Tetrahedron Vol. 37, No. 25, pp. 4371 to 4383, 1981
Printed in Great Britain

0040-4020/81/254371-13$02.00/0

1,3-DIYL TRAPPING REACTIONS. FUNDAMENTAL INVESTIGATIONS WITH APPLICATION TO THE SYNTHESIS OF LINEARLY FUSED TRICYCLOPENTANOIDS

R. DANIEL LITTLE*†, GEORGE W. MULLER, MANUEL G. VENEGAS, GARY L. CARROLL, AHMED BUKHARI, LARRY PATTON and KEITH STONE

Department of Chemistry, University of California, Santa Barbara, CA 93106, U.S.A.

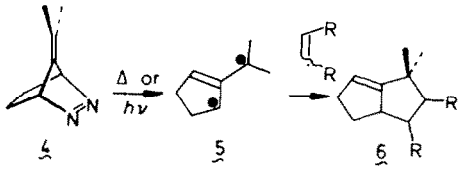
(*Received in U.S.A.* 15 *January* 1981)

Abstract—A comparison of the inter- and intramolecular diyl trapping routes to linearly fused tricyclopentanoids is presented. In addition, several of the factors which are responsible for the stereoselectivity which is associated with the intramolecular process are examined and it is concluded that conformational rather than electronic (secondary orbital) factors play the dominant role. It is shown that *gem* methyl groups located on the acyclic chain which joins the diyl and diylophile (in reference to **32** and **35**, but not to **47**) have no practical effect upon the outcome of the trapping reaction. The intramolecular process is stereospecific with respect to diylophile geometry, and highly stereoselective with respect to the ring junction stereochemistry. Finally, an abortive attempt to synthesize the marine natural product $\Delta^{9(12)}$-capnellene (**19**) as well as a successful synthesis of the mold metabolite *d,l*-hirsutene (**18**) is presented.

In 1966, Dowd reported the generation of the highly reactive diradical (diyl) called trimethylenemethane (TMM, **1**) and demonstrated, using ESR, that TMM possesses a triplet ground state with D_{3h} symmetry.[1] Until that time, TMM was primarily of interest to theoreticians only.[2]

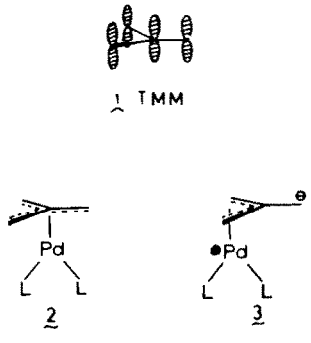
In general, attempts to trap TMM with olefins have not been successful. The principle competing side reaction which thwarted most efforts involved a simple intramolecular closure to form methylenecyclopropane.[3] In contrast, metal complexes of TMM have been trapped with greater efficiency.[4] Certainly the most successful approach to the use of metal complexed TMM has stemmed from the efforts of Trost and Chan who demonstrated that a variety of electron poor olefins react with TMM-PdL_2 in high yield.[5] However, even in these cases, the nature of the metal complex is such that, in contrast with TMM itself, the methylene carbons are nonequivalent; the complex behaves as though it is best represented by structure **3** rather than **2**.

To obtain a TMM system which was not metal complexed and which was not prone to undergo closure to form methylenecyclopropane, Berson *et al.* joined two of the methylene carbons of TMM with an ethano bridge, thereby imposing a strain barrier with respect to closure and allowing sufficient time for the diyl trapping reaction to compete. For example, the thermally induced (ca. 60°) extrusion of nitrogen from the azo compound **4** produced the dimethyl diyl **5** which, in the presence of a variety of different olefins (the diylophile), was trapped to produce a bicyclo(3.3.0)octane (fused adduct, **6**) and/or a 7-alkylidenebicyclo(2.2.1)heptane (bridged adduct, **7**). Fortunately, the course of the reaction could be controlled to favor the formation of the fused cycloadduct by simply operating under conditions wherein the diylophile concentration was "high".[6]



4 5 6 7 (1)

Since there are a number of natural products which possess a single or a series of fused five membered rings, we considered the possibility of utilizing the diyl trapping reaction in a synthetically useful sense. Potential target skeleta include, *inter alia*, those common to prostanoids, linearly and angularly fused tricyclopentanoids, hydroazulenes, and spiro(4.5)decanes. Thus far, our work has focused upon the construction of the four ring systems illustrated in Diagram I.[7-10] While we have been able to successfully utilize cyclopenta-1,3-diyls to construct each of these systems, most of our attention has been directed toward the linearly fused tricyclopentanoid system wherein the primary target molecules include hirsutic acid (**13**), complicatic acid (**14**), coriolin (**15**), coriolin B (**16**), diketocoriolin B (**17**), hirsutene (**18**), and the capnellanes (**19–24**).[11] Note Diagram II.



1 2 3

†Alfred P. Sloan, Foundation Fellow, 1980–82.

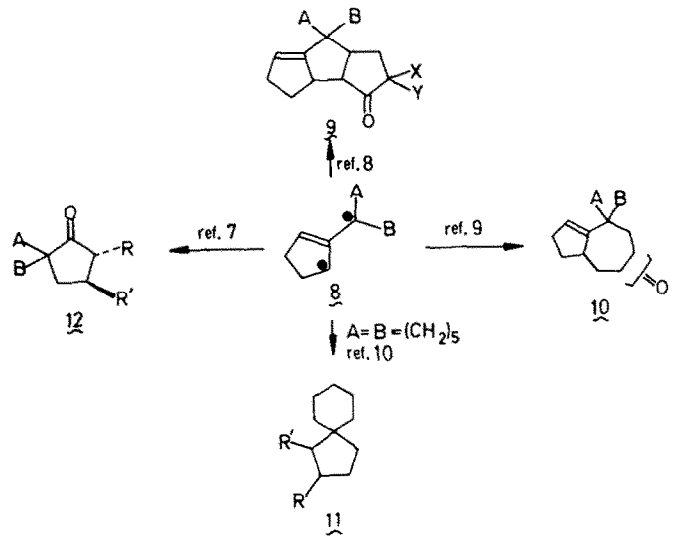


Diagram I

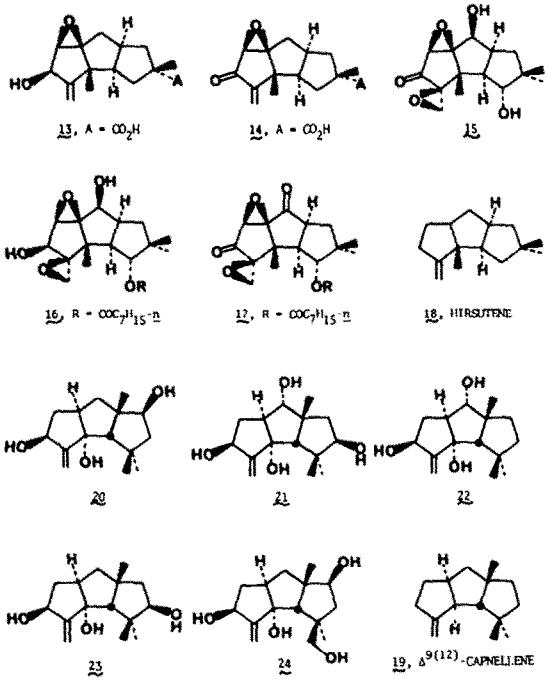
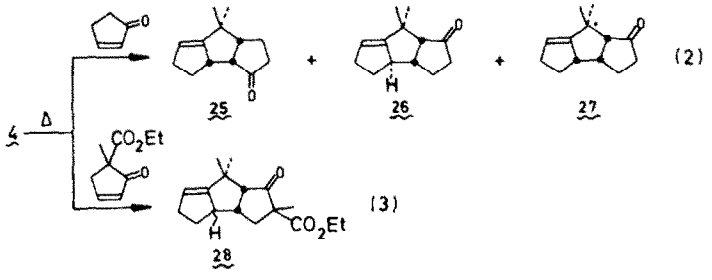


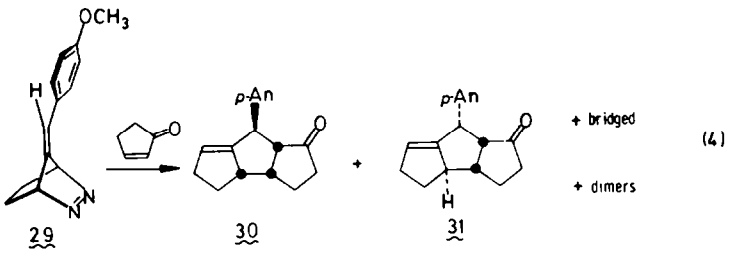
Diagram II

Our initial approach to the tricyclopentanoid skeleton utilized an *inter*molecular cycloaddition between the dimethyl diyl **5** and an excess of cyclopentenone. We were pleased to find that the reaction did in fact efficiently afford the desired ring system (isolated yield > 90%).[8a] However, several disturbing factors were also noted. Thus, while the reaction did show a slight regio- and stereo-selection for the formation of tricyclopentanoid **25**, two other products, **26** and **27**, were also formed. Furthermore, the major adduct **25** possessed a *cis, syn* ring fusion rather than the *cis, anti* fusion which is characteristic of each of the naturally occurring tricyclopentanoids illustrated in Diagram II.

In a similar experiment, **5** was trapped with 5-carbomethoxy-5-methylcyclopentenone to obtain a mixture of tricyclopentanoids in 50% yield. Once again, the reaction was not regio- or stereoselective.

In an effort to further examine the scope of the reaction and simultaneously, albeit awkwardly, provide a B-ring carbonyl or methylene unit as required in the synthesis of a variety of the naturally occurring systems, the anisyl azo compound **29** was heated to reflux in the presence of cyclopentenone for a period of 1 h. This time, the result was rather abysmal. Only a 23% yield of a mixture of two tricyclopentanoids was obtained.[8] The remainder of the material was accounted for in terms of bridged cycloadducts (33%) and diyl dimers (44%).





(4)

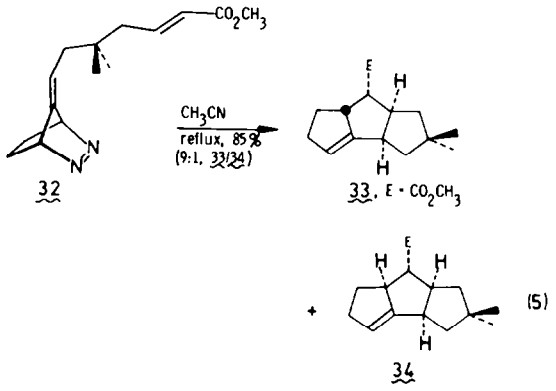
Attempts to rationalize this result have led us to explore some new chemistry which will be described on another occasion. For now, suffice it to say that when the reactions discussed above were reviewed collectively, it was clear that we would do well to consider alternate plans. It was to remain our objective, however, to continue with efforts to utilize the diyl trapping reaction as the key step of the sequence.

To that end, we reasoned that an *intra*molecular diyl trapping reaction would surely offer the ususal entropic advantages over the intermolecular version and like the intramolecular Diels–Alder reaction, it might also represent a more highly regio- and stereoselective process. Furthermore, it was clear that a number of the problems which are associated with the intermolecular process could be completely eliminated. First, there would be no need to remove the excess diylophile, since it would be built into the starting bicyclic azo compound. Second, regiochemical ambiguities would be eliminated since the relationship between the B and C ring substituents would be determined unambiguously in the synthesis of the acyclic chain containing the diylophile. Third, the difficulties associated with obtaining a suitable C_7 carbonyl or methylene unit synthon would be eliminated since the electron withdrawing group attached to the diylophile ultimately becomes the C_7 substituent and can surely be fashioned into nearly any desired functional group. (Note Scheme I).

To test this hypothesis, azo compound **32** was synthesized as previously described.[12] After heating to reflux for 6 h in acetonitrile, removal of the solvent, and chromatographic purification, two tricyclopentanoids, **33** and **34**, were isolated in 85% yield in a ratio of 9:1.

The regio- and stereochemical outcome of this reaction is clearly much more satisfactory than the intermolecular counterpart, especially in relation to the *cis, anti* ring fusion stereoselectivity which is observed.

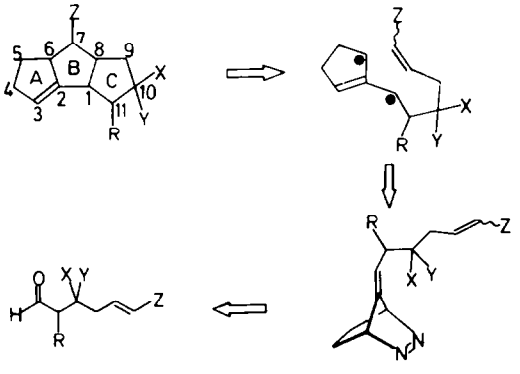
We have previously rationalized the stereoselective



(5)

nature of the intramolecular process through the use of secondary orbital overlap arguments.[12–14] Consider, for example, the two diyl conformers **33*** and **34*** (Note Diagram III). In **33*** there exist steric interactions between the ester and the diyl ring which are absent in **34***. On the other hand, if one consideres the form of the diyl HOMO and the diylophile LUMO, then it can be seen that two bonding secondary orbital interactions can occur between the ester carbonyl carbon and the diyl ring carbon atoms labeled A and B in **33***; these interactions are absent in **34***. Therefore, to the extent that the secondary interactions lower the energy of the pathway proceeding *via* **33*** more than the steric interactions raise the energy, one would anticipate the preferred formation of the *cis, anti* product, as observed.

