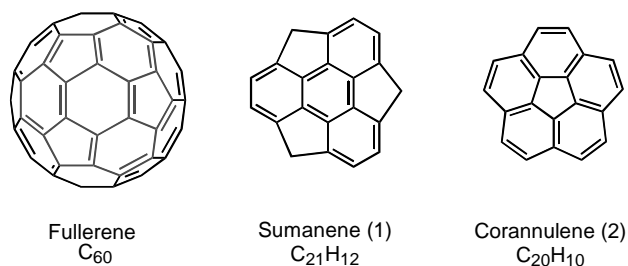


First Synthesis of Sumanene, a Fullerene Fragment

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Bowl-shaped π -conjugated compounds are important not only as model compounds of fullerenes but also as possible synthetic intermediates for artificially-designed fullerene derivatives such as hetero-fullerenes. Most of the attention has been focused on the compounds derived from C_{5v} symmetric corannulene. Sumanene (**1**), which is a key partial C_{3v} symmetric structure of fullerenes, has some advantages over corannulene (**2**) derivatives, including the presence of three benzylic positions that should permit further functionalization to create new bowl-shaped species via the corresponding radicals, cations, anions, carbenes, etc.¹ Although several approaches to sumanene have been attempted,¹⁻³ there is no report of a successful route to synthesize it. We now report the synthesis of sumanene, which can be prepared in short steps from commercially available norbornadiene under mild conditions.



Our strategy for synthesis lies in constructing the three-dimensional framework using tetrahedral sp^3 carbons, which leads to the required π -conjugated structure by oxidative aromatization. In our synthetic route (Figure 1), the key intermediate is hexahydrosumanene **4**, which may be prepared from the isomer **3** by transferring the alkene bridges.

Trimerization of norbornadiene yielded *syn*- and *anti*-benzotris(norbornadiene)s, which was achieved by a modified procedure based on the organocopper-mediated cyclization. Stepwise transmetalation via an organotin compound afforded *syn*-**3**.⁴ The alkene-bridge exchange was achieved by the Ru-catalyzed tandem ring-opening metathesis (ROM) and ring-closing metathesis (RCM) reaction. *Syn*-**3** was treated with 10 mol% of $Cl_2(PCy_3)_2Ru=CHPh$ in toluene at 0 °C, then at room temperature under an atmospheric pressure of ethylene, giving **4**. Finally, **4** was oxidized by DDQ to give sumanene (**1**). All of these steps were performed under mild conditions without severe conditions such as flash vacuum pyrolysis.

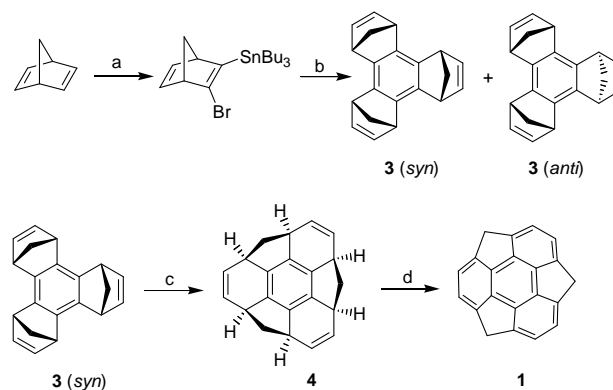


Figure 1. Synthetic routes to sumanene (**1**). Conditions: a) butyllithium, potassium *t*-butoxide, $BrCH_2CH_2Br$, THF, -78 °C to -45 °C then tributylstannyl chloride, room temperature. *Syn* : *anti* = 1:3. b) $Cu(2-C_4H_3SCO_2)_2$, -20 °C to room temperature. c) cat. $[P(C_6H_{11})_3]_2RuCl_2=CHPh$, $CH_2=CH_2$, toluene, -78 °C to room temperature, 24 h. d) dichlorodicyanoquinone (DDQ), toluene, 110 °C, 3 h.

The NMR spectra of **1** indicate that sumanene is present as a C_3 symmetric structure in solution. The dynamic behavior of the bowl-shaped compound is of interest. Corannulene exhibits rapid bowl-to-bowl inversion at room temperature. On the other hand, variable temperature NMR of sumanene in *p*-xylene- d_{10} solution revealed that sumanene is rigid.

Reference

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