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THE KOH/CCl_4-INDUCED REARRANGEMENT OF CYCLIC SULFONES INTO ALKENES AND VINYL CHLORIDES

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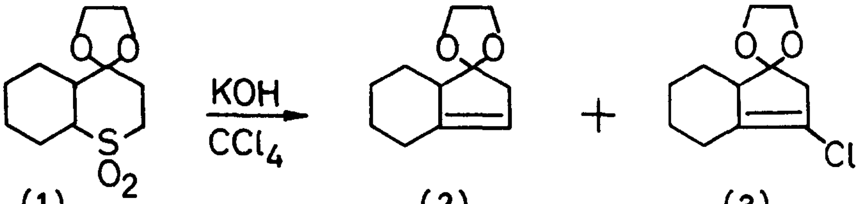
The base-induced rearrangement of α-halo sulfones (Ramberg-Bäcklund reaction) has received considerable attention. Examples starting from both acyclic and cyclic sulfones have been described[1,2]. The steric requirements of the reaction are well understood and have been formulated in terms of an easily obtainable semi-W conformation demanded for the transition state, going from the initial α-carbanionic centre through S_N2 substitution of the α'-halo atom to the intermediate episulfone[1].

Not surprisingly, no mention has been made of the successful rearrangement of cyclic sulfones in which the α-carbon occupies a bridgehead position in a bicyclo [n.m.0]system, since only a combination of the correct configuration at the halogenated carbon atom with the required conformation at the anionic centre will allow an easy reaction to proceed.

As part of a broader investigation into improved methods for α-halogenation and rearrangement of cyclic sulfones we wish to report the smooth conversion of 1 and 4 to hydroindenone systems, using the convenient in situ procedure published recently by Meyers and collaborators[3].



(1) (2) (3)

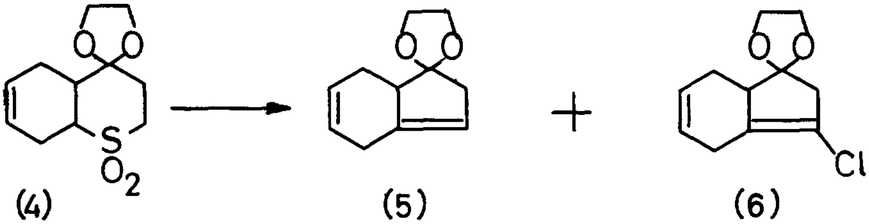
Treatment of cis-4-thiadecalone-S,S-dioxide ethylene glycol acetal (1)[4] with KOH/CCl_4 (2 mmol of sulfone, 5 g of powdered KOH, 30 ml of tBuOH and 75 ml of CCl_4) at 50° overnight resulted in complete conversion into a mixture of 2 and 3. GLC-separation of this mixture furnished pure 2 and 3 in 32 and 48% yield, respectively. The spectral data testify to the structures.

1-Oxo-2,4,5,6,7,8-hexahydroindene ethylene glycol acetal (2), $\nu_{max}^{CHCl_3}$ 1640, 1120 and 1020 cm^{-1}; $\delta_{TMS}^{CDCl_3}$ (100 MHz) 5.22 (multiplet, 1H, vinyl), 3.90 (singlet, 4H, acetal), 2.45 (multiplet, 5H, allylic), 1.75 and 1.30 (unresolved absorptions, 6H); m/e = 180.

3-Chloro-1-oxo-2,4,5,6,7,8-hexahydroindene ethylene glycol acetal (3), $\nu_{max}^{CHCl_3}$ 1665, 1080 and 1020 cm^{-1}; $\delta_{TMS}^{CDCl_3}$ (100 MHz) 3.90 (multiplet, 4H, acetal), 2.65 (multiplet, 5H, allylic), 1.70 and 1.30 (unresolved multiplets, 6H); m/e = 214.

The high yield of 3 reflects the increased tendency of the immediate precursor, the chloro episulfone, to expel SO_2. Although the OH-induced ring opening of chloro episulfones is a very important competing reaction in less strained molecules[5], no sulfonic acids were isolated.

The presence of a double bond, as in 4[4], introducing different torsion angles in the intermediate chloro episulfone constitutes no barrier to the Ramberg-Bäcklund reaction, since treatment of 4 with KOH/CCl_4 leads to complete conversion to a 1 : 1 mixture of 5 and 6. The mixture was submitted to GLC-separation and provided 5 and 6 in a pure state.



5: $\nu_{max}^{CHCl_3}$ 1640, 1120 and 1030 cm^{-1}; $\delta_{TMS}^{CDCl_3}$ (100 MHz) 5.70 (multiplet, 2H, vinyl), 5.35 (multiplet, 1H, vinyl), 3.95 (singlet, 4H, acetal), 2.74 (multiplet, 5H, allylic), and 2.2 (multiplet, 2H, allylic); m/e = 178.

6: $\nu_{max}^{CHCl_3}$ 1660, 1090 and 1030 cm^{-1}; $\delta_{TMS}^{CDCl_3}$ (100 MHz) 5.70 (multiplet, 2H, vinyl), 3.95 (multiplet, 4H, acetal), 2.85 (multiplet, 5H, allylic), 2.2 (multiplet, 2H, allylic); m/e = 212.

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