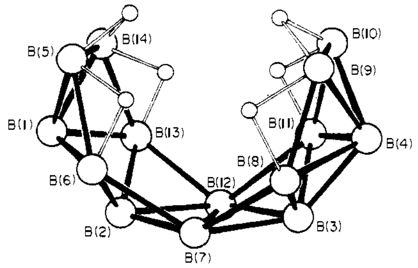

Figure 1. Terminal hydrogens have been omitted for clarity.

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.

Acknowledgment. We acknowledge support from the National Science Foundation Grant No. GP40499X.

References and Notes

(1) J. Dobson, P. C. Keller, and R. Schaeffer, *Inorg. Chem.*, **7**, 339 (1968).
(2) H. D. Johnson, II, R. A. Geanangel, and S. G. Shore, *Inorg. Chem.*, **9**, 908 (1970).
(3) Chemical shifts relative to $BF_3{\cdot}OEt_2$.
(4) J. C. Huffman, D. C. Moody, J. W. Rathke, and R. Schaeffer, *J. Chem. Soc., Chem. Commun.*, 308 (1973).
(5) L. B. Friedman, R. E. Cook, and M. D. Glick, *Inorg. Chem.*, **9**, 1452 (1970).
(6) P. G. Simpson and W. N. Lipscomb, *J. Chem. Phys.*, **39**, 26 (1963).
(7) P. G. Simpson, K. Folting, R. D. Dobrott, and W. N. Lipscomb, *J. Chem. Phys.*, **39**, 2339 (1963).

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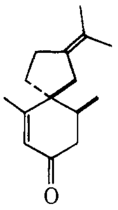
The Total Synthesis of Spirovetivanes[1]

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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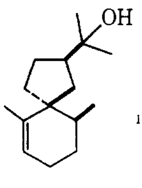

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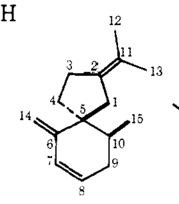

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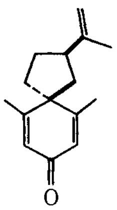

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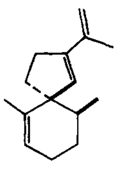

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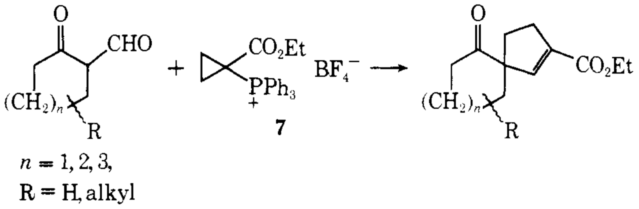
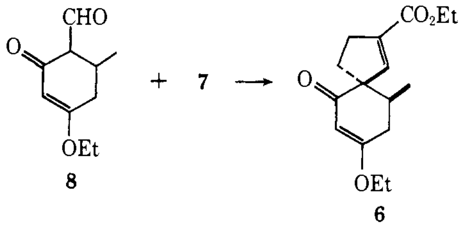
A general synthesis of spirocycles has been developed through an extension of the synthesis of ethylcyclopent-1-ene carboxylates by the closure of ylids derived from carboethoxycyclopropyltriphenylphosphonium tetrafluoroborate (**7**) and β-ketoesters or symmetrical 1,3-diketones.[8] The reaction of **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.

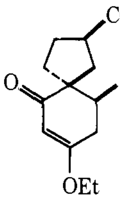


Application of this method to the synthesis of spirovetivanes **1–5** proceeded as follows. Treatment of an HMPT solution of the sodium enolate of formyl ketone **8**[11] with **7** produced a *single* crystalline spiroketoester in 38% yield (mp 82–84°; ir 1720, 1668, 1617 cm^{-1}; NMR (CCl$_4$) δ 1.00 (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



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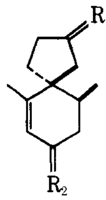
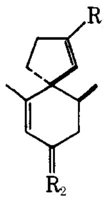
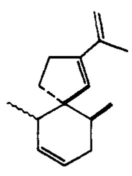


10-13



14-17



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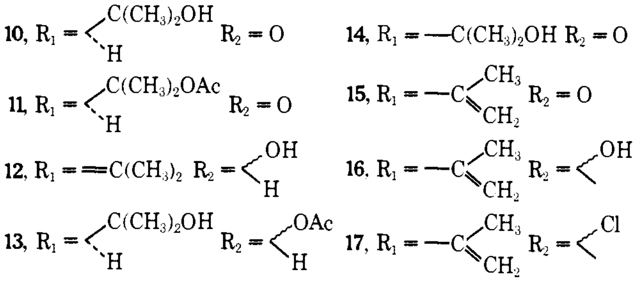

