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THE FIRST ISOLATION OF AN EPISULPHONE INTERMEDIATE FROM A RAMBERG- BÄCKLUND REACTION

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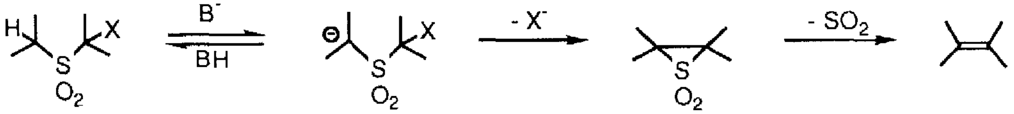
Abstract: Episulphone **6** was isolated as a crystalline solid in 69% yield from the low temperature Ramberg-Bäcklund reaction of α-iodosulphone **5** . The expected cyclopentene **7** was obtained when episulphone **6** was heated or treated with base and when the Ramberg-Bäcklund reaction was carried out under more forcing conditions.

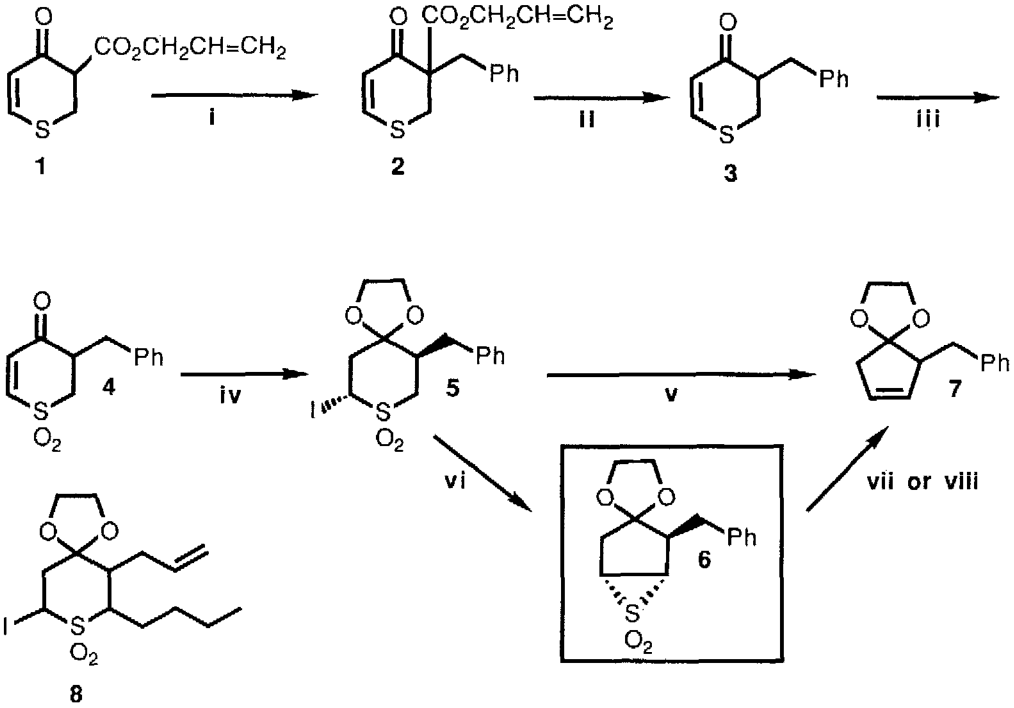
Since it was first described in 1940,[1] the Ramberg-Bäcklund reaction, the conversion of an α-halo sulphone into a regio-defined alkene (Equation 1), has attracted considerable mechanistic and synthetic interest.[2] It is widely accepted that the reaction proceeds by way of an episulphone (thiiran-1,1-dioxide) intermediate, indeed it has been shown that episulphones prepared by other methods[3] give alkenes under the conditions normally employed for the Ramberg-Bäcklund reaction.[2,3] To date, however, no-one has isolated an episulphone by treatment of an α-halo sulphone with base.[4] We now report the first such example made possible by the facile Ramberg-Bäcklund reaction of α-iodo-thiane dioxides we reported recently.[5]

EQUATION 1



The key Ramberg-Bäcklund precursor, the benzyl α-iodo-sulphone **5**, was prepared as shown in Scheme 1[6] using a similar sequence of reactions to those recently described for the preparation of the corresponding 2,3-dialkylated compounds (e.g. **8**).[5] Alkylation of 2,3-dihydro-3-allyloxycarbonylthiin-4-one (**1**) using $K_2CO_3/PhCH_2Br$, which proceeded in almost quantitative yield, was followed by palladium-catalyzed decarboxyallylation of adduct **2** to give sulphide **3**. Oxidation to sulphone **4** and treatment with Me_3SiI/ethylene glycol gave α-iodosulphone **5** as a stable, crystalline solid. Iodo-sulphone **5** was predominantly the trans-isomer with iodine equatorial as shown by 400 MHz ^{1}H-NMR spectroscopy (H-6, δ5.07, dd, J=12.8

