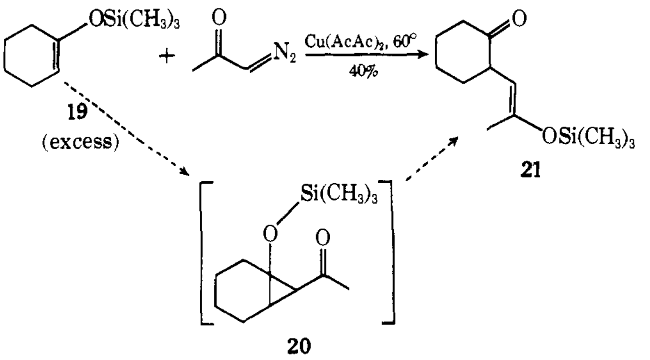

sumably by way of cyclopropyl ketone **20** which then undergoes a silatropic retro-aldol reaction.[20] Although the sensitivity of enol ether **21** hampered purification, its structure was established by spectral data (ir 1705 (C=O), 1675 (C=C—O), 850 (Si—C) cm^{-1}; NMR 4.61 (d, J = 8 Hz, C=CH), 1.63 (s, CH_3), 0.17 (s, $Si(CH_3)_3$) and hydrolysis to the known 2-acetonylcyclohexanone.[21]

Acknowledgment. We wish to thank the National Science Foundation and the National Institutes of Health for partial support of this research.

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A New Boron Hydride. Tetradecaborane(20)

Sir:

We wish to report the synthesis and novel structure of a stable new boron hydride, tetradecaborane(20). The synthesis of this material in low yield was accomplished by reaction of excess octaborane(12)[1] with potassium nonahydrohexaborate[2] in diethyl ether solution, solvent removal at room temperature, and treatment of the solid with liquid HCl at −78°. Fractional distillation of the volatile components yielded a mixture (stopping in a 0° trap) of a white solid ($B_{16}H_{20}$) and a yellow semicrystalline solid ($B_{14}H_{20}$) embedded in a small amount of yellow oily material. The mixture was placed in an oven maintained at 32°, and yellow crystals of $B_{14}H_{20}$ slowly formed over a period of several weeks. The yellow $B_{14}H_{20}$ was then manually separated from the colorless $B_{16}H_{20}$ in the open air. The yield of $B_{14}H_{20}$ could not be measured accurately, since only extremely small quantities of this material were obtained, but probably does not exceed 2%.

The mass spectrum of a sample purified in this manner contained a base peak at 162 amu and a parent peak at 174 amu, corresponding to the molecular ion $^{11}B_{14}H_{20}$. The 70.6-MHz ^{11}B NMR spectrum of a very dilute solution of $B_{14}H_{20}$ in dichloromethane suggested a high degree of molecular symmetry since only five resonances were observed: a low field area 1 doublet at −34.6 ppm (J_{BH} = 150 Hz), two overlapping area 2 doublets at −8.8 (J_{BH} = 160 Hz) and −6.0 ppm (J_{BH} = 160 Hz), and two upfield area 1 doublets at +10.6 (J_{BH} = 150 Hz) and +36.1 ppm (J_{BH} = 160 Hz).[3]

A well-formed single crystal of approximately 0.7 mm diameter was utilized in a single-crystal structure determination at −164°. The compound is thermochromic; the crystals became colorless upon cooling although there was no indication of a phase transition. The compound crystallizes in space group $P2_12_12_1$, with a = 13.119 (4), b = 9.976 (3), and c = 8.963 (3) Å (at −164°) and with ρ_{calcd} = 0.971 g/cm^3 for Z = 4.

The structure was solved using direct methods. The initial E map showed all 14 boron atoms. A difference Fourier located the 20 hydrogen atoms. Anisotropic least-squares

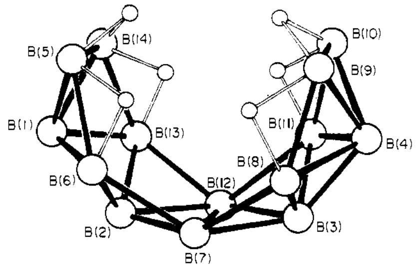

Figure 1. Terminal hydrogens have been omitted for clarity.

refinement of boron atoms and isotropic refinement of hydrogen parameters led to a final *R* value of 0.047 for all data (913 reflections). As shown in Figure 1, the molecule consists of two B_8H_{12} fragments fused at the B(7)-B(12) positions. All bond distances and angles appear normal. The novel structural feature is that the open faces are cis to one another, while all previous "fused fragment" boranes, for which structures have been established (e.g., $B_{13}H_{19}$, $B_{16}H_{20}$, n-$B_{18}H_{22}$, i-$B_{18}H_{22}$),[4-7] have the open faces in a trans configuration. Another interesting point is the unusual fact that the B(3)-B(7)-B(2)-B(12) portion of the molecule is nearly planar. The molecule in the solid state has nearly C_{2v} symmetry, in agreement with the room temperature NMR data.

