Mercury(II) Ion-catalysed Rearrangements of Cyclodeca-1,2,5,8-tetraene

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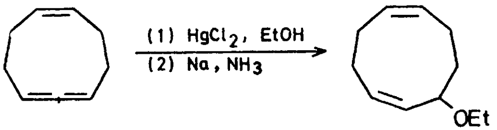
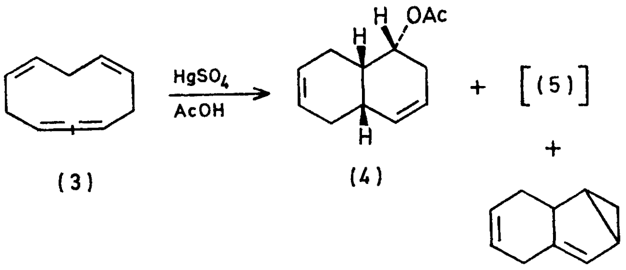
Summary Unlike most oxymercurations, cyclodeca-1,2,5,8-tetraene gives only rearranged products, one of which may derive from a 'metal complexed carbene' intermediate.

Oxymercuration[1] of (**1**) gives the normal adduct (**2**), but in marked contrast, treatment of (**3**) with $HgSO_4$ and AcOH produces only rearranged products (**4**), (**5**), and (**6**) in yields of 27, 1, and 22%, respectively. Skattebol's method[2] was used to prepare the title allene (**3**) from cyclonona-1,4,7-triene.[3]

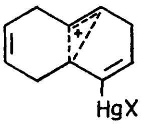
The carbon skeleton and stereochemistry of (**4**) were assigned by reduction to the known *cis,syn*-decalin-2-ol. The positions of the double bonds were established by decoupling experiments after the chemical shifts had been separated with Eu(fod)$_3$.[4] The structure of (**5**) has not been fully elucidated. Hydrogenation followed by oxidation gives bicyclo[5,3,0]decan-2-one. Compounds (**3**), (**4**), and (**6**) gave satisfactory analyses.



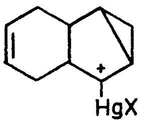
(1) (2)



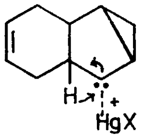
(3) (4) (6)



(7)



(8)



(9)

Reduction of (**6**) gave *cis*- and *trans*-decalin. The structure of (**6**) was assigned from its spectral data [λ_{max}, end absorption; ν_{max} 3060, 3020, 2993, 2840, and 2900 cm^{-1}; δ (CCl_4) 5·4—5·7 (3H, m), 2·3—3·1 (4H, m), 1·4—2·0 (3H, m), 0·5 (t of d, 1H, *J* 8 and 4 Hz, and −0·1 (q, 1H, *J* 4 Hz) p.p.m.]. The chemical shifts and coupling patterns of the cyclopropyl protons are similar to those of bicyclo[3,1,0]-hex-2-ene. Of the two nonconjugated positions that remain for the other double bond, only the isomer shown fits the chemical shift data reasonably.[5,6] The *cis-syn* stereochemistry fits the data best.

The formation of (**4**) and (**5**) represents transannular rearrangement during oxymercuration of the allene. The high stereospecificity implicates a bridged intermediate (**7**). Homoallyl–cyclopropyl carbinyl rearrangement leads to (**8**) which may be considered to be a 'metal-complexed carbene' intermediate,[8] (**9**). Such intermediates are known to undergo hydride shifts as shown.[8]

The reaction of (**3**) with HgSO$_4$ and AcOD leads to deuterium incorporation into (**4**) at the 4- position as required by the known[7] addition–elimination mechanism whereby mercury is lost. *Deuterium is not incorporated into* (**6**) consistent with intermediate (**9**).

Other solvents gave similar results but the ratio of products depends on solvent nucleophilicity. The ratio of products of solvent-capture to hydrocarbon (**6**) increases from the less nucleophilic solvent, CF_3CH_2OH (30:70), to AcOH (57:43), to the more nucleophilic system, 80% aqueous acetone (90:10). The overall yields of volatile products are 75% (from CF_3CH_2OH), 50% (AcOH), and 70% (aqueous acetone). The products do not interconvert but (**6**) apparently decomposes to non-volatile material. The above ratios thus may underestimate the relative amount of hydrocarbon (**6**) that is actually formed.

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