SCHEME 1



Reagents and conditions

i. $PhCH_2Br$, K_2CO_3, acetone (95%)

ii. $Pd(PPh_3)_4$-morpholine, THF (54%)

iii. OXONE, aq. MeOH (85%)

iv. 2.2 Me_3SiI, CH_3CN then 5 $HOCH_2CH_2OH$ (79%)

v. 2.5 $KOBu^t$, THF, -20°C to room temperature (85%)

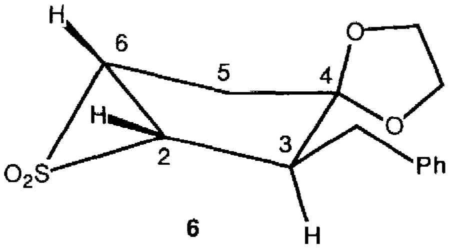
vi. 1.2 $KOBu^t$, THF, -78°C to 0°C, 2h (69% + 28% **7**)

vii. 2.5 $KOBu^t$, THF, -20°C to room temperature (81%)

viii. 100°C, 20 min (88%)

& 4.3 Hz). Treatment of compound **5** with 2.5 equivalents of $KOBu^t$ in THF at -20°C followed by warming to room temperature produced the expected cyclopentene **7** (a known[7] compound) in 85% yield. When the reaction was carried out at -78 to 0°C with 1.2 equivalents of $KOBu^t$, however, cyclopentene **7** was the minor product, episulphone **6** being obtained as a white crystalline solid in 69% yield. Episulphone **6** gave consistent ^1H and ^{13}C-NMR, mass spectral, analytical and IR data (see Scheme 2). In addition, nuclear Overhauser enhancements were observed between H-2 and H-6. Treatment of **6** with excess $KOBu^t$ at -20°C to room temperature under the conditions of the Ramberg-Bäcklund reaction gave the cyclopentene **7** as the only observable product in 81% yield. Episulphone **6** melted at 105-108°C with decomposition (to cyclopentene **7** according to chromatographic analysis). Thermolysis of episulphone **6** at ca. 100°C under nitrogen for 20 minutes gave cyclopentene **7** in 88% yield. Episulphone **6** can be stored as a solid at -18°C without noticeable decomposition (< 5%) over a 2 month period whereas storage in solution at room temperature leads to significant decomposition to cyclopentene **7** (ca. 66% conversion after 28 days according to ^1H-NMR spectroscopy).

SCHEME 2



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IR ($CDCl_3$): 1310, 1135 $cm.^{-1}$
MS (E.I.): *m/z* 216 (M^+-SO_2, 27%),
125 (M^+-SO_2- $PhCH_2$, 100%).
MS (NH_3 C.I.): Found: (M + NH_4)$^+$: 298.11201.
$C_{14}H_{20}NO_4S$ requires 298.11128.
Analysis: Found: C,60.1; H, 5.68.
$C_{14}H_{16}O_4S$ requires C, 59.98; H, 5.75%.

^{1}H-NMR ($CDCl_3$): δ 7.32-7.17 (5H,m, Ph), 4.07-3.84 (4H,m, OCH_2CH_2O), 3.56 (1H, dt, J=7.2,10.3 Hz, H-6), 3.35 (1H, dd, J=6, 10.3Hz, H-2), 3.08-3.02 (1H, m, H-3), 2.95 (1H, dd, J= 5.0, 14.2 Hz) and 2.73 (1H, dd, J=11.1 and 14.2Hz, CH_2Ph), 2.36-2.33 (2H, m, H-5).

^{13}C-NMR ($CDCl_3$): δ 138.4, 128.7, 128.4 and 126.6(Ph), 121.4 (s, C-4), 76.9 and 76.6 (2xt, OCH_2CH_2O), 50.3(d), 46.6(d), 44.8(d), 34.5(t), 32.1(t).

It should be noted that the related α-iodosulphone **8** undergoes a facile Ramberg-Bäcklund reaction at -78°C giving the corresponding cyclopentene in 78% yield with no trace of the episulphone intermediate.[5] Presumably the presence of adjacent substituents on C-2 and C-3 destabilises the resulting episulphone intermediate, leading to rapid SO_2 extrusion. Further work is under way to establish this point and to determine the scope and limitations of this new route[3] to episulphones.

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