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NOVEL RING BRIDGING REACTIONS INVOLVING ELEMENTAL SULPHUR AND SELENIUM

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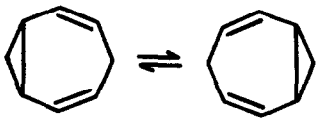
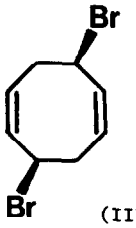
Recent interest[1] has centred round 9-heterobicyclo[3.3.1]nona-2,6-dienes (I) owing to their importance as synthetic precursors to diheteroadamantanes.[2] We now report that thermal reaction of bicyclo[5.1.0]octa-2,5-diene (II) with elemental sulphur or selenium in toluene leads to the direct introduction of a one atom bridge giving 9-thiabicyclo[3.3.1]nona-2,6-diene (Ia) and its selena-analogue (Ib).

(I) a; Z=S
b; Z=Se



(II) (II')



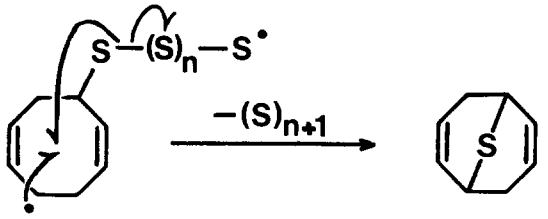
(III)

The pure homotropylidene (II) used was very readily prepared,[3] in 50% yield (unoptimised), by the action of excess activated zinc[4] on the known[5] (Z,Z)-cis-3,7-dibromocyclo-octa-1,5-diene (III), a 2 hr reflux in dry ethanol under N_2 being employed; following aqueous work-up, pentane extraction, and distillation, (II) showed a temperature-dependent ^1H n.m.r. spectrum which was consistent with the fluxional behaviour (II) $\rightleftharpoons$ (II') previously reported.[6] Reactions were typically performed in sealed thick-walled n.m.r. tubes, employing degassed toluene-d_8 as solvent and hexamethyldisiloxane as internal reference, so that reaction progress could be conveniently monitored. For reaction runs of (II) with selenium, grey selenium powder (initially about one half, and subsequently one molar equivalent) was employed. In the first run, reaction at 205° for 5 hrs produced prominent ^1H n.m.r. signals from the bridged selenide (Ib); further monitoring at this temperature over one week showed progressive disappearance of (Ib) and formation of ethyl benzene and o-xylene, detected by n.m.r. and ultimately by g.l.c. (50 m x 0.5 mm SCOT APL capillary column), along with other unidentified products. In a second run, stopped at an intermediate stage, a 25% yield (unoptimised) of crystalline selenide (Ib) was obtained by chromatography (Mallinckrodt silicic acid, 20%

CH_2Cl_2/n-pentane as eluent), and was positively identified by comparison of spectral properties (^{1}H n.m.r., i.r., and m.s.) with those of authentic (Ib) independently prepared.[1] In a separate run starting with selenide[1] (Ib), heating at 200° for 9 days caused selenium extrusion with clean conversion to a 2:3 mixture of o-xylene and ethyl benzene, it being noteworthy that the combined total of m- and p-xylenes constitutes, at most, ca. 2% of the product (g.l.c. analysis).

For the bridging reaction of (II) with sulphur, three molar equivalents of flowers of sulphur were employed, and after reaction at 170° for 2 hrs, chromatographic purification gave the highly volatile sulphide (Ia) which was identified by comparison of its g.l.c., t.l.c., m.s., and ^{1}H n.m.r. parameters with those from a sample of (Ia) independently prepared.[1]

The mechanism of these bridging processes is of interest. An attractive possibility is that (II) may act, formally at least, as a source of a bis-allyl diradical system.[8] So that with sulphur, for example, interaction of a linear sulphur diradical species, formed at elevated temperature, with (II) could be envisaged as producing the resonance-stabilised intermediate (IV) which goes on to give (Ia) as indicated.



(IV) (Ia)

An analogous mechanism is also possible for the selenium bridging process.

Further studies of related bridging reactions are underway.

References

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2. See, e.g., C. Ganter, Topics in Current Chemistry, 1976, 67, 15.
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6. W. von E. Doering and W.R. Roth, Tetrahedron, 1963, 19, 715.
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8. Cf., H. Kessler and W. Ott, J. Amer. Chem. Soc., 1976, 98, 5015.