Tetrahedron Letters, Vol. 34, No. 40, pp. 6371-6374, 1993
Printed in Great Britain

0040-4039/93 $6.00 + .00
Pergamon Press Ltd

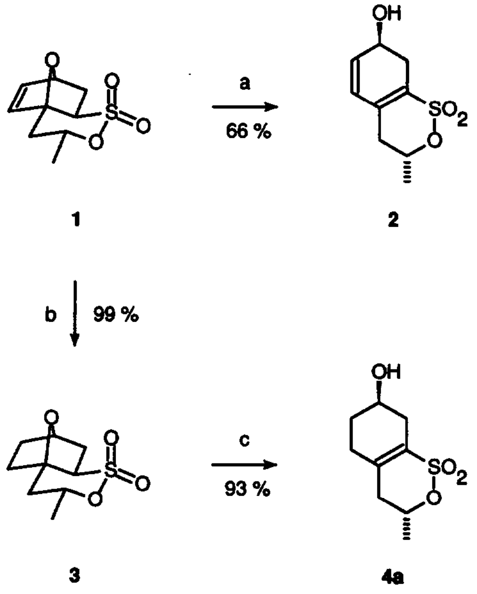
Reductive Desulfurization of Sultones Prepared via Intramolecular Diels-Alder Reaction of a Furan-Containing Vinylsulfonate

Peter Metz* and **Eva Cramer**

Organisch-Chemisches Institut der Universität Münster, Correnstrasse 40, D-48149 Münster, Germany

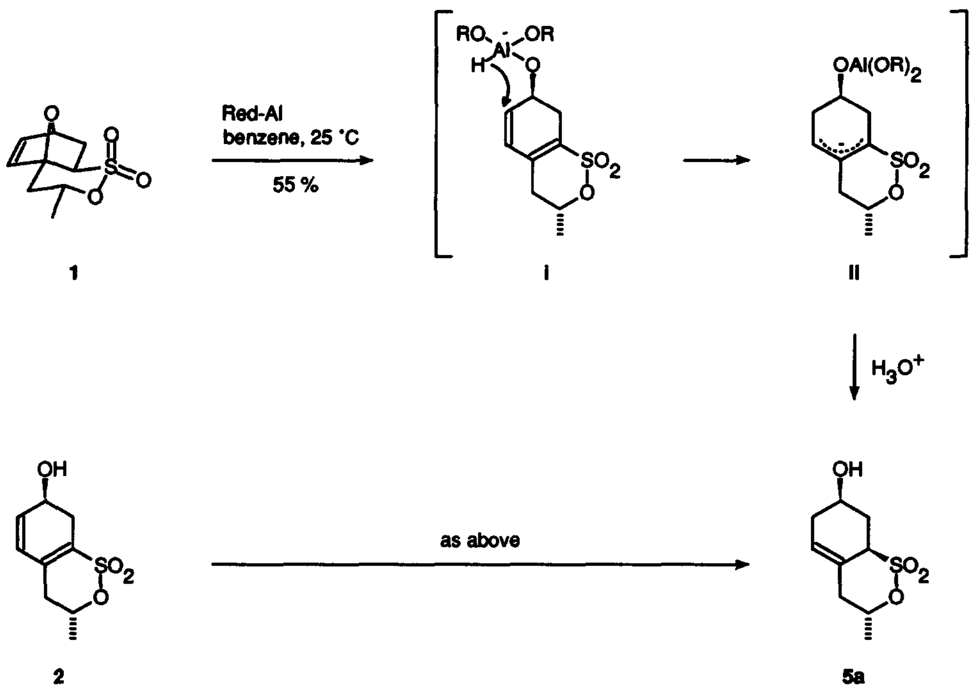
Abstract: Treatment of sultone 1 and the saturated derivative 3 with strong bases or reaction of 1 with Red-Al caused a cleavage of the oxygen bridge. The resultant vinylic or allylic sultones 4 and 5 were efficiently desulfurized by metal/ammonia reduction. While a mixture of cyclohexenes 6 and 7 was produced from allylic sultones 5, the vinylic sultones 4 reacted with complete regioselectivity to yield only 7.

