step (21% yield) by lithium-ammonia reduction of epoxide **15**. Finally, triol **18** was converted to (±)-calameon (**19**, 81% yield)[16] according to the method reported by Grieco, Gilman, and Nishizawa.[17]

It is a noteworthy consequence of the reagents, solvent, and reaction conditions used in this method for *trans*-decalin synthesis that the conversion of starting materials to product may be conducted without isolation of intermediates. Moreover, since the photolysis and thermolysis can be conducted at high reactant concentration (e.g., ca. 0.5–2.0 M), preparative-scale reactions are easily performed. Further studies on this method and its extension[18] are in progress.

Acknowledgment. This investigation was supported by Grant No. CA21136, awarded by the National Cancer Institute, DHEW. We thank Professor S. Yamamura for samples of calameon and isocalamenediol.

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[16] The IR and NMR spectroscopic data and chromatographic properties of synthetic calameon were identical in all respects with authentic material kindly provided by Professor S. Yamamura.

[17] Grieco, P. A.; Gilman, S.; Nishizawa, M. *J. Org. Chem.* **1976**, *41*, 1485.

[18] Wender, P. A.; Letendre, L. J. *J. Org. Chem.*, following paper in this issue.

[19] Fellow of the Alfred P. Sloan Foundation, 1979–1981.

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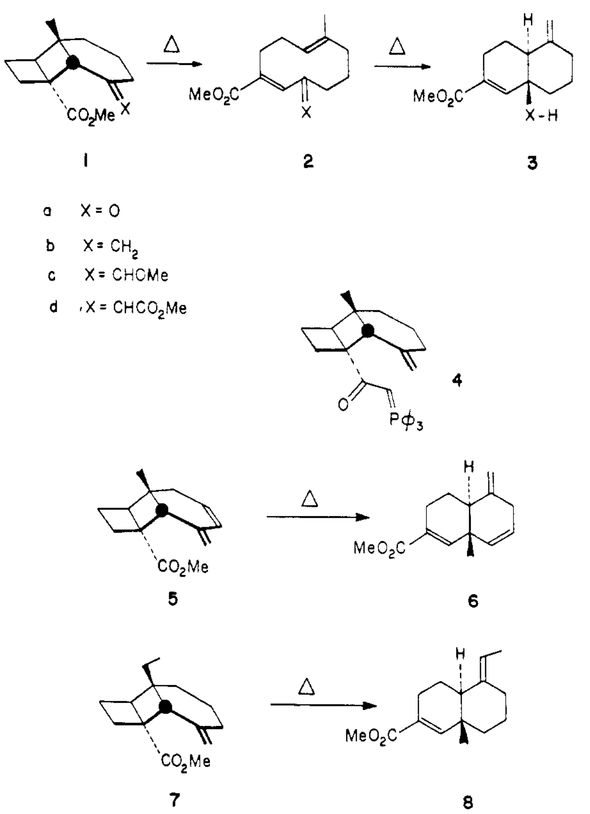
Olefin Metathesis-Transannular Ene Sequence. A Method for the Stereocontrolled Synthesis of *trans*-Decalin Derivatives. 2. Formal Eudesmane Syntheses[1]

Summary: *trans*-Decalin derivatives with an alkyl substituent at the ring junction can be prepared by thermolysis of readily available derivatives of photoadducts derived from methyl cyclobutenecarboxylate and 3-alkylcyclohex-2-enones.

Sir: In the preceding communication, we presented the mechanistic and synthetic groundwork for a method for the conversion of readily available cycloalkenones to *trans*-decalin derivatives with a hydroxyl group at the ring junction (**1a** → **2a** → **3a**).[2] In view of the potential value of this concept in the synthesis of *trans*-decalin natural products characterized by a methyl or other alkyl group at the ring junction, we became interested in determining whether methylene analogues (e.g., **1b**) of the readily available photoadducts would undergo the efficient reorganization observed for the parent ketones.[2] The salient results of these studies are presented below.

