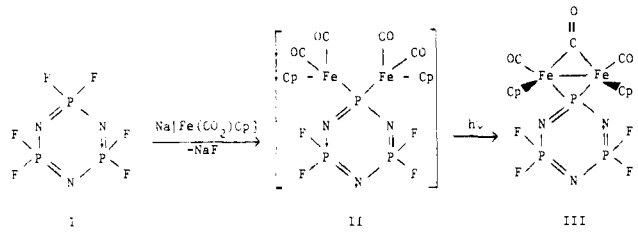

I II III

direct phosphorus–metal side group bonds and a three-membered organometallic ring. The structure is depicted as III.

Specifically, hexafluorocyclotriphosphazene (I, 2.0 g, 8×10^{-3} mol) was allowed to react with sodium dicarbonylcyclopentadienylferrate (1.6×10^{-2} mol) at 25 °C in tetrahydrofuran to give a mixture of products. Chromatographic separation yielded a bright yellow powder (II) in 10% yield. This product was photolytically sensitive, even under weak laboratory illumination, and underwent a transformation to a red, air-stable compound (III). Purification of III was effected by recrystallization from hexane–methylene chloride mixed solvent systems.

The structure of III was deduced by infrared spectroscopy, mass spectrometry, elemental analyses, NMR analysis, and by single-crystal X-ray structure determination. The infrared spectra show absorbances for P—N bonds at 1260 and 1220 (KBr disks), for bridging C=O groups at 1805 (br) (CH_2Cl_2 solution), and for terminal C≡O units at 2019 (s) and 1984 (br) cm^{-1}. Mass spectra showed a parent peak at *m/e* 537 (mol wt of III 537) with the successive loss of three carbonyl groups (*m/e* −28) at 509, 481, and 453. Elemental microanalysis was compatible with structure III. A ^1H NMR spectrum of III showed a singlet at 4.9 ppm downfield from Me_4Si, and the ^{19}F NMR spectrum consisted of a doublet centered at 44.7 ppm relative to C_6H_5F, with a P–F coupling of 897 Hz. These data were compatible with structure III. A fluorine-decoupled ^{31}P NMR spectrum showed a broad set of multiplet peaks centered at 1.5 ppm relative to H_3PO_4.

Finally, a single-crystal X-ray analysis of III confirmed the structure shown. The space group found for III was $P\bar{1}$, with the unit cell parameters $a = 9.116$ (14), $b = 14.219$ (09), $c = 7.735$ (17) Å; $\alpha = 90.48$ (3), $\beta = 113.93$ (4), and $\gamma = 92.83$ (2)° (with $Z = 2$). The Fe–Fe distance is 2.60, the P–Fe distances are 2.19, the Fe–C (bridging) distances are 1.92, and the Fe–C (terminal) distances are 1.74–1.77 Å. The P—N skeletal bonds that flank the spiro unit are 1.63 Å long, considerably longer than the other skeletal bonds (1.54–1.57 Å). The Fe–P–Fe bond angle is 72.9 and the Fe–C–Fe angle is 84.4°. The two cyclopentadiene ligands are cis to each other with respect to the metal–metal bond. The final *R* factor was 0.05. The arrangement of atoms in the carbonylcyclopentadienyl unit is reminiscent of the carbonyl-bridged Fe–Fe structures reported by Pauson[1] and Mills[2], and the structural parameters of the bridging phosphorus atoms are similar to those discussed by Clegg[3] for a phosphido-bridged diiron carbonyl compound.

The structure of II has not yet been confirmed unambiguously because of the photolytic lability of the compound and the difficulties encountered in the preparation of single crystals. However, the infrared spectrum gave clear evidence for the presence of the cyclic trimeric phosphazene ring, with peaks at 1240 and 1210 cm^{-1}, and also showed terminal C≡O absorbances at 2038 (sh), 2020 (s), and 1977 (br) cm^{-1}. The ^1H NMR spectrum showed a singlet at 5.3 ppm. We are continuing to investigate this intermediate.

Compound III is unusual in a number of ways. It is the first phosphazene reported in which the side-group bonds connect phosphorus directly to a metal. In this respect, the electronic and chemical properties of this and similar species are of considerable interest. This compound is the first phosphazene synthesized that possesses a three-membered spiro ring fused to the phosphazene skeleton. It is also a valuable new derivative for structural comparisons with related Fe–Fe species.[1-3] Moreover, compound III is the first member of a potentially large group of compounds in which a variety of catalytic transition metals are linked to and perhaps modified by a cyclic oligomeric or linear high polymeric phosphazene skeleton.