However, there is another factor which clearly ought to be considered in the analysis. What role, for example, is played by conformational factors? It is, after all, possible that the extended pseudochair conformer **33*** may be of lower energy than the folded pseudochair conformer **34*** and that conformational factors in fact play a



Scheme 1

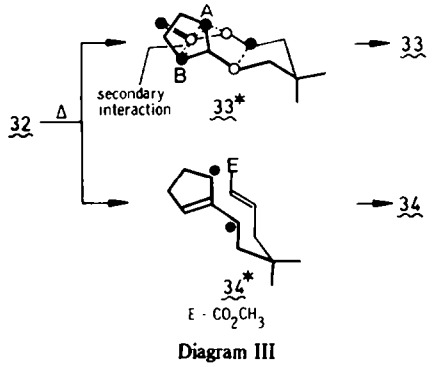


Diagram III

more significant role in determining product stereochemistry than electronic factors.

To test this hypothesis, the (*Z*)-isomer **35** of the azo compound **32** was synthesized following a scheme which exactly paralleled that used in the construction of **32**.[12] If electronic (secondary orbital) factors are controlling, then one would predict that the *cis, syn* tricyclopentanoid **37** originating from the folded pseudochair conformer **37*** wherein secondary orbital interactions can exist, should be the major product rather than the *cis, anti* tricyclopentanoid **36**.

In practice, after heating **35** to reflux in acetonitrile for 6 hr, the reaction mixture was cooled, the solvent was removed, and the cycloadducts were isolated and purified by medium pressure liquid chromatography (MPLC). Two tricyclopentanoids were formed in 87% yield in a ratio of 3:1; neither corresponded to either one of the adducts produced from **32**. Clearly, the reaction was not as stereoselective as that proceeding from the (*E*)-isomer **32**.

To ascertain the stereochemical outcome of the reaction, a combination of equilibration and shift reagent experiments were performed. Thus, treatment of the minor product from the trap of the (*Z*)-isomer **35** (*viz.* **37**) with sodium methoxide in refluxing methanol converted it entirely to the minor product **34** from the trap of the (*E*)-isomer **32**, thereby establishing that **34** is the thermodynamically more stable of the two, and more significantly, that the two compounds possess the same ring fusion sterochemistry.

In a similar experiment, the major product from the trap of the (*Z*)-isomer **35** (*viz.*, **36**) was treated with sodium methoxide in refluxing methanol; a 1:4 mixture of **33**, the major product from the trap of the (*E*)-isomer **32**, and the starting tricyclopentanoid was obtained. Since **33** is known to possess *cis, anti* ring fusion (*vide supra*)[12], it follows that the major product from **35** (*viz.* **36**) also possesses *cis, anti* fusion and *not* the *cis,syn* fusion anticipated on the basis of secondary orbital overlap control. Furthermore, if only *cis* BC ring fused tricyclopentanoids are formed, then one can conclude that the minor products possess *cis,syn* fusion, and that in the thermodynamically more stable isomer **34**, the C_7 ester group is located on the sterically less encumbered convex face of the molecule. This assignment is corroborated by the fact that the ester methyl group in **34** moves 1.8 times faster than the methyl group in **37** when treated with progressively increasing amounts of $Eu(fod)_3$. These experiments are summarized in Table I.

From these results, one can draw a number of conclusions. First, the intramolecular diyl trapping reaction is *stereospecific with respect to the olefin geometry*, regardless of whether one starts with the (*E*)- or the (*Z*)-olefin (**32** or **35**), the olefin geometry is maintained in the product. Second, the intramolecular diyl trapping reaction is *highly stereoselective with respect to the ring fusion stereochemistry*; the desired *cis, anti fusion is predominant regardless of the geometry about the diylophile π bond.* Third, while *both* secondary orbital interactions and conformational factors play a role in determining the ring fusion stereochemical outcome, *conformational factors appear to play a more significant role.* Let us explore the latter point in greater detail.

Consider the four diyl conformers **33***, **34***, **36***, and **37*** (note Diagram V). In **33*** and **36***, the acyclic chain has assumed an extended pseudochair conformation while in **34*** and **37***, a folded pseudochair conformation is illustrated. Notice, once again, that while secondary orbital interactions are possible starting with either **33*** or **37***, the major product in both cases can be explained as arising from a preferred extended pseudochair conformation. The fact that the trapping reaction

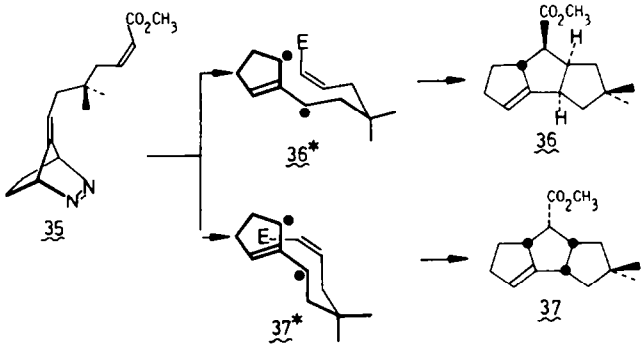


Diagram IV

Table I

AZO (OLEFIN GEOMETRY)	PRODUCT PREDICTED BASED ON SECONDARY INTERACTION	FOUND	PRODUCT RATIO	EQUILIBRATION RESULTS (NaOMe, MeOH)
32 (E)	33	33+34	9:1	33 ⇄ 36 (1:4)
35 (Z)	37	36+37	3:1	37 ⇄ 34 (0:100)

which originates from **32** is more stereoselective than that from **35** is therefore simply a reflection of the fact that the formation of **33** can benefit from both a lower energy diyl conformation as well as an energy lowering secondary orbital interaction in the transition state leading to product.

From the data presented thus far, one can determine the *approximate* order of magnitude of the secondary orbital interaction. Thus, if one assumes that the diyl trapping reactions occur at 81° (refluxing acetonitrile), then from a knowledge of the product ratio **33/34** = 9:1, one can estimate that $\Delta\Delta G^{\ddagger}_{12} = \Delta G_2^{\ddagger} - \Delta G_1^{\ddagger} = 1.55$ kcal/mole; similarly, knowing that **36/37** = 3:1, allows one to determine that $\Delta\Delta G^{\ddagger}_{34} = \Delta G_4^{\ddagger} - \Delta G_3^{\ddagger} = 0.78$ kcal/mole. Furthermore, if one *assumes* that the magnitude of the secondary interaction in conformer **33*** is the same as that in **37*** (note that there are two such interactions per conformer), then one can estimate that, for diyls of the same conformation: $\Delta G_3^{\ddagger} - \Delta G_1^{\ddagger} = 2$ (secondary orbital interaction) $= \Delta G_2^{\ddagger} - \Delta G_4^{\ddagger}$. Therefore, (secondary orbital interaction) $= 1/4[(\Delta G_3^{\ddagger} - \Delta G_1^{\ddagger}) + (\Delta G_2^{\ddagger} - \Delta G_4^{\ddagger})] = 1/4[(\Delta G_2^{\ddagger} - \Delta F_1^{\ddagger}) - (\Delta G_4^{\ddagger} - \Delta G_3^{\ddagger})] = 770/4 \sim 0.2$ kcal/mole^{-1}.

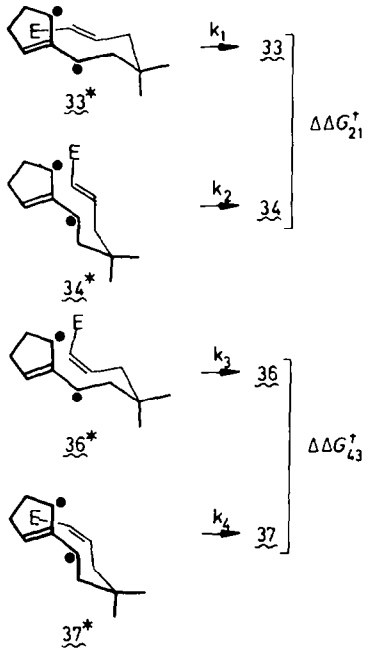
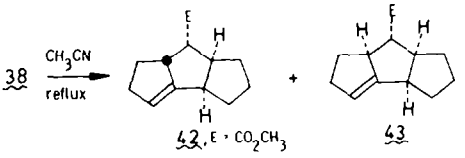


Diagram V

With the realization that conformational factors play a critical role in determining the stereochemical outcome of the trapping reaction, one might enquire as to whether or not the *gem* methyl group located on the acyclic chain interconnecting the diyl ring and the diylophile, facilitates the bending of the chain into a folded rather than a linear conformation.[15] To qualitatively test this idea, the normethyl azo compound **38** was synthesized using the methodology illustrated in Scheme II.

When **38** was subjected to the same reaction conditions as its *gem* methylated counterpart **32**, tricyclopentanoids **42** and **43** were isolated in 87% yield (7:1). Thus, for all *practical* purposes, one can conclude that the *gem* methyl groups do not play a role which manifests itself in terms of increased product yield. At present, we prefer to defer speculation concerning the effect of the *gem* methyls upon the *cis*, *anti*/*cis*, *syn* ratio derived from compounds **32** and **38**.



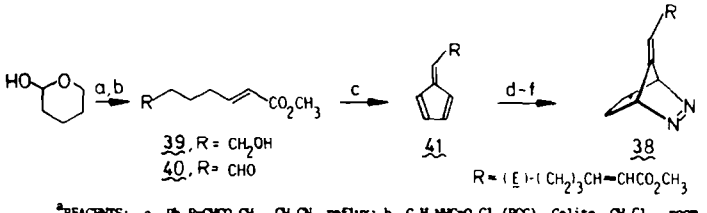
(6)

Having established several of the fundamental features of the trapping reaction, we felt well-suited to tackle a natural product total synthesis; *d,l*-hirsutene (**18**) and the marine natural product $\Delta^{9(12)}$-capnellene (**19**) were selected as the initial target molecules.

$\Delta^{9(12)}$-Capnellene (**19**). $\Delta^{9(12)}$-Capnellene (**19**) is a naturally occurring tricyclopentanoid produced by the soft coral *Capnella Imbricata* which is found off the shores of Serwaru, Leti Island in Indonesia. The compound, as well as many of its more complex, more fully oxygenated analogues, was first isolated and characterized by Djerassi *et al.*[11] Unlike the hirsutanes, two of the three methyl groups found in capnellene are located as a geminal pair at C_{11} rather than C_{10}, while the angular methyl group is located at C_8 rather than C_2 (note Diagram II). $\Delta^{9(12)}$-Capnellene (**19**) has not yet been synthesized; our efforts to do so are described below.

A retrosynthetic analysis of the problem is illustrated in Diagram VI. The intramolecular diyl trapping reaction *appeared* to be ideally suited to the task at hand. Thus, for example, the geminal and angular methyl groups which might be "difficult" to assemble using a more conventional approach to the ring system, were to be obtained in a straightforward fashion simply as substituents on the acyclic chain containing the diylophile.

In practice, the key azo compound **47** was readily



[a]REAGENTS: a, $Ph_3P{=}CHCO_2CH_3$, CH_3CN, reflux; b, $C_5H_5NHCrO_3Cl$ (PCC), Celite, CH_2Cl_2, room temp; c, cyclopentadiene, Et_2NH, CH_3OH, 5° to room temp; d, $Cl_3CCH_2O_2CN{=}NCO_2CH_2CCl_3$, ether, 0°C; e, $KO_2CN{=}NCO_2K$, AcOH; f, e^-, DMF, 0.1 N $LiClO_4$, room temp, then $K_3Fe(CN)_6$, H_2O, 0°C.

Scheme II[a]

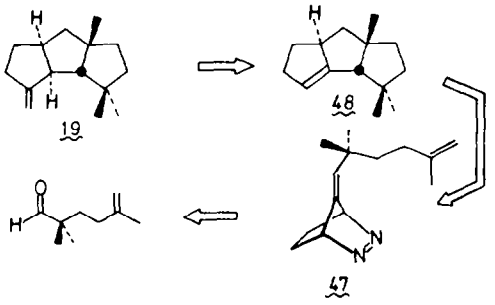
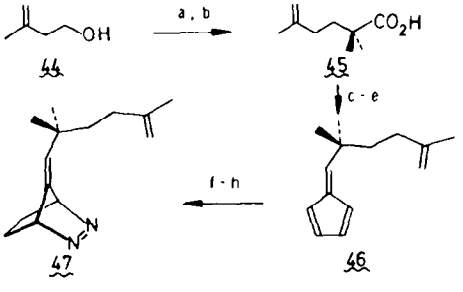


Diagram VI

synthesized following the pathway which is outlined in Scheme III. The basic plan is the same as that which we have adopted as a general route to these compounds and involves initial construction of the acyclic chain, followed by fulvene formation, Diels–Alder reaction, selective reduction of the C_5–C_6 pi bond of the bicyclic dicarbamate, and generation of the azo linkage.

