A Novel Synthesis of (±)-Sesquicarene

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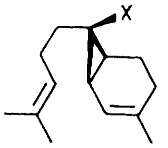
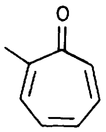
A highly stereospecific total synthesis of (±)-sesquicarene was accomplished by the photochemical transformation of the bicyclo[3.2.2]nona-3,6-dien-2-one (**7**), which was derived from 2-methyltropone (**5**), into the bicyclo[4.1.0]hept-2-ene (**3**).

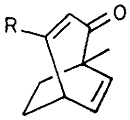
Sesquicarene (**1**)[1] is a sesquiterpene analogue of Δ^2-carene and it has been synthesised.[2-4] A major synthetic problem is the stereospecific elaboration of the bicyclo[4.1.0]heptane skeleton, which strongly suggests methods based on carbene



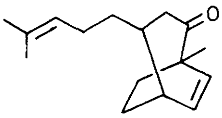
(1) X = Me
(2) X = CH=C=O
(3) X = CH_2CO_2Me
(4) X = CH_2CHO



(5)



(6) R = H
(7) R = $CH_2CH_2CH{=}CMe_2$



(8)

additions.[2,4] We now report a new and short synthesis of racemic sesquicarene (**1**) based on photochemical transformation of the bicyclo[3.2.2]nonadienone (**7**) into the Δ^2-carene derivative (**3**).

The dienone (**6**) was prepared from 2-methyltropone (**5**) by heating with ethylene.[5] Regioselective addition of 4-methylpent-3-enylmagnesium bromide to the α,β-unsaturated ketone (**6**) in the presence of copper(I) iodide in tetrahydrofuran afforded the enone (**8**)† (66%), ν_{max} 1700 cm^{-1}; 2,4-DNP (dinitrophenylhydrazone), m.p. 108—109 °C (decomp.). The trimethylsilyl enol ether of (**8**) was treated with *N*-bromosuccinimide,[6] and the resulting mixture of α-bromoketones was converted into the dienone (**7**) by dehydrobromination by heating with lithium bromide and carbonate in *N*,*N*-dimethylformamide [(**7**) (81%), ν_{max} 1660 and 1630 cm^{-1}; 2,4-DNP, m.p. 117—118 °C].

The dienone (**7**) was photochemically transformed into the Δ^2-carene derivative (**3**) by irradiation of a methanolic solution of (**7**) using a 100 W high-pressure mercury lamp through a Pyrex filter [(**3**) (66%), ν_{max} 1740 cm^{-1}]. This process is general for bicyclo[3.2.*x*]dienones[7] and presumably involves the initial [3,3] sigmatropic rearrangement of (**7**) to the keten intermediate (**2**) followed by addition of methanol.

In order to remove one carbon atom from the *syn* side chain as carbon monoxide, the ester (**3**) was reduced by lithium aluminium hydride, and the resulting alcohol was oxidized by Collins reagent to give the aldehyde (**4**) (80%), ν_{max} 2720 and 1725 cm^{-1}; 2,4-DNP, m.p. 140—142 °C. When a solution of the aldehyde (**4**) and tris(triphenylphosphine)chlororhodium (1.0 equiv.) in acetonitrile[8] was heated under reflux vigorously for 15 min, decarbonylation took place to give the hydrocarbon (**1**) (43%) which was identical spectroscopically with natural sesquicarene.

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† Satisfactory ^{1}H n.m.r. spectra have been obtained for all new compounds; the stereochemistry of the homoprenyl side chain of (**4**) is uncertain. All 2,4-DNP derivatives and (**3**) gave appropriate combustion data.