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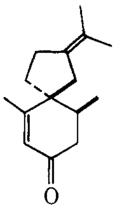
The Total Synthesis of Spirovetivanes[1]

Sir:

In recent years much attention has been directed toward developing synthetic routes to the rapidly expanding class of sesquiterpenes known as the spirovetivanes.[2-7] Representatives of the spirovetivanes are β-vetivone (**1**),[3] hinesol (**2**),[4] β-vetispirene (**3**),[5] anhydro-β-rotunol (**4**),[6] and α-vetispirene (**5**).[5a,7] Due in part to the widely variant oxidation states at carbons 1, 2, 6, 7, 8, 11, 12, and 14 throughout this series, previous synthetic work has concentrated on the construction of specific spirovetivanes. Only one study has dealt with the preparation of an intermediate suitable for transformation into a variety of these sesquiterpenes.[7] We would like to report the facile preparation of 2-carboethoxy-8-ethoxy-10-methylspiro[4.5]deca-1,7-dien-6-one (**6**), a versatile intermediate which we have transformed into spirovetivanes **1-5**.



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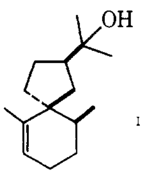

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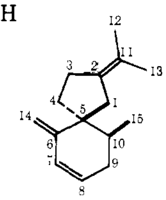

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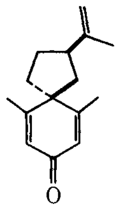

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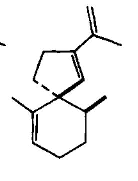

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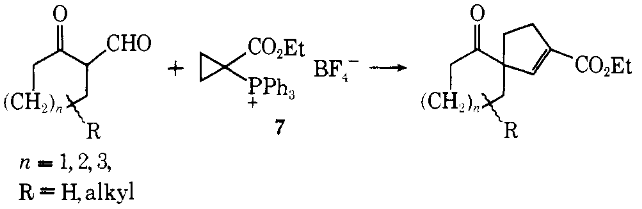
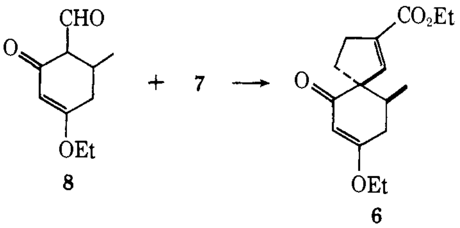
A general synthesis of spirocycles has been developed through an extension of the synthesis of ethylcyclopent-1-ene carboxylates by the closure of ylids derived from carboethoxycyclopropyltriphenylphosphonium tetrafluoroborate (**7**) and β-ketoesters or symmetrical 1,3-diketones.[8] The reaction of **7** with sodium enolates of 2-formylcycloalkanones produces spiro compounds in moderate yields.[9] For example, successive treatment of an HMPT solution of 2-formylcyclohexanone with sodium hydride and **7** produced 2-carboethoxyspiro[4.5]dec-1-en-6-one in 40% yield as the major isolable non-phosphorous-containing compound. The generality of this spiroannelation was illustrated by the preparation of five additional spiroketoesters in yields of 30-44%.[10] No products from reaction at the ketone carbonyl were ever detected.



Application of this method to the synthesis of spirovetivanes **1-5** proceeded as follows. Treatment of an HMPT solution of the sodium enolate of formyl ketone **8**[11] with **7** produced a *single* crystalline spiroketoester in 38% yield (mp 82-84°; ir 1720, 1668, 1617 cm^{-1}; NMR (CCl_4) δ 1.00 (d, 3 H), 1.30 (t, 3 H), 1.38 (t, 3 H), 1.6-2.8 (m, 7 H), 3.90 (q, 2 H), 4.12 (q, 2 H), 5.19 (s, 1 H), 6.33 (t, 1 H)) whose structure was shown to be **6** by subsequent transformation into known compounds.[12] None of the C-10 epimer of **6** was detected. The stereoselectivity of the attack of the enolate on the activated cyclopropane most likely is due to steric factors arising from the preferred pseudoaxial conformation of the incipient C-10 methyl group.[3b,13]



Catalytic hydrogenation of **6** in ethanol over palladium on charcoal produced ketoester **9** in a regiospecific, stereospecific manner (ir 1730, 1653, 1613 cm^{-1}; NMR (CCl_4) δ 1.00 (d, 3 H), 1.27 (t, 3 H), 1.37 (t, 3 H), 1.6-2.8 (m, 10 H), 3.88 (q, 2 H), 4.07 (q, 2 H), 5.09 (s, 1 H)). Successive treatment of **9** with excess methyllithium and 1.2 *N* HCl gave crystalline ketol **10** in 64% yield from **6** (mp 116-119°; NMR ($CDCl_3$) δ 1.00 (d, 3 H), 1.25 (s, 6 H), 1.6-2.6 (envelope with doublet at 1.95, 14 H), 5.72 (q, 1 H)). Since one optical antipode of **10** has previously been converted to **4**,[6b] a stress metabolite recently isolated from blight infected potato tubers, this reaction sequence represents a formal synthesis of (±)-anhydro-β-rotunol.

Ketol **10** also served as a simple precursor to sesquiterpenes **1-3**. Acetylation of **10** followed by treatment of the resulting tertiary acetate **11** with boron trifluoride etherate