When a dilute (*ca.* 10^{-3} *M*) acetonitrile solution of **47** was refluxed for 10 hr, nitrogen was extruded, and following careful removal of the solvent, two tricyclopentanoids, *tentatively* assigned to be **48** and **49** (*ca.* 2:1 by PMR), were isolated. In stark contrast with other intramolecular diyl trapping reactions, the yield was only 40%! This is undoubtedly due in part to material loss during isolation of the volatile cycloadducts and is perhaps related to the fact that an unactivated olefin was used as the diylophile.[6] However, as indicated below, other factors probably play a more significant role.

While the reason(s) for the failure of this approach are not entirely clear at this time, we suggest that the presence of an adverse nonbonded interaction between the pseudoaxial methyl group and H_A of the diyl ring in the conformer **48*** which would be expected to lead to the *cis,anti* fused tricyclopentanoid **48** may be responsible. This interaction can be diminished substantially if the diyl assumes the alternate conformation **49***, the anticipated precursor of the *cis,syn* product, **49**. Note



[a]REAGENTS:
a, p-TsCl, pyr, 0°C; b, $Me_2CCO_2Li_2$, THF, 0°C to room temp; c, $LiAlH_4$, Et_2O, reflux; d, PCC/Celite, CH_2Cl_2; e, cyclopentadienyllithium, THF, 0°C; f, $CH_3O_2CN{=}NCO_2CH_3$, 1:1 Et_2O/pentane, 0°C; g, $KO_2CN{=}NCO_2K$, AcOH, CH_2Cl_2, 0°C; h, KOH, $HOCH_2CH_2OH$, reflux then cool to 0°C and add $K_3Fe(CN)_6/H_2O$.

Scheme III[a]

Diagram VII. At the present time, experiments designed to test this hypothesis and complete the capnellene synthesis are in progress.

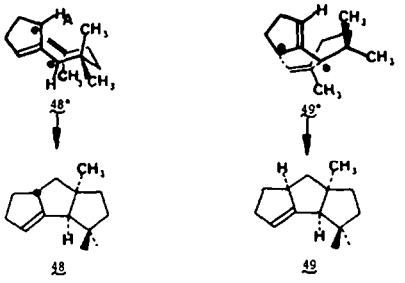


Diagram VII

d,l-*Hirsutene* (**18**). While the use of the intramolecular diyl trapping reaction to synthesize $\Delta^{9(12)}$-capnellene (**19**) has not yet culminated in success, the reaction has been of the utmost utility in our recently completed total synthesis of the mold metabolite *d,l*-hirsutene (**18**).[17] Thus, as illustrated in equation 5, the tricyclopentanoid skeleton was readily constructed starting from the bicyclic azo compound **32**. From **33** to hirsutene requires removal of the ester group located at C_7 and elaboration of the A-ring π bond.

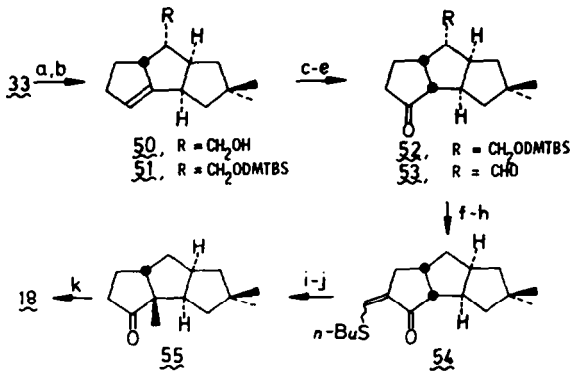
To this end, the ester was reduced to the corresponding alcohol **50** ($LiAlH_4$, Et_2O, quant) which was then protected as the dimethyl *tert*-butyl silyl ether **51** (Me_2t-BuSiCl, imidazole, DMF, 95%).[18] (Note Scheme IV). The presence of the bulky dimethyl *tert*-butyl silyl ether (DMTBS ether) on the α-face of the molecule assured that the subsequent delivery of borane to the $\Delta^{2,3}$-π bond would occur on the less hindered β-face, as required, Thus, hydrobaroation of **51** followed by oxidation with PCC/Celite afforded the C_3 carbonyl of compound **52** (54–57%).

Having served the dual role of activating the diylophile in the diyl trapping reaction and blocking access of borane to the α-face of the tricyclopentanoid, the C_7 substituent was removed by first treating the silyl ether with $(n\text{-Bu})_4NF$ (THF, 89–93%) followed by oxidation with PCC/Celite and finally, decarbonylation using Wilkinson's catalyst ($(Ph_3P)_3RhCl$, $ClCH_2CH_2Cl$, 76–91%).[19]

The synthesis was completed by appending the C_2 angular methyl group using a traditional sequence involving blocking C_4 with the *n*-butylthiomethylene unit followed by alkylation and removal of the blocking group to afford **55**, a compound which has previously been converted into hirsutene (**18**) using a simple Wittig reaction.[20] Comparison of the spectral data for **18** with those provided to us by Professor Hudlicky, confirmed that the synthesis had been successfully completed.

Concluding remarks

Efforts are presently underway to utilize the intramolecular diyl trapping reaction in the synthesis of the antitumor agent diketocoriolin B (**17**) in both racemic and chiral forms (*via* asymmetric induction), as well as the pseudoguaniolides confertin and damsin,[21] and in the construction of angularly fused tricyclopentanoids such as isocomene.[22]



[a]REAGENTS: a, $LiAlH_4$, Et_2O, room temp; t-BuMe$_2$SiCl, imidazole, DMF, room temp; c, BH_3·THF 0°C to room temp; PCC/Celite, CH_2Cl_2, room temp; d, n-Bu_4NF, THF, room temp; e, PCC/Celite, CH_2Cl_2, room temp; f, $(Ph_3P)_3RhCl$, $ClCH_2CH_2Cl$, reflux; g, $NaOCH_3$, EtOCHO, PhH, 0°C to room temp; h, n-BuSH, p-TsOH (cat), $MgSO_4$, PhH, reflux; i, KOt-Bu, t-BuOH, CH_3I, 0°C to reflux; j, 25% aq KOH, $HOCH_2CH_2OH$, reflux; k, $Ph_3P{=}CH_2$, DMSO [20]

Scheme IV[a]

EXPERIMENTAL

Proton magnetic resonance (PMR) spectra were obtained using a Varian T-60, and on occasion, an FT-80 spectrometer. A Varian CFT-20 was used to obtain ^{13}C-NMR (CMR) spectra; both fully decoupled and off-resonance decoupled spectra were recorded. Chemical shifts are given as parts per million (ppm) downfield from tetramethylsilane (Me_4Si, TMS) in δ units and coupling constants are given in cycles per second (Hz). The data are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, dd = doublet of doublets, br s = broad singlet, etc.), number of protons, coupling constants, assignments.

Infrared (IR) spectra were recorded on a Perkin-Elmer 283 spectrometer.

High resolution mass spectra or exact mass measurements were obtained from an AIE MS902 or a ZAB 2-F mass spectrometer. The observed and calculated values for the ion of the given formula are reported. Low resolution mass spectra were obtained from a Hewlett-Packard 5992A GC/MS system. The spectra are reported by giving the parent peak first (if it appeared), followed by the fragment peaks in order of decreasing mass. Carbon-hydrogen analyses were performed by Galbraith Laboratories of Knoxville, Tennessee or by Guelph Chemical Laboratories, Ltd of Guelph, Ontario, Canada or by Dr. Robert Petty of the Marine Science Institute at UCSB.

Medium pressure liquid chromatography (MPLC) was performed on a variety of Altex columns packed with Silica Gel 60 Merck (230–400 mesh, ASTM). The identity of the columns used (connected in series) are reported for each experiment. The distilled solvents (mixed by volume) were passed through the system with a FMI Model RPS 4 lab pump. The eluent was continuously monitored at 280 nm using an Altex Model 150 monitoring system or by TLC (Merck 60F-254, 70-230 mesh, ASTM). For gravity flow chromatography, E. Merck Silica Gel 60 (70-230 mesh, ASTM) was used. Florisil refers to Fischer 100–200 mesh gel. The term "flash chromatography" refers to the method of Still, Kahn and Mitra.[23]

Reagent grade solvents were used for all reactions. Anhydrous diethyl ether (Mallinkrodt) from freshly opened cans was sufficiently dry to be used without further treatment. In addition, acetonitrile and anhydrous methanol were purchased from Mallinkrodt and were used without further purification. Solvents referred to as "dry" were distilled from calcium hydride onto activated molecular sieves (4 Å). Tetrahydrofuran (THF) was tested for peroxides (EM test strips), collected from a calcium hydride pre-still after refluxing for at least one day, then distilled from sodium benzophenone ketyl. Pentane was distilled through a 30 cm glass column packed with glass helices.

Diisobutylaluminum hydride (Dibah, 1.1 M in hexane) and lithium aluminum hydride (LAH) were purchased from Ventron. Pyridinium chlorochromate (PCC), 3,3-dimethylglutaric anhydride, borane-THF, Wilkinson's catalyst, and tetra-*n*-butylammonium hydroxide (40% aqueous solution used in the preparation of the corresponding fluoride) were purchased from Aldrich.

Cyclopentadiene was freshly distilled prior to use. Dipotassium azodicarboxylate was prepared from the corresponding commercially available amide, according to the procedure of Berson.[24] Di(2,2,2-trichloroethyl) azodicarboxylate was prepared according to the procedure of Venegas and Little.[25]

Brine refers to a saturated solution of sodium chloride. Removal of the solvent "*in vacuo*" refers to the initial use of a rotary evaporator at water aspirator pressure followed by pumping on the material at 1 mm or less to remove the last traces of solvent.

Unless otherwise indicated, all reactions were conducted under an atmosphere of nitrogen.

In several of the descriptions which follow, a detailed procedure is presented for the preparation of the (*E*)-olefin; the procedure for preparation of the (*Z*)-olefin is entirely analogous and was simply carried out on a smaller scale. Complete details for the (*Z*)-olefin can be found in the Ph.D. Thesis of George W. Muller, UCSB, 1981, and are available upon request. The spectral data for both the (*E*) and the (*Z*)-olefins is presented below.

Pyrolysis of Diazene 4 in the Presence of Cyclopentenone. Typically, sample sizes ranging from 100 mg to 16 g of diazene **4** were heated to 65–70° for 1 hr in the presence of a ten-fold excess of cyclopentenone. Following removal of the excess cyclopentenone, the remaining material was chromatographed using MPLC (5% ether in pentane, column sizes of 1.5 × 20 cm and 2.5 × 100 cm connected in series for large scale runs). Tricyclopentanoids **25–27** were isolated in 90–98% yield in a ratio of 3/1.3/1 respectively. For **25**: IR (NaCl, film) 2950, 2850 1735 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 5.40 (X portion of ABX pattern, 1 H, $J_{AX}+J_{BX}$ = 7.8 Hz, vinyl), 3.0–3.7 (br m, 1 H, C_7–H), 1.2–3.0 (m, 10 H), 1.13 (s, 3H, CH_3), 1.10 (s, 3H, CH_3); MS (*m/e*) 190, 175, 109, 108 (base peak); exact mass *m/e* 190.1358 (calcd for $C_{13}H_{18}O$, 190.1381); ^{13}C NMR ($CDCl_3$) 221.2 (s), 158.4 (s), 119.2 (d), 56.0 (d), 50.0 (d), 49.8 (d), 40.5 (s), 40.0 (t), 35.3 (t), 31.8 (t), 27.3 (q), 24.4 (t), 20.1 (q); for **26** IR (NaCl, film) 2950, 2850, 1732 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 5.20 (X portion of ABX pattern, 1H, $J_{AX}+J_{BX}$ = 7.2 Hz, vinyl), 2.73–3.3 (br m,1H), 1.4–2.7 (m, 10 H), 1.30 (s, 3H, CH_3), 1.03 (s, 3H, CH_3); ^{13}C NMR ($CDCl_3$) 220.4 (s), 161.8 (s), 116.0 (d), 64.5 (d), 55.8 (d), 49.9 (d), 40.2 (s) 39.6 (t), 36.1 (t), 32.7 (t), 28.1 (q), 26.8 (t), 24.1 (q); MS (*m/e*) 190, 175, 162, 147, 133, 119, 108 (base peak); exact mass (*m/e*) 190.1358 (calc.

for $C_{13}H_{18}0$, 190.1344); for **27**: IR (NaCl, film) 1732 cm^{-1}; ^1H NMR ($CDCl_3$) δ 5.29 (X portion of an ABX pattern, 1H, $J_{AX}+J_{BX}$ = 7.8 Hz, vinyl), 3.13–3.76 (br m, 1H), 1.3–3.0 (m, 10 H), 1.19 (s, 3H, CH_3), 1.09 (s, 3H, CH_3); ^{13}C NMR ($CDCl_3$) 221.4, 160.0, 117.3, 66.8, 51.8, 41.9, 39.4, 38.4, 37.0, 31.9, 25.0, 24.9, 22.3; *MS* (*m/e*) 190, 175, 162, 147, 119, 108 (base peak).