Our attention was focussed initially on the suitability of this method for the preparation of derivatives with an angular methyl group (e.g., **3b**) due to the widespread occurrence of this structural element in various natural products. However, the ketone-to-methylene transformation (**1a** → **1b**) required in this regard was found to be unexpectedly nontrivial. For example, reaction of photoadduct **1a**[2a] with methylenetriphenylphosphorane generated by treatment of methyltriphenylphosphonium bromide with *n*-butyllithium in THF or sodium hydride in Me$_2$SO produced the desired product **1b**[3,4] in reproducibly low yields (30–47%) along with varying amounts of **4**. Other olefination procedures provided no improvement in yield. However, it was eventually found that the formation of the undesired byproduct (**4**) in this Wittig methylenation could be eliminated when the ylide was generated with sodium *tert*-amylate and the olefination reaction conducted in toluene.[5] Under these conditions, methylene ester **1b** was formed in 88% yield. Commercially available potassium *tert*-amylate/cyclohexane was also found to be equally effective. It is conceivable that relative to Me$_2$SO the nonpolar solvent (toluene or cyclohexane) serves to inhibit the ion formation required in the penultimate step of the undesired ester-to-ylide transformation, leading to **4**.

Scheme I



The subsequent study on the thermal reorganization of the methylene ester **1b** was found to be less problematic. Thus, when this compound (**1b**) was heated at 210 °C for 2 h in toluene (resealable Pyrex tube), the *trans*-decalin derivative **3b**[6] was formed in 95% yield. The course of this reorganization is presumably analogous to that described for the rearrangement of **1a** to **3a**,[2a] and, as such, its efficiency is similarly decreased in the case of unsaturated systems (e.g., **5** → **6**; 245 °C, 6 h, 78% yield)[7] and relatively

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[1] Presented in part at the ACS/CSJ Chemical Congress, Honolulu, Hawaii, Apr 1–6, 1979, No. ORGN 115.

[2] (a) Wender, P. A.; Hubbs, J. C. *J. Org. Chem.*, preceding paper in this issue. (b) For related independent studies, see: Lange, G. L.; McCarthy, F. C. *Tetrahedron Lett.* **1978**, 4749. Williams, J. R.; Callahan, J. R. *J. Chem. Soc., Chem. Commun.* **1979**, 404, 405.

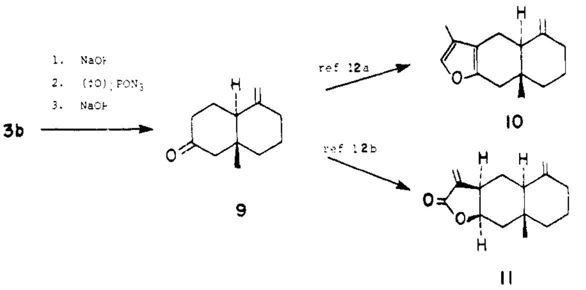
[3] Satisfactory spectroscopic data and elemental and/or exact mass analyses were obtained for all new compounds.

[4] **1b**: IR (CCl$_4$) 2910, 1735, 1650 cm^{-1}; NMR (CDCl$_3$) δ 1.05 (s, 3 H), 1.1–2.8 (m, 11 H), 3.08 (s, 1 H), 3.61 (s, 3 H), 4.74 (d, 2 H).

[5] Conia, J.-M.; Limasset, J.-C. *Bull. Soc. Chim. Fr.* **1967**, 1936.

[6] **3b**: IR (film) 2910, 1730, 1650 cm^{-1}; NMR (CDCl$_3$) δ 0.84 (s, 3 H), 1.50–2.50 (m, 11 H), 3.73 (s, 3 H), 4.52 (m, 1 H), 4.80 (m, 1 H), 6.77 (t, 1 H, J = 1.9 Hz); UV (95% EtOH) 222 nm (ε 6500).

Scheme II



unaffected by substitution on the cyclohexane ring (e.g., 7 → 8; 225 °C, 3 h, ca. 100% yield).[8] The latter transformation is noteworthy in that a single ethylidene isomer is obtained.[9]

The influence of methylene substituents on this reorganization and, consequently, the type of angular substituent which can be introduced were evaluated by using the methoxymethylene derivative **1c** (obtained in 85% yield as a mixture of *E* and *Z* isomers by reaction of **1a** with $Ph_3PCHOMe$ in toluene) and the carbomethoxymethylene derivative **1d** (formed in 79% yield as a mixture of *E* and *Z* isomers by reaction of **1a** with Ph_3PCHCO_2Me in glyme). Thermolysis (212 °C, 6 h, toluene) of the latter derivative (**1d**, 1:1 mixture of *E* and *Z* isomers) provided the diester **3d**[10] in quantitative yield. Thermolysis of **1c** (either a single isomer or a 6:1 mixture of *E* and *Z* isomers) under similar conditions (210 °C, 1 h, toluene) afforded a mixture of cyclodecadienes **2c** and none of the closure product **3c**. However, when this cyclodecadiene mixture (**2c**) or its tricyclic precursor **1c** was heated at 260 °C for 5 h (toluene), **3c**[11] was obtained in 60% yield. It is apparent from these studies on **1a–d**, **2a**,[2a] and **2c** that electronic perturbations have a substantial effect on the facility of the closure reaction.

