presented here prior to publication, and acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this research.

Registry No.—*cis*-4-*tert*-Butylcyclohexanol, 937-05-3; *trans*-3-methylcyclohexanol, 7443-55-2; *cis*-4-methylcyclohexanol, 7731-28-4; *cis*-2-methylcyclohexanol, 7443-70-1; Li-*sec*-Bu_3BH, 38721-52-7; $LDMBH_2$, 51899-21-9; LTMBH, 60284-40-4; LTSBH, 61075-97-6.

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(1) Lithium tri-*sec*-butylborohydride (Li-*sec*-Bu_3BH, L-Selectride): H. C. Brown and S. Krishnamurthy, *J. Am. Chem. Soc.*, **94**, 7159 (1972).
(2) Potassium tri-*sec*-butylborohydride (K-*sec*-Bu_3BH, K-Selectride): C. A. Brown, *J. Am. Chem. Soc.*, **95**, 4100 (1973).
(3) Lithium dimesitylborohydride bis(dimethoxyethane) ($LDMBH_2$·2DME): J. Hooz, S. Akiyama, F. J. Cedar, M. T. Bennett, and R. M. Tuggle, *J. Am. Chem. Soc.*, **96**, 274 (1974).
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(5) For an example of an application of hindered borohydrides to prostaglandin synthesis see E. J. Corey, K. B. Becker, and R. K. Varma, *J. Am. Chem. Soc.*, **94**, 8616 (1972).
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(7) Expansion of the equation given by Eliel[8] to the situation where each conformer yields two products gives

$$\frac{d\,\%_{cis}/dt}{d\,\%_{trans}/dt} = \frac{k_a[E] + k_e[A]}{k_a[A] + k_e[E]} = \frac{k_aK + k_e}{k_a + k_eK}$$

$$= \frac{k_a(n_E/n_A) + k_e}{k_a + k_e(n_E/n_A)} = \frac{n_Ek_a + n_Ak_e}{n_Ak_a + n_Ek_e} = \frac{n_E(k_a/k_e) + n_A}{n_E + n_A(k_a/k_e)}$$

$$= \frac{n_E(\%\ A/\%\ E) + n_A}{n_E + n_A(\%\ A/\%\ E)} = \frac{n_E\ \%\ A + n_A\ \%\ E}{n_E\ \%\ E + n_A\ \%\ A}$$

Integration over the entire course of reaction gives fraction (or %) cis product/fraction (or %) trans product = $(n_E\%\ A + n_A\%\ E)/(n_E\%\ E + n_A\%\ A)$ as indicated in the discussion. If the Curtin–Hammett principle does not apply (i.e., fast reactions, slow conformer interconversion) each conformer is converted independently to the two products as in Scheme I. Since the initial mole fractions of A and E are n_A and n_E, the result in the above discussion follows directly.
(8) E. L. Eliel, "Stereochemistry of Carbon Compounds", McGraw-Hill, New York, N.Y., 1962, p 238.
(9) J. A. Hirsch, *Top. Stereochem.*, **1**, 199 (1967).
(10) Calculated from $-\Delta G = RT \ln K_{eq}$.
(11) Along these lines, the data in Table II further suggest that Hoozs' reagent, $LDMBH_2$[3], should also show superior selectivity at low (i.e., −78 °C) temperatures.
(12) The situation is complicated for the 3-alkylcyclohexanones at temperatures high enough so that the axial conformer makes a significant contribution. In this situation, the axial alkyl group may interfere with axial approach of the bulky reagents. In addition, equatorial attack may be slowed by the developing syn-axial OX/alkyl interaction. These possible complications disappear at low temperatures where only the equatorial alkyl conformer is significantly populated.