Pyrolysis of diazene **4** *in the presence of 5-carboethoxy-5-methylcyclopentenone.* In a 100-ml round bottom flask equipped with a reflux condenser was added 0.15 g (1.13 mmol) of the dimethyl diazene **4** dissolved in 2.2 g (13.1 mmol) of 5-carboethoxy-5-methylcyclopentenone. The resulting solution was heated to 60–70° for 1 h and was then cooled to room temperature prior to the removal of the excess enone at reduced pressure. The residue was purified by MLPC using a mixture of 15% ether in pentane as the eluant (column size 1.5 × 100 cm). The yield of tricyclopentanoid product varied from 40–50%. For tricyclopentanoid **28**: IR (NaCl, film) 3010, 2960, 1740, 1710 cm^{-1}; ^1H NMR ($CDCl_3$) δ 5.15 (X portion of ABX pattern, 1H, J = 7.0 Hz, vinyl), 4.08 (q, 2H, J = 8.0 Hz, $CO_2CH_2CH_3$), 2.20–2.90 (m, (m, 9H), 1.30 (s, 3H, CH_3), 1.18 (s, 3H, CH_3), 1.20 (t, 3H, J = 8.0, CO_2CH_3), 0.86 (s, 3H, CH_3); ^{13}C NMR ($CDCl_3$) 215.8 (s), 172.8 (s), 161.9 (s), 116.7 (d), 61.2 (t), 64.6(d), 60.6 (s), 52.2 (d), 44.4 (t), 43.4 (d), 40.5 (s), 35.3 (t), 34.3 (t), 26.3 (q), 23.8 (q), 18.9 (q), 13.9 (q).

Pyrolysis of the anisyl azo compound **29** *in the presence of cyclopentenone.* In a 100-mL round bottom flask equipped with a magnetic stirring bar, reflux condenser, and nitrogen inlet tube, was placed a solution of 1.0 g (4.67 mmol) of the anisyl azo compound **29** dissolved in 33.3 g (406 mmol) of cyclopentenone. The flask was then immersed in an oil bath and was slowly heated to 100° over a period of 1 hr. After an additional 1 hr at 100°, the reaction mixture was cooled to room temperature and the excess enone was recovered by bulb-to-bulb distillation. The resulting oil was dissolved in a minimal amount of dichloromethane and was chromatographed via MPLC on a 15 × 1000 mm column packed with silica gel. Elution with 30% ether in pentane afforded 287 mg of dimers (0.77 mmol), 169 mg (0.63 mmol) of tricyclopentanoid **30**, 315 mg (1.17 mmol) of bridged cycloadduct, 75 mg (0.28 mmol) of another bridged cycloadduct, 104 mg (0.39 mmol) of tricyclopentanoid **31**, 70 mg of 2(*p*-methoxy phenycarbonyl)cyclopenten-1-ol, and 28 mg of an unknown substance (mass balance 92%). For tricyclopentanoid **31**: IR (NaCl, film) 1730 cm^{-1}; ^1H NMR ($CDCl_3$) 7.15 (AA'BB', 2H, aromatic), 6.80 (AA'BB', 2H, aromatic), 4.95 (dd, 1H, vinyl), 3.75 (s, 3H, OCH_3), 3.65 (br s, 1H, CH Ar), 1.4–2.9 (m, 11 H, aliphatic); m.p. 91.5–92°; exact mass (*m/e*) 268.148, Calc. for $C_{18}H_{20}O_2$ 268.147; for **30**: IR (NaCl, film) 1730 cm^{-1}; ^1H NMR ($CDCl_3$) δ 6.95 (AA'BB', 2H, aromatic), 6.70 (AA'BB', 2H, aromatic), 5.15 (dd, 1H, vinyl), 3.80 (br s, 1H, CHAr), 3.70 (s, 3H, OCH_3), 3.2 (m, 1H), 1.6–2.8 (m, 11 H, aliphatic), m.p. 81.5–82°; Calc. for $C_{18}H_{20}O_2$: C, 80.56; H, 7.51. Found: C, 80.52; H, 7.42%.

5-Hydroxy-3,3-dimethylpentanoic acid lactone. To a cold (0°), stirred suspension of sodium borohydride (8.00 g, 211 mmol) in 40 mL of THF, was added over 0.5 hr, a solution of 3,3-dimethylglutaric anhydride (20.0 g, 141 mmol) dissolved in 100 ml of THF. The resulting solution was allowed to warm to room temperature and was stirred for 3.5 hr. The solution was then cooled to 0° and was quenched by the addition of 70 ml of 6N HCl. The solution was washed with brine (5 × 100 ml) and was then extracted with ether (3 × 75 mL). The combined ether extracts were dried ($MgSO_4$) and the solvent was removed *in vacuo*. The resulting oil was purified by chromatography on 60 g of silica gel. Elution with 70% ether in pentane afforded 11.11 g (61%) of 5-hydroxy-3,3-dimethyl- pantanoic acid lactone. PMR ($CDCl_3$) δ 4.35 (t, 2H, J = 6, CH_2OH), 2.30 (s, 2H, CH_2CO_2R), 1.70 (t, 2H, J = 6, $HOCH_2CH_2$), 1.10 (s, 6H, *gem*-methyls); IR (NaCl, film) 3500, 2960, 1735 (broad), 1395, 1372, 1230 cm^{-1}.

2-Hydroxy-4,4-dimethyltetrahydropyran. To a stirred solution of 5-hydroxy-3,3-dimethylpentanoic acid lactone (25.2 g, 197 mmol) in 500 ml of ether at −20°, was added dropwise over a 1 hr. a solution of Dibah (205 ml of 1.1 M = 226 mmol) in hexane. The resulting solution was stirred for an additional 0.5 h and was then quenched by the addition of 150 ml of methanol. The solution was allowed to warm slowly to room temperature and was stirred overnight. The resulting suspension was diluted with 250 ml of a 30% aqueous solution of sodium potassium tartrate, and was stirred for 0.5 hr. The organic layer was separated and was washed with 30% aqueous sodium potassium tartrate (2 × 100 ml and 1 × 50 ml). The combined aqueous layers were then extracted with ether (3 × 50 ml). The combined organic layers were dried ($MgSO_4$) and concentrated *in vacuo*. The resulting liquid was purified by trap-to-trap distillation (40°, $< 5 \times 10^{-3}$ Torr) to afford 19.43 g (76%) of 2-hydroxy-4,4-dimethyltetrahydropyran. PMR ($CDCl_3$) δ 4.96 (m, 1H, CHOH), 4.8 (d, 1H, J ~ 4, OH), 4.18-3.37 (m, 2H, CH_2O), 1.95–1.10 (m, 4H, $CH_2C(CH_3)_2CH_2$), 1.05 (s, 6H, CH_3CCH_3); IR (NaCl, film) 3390, 2950, 2870, 1555, 1385, 1365, 1195, 1115, 1080, 1030, 990 cm^{-1}.

Methyl 7-Hydroxy-5,5-dimethylhept-2-enoate. A stirred solution of pyran (12.0 g, 92.3 mmol) and methyl (triphenylphosphoranylidene) acetate (46.2 g, 138 mmol) in 600 ml of acetonitrile was heated to reflux for 34.5 hr. Most of the solvent was removed *in vacuo*; 100 ml of ether was then added and the mixture was stirred for 2 hr. The resulting mixture was filtered and the filtrate was washed with 50 ml of ether. The solvent was again removed *in vacuo* and 50 ml of 70% ether in pentane was added. After stirring for 0.5 hr, the resulting suspension was once again filtered and the filter cake was washed with 25 ml of 70% ether in pentane. The solvent was removed *in vacuo* and the resulting material was purified by chromatography in two batches on 90 and 160 g of silica gel. Elution with 70% ether in pentane afforded 16.5 g (96%) of *cis*- and *trans*- (1:4, respectively) unsaturated hydroxy esters. Complete separation is readily achieved after the next step. PMR (*cis* isomer, $CDCl_3$) δ 6.32 (overlapping dt, 1H, J = 12 and 8 Hz, β-vinyl), 5.81 (dt, 1H, J = 12 and 1 Hz, α-vinyl), 3.68 (s, 3H, CO_2CH_3), 3.68 (t, 2H, J = 8, CH_2OH), 2.62 (dd, 2H, J = 8, J = 1, allylic), 2.55 (s, 1H, OH), 1.55 (t, 2H, J = 8, CH_2CMe_2), 1.12 (s, 6H, *gem* methyls); CMR ($CDCl_3$) 166.6(s), 147(d), 120.5(d), 59(t), 50.7(q), 43.89(t), 40.36(t), 32.76(s), 26.9(q). PMR (*trans*, $CDCl_3$) δ 6.97 (overlapping dt, 1H, J = 16 and 8, β-vinyl), 5.77 (dt, 1H, J = 16 and 1, α-vinyl), 3.71 (s, 3H, CO_2CH_3), 3.60 (t, 2H, J = 8, CH_2OH), 2.90 (br s, 1H, OH), 2.13 (dd, 2H, J = 8 and 1, allylic CH_2), 1.53 (t, 2H, J = 8, CH_2CH_2OH), 0.98 (br s, 6H, *gem*-methyls); IR (NaCl, film) 3420, 2980, 1725, 1655, 1390, 1370 cm^{-1}; exact mass *m/e* 186.12473 (calc. for $C_{10}H_{18}O_3$, 186.12559).

Methyl (Z)- *and* (E)-*7-oxo-5,5-dimethylhept-2-enoate.* To a stirred suspension of pyridinium chlorochromate (PCC, 13.9 g, 64.5 mmol) and 13.9 g of Celite in 90 mL of dichloromethane at room temperature, was added a solution of methyl 7-hydroxy-5,5-dimethylhept-2-enoate 8.00 g, 43.0 mmol) in 16 mL of dichloromethane. The resulting suspension was stirred for 2 hr and was then diluted with 500 ml of ether. The suspension was then filtered through a pad of Florisil which was rinsed with an additional 200 ml of ether. The solvent was removed *in vacuo* to afford an oil which was subjected to MPLC (17 ml/min, 15 × 250 mm and 25 × 1000 mm columns connected in series) on silica gel. Elution with 20% ethyl acetate in pentane afforded 1.34 g (17%) of the (*Z*)-isomer and 5.19 g (66%) of the (*E*)-isomer. PMR (*cis* isomer, $CDCl_3$) δ 9.85 (t, 1H, J = 3, CHO), 6.20 (overlapping dt, 1H, J = 7 and 12, β-vinyl), 5.88 (dt, 1H, J = 12 and 1, α-vinyl), 3.68 (s, 3H, CO_2CH_3), 2.75 (dd, 2H, J = 7 and 1, allylic CH_2), 2.32 (d, 2H, J = 3, CH_2CHO), 1.12 (s, 6H, *gem* methyls); IR (NaCl, film, *cis*-isomer) 3420, 3030, 2950, 2870, 2830, 2730, br carbonyl 1720, 1640, 1440, 1390, 1370 cm^{-1}. PMR (*trans*-isomer, $CDCl_3$) δ 9.89 (t, 1H, J = 3, CHO), 7.02 (overlapping dt, 1H, J = 16 and 8, β-vinyl), 5.75 (dt, 1H, J = 16 and 1, α-vinyl), 3.75 (s, 3H, CO_2CH_3), 2.34 (d, 2H, J = 3, CH_2CHO), 2.30 (dd, 2H, J = 8 and 1, allylic CH_2), 1.15 (s, 6H, *gem* CH_3); IR (NaCl, film, *trans*-isomer) 2980, br carbonyl from 1710–1740, 1655, 1390, 1370 cm^{-1}; exact mass (*m/e*) 184.11015 (calc. for $C_{10}H_{16}O_3$, 184.10944).

