Thermal Racemization and *cis,trans*-Isomerization of Allylically Unsaturated Di- and Poly-sulphides: a Mechanism involving Branched Sulphur Chains

By D. Barnard, T. H. Houseman, M. Porter,* and B. K. Tidd

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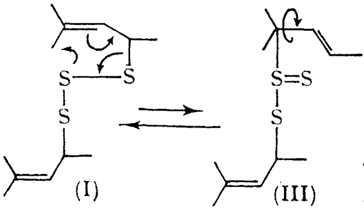
Summary The ready isomerization of allylically unsaturated di- and poly-sulphides is ascribed to their being in thermal equilibrium with the corresponding isoallylic species having a branched sulphur chain.

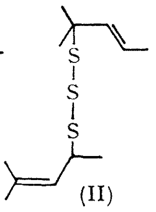
At elevated temperatures, dialkyl polysulphides undergo exchange[1,2] and disproportionation[2,3] reactions which appear to proceed by S–S bond homolysis. We now report that allylically unsaturated di- and poly-sulphides undergo an additional type of thermal reaction which proceeds much faster than either exchange or disproportionation.

Bis-(1,3-dimethylbut-2-enyl) trisulphide (I), as prepared from the corresponding Bunte salt,[4] consists of *meso*- and racemic forms which can be separated by fractional crystallization. The isomer of higher m.p. (33·5—34°) is converted rapidly ($t_{\frac{1}{2}}$, 46·5 min.) into a 1 : 1 mixture of the two isomers upon being heated either alone or in solution at 75°, isomer ratios being determined by isotope dilution analysis. Under these conditions no disproportionation to di- and tetra-sulphides takes place; neither is any of the trisulphide (II) formed by allylic rearrangement (g.l.c.).

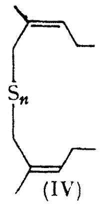
Such interconversion could involve racemization by C–H or C–S bond fission at asymmetric carbon or end-group exchange by S–S bond fission. Mechanisms involving charge separation in the transition state can be ruled out since there is no alteration in the reaction rate on changing the solvent from benzene to methanol. Similarly, failure of oxygen or 2,6-di-t-butyl-4-methylphenol to influence the rate, and the total absence of isoallylic compounds, such as (II), from the products argue against a mechanism involving homolytic C–H or C–S bond fission. Random exchange of trisulphide end-groups by an intermolecular chain mechanism involving homolytic S–S bond fission[2] cannot be operative here since the observed reaction rate is independent of concentration, and no mixed trisulphides are formed when the interconversion is carried out in the presence of another trisulphide such as dibenzyl or diethyl trisulphide. Furthermore, the rate is unaffected by the presence of tetrasulphides which are known[3,5] to produce $RS_2\cdot$ radicals under similar conditions.



(I) (III)



(II)



(IV)

As a consequence we suggest the electron-shift mechanism [(I)→(III)] in which racemization is a consequence of free rotation about the C–C bond indicated in (III). The observed negative entropy of activation for the interconversion ($\Delta S^{\ddagger}$, −7 e.u.) is consistent with such a concerted, cyclic mechanism; the entropy of activation for the formally similar, reversible sulphoxide–sulphenate rearrangement is −5 e.u. (in benzene[6] whereas a typical value for homolytic fision is +24·6 e.u.[7] We have chosen to write the sulphur-branched species (III) in the double-bonded, rather than the ylide, form in view of the lack of response to solvent polarity (a ten-fold decrease in rate obtains[6] for the racemization of allyl *p*-tolyl sulphoxide on changing the solvent from benzene to ethanol at 60·7°).

The suggested mechanism implies that thermal *cis,trans*-double-bond isomerization should occur in suitably substituted analogues of (I) which contain sulphur chain-lengths greater than one. In agreement with this, the double bonds in the trisulphide (IV; $n = 3$) have been found to isomerize with a rate constant of the same order as that found for the isomer interconversion of (I) and preliminary indications are that (IV, $n = 2$) also isomerizes. The diastereoisomers of bis-(1,3-dimethylbut-2-enyl) monosulphide are, however, completely stable under the given conditions.

There is an apparent mechanistic similarity between the above reaction and the allylic[6,8] and acetylenic[9] sulphenate–sulphoxide rearrangements, the O → S shifts of allylic sulphoxylates,[10] allylic[11] and acetylenic[12] sulphinates, and the S → C shifts of allylic[13] and acetylenic[14] sulphonium ylides. The findings also allow an alternative interpretation of the desulphurisation of allylic disulphides by triphenylphosphine.[15]

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