

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

By RICHARD W. THIES,* P. K. HONG, and R. BUSWELL

(Department of Chemistry, Oregon State University, Corvallis, Oregon 97331)

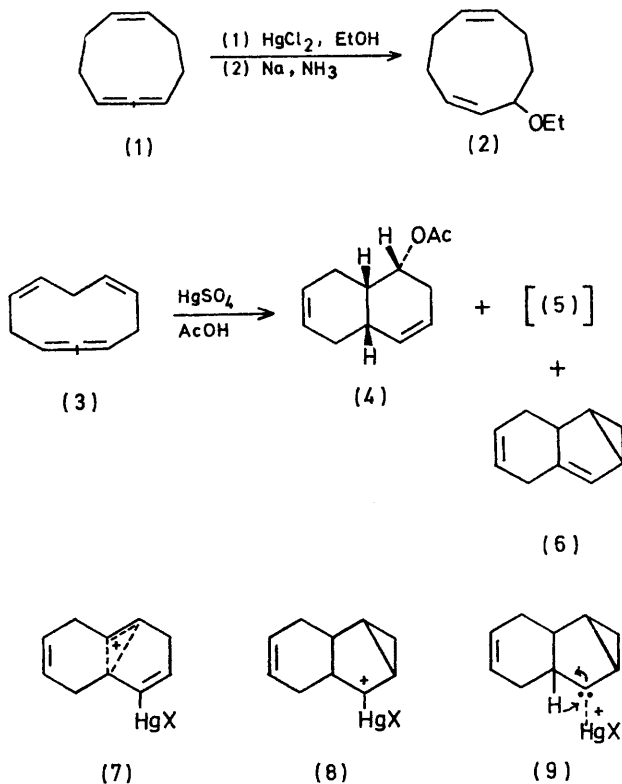
Summary Unlike most oxymercuration, cyclodeca-1,2,5,8-tetraene gives only rearranged products, one of which may derive from a 'metal complexed carbene' intermediate.

produces only rearranged products (4), (5), and (6) in yields of 27, 1, and 22%, respectively. Skattebol's method² was used to prepare the title allene (3) from cyclonona-1,4,7-triene.³

OXYMERCURATION¹ of (1) gives the normal adduct (2), but in marked contrast, treatment of (3) with HgSO₄ and AcOH

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 $\text{Eu}(\text{fod})_3$.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.



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 known⁷ 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, $\text{CF}_3\text{CH}_2\text{OH}$ (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 $\text{CF}_3\text{CH}_2\text{OH}$), 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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