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TELLURIUM EXTRUSION: SYNTHESIS OF BENZOCYCLOBUTENE AND NAPHTHO[b]CYCLOBUTENE

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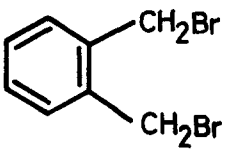
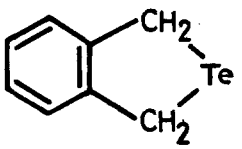
We have recently described[1] the pyrolysis of 9-tellurabicyclo[3,3,1]nona-2,6-diene in which loss of elemental tellurium leads to quantitative production of bicyclo[5,1,0]octa-2,5-diene (3,4-homotropylidene). We now report that tellurium extrusion allows ready synthesis of the title compounds which both possess four-membered carbocyclic rings.

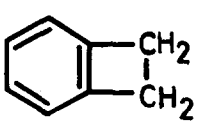
Treatment of α,α'-dibromo-o-xylene (I) with dry sodium telluride (Na_2Te) in dry, N_2-purged DMF for 16 hr at room temperature gave, in moderate yield, 1,3-dihydrobenzo[c]tellurophene (II)



(I)



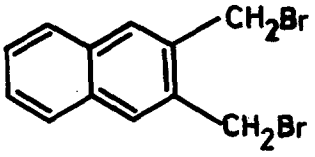
(II)



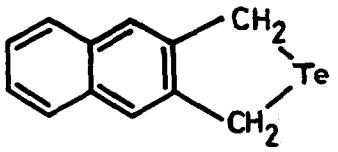
(III)

as plates m.p. 44-46° (evacuated sealed capillary) from petroleum spirit (b.p. 40-60°). Compound (II) gives a satisfactory high-resolution mass spectrum and the ^1H n.m.r. has signals, τ($CDCl_3$) 2.4-3.0 (4H, m) and 5.41 (4H, s). Pyrolysis of the tellurophene (II) was carried out at ca 500° in a low-pressure stream of He gas (0.4-0.5 mm Hg) over loosely packed quartz wool in the heated silica tube of a flow system and gave as product, collected in a receiver cooled in liquid N_2, a 74% yield of benzocyclobutene (III) which had m/e 104 (M^+) and an ^1H n.m.r. spectrum identical to an authentic sample independently prepared;[2] τ($CDCl_3$) 2.90 (centre; 4H, m), 6.83 (4H, s).

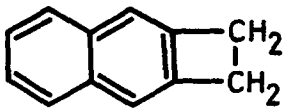
In a preparation corresponding to that of compound (II) described above, the action of Na_2Te on 2,3-bis-(bromomethyl)-naphthalene,[3] (IV), gave, in moderate yield, 1,3-dihydronaphtho-



(IV)



(V)



(VI)

-[2,3-c]tellurophene (V) as glistening scales, m.p. 192-194°, giving m/e 284 (M^+) and a satisfactory high resolution mass spectrum for $C_{12}H_{10}{}^{130}Te$; the ^1H n.m.r. comprises signals, $\tau(CDCl_3)$ 2.1-2.8 (6H, m) and 5.32 (4H, s). Pyrolysis of (V) under similar conditions to those employed for compound (II) gave, in good yield, crystalline naphtho[b]cyclobutene (VI) which on recrystallisation from petroleum spirit (b.p. 60-80°) had m.p. 85-87° (lit.[4] m.p. 86.5°). Compound (VI) had m/e 154 and a satisfactory high-resolution mass spectrum; its ^1H n.m.r. has resonances $\tau(CDCl_3)$ 2.1-2.8 (6H, m) and 6.66 (4H, s) and its u.v. spectrum is in agreement with that reported earlier.[4]

The convenient production of the fused cyclobutenes[5] (III) and (VI) in the above processes suggests the ready extension of the use of tellurium extrusion to the synthesis of other systems, including those related to (III) and (VI) which may be expected to exhibit interesting ring strain effects.[6]

References

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5. For a review on the synthesis of benzocyclobutene and derivatives see, I.L. Klundt, Chem. Revs., 1970, 70, 471.
6. Cf., for example, R.D. Rieke, S.E. Bales, C.F. Meares, L.I. Rieke, and C.M. Milliren, J. Org. Chem., 1974, 39, 2276.