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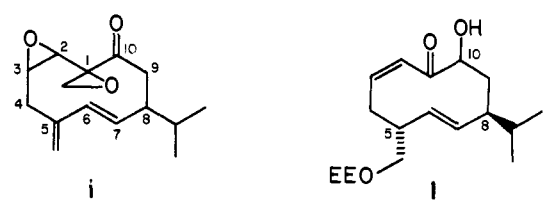
(±)-Periplanone-B. Total Synthesis and Structure of the Sex Excitant Pheromone of the American Cockroach[1]

Sir:

Females of the species *Periplaneta americana*, the American cockroach, have long been known to produce an extraordinarily potent sex pheromone. Unlike the long-range sex attractants which help many insects to locate a receptive mate, the cockroach pheromone acts over relatively short distances and functions largely as a close proximity sex excitant. Human interest in this material has intensified since its discovery[2] some 25 years ago and has resulted in a large number of behavioral studies as well as attempts to isolate and identify its active components.[3] Early efforts to isolate the material were foiled since the pheromone is stored only in minute amounts (≪1 μg) by individual cockroaches and is so active (threshold $<10^{-6}$ μg) that its presence as a trace impurity in otherwise inactive materials easily misleads bioassay-guided evaluations. A few years ago Persoons et al. reported the results of a massive cockroach rearing and extraction program which utilized more than 75 000 virgin female cockroaches and led to the isolation of two extremely active compounds, periplanones-A (~20 μg) and -B (~200 μg). The latter material was characterized spectrally and tentatively assigned a germacranoid structure, i (stereochemistry unknown).[4] Reported here are highly stereoselective syntheses of three of the four possible diastereomers of i and the identification of one of these stereoisomers as the major component of the American cockroach pheromone, periplanone-B.



i I

Except for the geometries of the endocyclic epoxide and olefin (cis and trans, respectively) the relative stereochemistry in periplanone-B was unknown. Therefore a flexible route to i had to be developed which allowed for the stereochemical uncertainties at C-1, C-2, and C-8. The basic plan called for the preparation of an advanced cyclodecanoid intermediate

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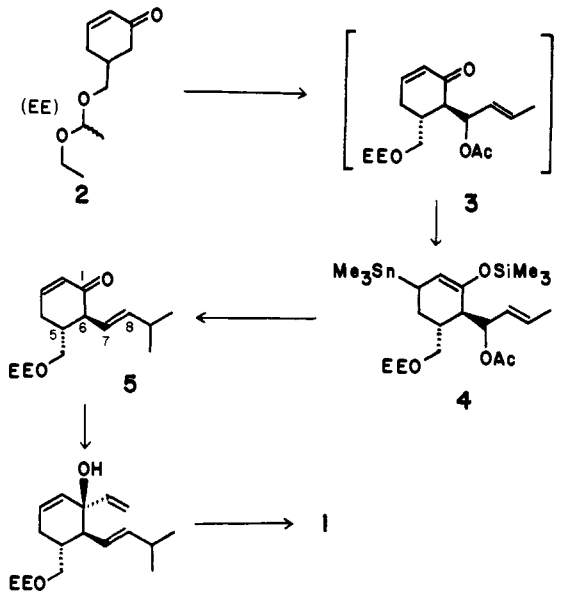
which could be converted in a stereorational fashion to each possible diastereomer of i for spectral and biological evaluation.

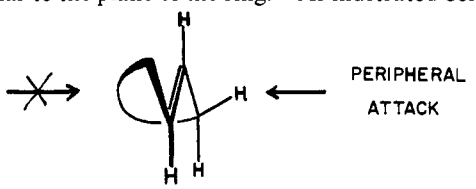
The cyclodecadienone **1** is the key intermediate mentioned above and its synthesis began with the ethoxyethyl ether of 5-(hydroxymethyl)cyclohexenone[5] (**2**). When **2** was subjected to kinetic aldolization[6] (a, LDA/THF, 0 °C; b, $CH_3CH{=}CHCHO$, −78 °C) and in situ acetylation (Ac_2O, −78 °C), the intermediate enone **3** was formed. This enone was not isolated but was protected by the further addition of Me_3SnLi[7] (1.1 equiv, −78 °C) and Me_3SiCl to give the β-stannyl enol silyl ether **4**. This form of enone protection was ideal for our



purposes since β-stannyl enol silyl ethers are relatively unreactive with most nucleophiles and yet are smoothly transformed back to starting enone by mild oxidation.[8] Thus coupling of the allylic acetate **4** with lithium dimethylcuprate[9] (Et_2O, 30 min, 0 °C) followed by an oxidative workup (1.5 equiv of MCPBA) led to the disubstituted cyclohexenone **5** (74% from **2**). The stereochemistry follows from the NMR of **5** which shows a diaxial relationship between the protons at C-5 and C-6 (J = 10 Hz) and a typical trans coupling constant (16 Hz) for the vinyl hydrogens at C-7 and C-8.