The intramolecular Diels-Alder reaction of vinylsulfonates[1-3] derived from hydroxyalkyl substituted furans provides an efficient and highly stereoselective access to δ-sultones like **1**.[1] In this letter, we report on reductive desulfurizations of allylic and vinylic sultones[4] readily available from **1** leading to substituted cyclohexenes with two stereogenic centers in a 1,6-relationship.[5]



Scheme 1. Conversion of cycloadduct **1** to vinylic sultones *via* elimination. a: LDA, THF, -78 °C; b: 1 atm H_2, 10 % Pd/C, MeOH, 20 °C; c: *n*-BuLi, THF, -78 °C.
(LDA = lithium diisopropylamide)

Deprotonation of **1** with lithium diisopropylamide or treatment of the saturated derivative **3** with *n*-butyllithium effected a fast elimination to hydroxy sultones **2** and **4a**, respectively, in good to excellent yield (Scheme 1).[6] In contrast to the behaviour of the cyclopentadiene-derived analogue of **1**,[2] the intermediate α-lithiated sultones could not be trapped with electrophiles even at -100 °C.

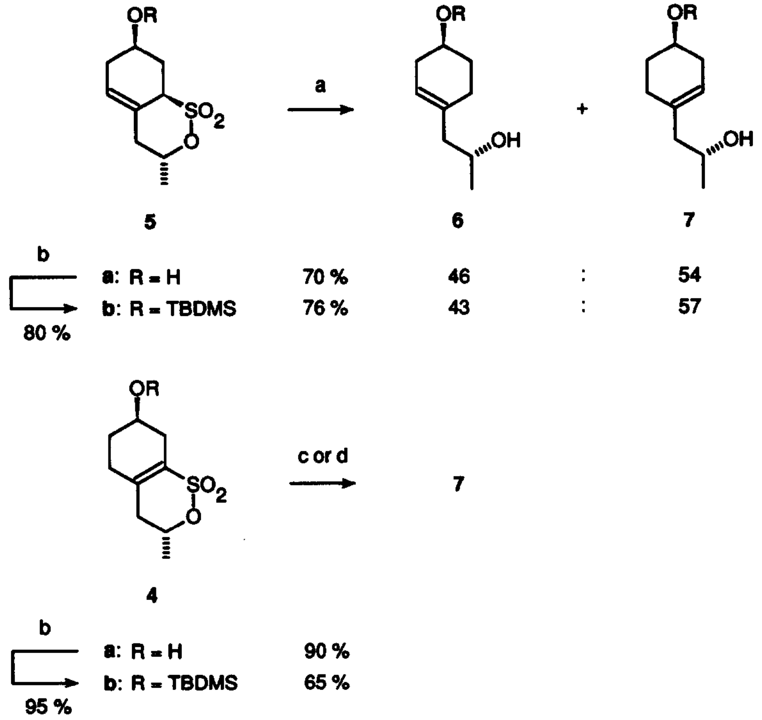


Scheme 2. Conversion of cycloadduct **1** to allylic sultone **5a** *via* one-pot elimination/reduction.
(Red-Al = sodium bis(2-methoxyethoxy)aluminum dihydride; R = 2-methoxyethyl)

Unexpectedly, hydroxy sultone **5a** was formed as a single diastereoisomer upon reaction of **1** with one equivalent of Red-Al (Scheme 2).[7] Since **5a** was also obtained from dienol **2** with one equivalent of Red-Al under identical conditions, sultone **1** is probably deprotonated by Red-Al to produce an aluminate **i** of **2** which in turn is converted to **5a** *via* intramolecular 1,6-addition of the second hydride and subsequent regio- and stereoselective protonation of the resultant allyl anion **ii** during aqueous work-up.[8,9]

Using sodium in liquid ammonia, an efficient reductive cleavage of the allylic C-S bond within sultones **5a,b** took place (Scheme 3).[10,11] Due to non-regioselective protonation of the nearly symmetrical intermediate allyl anions, two isomeric products **6** and **7** were formed in approximately equimolar amounts.[12] While a regiodiscriminating intramolecular protonation[13] through solely the side chain hydroxyl group might have been a feasible pathway for the *tert*-butyldimethylsilyl ether **5b**, the observed ratio of **6b** : **7b** renders such a route rather unlikely.