In order to experimentally verify the stereochemical outcome of this reorganization and to calibrate its synthetic potential against a known standard,[12] we converted **3b** to ketone **9** (78% yield), which has figured in numerous synthesis studies, including the synthesis of (±)-atractylon (**10**)[12a] and (±)-isoalantolactone (**11**).[12b] Thus, ester **3b** provided upon hydrolysis (10% NaOH/MeOH) the corresponding unsaturated acid (mp 139–140 °C). This acid was then converted with diphenylphosphoryl azide[13] to the isocyanate which was hydrolyzed in situ with 10% NaOH to afford the ketone **9** (Scheme II).

New synthetic approaches to a variety of natural product families, in addition to the eudesmane and cadinane families,[2a] can be envisaged on the basis of the mechanistic and synthetic studies presented in this and the preceding communication and in the work of others.[2] Furthermore, this methodology should be readily extended to heterocyclic synthesis and should service a number of objectives in fused-ring synthesis in addition to those presented by the decalin unit. Further studies are in progress.

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[7] The starting material (5) was prepared from the corresponding enone.[2a] Pyrolysis of 5 at 180 °C gave a divinyl compound which, upon heating at 246 °C, gave 6. 6: IR (CCl_4) 2940, 1720, 1650 cm^{-1}; NMR ($CDCl_3$) δ 0.89 (s, 3 H), 1.0–3.0 (m, 7 H), 3.73 (s, 3 H), 4.69 (s, 1 H), 4.92 (s, 1 H), 5.6–5.85 (m, 2 H), 6.93 (t, 1 H, J = 2 Hz); UV (95% EtOH) 222 nm (ε 6100).

[8] 8: IR (CCl_4) 2910, 1720, 1655 cm^{-1}; NMR ($CDCl_3$) δ 0.79 (s, 3 H), 1.25–2.80 (m, 14 H), 3.72 (s, 3 H), 5.02 (q, 1 H, J = 6 Hz), 6.75 (t, 1 H, J = 2 Hz); UV (95% EtOH) 223 nm (ε 5500).

[9] Models indicate that the *E* isomer of 8 should be formed preferentially under kinetic or thermodynamic control. Proof of this assignment must await further analysis. Cf.: Steinberg, N. G.; Rasmusson, G. H.; Reamer, R. A. *J. Org. Chem.* **1979**, *44*, 2294.

[10] **3d**: IR (film) 2920, 1735, 1710, 1650 cm^{-1}; NMR ($CDCl_3$) δ 1.00–2.65 (m, 11 H), 3.63 (s, 3 H), 3.72 (s, 3 H), 4.56 (s, 1 H), 4.84 (s, 1 H), 6.97 (t, 1 H, J = 2 Hz); UV (95% EtOH) 222 nm (ε 7200).

[11] **3c**: IR (CCl_4) 2930, 1720, 1650 cm^{-1}; NMR ($CDCl_3$) δ 1.0–2.5 (m, 11 H), 3.17 (d, 1 H, J = 7.8 Hz), 3.24 (s, 3 H), 3.45 (d, 1 H, J = 7.8 Hz), 3.73 (s, 3 H), 4.55 (s, 1 H), 4.80 (s, 1 H), 6.90 (t, 1 H, J = 1.9 Hz); UV (95% EtOH) 222 nm (ε 8900).

[12] (a) Minato, H.; Nagasaki, T. *J. Chem. Soc., Chem. Commun.* **1965**, 377. (b) Minato, H.; Horibe, I. *J. Chem. Soc. C* **1967**, 1575. (c) Miller, R. B.; Nash, R. D. *J. Org. Chem.* **1973**, *38*, 4424. (d) Miller, R. B.; Nash, R. D. *Tetrahedron* **1974**, *30*, 2961. (e) Harding, K. E.; Cooper, J. L. *Tetrahdedron Lett.* **1977**, 3321.

[13] Yamada, S.-i.; Shioiri, T.; Ninomiya, K. *J. Am. Chem. Soc.* **1972**, *94*, 6203.

[14] Fellow of the Alfred P. Sloan Foundation, 1979–1981.