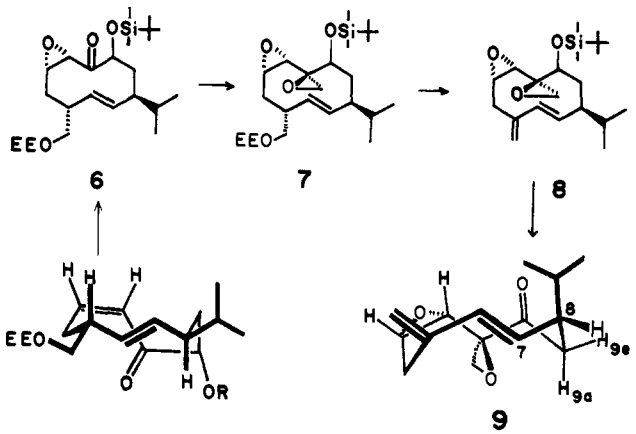
Ring expansion to the cyclodecadienone **1** required two more steps and followed an oxy-Cope pathway. Thus addition of ethereal vinyllithium[10] to **5** gave a divinylcyclohexenol which smoothly underwent an oxy-Cope rearrangement on conversion to its potassium salt (KH/THF-18-crown-6, 1 h, 70 °C).[8,11] The reaction mixture was then chilled to −78 °C, treated with Me_3SiCl, and finally worked up with *m*-chloroperbenzoic acid. The product **1** was isolated by flash chromatography in 57% yield.[12] Interestingly, virtually all the material having gross structure **1** was produced as a single stereoisomer. The stereochemistry assigned above is that required by a chair-like oxy-Cope transition and is supported by analysis of the vinyl hydrogen splitting patterns in the NMR.

The approach to stereocontrol in the synthesis of the various diastereomers of i was based on the fact that 1,4- and 1,5-cyclodecadienes generally exist in predictable well-defined conformations having the planes of the olefinic linkages perpendicular to the plane of the ring.[13] As illustrated below, this



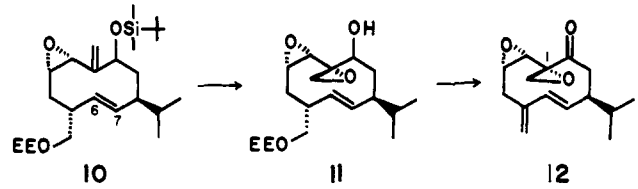
situation quite effectively differentiates the two faces of a medium-ring double bond and strongly favors the approach of a reagent from the less-hindered peripheral face of the π system. This principle of peripheral attack appears to be general as a strategy for stereochemical control in the synthesis and modification of germacranes and related medium-ring compounds.[14] It does, however, require knowledge of the conformation of the starting olefin. With 1,4- and 1,5-cyclodecadiene derivatives, the typical lack of serious transannular nonbonded interactions makes it possible to consider only those conformers composed totally of minimum energy torsional fragments (A—C—C—B staggered; A—C—C=B eclipsed[15]). Consideration of these torsional constraints along with the usual nonbonded repulsions for proximate atoms often points to a single conformation with a fair degree of certainty. Although this approach to stereochemical control in medium-ring systems must be used with caution, it has proven to be a successful strategy for the current problem and its predictions regarding the stereochemistry of products have been largely confirmed by NMR and X-ray crystallography.

Synthesis of the first diastereomer of structure i proceeded as follows. Compound **1** was first protected (Me_2-*t*-BuSiCl)[16] and then epoxidized (*t*-BuOOH, Triton B/THF).[17] Since silyl-protected **1** should exist in the conformation shown, peripheral epoxidation would be expected to produce the α-epoxy ketone **6** stereoselectively. In fact, a single *cis*-epoxy ketone



was produced in 66% yield. Conversion to the bisepoxide **7** should also be subject to peripheral stereocontrol since one of the two faces of the carbonyl is highly hindered by the opposite side of the medium ring. As expected, ketone epoxidation with dimethylsulfonium methylide (THF-Me_2SO, −5 °C) gave rise to a single bisepoxide (75%) to which we assign structure **7**. Generation of the *exo*-methylene followed by deprotection of the primary alcohol (1:1 H_2O-HOAc, 25 °C, 15 min), selenylation[18] (*o*-$NO_2C_6H_4SeCN$, Bu_3P/THF, 5 min, 0 °C), and selenoxide elimination (H_2O_2/THF, 18 h, 25 °C) gave **8** (68% from **7**). Finally, removal of the silyl protecting group ($Bu_4N^+F^-$/THF) and oxidation (CrO_3·2Pyr) gave **9** (>95%). Although spectral comparison of **9** with authentic periplanone-B showed the compounds to be nonidentical, similarities in the 300-MHz NMR spectra strongly suggested that the only difference between **9** and periplanone-B was the configuration of the C-8 isopropyl. In **9** the isopropyl was pseudoaxial ($J_{7,8}$ = 5, $J_{8,9a}$ = 7.5, $J_{8,9e}$ = 2 Hz), whereas in periplanone-B the isopropyl appears pseudoequatorial ($J_{7,8}$ = 10, $J_{8,9a}$ = 10, $J_{8,9e}$ = 5.5 Hz).