6-[(E)-5-Carbomethoxy-2,2-dimethyl-4-pentenyl]fulvene. To a stirred solution of methyl (*E*)-7-oxo-5,5-dimethylhept-2-enoate (5.19 g, 28.2 mmol) and freshly distilled cyclopentadiene (5.8 ml, 4.65 g, 70.5 mmol) in 50 ml of anhydrous methanol cooled in a 5–10° ice bath, was added dropwise, a solution of diethylamine (4.4 ml, 3.09 g, 42.3 mmol) in 40 ml of anhydrous methanol. The resulting solution was allowed to warm to room temperature where it was stirred for 2 hr prior to cooling to 0° and the

dropwise addition of 3.4 ml of glacial acetic acid. Most of the solvent was removed *in vacuo* and the resulting solution was extracted with 50 ml of ether and was washed with saturated aqueous sodium bicarbonate (2 × 25 ml) and brine (2 × 25 ml). The organic layer was dried ($MgSO_4$) and the solvent was removed *in vacuo*. The resulting oil was purified by chromatography on 120 g of neutral alumina (activity II). Elution with 7% ether/pentane afforded 5.96 g (91%) of 6-[(*E*)-5-carbomethoxy-2,2-dimethyl-4-pentenyl]fulvene. PMR (*cis*-isomer, $CDCl_3$) δ 6.00–6.60 (m, 6H, ring H's and β-vinyl), 5.82 (dt, 1H, J = 12 and 1, α-vinyl), 3.65 (s, 3H, CO_2CH_3), 2.67 (dd, 2H, J = 7 and 1, $CH_2CO_2CH_3$), 2.43 (d, 2H, J = 8, C_6CH_2), 1.00 (s, 6H, *gem* CH_3); IR (NaCl, film, *cis*-isomer) 2940, 2860, 1720, 1640, 1465, 1435, 1405, 1380, 1365 cm^{-1}. PMR (*trans*-isomer, $CDCl_3$) δ 7.05 (overlapping dt, 1H, J = 16 and 8, β-vinyl), 6.10–6.70 (m, 5H, ring H's), 5.78 (dt, 1H, J = 16 and 1, α-vinyl), 3.75 (s, 3H, CO_2CH_3), 2.45 (d, 2H, J = 8, C_6HCH_2), 2.17 (dd, 2H, J = 8 and 1, $C(CH_3)_2CH_2$), 1.02 (br s, 6H, *gem* methyl); IR (NaCl, film, *trans*-isomer) 2960, 1725, 1655, 1650, 1385, 1370 cm^{-1}; exact mass *m/e* 232.1475 (calc. for $C_{15}H_{20}O_2$, 232.1463).

N,N' - [*Di* - (2,2,2 - *trichloroethoxycarbonyl*)] - 2,3 - *diaza* - 7 - (*trans* - 6 - *carbomethoxy* - 3,3 - *dimethylhex* - 5 - *enylidene*)*bicyclo*(2.2.1)*heptane*. To a stirred solution of 6 - [(*E*) - 5 - carbomethoxy - 2,2 - dimethyl - 4 - pentenyl]fulvene (5.937 g, 25.59 mmol) in 7 ml of ether at 0°, was added dropwise over 15–30 min, a solution of di(2,2,2-trichloroethyl) azodicarboxylate (9.699 g, 25.59 mmol) in 75 ml of ether. The resulting solution was stirred an additional 0.75 hr and was then concentrated *in vacuo* to afford a quantitative yield of the desired Diels–Alder adduct which was used without purification in the next step of the sequence. PMR (*cis*-isomer, $CDCl_3$) δ 6.80 (t, 2H, J = 2, C_5H = C_6H), 6.28 (overlapping dt, 1H, J = 7 and 12, β-vinyl), 5.85 (dt, 1H, J = 12 and 1, α-vinyl), 5.50 and 5.28 (br s, 2H, bridgeheads), 5.05 (t, 1H, J = 8, C_7 = $CHCH_2R$), 4.82 (s, 4H, $CO_2CH_2CCl_3$), 3.70 (s, 3H, CO_2CH_3), 2.58 (dd, 2H, J = 1 and 7, $CH_2CH{=}CHCO_2CH_3$), 1.95 (d, 2H, J = 8, $RC_8HCH_2CMe_2R$), 0.88 (s, 6H, *gem*-methyls); IR (NaCl, film, *cis*-isomer) 2960, 2870, br carbonyl from *ca* 1780–1700, 1640, 1440, 1380 cm^{-1}. PMR (*trans*-isomer, $CDCl_3$) δ 6.97 (overlapping dt, 1H, J = 16 and 8, β-vinyl), 5.82 (dt, 1H, J = 16 and 1, α-vinyl), 5.52 and 5.33 (br s, 2H, bridgeheads), 6.87 (t, 2H, J = 2, C_5C_6H), 5.33 (t, 1H, J = 8, C_7 = $CHCH_2R$), 4.85 (s, 4H, $CO_2CH_2CCl_3$), 3.75 (s, 3H, CO_2CH_3), 2.05 (d, 2H, J = 8, CH_2CH = $CHCO_2CH_3$), 1.92 (d, 2H, J = 8, $RC_8HCH_2CMe_2R$), 0.54 (s, 6H, *gem*-methyls); IR (NaCl, film) 2960, 2930, broad carbonyl centered at 1735, 1660, 1440, 1385, 1300, 1290, 1120, 1060, 990 cm^{-1}.

To a stirred suspension of dipotassium azodicarboxylate (24.56 g, 12.79 mmol) and the Diels–Alder adduct (15.63 g, 25.58 mmol) in 100 ml of dry dichloromethane in an ice bath cooled to 9–13°, was added dropwise over 25 min, a solution of acetic acid (16 ml, 289 mmol) in 27 ml of dry dichloromethane. The mixture was stirred an additional 1 hr. The resulting suspension was filtered and the filter cake was rinsed with 150 ml of ether. The solvent was removed *in vacuo*. PMR analysis indicated that approximately 60% of the Diels–Alder adduct was not hydrogenated; therefore, the reaction was continued. To a stirred suspension of the partially hydrogenated adduct and dipotassium azodicarboxylate (14.74 g, 76.74 mmol) in 60 ml of dry dichloromethane cooled in an ice bath to 9–13°, was added dropwise over 20 min, a solution of acetic acid (9.6 ml, 170 mmol) in 16 ml of dry dichloromethane. After stirring for 1 hr, the resulting suspension was filtered and washed with 100 ml of ether. The solvent was removed *in vacuo* and the resulting thick oil was purified by MPLC (silica gel, 16 ml/min, 15 × 250 and 25 × 1000 mm columns connected in series) in three portions. Elution with 40% ether in pentane afforded 13.62 g (87%) of the desired hydrogenated adduct. PMR (*cis*-isomer, $CDCl_3$) δ 6.22 (overlapping dt, 1H, J = 7 and 12, β-vinyl), 5.78 (dt, 1H, J = 12 and 1, α-vinyl), 5.4 (t, 1H, J = 7, C_8H), 4.42–5.08 (m, 6H, CH_2CCl_3 and bridgeheads), 3.65 (s, 3H, CO_2CH_3), 2.55 (dd, 2H, J = 7 and 1, CH_2CH = $CHCO_2CH_3$), 1.58–2.25 (m, 4H, CH_2CH_2), 2.00 (d, 2H, J = 8, C_8HCH_2), 0.90 (s, 6H, *gem* methyl); IR (NaCl, film, *cis*-isomer) 2945, 2865, 1715–1760, 1440, 1385 cm^{-1}. PMR (*trans*, $CDCl_3$) δ 6.93 (overlapping dt, 1H, J = 16 and 8, β-vinyl), 5.80 (dt, 1H, J = 8 and 1, α-vinyl), 5.45 (t, 1H, J = 8, RC_7H = $CHCH_2R$), 5.08–4.48 (m, 6H, $CO_2CH_2CCl_3$ and bridgeheads), 3.73 (s, 3H, CO_2CH_3), 2.32–1.75 (m, 8H, allylic CH_2's and CH_2CH_2), 0.92 (s, 6H, *gem*-methyls); IR (NaCl, film) 2945, 2925, 2865, 1715, 1430, 1380, 1360, 1270, 1195, 1140, 1100 cm^{-1}; exact mass *m/e* 611.9878 (calc. for $C_{21}H_{26}O_6Cl_6N_2$, 611.99216).

2,3 - *Diaza* - 7 - (*trans* - 6 - *carbomethoxy* - 3,3 - *dimethylhex* - 5 - *enylidene*)*bicyclo*(2.2.1) *hept* - 2 - *ene* (**32**). *N,N'* - [*Di* - 2,2,2 - (trichloroethoxycarbonyl)] - 2,3 - diaza - 7 - (*trans* - 6 - carbomethoxy - 3,3 - dimethylhex - 5 - enylidene)bicyclo(2.2.1)heptane (1.286 g, 2.09 mmol) was treated according to the method of Little and Carroll,[8c] at a potential of −1.76 V (vs Ag/AgCl) to afford an oil which was purified by chromatography on 80 g of silica gel. Elution with 30–100% ether in pentane afforded 300 mg (55%) of the azo compound **32**. PMR (*cis*-isomer **35**, $CDCl_3$) δ 6.23 (dt, 1H, J = 12 and 7, β-vinyl), 5.80 (dt, 1H, J = 1 and 12, α-vinyl), 4.97–5.40 (m, 3H, bridgeheads and C_8H), 3.67 (s, 3H, CO_2CH_3), 2.55 (m, 2H, CH_2CH = $CHCO_2CH_3$), 1.92 (d, 2H, J = 8, C_8HCH_2R), 0.93–1.9 (m, 4H, CH_2CH_2), 0.90 (s, 6H, *gem* methyl); IR (NaCl, film, *cis*-isomer **35**) 3010, 2950, 2870, 1725, 1601, 1440, 1405, 1385, 1365 cm^{-1}. PMR (*trans*-isomer **32**, $CDCl_3$) δ 7.01 (dt, 1H, J = 16 and 8 Hz, β-vinyl), 5.87 (dt, 1H, J = 16 and 1, α-vinyl), 5.40 (br s, 1H, bridgehead), 5.20 (t, 1H, J = 8, C_7 = CHR), 5.17 (br s, 1H, bridgehead), 3.78 (s, 3H, CO_2CH_3), 2.13 (2H, gamma to the ester), 1.90 (d, 2H, J = 8, $HC_8CH_2CMe_2R$), 1.2 (m, 4H, ethano bridge), 0.92 (s, 6H, *gem*-methyls).

(3aα,6aβ,7aα,7aα) - 2,3,3a,5,6,6a,7,7a - *Octahydro* - 2,2 - *dimethyl* - 1H - *cyclopenta*(a) - *pentalene* - 7 - *carboxylic acid methyl ester* (**33**). A stirred solution of azo compound **32** (300 mg, 1.14 mmol) in 500 ml of acetonitrile was refluxed for 6 hr. The solvent was removed *in vacuo* to afford 260 mg of an oil which was purified by MPLC (16 ml/min, 15 × 250 mm and 25 × 1000 mm columns connected in series) on silica gel. Elution with 6% ether in pentane afforded 214 mg (85%) of tricyclopentanoids as a 9:1 mixture of two isomers. Complete separation of the isomers was accomplished by further chromatography under the same conditions. For (3aα,6aα,7aα,7aα) - 2,3,3a,5,6,6a,7,7a - octahydro - 2,2 - dimethyl - 1H - cyclopenta(a) - pentalene - 7 - carboxylic acid methyl ester **34**. PMR ($CDCl_3$) δ 5.18 (m, 1H, vinyl), 3.72 (s, 3H, CO_2CH_3), 1.05 and 0.95 (two s each, 6H, *gem* methyl); IR (NaCl, film) 3040, 2920, 2850, 1730, 1450, 1430, 1365 cm^{-1}; CMR ($CDCl_3$) 175.2, 156.1, 117.7, 58.7, 58.0, 52.3, 51.3, 47.8, 45.5, 43.96, 41.2, 37.1, 30.1, 28.9, 27.5. For tricyclopentanoid **33**. PMR ($CDCl_3$) δ 5.2 (overlapping dt, 1H, J = 2 and 3, vinyl), 3.61 (s, 3H, CO_2CH_3), 2.58 (d, 1H, J = 8, $CHCO_2CH_3$), 1.03 (s, 3H, CH_3), 0.92 (s, 3H, CH_3); IR (NaCl, film) 3050, 2950, 1735, 1370, 1160 cm^{-1}; CMR ($CDCl_3$) 26.7, 25.9 and 28.2 (*gem*-methyls), 37.0, 39.9, 40.9 (CMe_2), 47.3, 47.6, 50.5, 50.7, 51.4 (CO_2CH_3), 51.6, 117.5 (CH_2CH = C), 154.5 (CH = CR_2), 175.1 (CO_2CH_3); exact mass *m/e* 234.15891 (calc. for $C_{15}H_{22}O_2$, 234.16197).

Thermolysis of the (*Z*)-*Azo compound* **35**. A stirred solution of azo compound **35** (487 mg, 1.86 mmol) in 750 ml of acetonitrile was refluxed for 6 hr. The solvent was removed *in vacuo* to afford 429.6 mg of an oil which was purified by MPLC (16 ml/min, 15 × 250 and 25 × 1000 mm columns connected in series) on silica gel. Elution with 3% ether in pentane afforded an 87% yield of two isomers **36** and **37** in a ratio of 3:1. For **36**: PMR ($CDCl_3$) δ 5.17 (m, 1H, vinyl), 3.63 (s, 3H, CO_2CH_3), 1.00 (s, 3H, CH_3), 0.88 (s, 3H, CH_3); IR (NaCl, film) 3045, 2925, 2860, 1730, 1465, 1440, 1385, 1370 cm^{-1}; CMR ($CDCl_3$) 174.1(s), 154.4(s), 117.9(d), 52.9(d), 50.95, 49.98, 49.60, 47.6(t), 43.3(t), 40.86(s), 40.4(d), 37.0(t), 30.2(t), 28.1(q), 25.7(q): Calc. for $C_{15}H_{22}O_2$: C, 76.92; H, 9.40. Found: C, 77.19; H, 9.46%. For tricyclopentanoid **37**: PMR ($CDCl_3$) δ 5.20 (m, 1H, vinyl), 3.62 (s, 3H, CO_2CH_3), 1.05 (s, 3H, CH_3), 0.95 (s, 3H, CH_3); IR (NaCl, film) 2945, 2865, 1735, 1465, 1435, 1385, 1370 cm^{-1}; CMR ($CDCl_3$) 175.1(s), 156.4(s), 119.0(d), 59.03(d), 52.8(t), 51.8, 49.7, 45.8, 45.4, 44.03, 43.21(d), 38.6(t), 30.7, 29.7, 28.5.

