Stereospecific Intramolecular Addition of α-Lithio Sulphoxides or Sulphones to Inactivated Double Bonds

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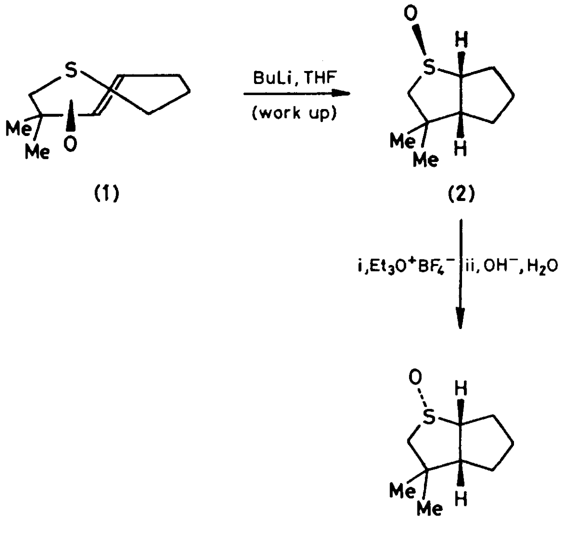
Summary Treatment of the 1-oxides or 1,1-dioxides of *trans* homoallylic 8—10 membered ring cyclic sulphides with BuLi in tetrahydrofuran results in transannular addition of the α-thio carbanion to the *E* double bond with formation of bicyclic products.

NUCLEOPHILIC additions to inactivated double bonds are rare.[1] We report the facile intramolecular addition of α-sulphinyl or -sulphonyl carbanions (lithio derivatives) to inactivated double bonds. The substrates were 1-oxides or 1,1-dioxides of cyclic n-membered (n = 8—10) homoallylic sulphides of the E-configuration.[2] Their structure is such that carbon atom n, α to sulphur, faces the transannular double bond.[3] When treated with BuLi in tetrahydrofuran (THF), α-lithio derivatives are formed which rapidly and quantitatively add to the double bond on the opposite side of the ring resulting in bicyclic products.† Under the same conditions the corresponding Z-isomers were inert. Thus,



(1)

(2)

(3)

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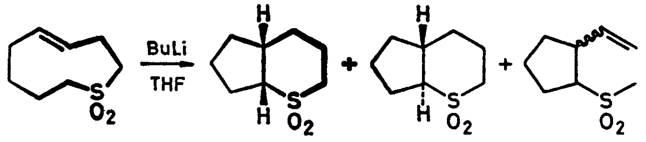
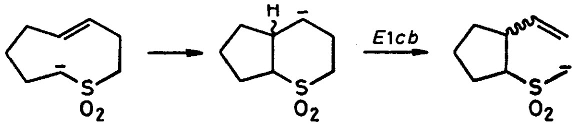
† Satisfactory analytical and spectral data (^{1}H and ^{13}C n.m.r.; m.s.) were obtained for all separated products.

from the 1-oxide‡ of (*E*)-3,3-dimethylthiacyclo-oct-4-ene[5] (**1**), a single product was formed, *exo*-4,4-dimethyl-2-thiabicyclo[3·3·0]octane 2-oxide (**2**), which implies attack of C-8 on the C-4 end of the double bond. The *exo* structure was established by comparison of the ^{13}C n.m.r. spectrum of (**2**) with that of (**3**), the isomeric sulphoxide obtained from (**2**) by sulphur inversion[6] *via* alkaline hydrolysis of the ethoxysulphonium derivative.§



(4) (5) (6) (7)

In an analogous reaction *E*-thiacyclodec-4-ene 1,1-dioxide gave a bicyclic product, identified as *trans*-1-thiadecalin 1,1-dioxide (m.p. 115—116 °C) by comparison with an authentic sample prepared by oxidation of *trans*-1-thiadecalin.[7] In this case attack of C-10 occurs on the C-5 end of the double bond.



SCHEME

The reaction of the analogous 9-membered sulphone (**4**) also yields products *via* intramolecular attack at C-5; three major products (all *m/e* 174) were formed, two of which are isomeric *cis*- and *trans*-2-thiabicyclo[4.3.0]nonane 2,2-dioxides (**5**) and (**6**). The third appears to be a ring-contracted methyl sulphone (**7**)¶ which probably arises by *E*1*cb* elimination from the carbanion initially formed by intramolecular addition at C-5, as depicted in the Scheme.

(*Received*, 22*nd April* 1981; *Com.* 477.)

‡ Oxidation ($NaIO_4$) of racemic *E*-thiacyclo-oct-4-enes yields a single sulphoxide.[4] Models show that for steric reasons only the sulphoxide may be formed where the oxygen atom projects outside. This is the (1*R*, 4*R*; 1*S*, 4*S*)-diastereoisomeric mixture.

§ ^{13}C N.m.r.: δ (p.p.m. from Me_4Si), (**2**) 75·2 (d), 62·2 (t), 59·2 (d), 46·3 (s), 30·5 (q), 29·2 (t), 28·6 (t), 26·7 (t), and 25·4 (q); (**3**) 64·4 (t), 61·2 (d), 59·6 (d), 40·3 (s), 30·6 (q), 29·8 (t), 27·3 (t), 24·9 (q), and 21·8 (t). Particularly revealing are the upfield shifts (*exo* → *endo*) of C-4 (46·3 → 40·3) and C-8 (minimum 26·7 to 21·7).

¶ Assignment of structure (**7**) is based on n.m.r. evidence which indicates the presence of a monosubstituted ethylene unit [^{13}C, δ 139·8 (d) and 115·9 (t) p.p.m.; ^{1}H, δ 6·07—4·87 (3H, m)] and a methyl sulphonyl group [^{13}C, δ 40·1 (q) p.p.m.; ^{1}H, δ 2·71 (3H, s)].

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