10, $R_1 = \langle^{C(CH_3)_2OH}_{H}$ $R_2 = O$

11, $R_1 = \langle^{C(CH_3)_2OAc}_{H}$ $R_2 = O$

12, $R_1 = {=}C(CH_3)_2$ $R_2 = \langle^{OH}_{H}$

13, $R_1 = \langle^{C(CH_3)_2OH}_{H}$ $R_2 = \langle^{OAc}_{H}$

14, $R_1 = -C(CH_3)_2OH$ $R_2 = O$

15, $R_1 = -C\langle^{CH_3}_{CH_2}$ $R_2 = O$

16, $R_1 = -C\langle^{CH_3}_{CH_2}$ $R_2 = \langle^{OH}$

17, $R_1 = -C\langle^{CH_3}_{CH_2}$ $R_2 = \langle^{Cl}$

afforded a 50% yield of (±)-β-vetivone (**1**), mp 43.5–47.0°. (lit. 43.5–46.0[3a]), spectrally and chromatographically identical with an authentic sample.[14] Lithium aluminum hydride reduction of **1** gave allylic alcohol **12**. Subsequent dehydration of **12** with 10-camphorsulfonic acid in benzene gave (±)-β-vetispirene (**3**), spectrally identical with (−)-β-vetispirene,[5a] in 86% overall yield.

Lithium aluminum hydride reduction of **10** followed by selective acetylation (acetic anhydride, pyridine) of the resulting diol produced a mixture of hydroxyacetates **13** in 81% yield (mp 45–55°; ir 3350, 1725, 1650, 1240 cm^{-1}; NMR (CCl_4) δ 0.97 (d, 3 H), 1.22 (s, 6 H), 1.3–2.1 (envelope with singlets at 1.75, 2.03, 17 H), 5.20 (m, 2 H)). Reduction of **13** with lithium in ethylamine[15] afforded a 75% yield of a 9:1 mixture of two compounds. The major component was shown to be (±)-hinesol (**2**), spectrally and chromatographically identical with an authentic sample.[14,16]

To make use of the C-1,2 double bond present in **6**, the following transformations were conducted. Successive treatment of **6** with methyllithium and 1.2 *N* HCl-ether (4:1) yielded ketol **14** which was dehydrated with 10-camphorsulfonic acid to trienone **15** in an overall yield of 78% (ir 1671, 892 cm^{-1}; NMR (CCl_4) δ 0.97 (d, 3 H), 1.83 (d, 3 H), 1.8–2.8 (envelope with singlet at 1.95, 10 H), 4.90 (broad s, 2 H), 5.58 (broad s, 1 H), 5.68 (q, 1 H)). Treatment of **15** with lithium aluminum hydride gave a mixture of solid isomeric alcohols **16** in quantitative yield (mp 51–62°). Conversion of **16** to the corresponding chlorides **17** with *N*-chlorosuccinimide-dimethyl sulfide complex[17] followed immediately by reduction with lithium aluminum hydride gave an 80% yield of a 37:63 mixture of trienes **18** and (±)-α-vetispirene (**5**),[18] separated and purified by preparative gas chromatography (10 ft × ¼ in. 10% SE-30, 190°, 60 ml He min^{-1}).

