimide	110 °C, 4.5 h	 8 (91%)
3	$(CH_2{=}CMeCH_2)_2SO$	N-Phenyl maleimide	127 °C, 12 h	 12 (85%)
4	$(CH_2{=}CHCH_2)_2SO$	Norbornene	87 °C, 3 d	 5 (40%)
5	$(CH_2{=}CHCH_2)_2SO$	(E)-$MeO_2CCH{=}CHCO_2Me$	107 °C, 4.5 h	 7 (95%)
6	$(CH_2{=}CHCH_2)_2SO$	(E)-PhCH=CHPh	150 °C, 3 h	 11 (28%)

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8. Use of stoichiometric ratios of reagents leads to lower yields.

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