A smooth desulfurization without interfering shift of the double bond was achieved for vinylic sultones **4a,b** *via* reduction with lithium in liquid ammonia. Whereas this transformation worked well for **4a** in the absence of an external proton donor, a prior silylation of **4a** to **4b** which allows for a chemical differentiation of the two secondary alcohol functions within the product demanded the presence of *tert*-butanol during reduction to obtain a good yield of **7b**[14] in a reproducible manner.



Scheme 3. Reductive desulfurization of sultones **5** and **4**. a: Na, NH_3, THF, -60 °C to -40 °C; b: TBDMSCl, imidazole, DMAP, DMF, 20 °C; c (for **4a**): Li, NH_3, THF, -60 °C to -40 °C; d (for **4b**): Li, NH_3, THF, *t*-BuOH, -60 °C to -40 °C.
(TBDMS = *tert*-butyldimethylsilyl; DMAP = 4-*N*,*N*-(dimethylamino)pyridine)

Acknowledgement. Financial support of this work by the Deutsche Forschungsgemeinschaft and the Fonds der Chemischen Industrie is gratefully acknowledged.

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12. Ratios were determined by capillary gas chromatography using HP Ultra II columns, 0.25 mm i. d., 0.25 µm film (**6a**/**7a**: after silylation with *N*-methyl-*N*-(trimethylsilyl)trifluoroacetamide, 50 m column, 135 °C; **6b**/**7b**: 25 m column, 180 °C).
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14. **7b**: To a solution of **4b** (1.16 g, 3.5 mmol) in dry THF (80 ml), liquid ammonia (80 ml, predistilled from sodium) and *t*-BuOH (0.33 ml, 3.5 mmol) small pieces of lithium are added at a temperature between -60°C and -40 °C until a blue color persists. Stirring is continued for further 15 min at the same temperature, excess lithium is destroyed by addition of EtOH, and sat. aq. NH_4Cl (30 ml) is slowly added. The cooling bath is removed and after evaporation of ammonia overnight, ethyl acetate (20 ml) is added. The aqueous layer is extracted with additional portions of ethyl acetate (4 x 20 ml), the combined organic layers are dried over $MgSO_4$, and the solvent is removed *in vacuo*. Filtration of the crude product through a short column filled with silica gel using ethyl acetate/petroleum ether 1 : 3 as eluent gives **7b** (614 mg, 65 %) as a colorless oil. - $R_f = 0.39$; ^1H NMR (300 MHz, $CDCl_3$) δ 0.04 (s, 3 H, Si-CH_3), 0.05 (s, 3 H, Si-CH_3), 0.87 [s, 9 H, Si-C(CH_3)$_3$], 1.17 (d, 3 H, $J = 6.2$ Hz, CH-CH_3), 1.55 - 1.80 (m, 3 H), 2.02 (m_c, 4 H), 2.19 (m_c, 2 H), 3.82 - 3.95 (m, 2 H, SiO-C*H*, HO-C*H*), 5.40 (m_c, 1 H, C=C*H*); ^{13}C NMR (75.47 MHz, $CDCl_3$) δ -4.7 [q, Si($\mathit{C}H_3$)$_2$], 18.1 [s, Si-*C*(CH_3)$_3$], 22.7 (q, CH-$\mathit{C}H_3$), 25.8 [q, Si-C($\mathit{C}H_3$)$_3$], 26.7 (t), 31.4 (t), 34.9 (t), 47.6 (t), 64.8 (d), 67.2 (d), 122.2 (d, C=*C*H), 134.5 (s, *C*=CH); IR ($CHCl_3$) 3600 - 3400 (O-H) cm^{-1}; MS (GC/MS, 70 eV) m/e (relative intensity) 255 (M - CH_3, 2), 213 (M - C_4H_9, 76), 195 (M - C_4H_9 - H_2O, 4), 169 (M - C_4H_9 - CH_3CHO, 100), 121 (M - *t*-BuMe$_2$SiO - H_2O, 63), 119 (22), 101 (26), 93 (M - *t*-BuMe$_2$SiOH - CH_3CHOH, 36), 75 [$(CH_3)_2Si{=}OH^+$, 82], 73 (23), 59 (6), 45 ($C_2H_5O^+$, 7). Anal. Calcd for $C_{15}H_{30}O_2Si$: C, 66.59; H, 11.20. Found: C, 66.77; H, 11.23.

(Received in Germany 21 July 1993; accepted 27 July 1993)