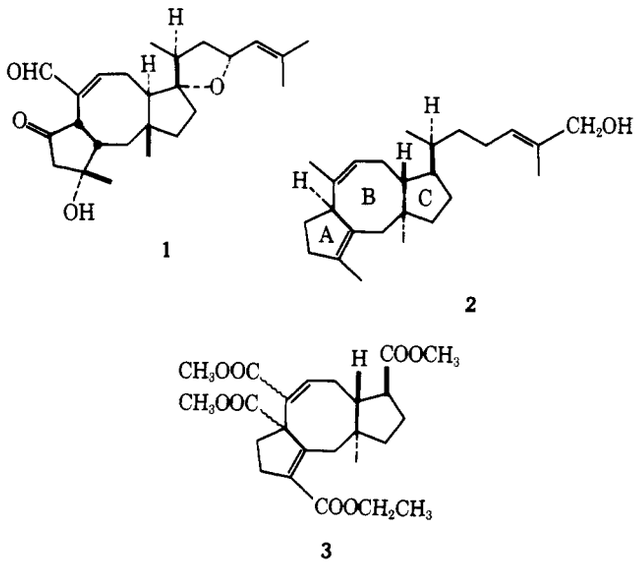
Communications

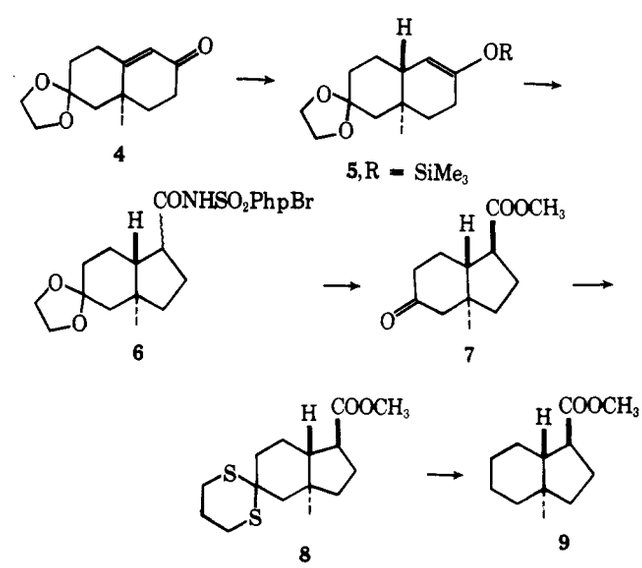
A Synthesis of the Ophiobolin Nucleus[1]

Summary: A ring contraction–ring expansion–annelation reaction sequence was followed for the synthesis of functionalized carbon skeleton of the ophiobolins.

Sir: The ophiobolins are the most abundant members of the relatively new class of C-25 terpenoids known as sesterterpenes.[2] Representatives of this class of natural products are ophiobolin A (**1**),[3] a metabolite of the plant pathogenic fungus *Cochliobolus miyabeanus,* and ceroplastol II (**2**),[4] a component of the desiccant wax produced by females of insect family *Ceroplastes albolineatus.*[5] The ring system of the ophiobolins is also found in a large family of diterpene aglycones known as fusicoccins.[6] The novel structure and biological activity[7] of the ophiobolins make them attractive targets for total synthesis. We would like to report the preparation of tetraester **3**, the first synthesis of the tricyclo[9.3.0.$0^{3,7}$]tetradecane ring system characteristic of the ophiobolins.[8] The synthesis described herein produces the trans BC ring juncture present in all ophiobolins. The location of substituents on the tricyclic nucleus makes **3** a potential intermediate in projected syntheses of several ophiobolins.

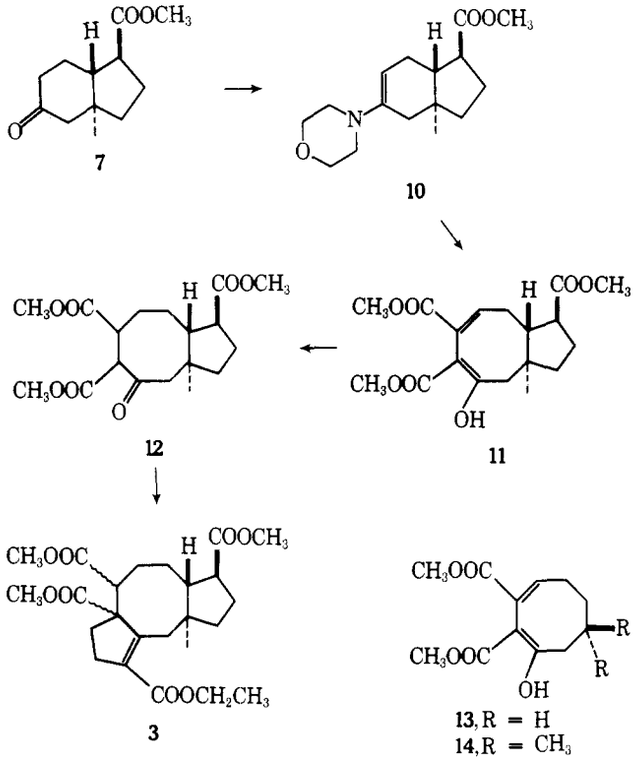
The known octahydronaphthalene **4**[9] was reduced with lithium in ammonia and the resulting enolate was trapped according to established procedures[10] to afford a high yield of enol ether **5**. The crude ether **5** was allowed to react with 1 equiv of *p*-bromobenzenesulfonyl azide in acetonitrile at 50 °C, followed by the addition of a small amount of water to effect hydrolysis of the intermediate imino ether.[11] The re-