Equilibration of (3aα,6aα,7β,7aα) - 2,3,3a,5,6,6a,7,7a - *octahydro* - 2,2 - *dimethyl* - 1H - *cyclopenta*(a)*pentalene* - 7 - *carboxylic acid methyl ester* (**37**) *and* (3aα,6aα,7α,7aα) - 2,3,3a,5,6,6a,7,7a - *octahydro* - 2,2 - *dimethyl* - 1H - *cyclopenta*(a)*pentalene*-7-*carboxylic acid methyl ester* (**34**). A solution of ester **37** (13 mg, 0.056 mmol) and sodium methoxide (93 mg,

1.72 mmol) in 3 ml of anhydrous methanol was heated to reflux for 8 hr. The resulting solution was diluted with 10 ml of ether and was then washed successively with saturated aqueous sodium bicarbonate (2 × 25 ml) and brine (2 × 25 ml). The organic layer was dried ($MgSO_4$) and the solvent was removed *in vacuo* to afford 7.7 mg of ester **34**; no indication of **37** was evident.

Equilibration of (3aα,6aβ,7α,7aα) - 2,3,3a,5,6,6a,7,7a - *octahydro* - 2,2 - *dimethyl* - 1H - *cyclopenta(a)pentalene* - 7 - *carboxylic acid methyl ester* (**33**) *and* (3aα,6aβ,7β,7aα) - 2,3,3a,5,6,6a,7,7a - *octahydro* - 2,2 - *dimethyl* - 1H - *cyclopenta(a)pentalene* - 7 - *carboxylic acid methyl ester* (**36**). A solution of ester **36** (61.5 mg, 0.26 mmol) and 8.7 equiv of sodium methoxide in 4 ml of methanol was heated to reflux for 19 hr. The resulting solution was diluted with 30 ml of ether and was washed with brine (3 × 25 ml). The organic layer was dried ($MgSO_4$) and the solvent was removed *in vacuo*. The resulting oil was purified by MPLC (16 ml/min, 15 × 250 and 15 × 1000 mm columns connected in series) on silica gel. Elution with 3% ether in pentane afforded an 84% recovery of tricyclopentanoids **33** and **36** in a ratio of 1:4.

Treatment of tricyclopentanoid methyl esters **34** *and* **37** *with lanthanide shift reagent* [*Eu(fod)*$_3$]. Treatment of tricyclopentanoid methyl esters **34** (18.3 mg) and **37** (11.7 mg), each dissolved in $CDCl_3$, with progressively increasing amounts of $Eu(fod)_3$ (Aldrich, 0.03 M in $CDCl_3$) led to $\Delta\delta_{34}^{CO_2CH_3} = 1.84(\Delta\delta_{37}^{CO_2CH_3})$. Thus, in conjunction with the equilibration study above, this result implies that the C_7 ester group in **34** is on the less hindered convex face of the molecule.

(3aα,6aβ,7α,7aα) - 2,3,3a,5,6,6a,7,7a - *octahydro* - 7 - (*hydroxymethyl*) - 2,2 - *dimethyl* - 1H - *cyclopenta(a)pentalene* (**50**). To a stirred suspension of lithium aluminum hydride (48.0 mg, 1.27 mmol) in 4 ml of ether at room temperature, was added dropwise over 15 min, a solution of tricyclopentanoid **33** (281 mg, 1.20 mmol) in 3 ml of ether. After stirring for 45 min, the resulting suspension was cooled to 0° and was quenched by the dropwise addition of 6 ml of 5% HCl. The organic layer was separated and the aqueous layer was extracted with ether (2 × 10 ml). The combined organic solutions were dried ($MgSO_4$) and the solvent was removed *in vacuo* to afford a quantitative yield of the desired alcohol **50**. PMR ($CDCl_3$) δ 5.20 (m, 1H, vinyl), 3.80–1.05 (m, 12H), 2.1 (s, 1H, OH), 1.00 (s, 3H, CH_3), 0.86 (s, 3H, CH_3); IR (NaCl, film) 3330, 2940, 2840, 1730, 1460, 1380, 1365 cm^{-1}; exact mass *m/e* 206.1643 (calc. for $C_{14}H_{22}O$, 206.1671).

(3aα,6aβ,7α,7aα) - 2,3,3a,5,6,6a,7,7a - *octahydro* - 2,2 - *dimethyl* - 7 - (tert - *butyldimethylsiloxymethyl*) - 1H - *cyclopenta(a)pentalene*. To a stirred solution of *tert*-butyldimethylsilyl chloride (223 mg, 1.48 mmol) and tricyclopentanoid **50** (252 mg, 1.23 mmol) in 2 ml of DMF at room temperature, was added in one portion as a solid, imidazole (209 mg, 3.07 mmol). The reaction mixture was stirred at room temperature for 67 hr. Addition of 15 ml of brine, extraction with ether (3 × 10 ml), drying ($MgSO_4$), and concentration *in vacuo*, afforded an oil which was chromatographed on 10 g of silica gel. Elution with 20% ether in pentane afforded 39.2 mg (15.5%) of the starting alcohol **50** and 320.2 mg (81.2%) of the desired protected alcohol. PMR ($CDCl_3$) δ 5.07 (m, 1H, vinyl), 3.72–1.06 (m, 14H), 0.99 and 0.86 (two s, 15H, *t*-butyl and *gem*-methyls), −0.01 (s, 6H, $SiMe_2$); IR (NaCl, film) 2950, 2920, 2850, 1465, 1385, 1365, 1255, 1095, 835 cm^{-1}.

(3aα, 3bβ, 6aβ, 7aα, 7aα)-*decahydro*-2,2-*dimethyl*-7-(*tert-butyl dimethylsiloxymethyl*) - 1H - *cyclopenta(a)pentalen* - 4 - *one*. To a stirred solution of the silylated alcohol **51** (440 mg, 1.37 mmol) in 5.5 ml of THF at 0°, was added over 3 min, 2.2 ml of 0.94 M borane-THF. The ice bath was removed and the solution was allowed to warm to, and stir at room temperature for 3.5 hr. The solvent was removed *in vacuo* to afford an oil. The oil was dissolved in 15 ml of dichloromethane and was added to a stirred suspension of PCC (2.67 g, 12.4 mmol) and 2.67 g of Celite in 16 ml of dichloromethane at room temperature. After stirring for 2 hr, the reaction mixture was diluted with 75 ml of ether and was filtered through a pad of Florisil (Fisher). An additional 100 ml of ether was used to rinse the Florisil. The solvent was removed *in vacuo* to afford an oil which was chromatographed on 40 g of silica gel. Elution with 18% ether in pentane afforded 263 mg (57%) of the desired ketone. PMR ($CDCl_3$) δ 3.54 (d, 2H, J = 7, CH_2O), 3.42–0.72 (m, 13H), 0.99 and 0.86 (two s, 15H, *gem*-methyls and *t*-butyl), −0.01 (s, 6H, $Si(CH_3)_2$); IR (NaCl, film) 2930, 2900, 2860, 1735, 1460, 1410, 1385, 1365, 1250, 1100, 1005, 835, 810, 770 cm^{-1}.

(3aα,3bβ,6aβ,7α,7aα) - *decahydro* - 2,2 - dimethyl - 7 - (*hydroxymethyl*) - 1H - *cyclopenta(a)pentalen* - 4 - *one*. To a stirred solution of tetra-*n*-butylammonium fluoride (354 mg, 1.35 mmol) in 2 ml of THF at 0°, was added over 2 min, a solution of (3aα,3bβ,6aβ,7α,7aα) - decahydro - 2,2 - dimethyl - 7 - (*tert* - butyldimethylsiloxymethyl) - 1H - cyclopenta(a)pentalen - 4 - one (182 mg, 0.542 mmol) in 3 ml of THF. The reaction mixture was allowed to warm to room temperature and was stirred for 1 hr. To the resulting solution was added 20 ml of brine; the solution was then extracted with ether (3 × 10 ml). The combined ether extracts were washed with brine (3 × 10 ml), dried ($MgSO_4$), and concentrated *in vacuo* to yield an oil which was chromatographed on 10 g of silica gel. Elution with ether afforded 112 mg (93%) of the desired product. PMR ($CDCl_3$) δ 3.65 (d, 2H, J = 6, CH_2O), 3.33–0.83 (m, 14H), 1.07 (s, 3H, CH_3), 0.95 (s, 3H, CH_3); IR (NaCl, film) 3430, 2950, 2930, 2870, 1740, 1465, 1385, 1365, 1030 cm^{-1}.

(3aα,3bβ,6aβ,7α,7aα) - *decahydro* - 7 - *formyl* - 2,2 - *dimethyl* - 1H - *cyclopenta(a)pentalen* - 4 - *one*. To a stirred suspension of PCC (290 mg, 1.34 mmol) and 290 mg of Celite in 2 ml of dichloromethane at room temperature, was added a solution of (3aα,3bβ,6aβ,7α,7aα) - decahydro - 2,2 - dimethyl - 7 - (hydroxymethyl) - 1H - cyclopenta(a)pentalen - 4 - one (149 mg, 0.672 mmol) in 3 ml of dichloromethane. The resulting mixture was stirred for 2 hr and was then diluted with 15 ml of ether. The mixture was filtered through a pad of Florisil which was rinsed with an additional 75 ml of ether. The solvent was removed *in vacuo* to afford an oil which was purified by chromatography on 9 g of silica gel. Elution with ether afforded 124 mg (84%) of the desired ketoaldehyde. PMR ($CDCl_3$) δ 9.61 (d, 1H, J = 1, CHO), 3.55–0.75 (m, 13H), 1.10 (s, 3H, CH_3), 0.97 (s, 3H, CH_3); IR (NaCl, film) 2940, 2860, 2710, 1740, 1720, 1460, 1410, 1385, 1365, 1165 cm^{-1}.

(3aα,3bβ,6aβ,7aα) -*decahydro* - 2,2 - *dimethyl* - 1H - *cyclopenta(a)pentalen* - 4 - *one*. A solution of tris(triphenylphosphine)rhodium(I) chloride (625 mg, 0.675 mmol) and (3aα,3bβ,6aβ,7α,7aα) - decahydro - 7 - formyl - 2,2 - dimethyl - 1H - cyclopenta(a)pentalen - 4 - one (124 mg, 0.563 mmol) in 16.6 ml of dry 1,2-dichloroethane was degrassed *via* two freeze-pump-thaw cycles under argon. The resulting solution was refluxed for 40.5 hr under an argon atmosphere. The solvent was removed *in vacuo*, 15 ml of ether was added, the resulting mixture was filtered and the filter cake was washed with a small amount of ether. The solvent was removed *in vacuo*; the same procedure was repeated using 30% ether in pentane. After removal of the solvent *in vacuo*, the mixture was purified by chromatography on 10 g of silica gel. Elution with 30% ether in pentane afforded 99.3 mg (92%) of the desired decarbonylated ketone. PMR ($CDCl_3$) δ 3.33–0.82 (m, 14H), 1.05 (s, 3H, CH_3), 0.90 (s, 3H, CH_3); IR (KBr disk) 2930, 1730, 1460, 1385, 1365 cm^{-1}; exact mass *m/e* 193.1563 (calc. for $C_{13}H_{20}O$, 193.1548).

(3aα,3bβ,6aβ,7aα) - *decahydro* - 5 - *formyl* - 2,2 - *dimethyl* - 1H - *cyclopenta(a)pentalen* - 4 - *one*. To a stirred suspension of sodium methoxide (Mallinkrodt, 110 mg, 1.66 mmol) in 1 ml of benzene at room temperature, was added a solution of ketone **28** (127.8 mg, 0.666 mmol) in 3.5 ml of dry benzene. The reaction mixture was stirred for 5 min and was then cooled to 0° using an ice bath. To the cold solution was added a neat solution of ethyl formate (0.11 ml, 98.6 mg, 1.33 mmol). The resulting mixture was allowed to warm to room temperature and stir overnight. The suspension was diluted with 25 ml of ether and washed with water (1 × 10 ml) and 2M NaOH (2 × 6 ml). The combined aqueous extracts were acidified to pH 1 with 3N HCl and were then extracted with ether (3 × 10 ml). The ether extracts were dried ($MgSO_4$), and the solvent was removed *in vacuo* to afford 141 mg (97%) of the desired product which was used in the next step without further purification. PMR ($CDCl_3$) δ 11.17 (br s,

1H, CHOH), 9.73 (br d, 1H, CHO), 7.20 (m, 1H, vinyl), 3.67–0.7 (m, 11H), 1.03 (s, 3H, CH_3), 0.90 (s, 3H, CH_3); GC/MS (1% OV-101, 0.125 in. × 1 foot glass column) *m/e* 220 (parent), 192, 111 (base), 110, 93, 82, 77.

