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ASYMMETRIC SELECTION DURING PYROLYSIS OF OPTICALLY ACTIVE 4-METHYLCYCLOHEXYL p-TOLYL SULFOXIDE

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Continuing our work on asymmetric selection *via* elimination (1), we wish to report on the preparation of a simple, optically active sulfoxide which, upon pyrolysis, gave rise to optically active olefin in remarkably high optical yield.

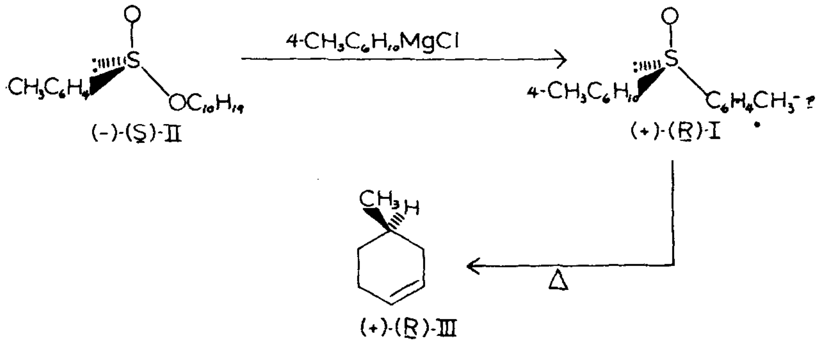
(+)-*trans*-4-Methylcyclohexyl *p*-tolyl sulfoxide (I), m.p. 126-7°, $[\alpha]_D^{28}$ + 165.5 ± 0.6° (c 1.02, methanol) was prepared *via* treatment of (-)-menthyl *p*-tolysulfinate (II) (2,3) with 4-methylcyclohexyl magnesium chloride.

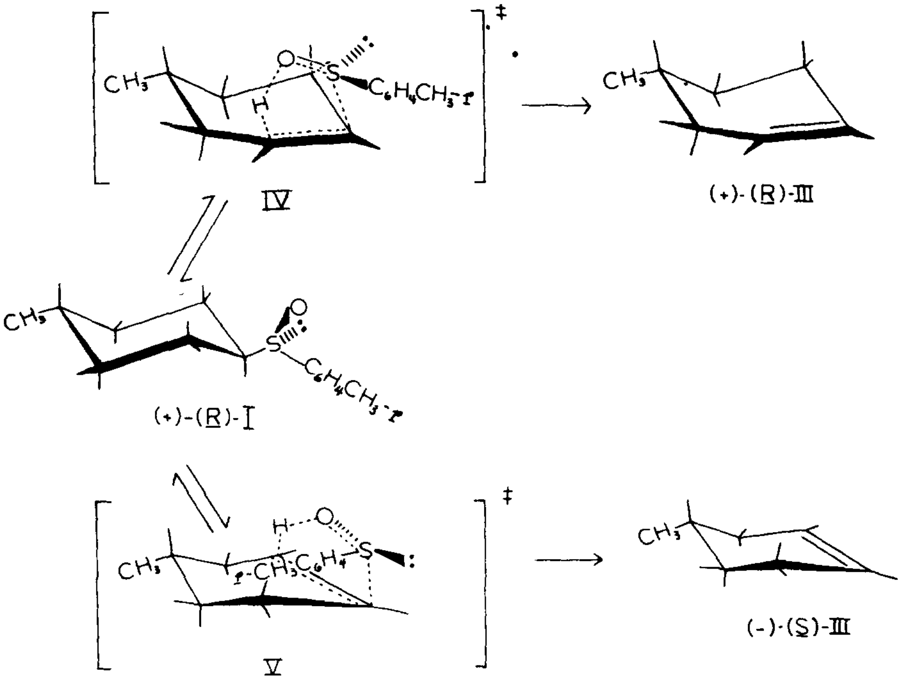
Pyrolysis of the sulfoxide was carried out in chloroform solution at 250° in the injection port of a gas chromatograph. The pyrolyzate was then carried in a helium stream on to a Carbowax column maintained at 80°. The pure collected olefinic product, shown to be 4-methylcyclohexene (II) by means of superimposable infrared spectra determined from it and from authentic

4-methylcyclohexene, was found to be optically active: $[\alpha]_D^{30} + 45.3 \pm 0.5^\circ$ (c 2.22, methanol).

On the basis of available information, the sulfoxide is indicated as possessing the trans-(R) configuration. This assignment is drawn from the facts that the levorotatory sulfinate (II) is known to possess the (S) configuration at sulfur (2) and that displacement of its menthyloxy group by Grignard reagent is also known to proceed with inversion (2). The 1,4-trans disposition of substituents on the cyclohexane ring is assumed since it is known from the work of Goering and McCarron (5) that the steric course of Grignard reagent formation from alkyl halide and magnesium is thermodynamically controlled.

Since the configuration of the dextrorotatory product olefin is also known [(R)] (4), it is possible to formulate a transition state topology which reconciles the configurational details of the starting material with those of the product. The two diastereomeric transition states may be represented by IV and V, and the more favored one (lower energy pathway) may be selected by evaluation of the extent of non-bonded interaction present in each case. In terms of this model transition state IV clearly possesses less strain than V since in the former the p-tolyl group is clear of close interactions with the cyclohexyl protons, while in the latter the p-tolyl group is involved in serious non-bonded interaction. Since transition state IV, but not V, leads to prediction of the experimentally observed olefin, the proposed topology appears to be satisfactory. A similar analysis has been found


4-CH₃C₆H₁₀MgCl
CH₃C₆H₄
OC₁₀H₁₉
(-)-(S)-II
4-CH₃C₆H₁₀
C₆H₄CH₃-p
(+)-(R)-I
Δ
CH₃ H
(+)-(R)-III


CH₃
O
H
S
C₆H₄CH₃-p
‡
IV
(+)-(R)-III
(+)-(R)-I
p-CH₃C₆H₄
V
(-)-(S)-III

to account for the stereospecificity noted in the pyrolysis of steroidal sulfoxides (6).

Additional work bearing on the proposed transition state topology is in progress. In the meantime we wish to point out the remarkably high degree of asymmetric selection that must have occurred during the pyrolysis of I. An optical yield [based on the highest specific rotation (+ 107°) reported (7) for III] near 42% is indicated, and this appears even more remarkable since I was probably not diastereomerically pure.

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