Tellurium Extrusion: A Novel Method for Carbon–Carbon Bond Formation

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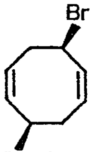
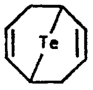
Summary Pyrolysis of 9-tellurabicyclo[3,3,1]nona-2,6-diene (II) in [$^2H_8$]toluene at 175° leads to loss of elemental tellurium and quantitative formation of bicyclo-[5,1,0]octa-2,5-diene (III) which was also formed independently by the action of Te^{2-} anion on the dibromide (I) during the preparation of (II).

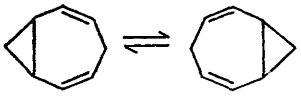
In a recent study[1] of bridging reactions of the dibromide (I) we have prepared 9-oxa-, 9-thia-, and 9-selena-bicyclo-[3,3,1]nona-2,6-dienes. We now report that treatment of (I) with Na_2Te in DMF yields not only the expected 9-tellura compound (II) in 18% yield [characterised by i.r., high resolution m.s., and ^1H n.m.r. τ ($CDCl_3$) 3·9—4·5 (4H, m, olefinic), 6·0—6·4 (2H, m, bridgehead), and 7·1—8·4 (4H, m, methylenes)] but also an appreciable amount of bicyclo[5,1,0]octa-2,5-diene (III) as the other major volatile product (*ca.* 20%) of the reaction. The hydrocarbon (III), separated chromatographically, showed a temperature-dependent ^1H n.m.r. spectrum which was consistent with the fluxional behaviour (III) ⇌ (III′) previously reported[2] for this compound. A control experiment, in which the pure telluride (II) was resubjected to similar aqueous work-up conditions to those used in its preparation did not lead to detectable amounts of hydrocarbon (III), showing that (III) did not arise from (II) by thermal or other means. The action of Te^{2-} ion on the dibromide (I), involving attack of the highly nucleophilic Te^{2-} anion on bromine, appears to have no precedent, though the isoelectronic I^- anion is well known[3] to effect analogous eliminations on dibromides.

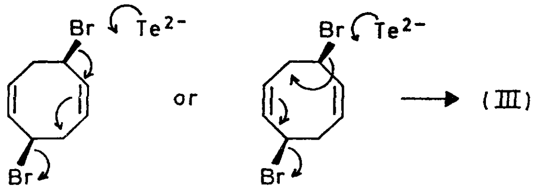


(I)



(II)


(III) (III′)



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† The corresponding 9-thiabicyclo[3,3,1]nona-2,6-diene shows no decomposition (n.m.r. monitoring) after 16 h at 200° in [$^2H_8$]-toluene in a sealed tube (ref. 1).

A mechanistically distinct mode of formation of (III) was discovered while investigating the thermal stability of telluride (II). While stable effectively indefinitely at ambient temperature under N_2 in the dark, (II), in degassed [$^2H_8$]-toluene (sealed tube), was found to undergo a quantitative tellurium extrusion reaction at 175°, the deposition of metallic tellurium being accompanied by the disappearance of (II) and the formation of diene (III) as the sole organic product detected by ^1H n.m.r. after 8 h. Interestingly, (III) and not its thermodynamically more stable[2] isomer, bicyclo[3,3,0]octa-2,6-diene is formed in this reaction. This process represents the first synthetically useful formation of a carbon–carbon bond by thermal loss of zero-valent tellurium, and the greater ease of thermal loss of tellurium compared to sulphur† leads us to explore further synthetic applications of tellurium extrusion.

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[1] E. Cuthbertson and D. D. MacNicol, *J.C.S. Perkin I*, in the press; R. K. Mackenzie, D. D. MacNicol, H. H. Mills, R. A. Raphael, F. B. Wilson, and J. A. Zabkiewicz, *J.C.S. Perkin II*, 1972, **1632**.

[2] W. von E. Doering and W. R. Roth, *Tetrahedron*, **1963**, **19**, 715.

[3] H. Finkelstein, *Ber.*, 1910, **43**, 1528.