(3aα,3bβ,6aβ,7aα) - *decahydro* - 5 - (n - *butylthiomethylene*) - 2,2 - *dimethyl* - 1H - *cyclopenta(a)pentalen* - 4 - *one* (**54**). A stirred suspension of magnesium sulfate (424 mg, 3.53 mmol), *p*-toluenesulfonic acid (10 mg, 0.052 mmol), *n*-butyl thiol (0.10 ml, 86.7 mg, 0.964 mmol), and (3aα,3bβ,6aβ,7aα) - decahydro - 5 - formyl - 2,2 - dimethyl - 1H - cyclopenta(a)pentalen - 4 - one (138.4 mg, 0.629 mmol) in 4.5 ml of dry benzene was heated to reflux for 20 hr. The resulting mixture was filtered and diluted with 25 ml of ether, washed with saturated sodium bicarbonate (2 × 10 ml) and brine (3 × 10 ml). The organic layer was dried ($MgSO_4$) and the solvent was removed *in vacuo* to afford a brown solid which was purified by chromatography on 10 g of silica gel. Elution with 10% ether in pentane provided 152 mg (82%) of **54**. PMR ($CDCl_3$) δ 7.42 (t, 1H, J = 2, vinyl), 3.38–0.68 (m, 19H), 1.02 (s, 3H, CH_3), 0.90 (s, 3H, CH_3); IR (NaCl, film) 3050, 2915, 2850, 1730, 1690, 1580, 1460, 1450, 1380, 1365, 1325, 1290, 1270, 1235, 1215, 1190, 1165, 1100, 1070, 1010, 890, 860, 830, 800, 785 cm^{-1}; GC/MS (0.125 in. × 1 ft glass column packed with 1% OV-101) *m/e* 292 (parent) 235, 109, 107, 95, 79, 72.

(3aα,3bβ,6aβ,7aα) - *decahydro* - 5 - (n - *butylthiomethylene*) - 2,2,3b - *trimethyl* - 1H - *cyclopenta(a)pentalen* - 4 - *one*. A stirred solution of potassium *t*-butoxide (2.07 mmol) in 1.5 ml of dry *t*-butanol at room temperature, was added compound **54** (148 mg, 0.507 mmol) in 3 ml of dry *t*-butanol. After the solution was stirred at room temperature for 2 min, it was cooled to 0°. To the cooled solution was added over 1 min, methyl iodide (0.64 ml, 1.47 g, 10.3 mmol). The resulting mixture was allowed to warm to room temperature and was then heated to reflux for 0.5 hr. The suspension was washed with 25 ml of brine and was extracted with ether (3 × 10 ml). The combined ether extracts were dried ($MgSO_4$) and the solvent was removed *in vacuo*. The resulting solid was purified by chromatography on 12 g of silica gel. Elution with 8% ether in pentane afforded 28 mg (15%) of starting material and 78 mg (50%) of the desired alkylation product. PMR ($CDCl_3$) δ 7.45 (t, 1H, J = 2, vinyl), 3.20–0.67 (m, 20H), 1.05 (s, 3H, CH_3), 0.92 (s, 3H, CH_3), 0.97 (s, 3H, angular methyl); IR (NaCl, film) 3005, 2915, 2865, 1730, 1695, 1585, 1455, 1380, 1365, 1290, 1275, 1230, 1210, 1185, 1155, 1100, 1010, 980, 890, 860, 840, 800, 780, 730 cm^{-1}; GC/MS (1% OV-101, 0.125 in. × 1 ft) *m/e* 306 (parent), 107, 95, 91, 81, 72.

(3aα,3bβ,6aβ,7aα) - *decahydro* - 2,2,3b - *trimethyl* - 1H - *cyclopenta(a)pentalen* - 4 - *one* (**55**). A stirred solution of (3aα,3bβ,6aβ,7aα) - decahydro - 5 - (*n* - butylthiomethylene) - 2,2,3b - trimethyl - 1H - cyclopenta(a)pentalen - 4 - one (68 mg, 0.22 mmol), 3 ml of 25% aqueous potassium hydroxide, and 4 ml of ethylene glycol was heated to reflux for 24 hr. The resulting mixture was washed with 25 ml of brine and extracted with ether (3 × 10 ml). The combined ether extracts were washed with aqueous saturated sodium bicarbonate (2 × 8 ml) and brine (10 ml). The organic layer was then dried ($MgSO_4$) and the solvent was removed *in vacuo*. The resulting oil was purified by chromatography on 5 g of silica gel. Elution with 10% ether in pentane afforded 23 mg (51%) of the desired norketone **55** whose spectral properties nicely matched those kindly furnished to us by Prof. Hudlicky. PMR ($CDCl_3$) δ 3.1–0.73 (m, 13H), 1.07 and 0.92 (two singlets, 3H each, *gem*-methyls), 0.95 (s, 3H, angular methyl); IR (NaCl, film) 2935, 2860, 1760, 1550, 1380, 1365 cm^{-1}; GC/MS (0.125 in. × 1 ft glass OV-101 column) *m/e* 206 (parent), 162, 123, 108, 107, 105, 95, 94, 79, 77; CMR ($CDCl_3$) 224.5 (C = O), 59.3 (s, C alpha to C = O), 48.9, 46.8, 43.4, 41.9, 41.2 (CMe_2), 37.7, 34.2, 29.7, 29.3, 26.6 (*gem*-methyls), 22.4, 17.3 (angular methyl).

2,2,5-trimethyl-5-hexenoic acid (**45**). To a stirred solution of freshly distilled diisopropylamine (20.84 g, 205.9 mmol) in 150 ml of THF and cooled in a dry ice–acetone bath, was added 145 ml (205.9 mmol, 1.48 M in hexane) of butyllithium. The mixture was warmed to and stirred at ice bath temperature for 0.25 hr prior to the addition of 8.646 g (98.1 mmol) of isobutyric acid. The resulting solution was stirred at room temperature for 0.5 hr. After cooling to 0°, 22.343 g (92.97 mmol) of 3-methyl-3-butenyl tosylate was added *via* syringe and the solution was allowed to stir at room temperature for 44 hr. Cold 10% HCl (250 ml) was added and the aqueous layer was extracted with ether (2 × 250 ml). The combined organic material was washed successively with 10% HCl (200 ml) and water (2 × 250 ml) then dried ($MgSO_4$), and concentrated *in vacuo* to afford 13.405 g of material which was chromatographed on silica gel (3 × 61 cm column) eluting with 30% ether in pentane to obtain 11.399 g (79%) of the desired acid. PMR ($CDCl_3$) δ 1.09 (s, 6H, CH_3), 1.77 (m, 3H, allylic methyl), 1.8 (m, 4H, CH_2CH_2), 4.70 (m, 2H, $=CH_2$), 12.0 (s, 1H, CO_2H); IR (NaCl, film) br absorption from 3500–2400, 3080, 1700, 1650, 885 cm^{-1}; *Anal.* Calc. for $C_9H_{16}O_2$: C, 69.19; H, 10.32. Found: C, 68.97; H, 10.18.

2,2,5-trimethyl-5-hexenal. To a 250-ml three-neck round bottom flask fitted with a condenser, a dropping funnel, and a magnetic stirring bar, was added 90 ml of ether and 2.824 g (79.34 mmol) of lithium aluminum hydride. This was followed by the addition of 8.910 g (57.02 mmol) of 2,2,5-trimethyl-5-hexenoic acid (**45**) in ether (50 ml) at a rate which maintained a gentle reflux. The solution was stirred for 0.5 hr and was then cooled in an ice bath. Following the dropwise addition of 10% H_2SO_4, the resulting solution was extracted with ether (3 × 50 ml), dried ($MgSO_4$), and concentrated *in vacuo* to obtain 7.855 g (97%) of the desired alcohol which was sufficiently pure to be used in the next step. PMR ($CDCl_3$) δ 1.83 (s, 6H, CH_3), 1.4 (m, 4H, CH_2CH_2), 1.7 (d, 3H, allylic CH_3), 2.00 (s, 1H, OH), 3.28 (s, 2H, OCH_2), 4.65 (m, 2H, $=CH_2$); IR (NaCl, film) 3360 (broad OH), 3080, 1650, 885 cm^{-1}.

To a 500-ml round bottom flask was added 250 ml of dichloromethane and 15.25 g (70.75 mmol, 1.5 equiv) of pyridinium chlorochromate along with 15 g of Celite. To the stirred suspension was added 3.004 g (21.11 mmol) of 2,2,5-trimethyl-5-hexen-1-ol dissolved in 15 ml of dichloromethane; the mixture turned dark immediately. After 2.5 hr, 100 ml of ether was added and the organic material was decanted away from the solid. The solid was washed with ether (4 × 25 ml), the organic material was combined and filtered through Florisil. The resulting solution was concentrated *in vacuo* to obtain 2.647 g (91%) of the desired aldehyde. PMR ($CDCl_3$) δ 1.08 (s, 6H, CH_3), 1.53 (s, 3H, allylic CH_3), 1.8 (m, 4H, CH_2CH_2), 4.7 (br s, 2H, $=CH_2$), 9.5 (s, 1H, CHO); IR (NaCl, film) 3080, 2800, 2700, 1730, 1650, 890 cm^{-1}.

6-(1,1,4-*trimethyl*-4-*pentenyl*)*fulvene* (**46**). To a cold (0°) flask containing 0.248 g (3.751 mmol) of freshly distilled cyclopentadiene in 15 ml of THF was added 2.50 ml (3.70 mmol) of *n*-butyllithium *via* syringe. The solution was stirred at 0° for 0.5 hr, allowed to warm to room temperature for 15 min, and then cooled to 0° at which time 0.505 g (3.597 mmol) of 2,2,5-trimethyl-5-hexenal dissolved in 1.0 ml of THF was added *via* syringe over 10 min. After 1.5 hr, the red solution was diluted with ether (30 ml) and washed with water (30 ml). The aqueous layer was extracted with ether (3 × 20 ml), and the combined organic material was washed with 25 ml of water, dried ($MgSO_4$), and concentrated *in vacuo*. Chromatography on activity II alumina, eluting with pentane, afforded 0.471 g (70%) of the desired pure fulvene **46**. PMR ($CDCl_3$) δ 1.23 (s, 6H, CH_3), 1.6 (m, 4H, CH_2CH_2), 1.70 (m, 3H, allylic CH_3), 4.68 (m, 2H, $=CH_2$), 6.18–6.60 (m, 5H, ring H's); IR (NaCl, film) 3070, 1630, 885 cm^{-1}; *Anal.* Calc. for $C_{14}H_{20}$: C, 89.36; H, 10.63. Found: C, 89.15; H, 10.50.

N,N - (*dimethoxycarbonyl*) - 2,3 - *diaza* - 7 - (1,1,4 - *trimethyl* - 4 - *hexenylidene*)*bicyclo*(2.2.1)*heptane*. To a solution of 4.216 g (22.404 mmol) of 6 - (1,1,4 - trimethyl - 4 - pentenyl)fulvene (**46**) in 45 ml of 1:1 ether/pentane was added dropwise with stirring 3.288 g (22.50 mmol) of dimethyl azodicarboxylate in 45 ml of 1:1 ether/pentane. After the addition was complete, the solution was stirred at 0° for 1 hr. The solvent was removed at reduced pressure and the resulting oil was used without purification (none required) in the next step. PMR ($CDCl_3$) δ 1.05 (s, 6H, CH_3), 1.3 (A_2B_2, 4H, CH_2CH_2), 1.65 (m, 3H, allylic CH_3), 3.75 (s, 6H, CO_2CH_3), 4.65 (m, 2H, $=CH_2$), 4.85 (s, 1H, vinyl), 5.0 (m, 1H, bridgehead), 5.65 (m, 1H, bridgehead), 6.75 (m, 2H, vinyl).

To the Diels–Alder adduct dissolved in 150 ml of freshly distilled dichloromethane was added 21.789 (112.2 mmol) of dipotassium azodicarboxylate. A solution of 13 ml of glacial acetic

acid in 30 ml of dichloromethane was added dropwide over a period of 1.25 hr and the resulting solution was stirred at 0° for 3 hr. The reaction mixture was filtered and the yellow solid was washed with CH_2Cl_2 and ether. Concentration *in vacuo* followed by chromatography on silica gel (2.5 × 46 cm column) eluting with 25% Et_2O/pentane produced 5.488 g (73%) of the desired adduct. PMR ($CDCl_3$) δ 1.05 (s, 6H, CH_3), 1.40 (m, 8H, CH_2), 1.70 (d, 3H, allylic CH_3), 3.70 (s, 3H, CO_2CH_3), 4.4 (m, 1H, bridgehead), 5.05 (m, 1H, bridgehead), 4.65 (m, 2H, $=CH_2$), 5.30 (s, 1H, vinyl); IR (NaCl, film) 3070, 2960, 2870, 1750, 1715, 1650, 1440, 1390, 1365, 890 cm^{-1}; *Anal.* Calc. for $C_{18}H_{28}N_2O_4$: C, 64.28; H, 8.33. Found: C, 64.08; H, 8.58.

