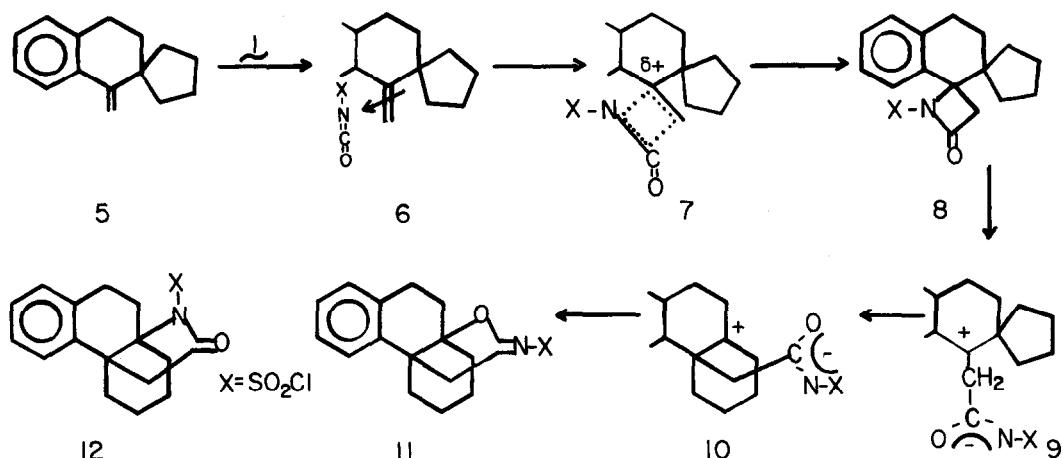


CHART I



yield in both cases) m.p. 164.5–166°C; λ (CHCl₃) C=O 1770 cm⁻¹. *

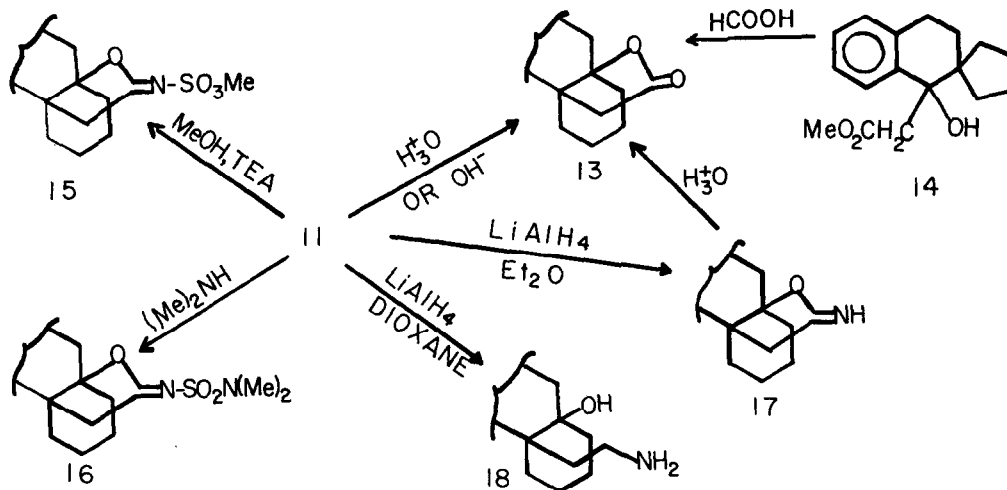
Treatment of 11 with methanol in the presence of triethylamine (TEA) gave 15 in 85% yield; m.p. 135–136°C; λ (CHCl₃) C=N 1633 cm⁻¹, SO₂ 1350, 1178 cm⁻¹; NMR (CDCl₃) δ 7.0–7.4 (multiplet, 4, aromatic), δ 3.82 (singlet, 3, OCH₃), δ 3.2–3.6 (multiplet, 2, CH₂-C=N), δ 2.7–3.0 (multiplet, 2, benzylic CH₂), δ 1.3–2.4 (multiplet, 10, CH₂ envelope). Similarly treatment of 11 with dimethylamine (excess) in ether gave 16 (ca 25% yield); m.p. 134–135°C; λ (CHCl₃) C=N 1633 cm⁻¹ SO₂ 1350, 1145 cm⁻¹; NMR (CDCl₃) δ 7.1–7.4 (multiplet, 4), δ 3.3–3.6 (multiplet, 2, CH₂-C=N), δ 2.7–3.0 (multiplet, 2, benzylic), δ 2.71 (singlet, 6, N(CH₃)₂), δ 1.3–2.3 (multiplet, 10, CH₂ envelope).