References and Notes

(1) This work was supported by National Science Foundation Grant No. GP-8700.
(2) For a review on the spirovetivanes, see J. A. Marshall, S. F. Brady, and N. H. Anderson, *Fortschr. Chem. Org. Naturst.*, **31**, 283 (1974); for the most recent report of a spirovetivane see A. Stoessl, J. B. Stothers, and E. W. G. Ward, *J. Chem. Soc., Chem. Commun.*, 709 (1974).
(3) (a) For the structure and first total synthesis of this substance see J. A. Marshall and P. C. Johnson, *J. Org. Chem.*, **35**, 192 (1970); (b) for a recent efficient synthesis see G. Stork, R. L. Danheiser, and B. Ganem, *J. Am. Chem. Soc.*, **95**, 3414 (1973).
(4) For the structure and first total synthesis of this substance see J. A. Marshall and S. F. Brady, *J. Org. Chem.*, **35**, 4068 (1970).
(5) (a) For the structure of this substance see N. H. Anderson, M. S. Falcone, and D. D. Syrdal, *Tetrahedron Lett.*, 1759 (1970); (b) for the first total synthesis see P. M. McCurry and R. K. Singh, *ibid.*, 3325 (1973).
(6) (a) For the structure of this substance see D. T. Coxon, K. R. Price, and B. Howard, *Tetrahedron Lett.*, 2921 (1974); (b) for a relay synthesis from hinesol and β-rotunol see H. Hikino, K. Aota, D. Kuwano, and T. Takemoto, *Tetrahedron*, **27**, 4831 (1971); (c) for a relay synthesis from nootkatone see D. Caine and C. Chu, *Tetrahedron Lett.*, 703 (1974).
(7) For the first total synthesis of this substance see K. Yamada, H. Nagase, Y. Hayakawa, K. Aoki, and Y. Hirata, *Tetrahedron Lett.*, 4963, 4967 (1973); in this report, a 16-step synthesis of an intermediate suitable for conversion to **1–5** is described.
(8) P. L. Fuchs, *J. Am. Chem. Soc.*, **96**, 1607 (1974).
(9) For a recent review on the synthesis of spiro compounds see A. P. Krapcho, *Synthesis*, 383 (1974); for another method of preparing spiro compounds form 2-formylcycloalkanones see V. Dave and J. S. Whitehurst, *Tetrahedron*, **30**, 745 (1974), and references therein.
(10) The 2-formylcycloalkanones were those derived from the condensations of cyclooctanone, cycloheptanone, 2-methylcyclohexanone, 3-methylcyclohexanone, and 4-*tert*-butylcyclohexanone with ethyl formate.
(11) Prepared in 61.5% yield from 3-ethoxy-5-methylcyclohex-2-en-1-one and ethyl formate, bp 133–135° (1 mm).
(12) All new compounds reported herein were fully characterized. All yields refer to isolated materials.
(13) F. Johnson and S. K. Malhotra, *J. Am. Chem. Soc.*, **87**, 5492 (1965).
(14) We wish to thank Professor J. A. Marshall for kindly supplying us with samples of (±)-**1**, (±)-**2**, and (−)-**2**.
(15) A. S. Hallsworth, H. B. Henbest, and T. I. Wrigley, *J. Chem. Soc.*, 1969 (1957).
(16) This material was also converted to hinesol acetate, spectrally and chromatographically identical with an authentic sample.
(17) E. J. Corey, C. V. Kim, and M. Takeda, *Tetrahedron Lett.*, 4339 (1972).
(18) Spectrally identical (ir, NMR, uv) to (+)-α-vetispirene (see ref 5a).

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Reactions of Transition Metal–Nitrogen σ-Bonds. II.[1] Pentakis(*N*,*N*-dimethylcarbamato)niobium(V) and Its Facile Exchange Reaction with Carbon Dioxide

Sir:

We wish to report the interesting structure and dynamic solution behavior of $Nb(O_2CNMe_2)_5$ (**1**) and to propose a mechanism which accounts for the observed facile carbon dioxide exchange reaction (eq 1).

$$\begin{gathered} Nb(O_2CNMe_2)_5 + x{*}CO_2 \rightleftharpoons \\ Nb(O_2{*}CNMe_2)_n(O_2CNMe_2)_{5-n} + (x-n){*}CO_2 + nCO_2 \quad (1) \\ \text{where } n = 0\text{–}5 \end{gathered}$$

A benzene solution of $Nb(NMe_2)_5$ reacts with CO_2 (5 or more equiv) in a sealed tube at room temperature to give $Nb(O_2CNMe_2)_5$ (**1**). **1** is an air-sensitive, pale yellow crystalline solid, only very sparingly soluble in alkane solvents but appreciably soluble in benzene and toluene. A cryoscopic molecular weight determination shows that **1** is monomeric in benzene. The ^1H NMR spectrum of **1** in toluene-d_8 at 60 MHz shows a single resonance at 2.56 ppm from HMDS (hexamethyldisiloxane) at ambient temperatures. On cooling the sample this resonance splits into a 3:2 doublet at 2.28 and 2.50 ppm (rel HMDS), $T_c = -65°$. No further change in the spectrum is observed on cooling the sample to −90°. A methylene chloride-freon 11 solution of **1** shows similar ^1H NMR spectroscopic properties; the 3:2 doublet persists to −120° (100 MHz) which is the limit of our low temperature capability. The ^1H NMR spectroscopic properties of **1** are independent of the concentration of **1**. These observations alone, however, are singularly uninformative with regard to the coordination properties of the metal.

Early transition metal *N*,*N*-dimethylcarbamato compounds show strong infrared absorptions in the region 1690–1550 cm^{-1} attributable to a stretching mode of the NCO_2 moiety.[2] We have sought a distinction between bidentate and monodentate $Me_2NCO_2^-$ ligands from a comparison of the ir spectra of $^{12}C^{16}O_2$, $^{13}C^{16}O_2$, and $^{12}C^{18}O_2$