2,3 - *Diaza* - 7 - (1,1,4 - *trimethyl* - 4 - *hexenylidene*)*bicyclo*(2.2.1)*hept* - 2 - *ene* (**47**). A solution of 1.493 g (22.61 mmol) of 85% KOH dissolved in 5 ml of degassed ethylene glycol was heated to 120° (oil bath) at which time 608 mg (1.81 mmol) of N,N - (dimethoxycarbonyl) - 2,3 - diaza - 7 - (1,1,4 - trimethyl - 4 - hexenylidene)bicyclo(2.2.1)heptane dissolved in 5 ml of degassed ethylene glycol was added. After stirring at 120° for 0.75 hr, the flask was cooled to 0° (ice bath) and 1.81 g (5.49 mmol) of potassium ferricyanide was added dropwise over *ca.* 5 min. The thick brown suspension was stirred for 0.5 hr, diluted with water (100 ml), extracted with pentane (6 × 15 ml), rewashed with water (2 × 25 ml), dried ($MgSO_4$), and concentrated *in vacuo*. The resulting brown oil was chromatographed on silica gel (2 × 20 cm column) eluting with 10% ether in pentane to afford 0.264 g (67%) of compound **47**. PMR ($CDCl_3$) δ 5.6 (br s, 1H, bridgehead), 5.02 (br s, 1H, C_8 vinyl), 5.0 (br s, 1H, bridgehead), 4.63 (br s, 2H, $=CH_2$), 1.63 (poorly resolved dd, 3H, allylic CH_3), 1.00 (s, 6H, *gem* CH_3); IR (NaCl, film) 3035, 2980, 2380, 1380, 1370, 1360, 885 cm^{-1}.

Thermolysis of azo compound **47**. A solution of 1.868 g (8.55 mmol) of 2,3 - diaza - 7 - (1,1,4 - trimethyl - 4 - hexenylidene)bicyclo(2.2.1)hept - 2 - ene (**47**) dissolved in 2.5 l of acetonitrile (clearly the use of syringe pump techniques to achieve high dilution seems warranted) was heated to reflux for 10 hr. Tlc analysis indicated the presence of two components possessing very similar R_f's; both components proved to be quite volatile. The acetonitrile was carefully removed at atmospheric pressure through a 33 cm Vigreux column packed with glass spheres. An oil, still consisting of two components present in unequal amounts (tlc and PMR analysis indicated roughly a 2:1 ratio; 0.656 g), was isolated. By comparison with the spectral data for numerous other tricyclopentanoids, it was clear that both compounds were tricyclopentanoids. Furthermore, GC/MS analysis indicated that the two compounds were isomeric with a molecular weight of 190. Attempts to separate the compounds by tlc and mplc were not successful. As indicated in the text, attempts to convert the material to $\Delta^{9(12)}$-capnellene (**19**) were unsuccessful. The ^1H NMR spectrum of the major adduct (tentatively assigned to be tricyclopentanoid **48**) showed: ($CDCl_3$) δ 5.5 (m, 1H, vinyl), 0.95 (s, CH_3), 0.90 (s, CH_3), 0.87 (s, CH_3).

Thermolysis of azo compound **38**. (3aα,6aβ,7α,7aα) - *and* (3aα,6aα,7α,7aα) - 2,3,3a,5,6,6a,7,7a - *octahydro* - 1H - *cyclopenta*(*a*)*pentalene* - 7 - *carboxylic acid methyl ester* (**42** *and* **43**). Azo compound **38** (409.4 mg, 1.75 mmol), prepared in a fashion which is entirely analogous to that reported herein for the construction of **33** (complete details are available upon request), dissolved in 1.5 l of acetonitrile, was heated to reflux for 6 hr. After cooling to room temperature, the solvent was removed in part at atmospheric pressure and in part *in vacuo*. Chromatography (MPLC, 15 × 200 and 25 × 1000 mm columns, 6% ether in pentane, 16 ml/min) on silica gel afforded 87% of tricyclopentanoids **42** and **43** in a ratio of 7:1. For **42**: IR (NaCl, film) 3050, 2950, 2860, 1735, 1450, 1435, 1370, 1275, 1225, 1190, 1165, 1000 cm^{-1}; PMR ($CDCl_3$) δ 5.25 (m, 1H, vinyl), 3.63 (s, 3H, CO_2CH_3), 2.65 (d, 1H, J = 8, $CHCO_2CH_3$), 3.62–0.77 (m, remaining H's); *Anal.* Calc. for $C_{13}H_{18}O_2$: C, 75.73; H, 8.74. Found: C, 76.03; H, 8.87. For **43**: IR (NaCl, film) 3050, 2950, 2860, 1735, 1435, 1370, 1315, 1295, 1255, 1230, 1160, 1025 cm^{-1}; PMR ($CDCl_3$) δ 5.23 (m, 1H, vinyl), 3.70 (s, 3H, CO_2CH_3), 3.60–0.67 (m, remaining H's); *Anal.* Calc. for $C_{13}H_{18}O_2$: 206.1307; Found: 206.1306.

Note added in proof: Since this manuscript was submitted, we have completed a total synthesis of capnellene using a modification of the route described herein. See: R. D. Little and G. L. Carroll, *Tetrahedron Letters*, in press.

Acknowledgements—Financial support for this work was provided by the Cancer Research Coordinating Committee of the University of California and by the National Cancer Institute, DHEW (Grant Number CA 21144-02, 03, 04), to whom we are most grateful. GM and AB thank the University of California, Santa Barbara for the receipt of Patent Funds. MV is grateful to the University of California for a followship. AB would like to thank the University of Petroleum and Minerals, Dhahran, Saudi Arabia for a fellowship. Finally, we are pleased to acknowledge the receipt of spectral data for comparison purposes, from Prof. Hudlicky of the Illinios Institute of Technology and Prof. Djerassi of Stanford University.

REFERENCES

[1]P. Dowd, *J. Am. Chem. Soc.* **88**, 2587 (1966). See also R. J. Baseman, D. W. Pratt, M. Chow and P. Dowd, *Ibid.* **98**, 5726 (1976).

[2a]W. Moffitt, *Trans. Faraday Soc.* **45**, 373 (1949); [b]H. C. Longuet-Higgins, *J. Chem. Phys.* **18**, 265 (1950).

[3a]P. Dowd, *Acc. Chem. Res.* **5**, 242 (1972); [b]F. Weiss, *Q. Rev., Chem. Soc.* **24**, 278 (1970).

[4]For example see (a) K. Ehrlich and G. F. Emerson, *J. Am. Chem. Soc.* **94**, 2464 (1972); (b) M. R. Churchill and K. Gold, *Inorg. Chem.* **8**, 401 (1969); (c) A. Almenningen, A. Haaland and K. Wahl, *Acta Chem. Scand.* **23**, 1145 (1969); (d) R. Noyori, M. Yamakawa and H. Takaya, *Tetrahedron Letters* 4823 (1978).

[5a]B. M. Trost and D. M. T. Chan, *T. Am. Chem. Soc.* **101**, 6429 (1979); [b]B. M. Trost and D. M. T. Chan, *Ibid.* **102**, 6359 (1980).

[6]J. A. Berson, *Acc. Chem. Res.* **11**, 446 (1978).

[7]R. D. Little and L. Brown, *Tetrahedron Letters* **21**, 2203 (1980).

[8a]R. D. Little, A. Bukhari and M. G. Venegas, *Tetrahedron Letters* 305 (1979); [b]M. G. Venegas and R. D. Little, *Ibid.* 309 (1979); [c]R. D. Little and G. L. Carroll, *J. Org. Chem.* **44**, 4720 (1979).

[9]Unpublished results with L. Losinski-Dang, UCSB.

[10]Unpublished results with G. M. Muller, UCSB.

[11]Hirsutic acid: F. W. Comer, F. McCapra, I. H. Qureshi and A. I. Scott, *Tetrahedron* **23**, 4761 (1967); B. M. Trost, C. D. Shuey and F. Dininno, *J. Am. Chem. Soc.* **101**, 1284 (1979); H. Hashimoto, K. Tsuzuki, F. Sakan, H. Shirahama and T. Matsumoto, *Tetrahedron Letters* 3745 (1974); P. T. Lansbury, N. Y. Wang and J. E. Rhodes, *Ibid.* 2053 (1972); K. Hayano, Y. Ohfune, H. Shirahama and T. Matsumoto, *Ibid.* 1991 (1978); Coriolin, coriolin B, diketocoriolin B: S. Takahashi, H. Naganawa, H. Iinuma, T. Takita, K. Maeda and H. Umezawa, *Tetrahedron Letters* 1995–1958 (1971); M. Tanabe, K. Suzuki and W. C. Jankowski, *Ibid.* 2271 (1974); T. Takeuchi, S. Takahashi, H. Iinuma and H. Umezawa, *J. Antibiot.* **24**, 631 (1971); N. Nakamura, T. Takita, H. Umezawa, M. Kunishima, Y. Nakayama and Y. I. Iitaka, *Ibid.* **27**, 301 (1974); T. Kunimoto and H. Umezawa, *Biochimica et Biophysica Acta*, **318**, 78 (1973); Y. Nishimura, Y. Koyama, S. Umezawa, T. Takeuchi, M. Ishizuka and H. Umezawa, *J. Antibiot.* **30**, 59 (1977); M. Shibasaki, K. Iseki and S. Ikegami, *Tetrahedron Letters* 3587 (1980); S. Danishefsky and R. Zamboni, *Ibid.* 3439 (1980); K. Tatsuta, K. Akimoto and M. Kinoshita, *J. Antibiot.* **23**, 100 (1980); S. Danishefsky, .R. Zamboni, M. Kahn, S. J Etheredge, *J. Am. Chem. Soc.* **102**, 2097 (1980); Hirstuene: S. Nozoe, J. Furukawa, U. Sankawa and S. Shibata, *Tetrahedron Letters* 195 (1976); Y. Ohfune, H. Shirahama and T. Matsumoto, *Ibid.* 2795 (1976); K. Hayano, Y. Ohfune, H. Shirahama and T. Matsumoto, *Ibid.* 1991 (1978); K. Tatsuta, K. Akimoto and M. Kinoshita, *J. Am. Chem. Soc.* **101**, 6116 (1979); A. E. Greene, *Tetrahedron Letters* 3059 (1980); T. Hudlicky, T. Kutchan, S. R. Wilson and D. T. Mao, *J. Am. Chem. Soc.* **102**, 6351 (1980); Norhirsutene: P. T. Lansbury and N. Nazarenko, *Tetrahedron Letters* 1833 (1971); Capnellene: M. Kaisin, Y. M.

Sheikh, L. J. Durham, C. Djerassi, B. Tursch, D. Daloze, J. C. Braekman, D. Losman and R. Karlsson, *Tetrahedron Letters* 2239 (1974); E. Ayanoglu, T. Gebreyesus, C. M. Beechan, C. Djerassi and M. Kaisin, *Ibid.* 1671 (1978); R. Karlsson, *Acta Crystallogr. Sect. B*, **B33**, 1143 (1977).
[12]R. D. Little and G. Muller, *J. Am. Chem. Soc.* **101**, 7129 (1979).
[13]R. Siemionko and J. A. Berson, *Ibid.* **102**, 3870 (1980).
[14]W. W. Schoeller, *J. Chem. Soc. Perkin II*, 366 (1979).
[15]See, for example, E. L. Eliel, N. L. Allinger, S. J. Angyal and G. A. Morrison, *Conformational Analysis* pp. 191-ff. Wiley-Interscience, New York (1967).
[16]E. J. Corey and J. W. Suggs, *Tetrahedron Letters* 2647 (1975).
[17]For a detailed account see: R. D. Little and G. M. Muller, *J. Am. Chem. Soc.* **103**, 2744 (1981).
[18]E. J. Corey and A. Venkateswarlu, *Ibid.* **94**, 6190 (1972).
[19]R. Campbell, Jr., C. F. Lochow, K. P. Vora and R. G. Miller, *Ibid.* **102**, 5824 (1980) and Refs. therein.
[20]See, for example: K. Tatsuta, K. Akimoto and M. Kinoshita, *J. Am. Chem. Soc.* **101**, 6118 (1979).
[21]Note, for example: G. J. Quallich and R. H. Schlessinger, *Ibid.* **101**, 7627 (1979) and Refs. therein.
[22a]L. A. Paquette and Y. K. Han, *J. Org. Chem.* **44**, 4014 (1979); [b]M. C. Pirrung, *J. Am. Chem. Soc.* **101**, 7130 (1979).
[23]W. C. Still, M. Kahn, and A. Mitra, *J. Org. Chem.* **43**, 2923 (1978).
[24]J. A. Berson, M. S. Poonian and W. J. Libbey, *J. Am. Chem. Soc.* **91**, 5567 (1969).
[25]R. D. Little and M. G. Venegas, *Org. Synth.* Preprints are available upon request.