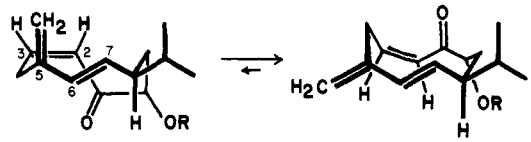
The second diastereomer of structure i to be prepared was epimeric with **9** at C-1. This epoxide epimer was derived from **6** by Peterson-Chan olefination[19] (1, Me_3SiCH_2MgCl/Et_2O; 2, KH/THF, 62%) and epoxidation. The latter reaction caused some problem since the C-6–C-7 olefin was found to be the more reactive; however, deprotection of **10** ($Bu_4N^+F^-$) and hydroxyl-directed epoxidation (*t*-BuOOH, $VO(acac)_2$/



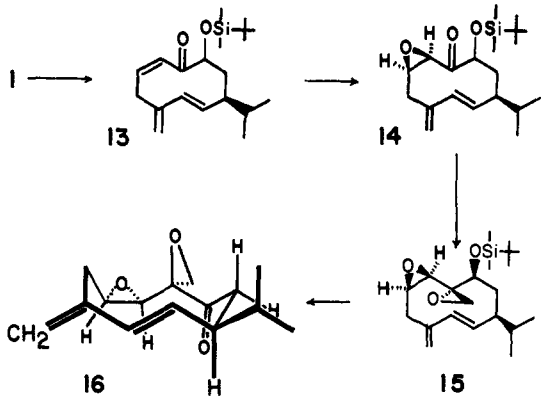
10 11 12

C_6H_6)[20] cleanly gave bisepoxide **11** (95%). Again the stereochemistry follows from peripheral attack and is supported by the observation that **11** is isomeric with desilylated **7**. Finally, oxidation (CrO_3·2Pyr), deprotection (H_2O-HOAc), and elimination via the selenoxide as before gave **12**. Like **9**, this material was also found not to be the same as periplanone-B. Interestingly, the NMR of **12** shows it to be conformationally very different from **9** and periplanone-B. This is not unexpected. By inverting the C-1 exocyclic epoxide in the stereostructure **9**, a transannular -O- interaction is replaced by a more severe $-CH_2-$ interaction. This interaction coupled with the axial isopropyl could easily drive a deep-seated conformational change to give **12** a totally different ring geometry.

Preparation of the third diastereomer of i required a method for construction of the stereoisomeric C-2–C-3 cis epoxide. It will be seen that the desired epoxide is now the more hindered one and, other things being equal, would require the disfavored antiperipheral approach of an epoxidant to a C-2–C-3 olefin. Since this was clearly a difficult process, an alternative tactic was chosen. It appeared possible that, if the C-5–C-7 conjugated diene were constructed before epoxidation, the inherent preference[21] of 1,3-dienes for the s-trans conformation might be enough to drive the medium ring into a new conformation in which the opposite face of the C-2–C-3 olefin would be exposed for reaction. Peripheral epoxidation would then give the desired epimeric epoxide. These expectations appear to have



been largely realized for, when silylated **1** was deprotected (H_2O-HOAc) and eliminated (1, *o*-$NO_2C_6H_4SeCN$, Bu_3P/THF; 2, H_2O_2/THF) to **13** (54%), epoxidation (*t*-BuOOH, KH[22]/THF, −20 °C) gave a 4:1 mixture of epoxy ketones in which the major component was the desired isomer **14** (74%). The product was readily purified by crystallization



13 14 15 16

(mp 113–114 °C) and treated with dimethylsulfonium methylide to give a single bisepoxide **15** (69%). Finally, deprotection ($Bu_4N^+F^-$/THF) and oxidation (CrO_3·2Pyr) gave **16** (81%). Comparison of (±)-**16** with periplanone-B by 300-MHz NMR, IR, and mass spectra showed the two substances to be identical. Bioassay showed (±)-**16** to be very active.[23] This synthesis firmly establishes the gross structure i as that of the elusive American cockroach sex excitant and strongly suggests the relative stereochemistry and conformation shown above. As reported in the following communication,[24] these stereochemical and conformational assignments were fully confirmed by an X-ray crystallographic structure determination of the intermediate alcohol, periplanol-B.

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Sex Pheromone of the American Cockroach: Absolute Configuration of Periplanone-B

Sir:

The identification of the sex pheromones of the American cockroach, *Periplaneta americana*, has been a long standing

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