Catalytic Synthesis of *endo*-Brevicomin and Related Di- and Tri-oxabicyclo[x.2.1] Systems

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Summary Palladium(II)-catalysed intramolecular cyclisation of terminal olefins containing a suitably located vicinal diol group gives the corresponding cyclic acetal.

DIOXABICYCLO[3.2.1]ALKANES have attracted interest because of the structures of various bark beetle pheromones such as brevicomin $(1a)^1$, frontalin (1b),² and the Dutch elm beetle pheromone $(2)^3$ and several syntheses of these pheromones have been reported.⁴ We have devised a short stereospecific synthesis of *endo*-brevicomin from butadiene which appears to have general applicability. Palladium catalysed dimerisation of butadiene with concomitant carbonylation in ethanol gave the nonadienoate $(3)^5$ which was converted by a standard reduction-tosylation-reduction sequence into the *trans*-nonadiene (4; 64%).

(II)-catalysed cyclisation. Yields for the final cyclisation step were moderate [(6), 30%; (7) 49%]. The spectroscopic properties of *endo*-brevicomin (*endo*-1a) and (7) were in accord with published data. The mass spectra of (*endo*-1a) and (7) contained M - EtCO, M - EtCHO and M - Me-CO, M - Me-CHO ions respectively. In contrast the mass spectrum of (6) did not contain the corresponding M - CHO, $M - \text{CH}_2\text{O}$ ions but did exhibit an M - 42 ion. The synthesis may be varied by palladium-catalysed conversion of the dienes into the keto-olefins followed by epoxidation and thermal (acid-catalysed) rearrangement⁸ to the dioxabicyclic system (*e.g.* $8 \rightarrow 9 \rightarrow 10 \rightarrow 7$).



Epoxidation (76%) followed by hydrolysis (74%) gave the diol (5) which was cyclised directly to *endo*-brevicomin $(45\%)^6$ using palladium chloride as catalyst⁷ in anhydrous dimethoxyethane with copper(II) chloride as reoxidant for the palladium. Octa-1,7-diene and octa-1,6-diene were similarly converted into the dioxabicyclo[4.2.1]nonane (6) and the dioxabicyclo[3.2.1]octane (7) respectively, by mono-epoxidation, ring opening to the olefinic diol, and palladium-

The reaction has been extended to the trioxabicyclo-[3.2.1]-series using diallyl ethers as precursors. The ethers (**11a**—c) were converted into the corresponding monoepoxides (**12a**—c) [*e.g.* (**12b**) τ (CDCl₃) 3·70—4·0 (1H, CH₂=CH-), 4·53—5·0 (2H, CH₂=CH-), 5·98, 6·45 (2 × 2H,

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m, CH2-O), 7.15 (2H, m, epoxide H), and 8.70 (3H, d, Me)]. The epoxides were hydrolysed (H₂SO₄ in tetrahydrofuran) to the diols (13a-c) which were cyclised, without purification, to (14a-c; ca. 20%) using PdCl2-CuCl2 [e.g. (14b) τ (CDCl₃) 5·40–6·40 (4H, m), 4·53 (2H, s), 8·53 (3H, d), and 8.65 (3H, s)]. The mass spectrum of (14b) indicates fragmentation of the largest bridge is preferred, i.e. M - 30(20% abundance).

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