

A NOVEL REACTION OF THE ETHYLENEDISULFONYL GROUP

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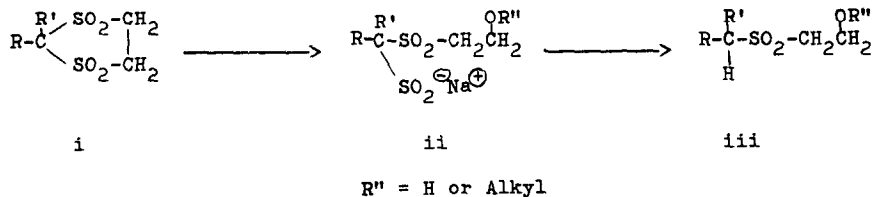
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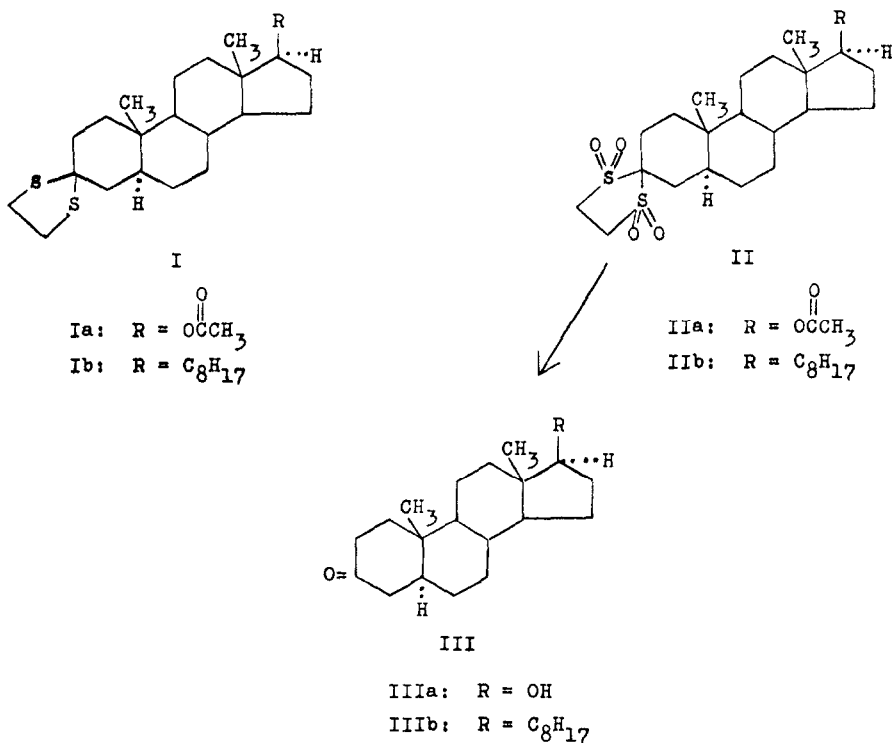
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Normally, protective groups for ketones such as ketals, thioketals and enol ethers have to be removed under acidic conditions. We have found that the thioketal group formed by the reaction of ethanedithiol with a steroidal ketone can be oxidized readily to a cyclic disulfone. Such ethylene disulfones can then be decomposed easily under alkaline conditions in the presence of oxygen to regenerate the original ketone.* This new protecting group is useful in cases where an acid-sensitive moiety has been introduced following protection of the ketone.

3,3-Ethylenedisulfonyl-5 α -androstan-17 β -ol acetate (IIa) was prepared in better than 90% yield by treatment of a tetrahydrofuran solution of the thioketal (Ia) (2) with an excess of monopero-phthalic

*It is known that γ -disulfonyl compounds (i), when treated with alkali, can give compounds of the type ii. These, on acidification, form sulfinic acids which lose sulfur dioxide to form compounds of the type iii. (1)





acid in ether. This compound melted at $315-318^\circ$, $[\alpha]_D^{25} + 12.2^\circ$ (1% CHCl_3). $\text{C}_{23}\text{H}_{36}\text{S}_2\text{O}_6$ requires C, 58.44; H, 7.67; S, 13.39. Found: C, 58.4; H, 7.7; S, 13.6. The integrated NMR spectrum (CDCl_3 , ext. TMS, Varian A-60) was consistent with this structure: singlets at 8.71, 8.63 (angular methyls), 7.92 (acetate) and 5.86 τ (ethylene hydrogens).

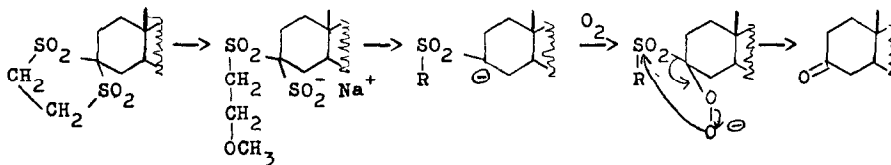
3,3-Ethylenedisulfonyl-5 α -cholestane (IIb) was prepared in the same fashion and in similar yield from the thioether (Ib) (3). This compound melted at $298-299.5^\circ$, $[\alpha]_D^{25} + 26.9^\circ$ (1% CHCl_3). $\text{C}_{29}\text{H}_{50}\text{O}_4\text{S}_2$ requires C, 66.11; H, 9.57; S, 12.12. Found: C, 66.3; H, 9.5; S, 12.1.

A methanolic suspension of IIA and an equal weight of sodium ethoxide were heated under reflux in an atmosphere of nitrogen to give a solution completely miscible with water. Oxygen, when bubbled through this aqueous solution for ten minutes, caused precipitation of crude 17 α -hydroxy-5 α -androstan-3-one (57%). Recrystallization from acetone gave a pure product (40% yield) which was identical with an authentic sample by mixture melting point, infrared spectral comparison and thin layer chromatography. A small sample was converted to its acetate which was identical with authentic 17 β -hydroxy-5 α -androstan-3-one acetate by the criteria mentioned above.

IIb, when treated in a similar fashion with only 2 equivalents of sodium methoxide,* afforded a 55% yield of impure 5 α -cholestan-3-one. Chromatography on silica gel and recrystallization of this crude product yielded 39% of pure 5 α -cholestan-3-one which was identical with an authentic sample by mixture melting point, infrared spectral comparison and thin layer chromatography.

When IIb was treated with one equivalent of sodium methoxide, half the weight of IIb was recovered.

A possible pathway for the observed reaction may be envisioned as shown below. This is similar to the mechanism proposed for the base catalysed autoxidation of α -sulfoxo carbanions (4).



REFERENCES

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* The solution obtained after heating under reflux and dilution with water was neutral to pH paper.