When 11 was treated with one equivalent of LiAlH₄ in refluxing ether for 15 min. there was obtained an oil (ca 75% yield) the structure of which we have assigned as 17, λ (neat) N-H 3200 cm⁻¹, C=N 1685 cm⁻¹. On treatment of 17 with methanol-hydrochloric acid only lactone 13 was isolated.

Finally, treatment of 11 with five equivalents of LiAlH₄ in refluxing dioxane for 24 hrs gave 4a-[2'-aminoethano]-10a-hydroxy-1,2,3,4,4a,9,10,10a-octahydro-phenanthrene 18 in 90% yield. Trituration with ether induced crystallization

* Lit. (4) m.p. 167–167.5°C. The infrared and NMR spectra were identical with those of the lactone prepared by rearrangement of 14 with formic acid (4).

CHART II



of the oil; m.p. 153-154°; λ (CHCl₃) OH, NH₂ 3300-3600 cm⁻¹ (broad, poorly defined); NMR (CDCl₃), δ 7.2-7.45 (multiplet, 4), δ 2.7-3.4 (multiplet, 7, OH, NH₂, benzylic CH₂, CH₂NH₂, 3H exchange with D₂O), δ 1.3-2.3 (multiplet, 12, CH₂ envelope).

We believe that the formation of the N-chlorosulfonylimino ether 11 from olefin 5 proceeds by the reaction pathway outlined in Chart I. The first step is probably the formation of the π -complex 6.^{*} This species then could proceed in a partly concerted process to 7. Intermediate 7 could then collapse to N-chlorosulfonyl β -lactam 8.^{**} Ring opening of 8 would lead to charge-separated intermediate 9. Intermediate 9 undergoes a Wagner-Meerwein rearrangement to give 10, which then ring closes via attack of the oxygen portion of the ambident anion upon the cationic center in 10 yielding the observed product.

* The intermediacy of a π -complex in CSI-olefin cycloaddition reactions has been suggested by Moriconi and Kelly (5).

** When the cycloaddition reaction was carried out in CDCl₃ at -60°C an unstable intermediate was observed; NMR (*inter alia*) δ 3.50 (singlet, CH₂-C=O), δ 2.87-3.23 (multiplet, benzylic CH₂). When the sample was allowed to warm to room temperature, the NMR spectrum of 11 was observed. We gratefully acknowledge the assistance of Mr. Victor Yu of McGill University in obtaining this spectrum.

The unusual aspect of this rearrangement is the ring closure onto oxygen this being, to our knowledge, the first reported instance of such an occurrence.* Originally, we had considered 12 as a possible structure for the CSI adduct with 5. We have discarded this possibility because: (a) lactone 13 was produced on hydrolysis; (b) the complete absence of C=O absorption in the IR spectrum of 11 (in CCl₄, CHCl₃, or KBr disc); (c) the methoxy 15 and N,N-dimethyl 16 derivatives also show C=N absorption in their IR spectra, (d) amino-alcohol 18 is produced on prolonged reduction with LiAlH₄.

Ring closure via the oxygen probably is favored in this case due to the steric hindrance of the nitrogen in the ambident anion by the bulky chlorosulfonyl group. We are currently exploring the scope and mechanism of this reaction.

* A number of CSI induced rearrangements have been reported (6,7,8). None of these involved cyclization to oxygen.

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