sulting *N*-acyl sulfonamide **6** [mp 185–188 °C; NMR ($CDCl_3$) δ 0.85 (s, 3), 1.1–2.5 (m, 12), 3.87 (m, 4), 7.63 (d, 2, J = 9 Hz), 7.91 (d, 2, J = 9 Hz), 8.55 (br s, 1)] was hydrolyzed with concommitant loss of the ketal and the resulting crude keto acid was esterified to give the trans-fused hydrindan **7** in overall yield of 42% from enone **4**.[12] The structure and stereochemistry of **7** was firmly established by converting it to the known ester **9**[13] via the crystalline thioketal **8** (mp 54–57 °C). The ester **9** produced from **7** was identical (IR, ^1H NMR, ^{13}C NMR, VPC, TLC) with a sample of **9** prepared by an established route.[13,14]

Having established the crucial trans BC ring juncture, attention was turned to expanding the six-membered ring to an eight-membered ring via the well-known reaction between enamines and acetylenic esters.[15] It had been suggested that a trans-fused hydrindanone such as **7** should enolize predominantly away from the ring juncture.[16] This suggestion was primarily an extrapolation from results obtained with trans-fused decalones and steroidal ketones. Thus, when a mixture of keto ester **7** and morpholine was heated in refluxing tetrahydrofuran over 4A molecular sieves, crude enamino ester **10** was obtained in a 90% yield. The appearance of the vinyl proton as a doublet (J = 4.5 Hz) at δ 4.50 (benzene-d_6) in the ^1H NMR spectrum of **10** confirmed that enamine formation had occurred predominantly, if not exclusively, away from the ring juncture. When crude **10** was allowed to react with dimethyl acetylenedicarboxylate and the crude mixture of products was hydrolyzed with aqueous acidic methanol, a 40% yield of a mixture of 1:1 adducts between **7** and dimethyl acetylenedicarboxylate was obtained. Keto ester **7** was also obtained in an 8% yield. The mixture of adducts was 75–80% dienol **11** which was obtained in pure form by crystallization from petroleum ether [mp 114–117 °C; IR (CCl_4) 1730, 1658, 1610 cm^{-1}; UV max (MeOH) 220 nm (ε 7200), 264 (9100); NMR ($CDCl_3$) δ 0.93 (s, 3), 1.3–2.9 (m, 10), 3.78 (sharp m, 9), 7.08 (t, 1, J = 9 Hz), 13.0 (br s, 1); mass spectrum (70 eV) m/e 352 (M^+)].[17] The similarity between the spectral properties of **11** and those of the related cyclooctadienols **13**[18] and **14**[19] support the assigned structure.



The A ring was grafted onto dienol **11** in the following manner. The mixture of adducts from the ring expansion was hydrogenated at 45 psi over 5% palladium on alumina to give a 90% yield of β-keto ester **12** after chromatography over silica gel. Sequential treatment of **12** with sodium hydride and 1-carbethoxycyclopropyltriphenylphosphonium tetrafluoroborate[20] gave a 30% yield of a *single* α,β-unsaturated ester **3** after chromatography over silica gel and recrystallization from petroleum ether [mp 120–121 °C; UV max (MeOH) 237 nm (ε 8700); NMR ($CDCl_3$) δ 0.82 (s, 3), 1.29 (t, 3, J = 7 Hz), 1.3–3.6 (m, 17), 3.70 (s, 3), 3.71 (s, 3), 3.74 (s, 3), 4.21 (q, 2, J = 7 Hz); exact mass calcd for $C_{24}H_{34}O_8$ 450.2254, found 450.2296].[21]

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(14) In order to rule out the possibility that **5** was rearranging to the more stable $\Delta^{2,3}$ isomer prior to ring contraction, methyl 3aβ-methyl-2,3,3aβ,4,5,6,7,7aα-octahydroindan-2-carboxylate was prepared by several routes. It was possible to distinguish this material from **9** by IR spectroscopy and VPC retention time on an SE-30 column.
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William G. Dauben,* David J. Hart
Department of Chemistry, University of California
Berkeley, California 94720
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Synthesis and Structural Determination of Dehydrocyclobutatusin, a Diterpenoid with a Four-Membered Ring

Summary: Irradiation of the diterpenoid, barbatusin (**2**), produces dehydrocyclobutatusin (**3**), which contains a new four-membered ring; the structure of **3** was determined by x-ray methods.

Sir: Cyclobutatusin (**1**), a diterpenoid isolated from *Coleus barbatus*,[1,2] retains the basic spiro[2,5]octane system of bar-