

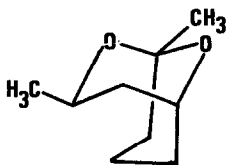
SHORT-STEP SYNTHESIS OF 1,3-DIMETHYL-2,9-DIOXABICYCLO
[3.3.1] NONANE: AN INSECT ATTRACTANT.

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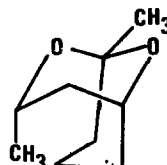
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Summary: Endo- and exo-1,3-dimethyl-2,9-dioxabicyclo [3.3.1] nonane were synthesized in a three-step sequence starting from acetylacetone involving intramolecular cyclization using palladium chloride as catalyst.

1,3-Dimethyl-2,9-dioxabicyclo [3.3.1] nonane, a host-specific substance in Norway spruce infested by the striped ambrosia beetle, Trypodendron lineatum OLIV., was isolated and identified as bicyclic structures (1) and (2) by W. Franke.^{1,2)} These compounds were first synthesized in low yield by Diels-Alder reaction of 3-buten-2-one and 4-penten-2-ol followed by cyclization.²⁾ Both isomers were later synthesized in higher yield but by a lengthy method.³⁾ Redlich⁴⁾ determined the absolute stereochemistry of both isomers and their enantiomers and synthesized all four compounds.

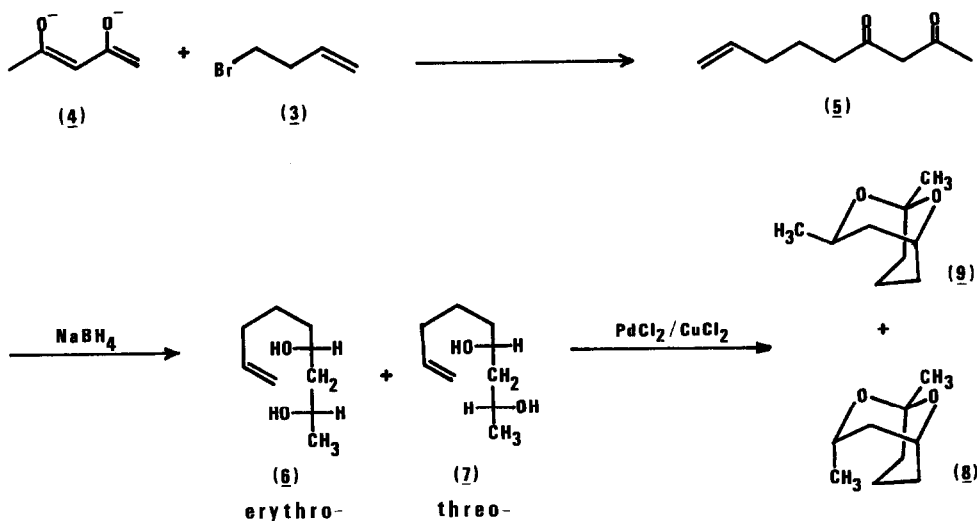


exo-(1)



endo-(2)

Our success in the synthesis of endo-brevicommin and related di- and tri-oxabicyclo [3.3.1] systems⁵⁾ led us to synthesize the insect attractant 1,3-dimethyl-2,9-dioxabicyclo [3.3.1] nonane in a three-step sequence starting from commercially available acetylacetone.



Alkylation of the acetylacetonate di-anion (4)³⁾ with 4-bromo-1-butene (3) was carried out at 0°C in anhydrous tetrahydrofuran for 20 min to give the dione (5) as a colorless liquid in 70% yield. Reduction of the ketone functions with NaBH_4 in 0.05N KOH at 50°C for 30 min gave nearly quantitatively a mixture of the erythro- and threo-8-nonen-2,4-diol (6) and (7) which was cyclised directly to endo- and exo-1,3-dimethyl-2,9-dioxabicyclo [3.3.1] nonane (8) and (9) (50% yield, ratio of endo:exo, 5:4) using palladium chloride as catalyst⁵⁾ in anhydrous tetrahydrofuran with copper (II) chloride as reoxidant for the palladium. The ratio of the endo- and exo-mixture was determined by GC/MS (2% OV-17 column) and separated on preparative GLC. The structures were identified with the authentic samples by spectral comparisons (IR, NMR, MS).^{2,3,4)}

Acknowledgment. We are indebted to Prof. Hartmut Redlich, Institut für Organische Chemie und Biochemie der Universität Hamburg, for providing the NMR spectra of authentic endo- and exo-1,3-dimethyl-2,9-dioxabicyclo [3.3.1] nonane, and to Prof. R.W. Rickards, Research School of Chemistry, The Australian National University, Canberra, for MS analysis.

Reference

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