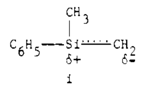
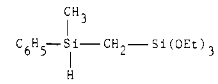


$$\mathrm{C_6H_5{-}\underset{\delta+}{\overset{CH_3}{Si}}\cdots\underset{\delta-}{CH_2}}$$

i

trapped by reaction with $(EtO)_3SiH$ as i. If the unsaturated silicon species is photochemically generated as a triplet diradical, it must rapidly change to the polarized double bond shown in i (the more stable ground-state form; see ref 9).

If trapping had involved addition of the silicon–hydrogen bond across the unsaturated linkage—thus suggesting a diradical structure—the product obtained would have had structure II. From NMR, IR and mass spectral data the

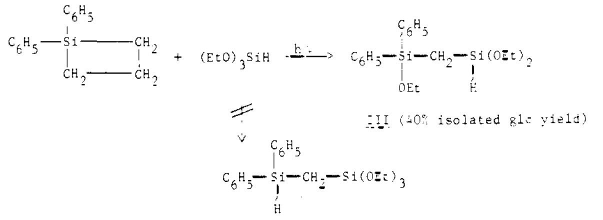


$$\mathrm{C_6H_5{-}\underset{H}{\overset{CH_3}{Si}}{-}CH_2{-}Si(OEt)_3}$$

II

product was found to have structure I. An especially significant spectral observation was found to be a clean *triplet* at δ 4.56 for the silicon–hydrogen bond in the product. Structure II would have given a sextet for the Si—H.

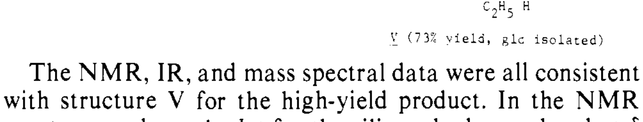
The product III from trapping 1,1-diphenyl-1-silaethene with triethoxysilane, shown in the reaction scheme below, also was characterized by NMR, IR, and mass spectral data and also had a clean triplet for the silicon–hydrogen bond at δ 4.56. In this case, the chemical shift of the Si—H in III being the same as for I, when considered along with Si—H chemical shifts of δ 4.84 for $(C_6H_5)_2(CH_3)SiH$ and 4.16 for $(EtO)_3SiH$, established III as the product instead of IV which would have resulted from addition of the Si—H bond across the unsaturated linkage.



III (40% isolated glc yield)

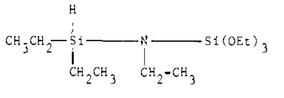
IV (not found)

We next turned to the problem of the nature of the unsaturated linkage generated by *photolysis* of silyl azides.[10] Facile reaction of such intermediates with silicon-oxygen bonds in substances such as $(Me_2SiO)_3$ previously led us to assign a polarized double-bond structure to these unsaturated intermediates: $R_2Si^{\delta+}\overline{\cdots}NR^{\delta-}$. We now report confirmation of this view by the experiment shown.



V (73% yield, glc isolated)

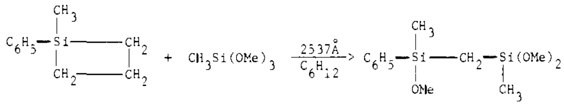
The NMR, IR, and mass spectral data were all consistent with structure V for the high-yield product. In the NMR spectrum a clean *singlet* for the silicon–hydrogen bond at δ 4.35 served to dispose of structure VI which would result from addition of the Si—H grouping across the unsaturated linkage and which would have a quintet for its Si—H bond. In further



$$\mathrm{CH_3CH_2{-}\underset{CH_2CH_3}{\overset{H}{Si}}{-}\underset{CH_2{-}CH_3}{N}{-}Si(OEt)_3}$$

VI (not found)

support of analogous highly polarized (p_π–p_π) double bonds for photochemically generated silicon-carbon and silicon-nitrogen unsaturated linkages, we carried out the experiments shown in which the unsaturated species both reacted similarly with $CH_3Si(OMe)_3$ which is an excellent trap. Products were characterized by NMR, IR, and mass spectra, consistent with the assigned structures. In the NMR, for both products, different chemical shifts for $-SiOMe$ and for $-Si(OMe)_2$ were found, thus showing that alternate structures resulting from addition of CH_3Si across the unsaturated linkages were not formed since such additions would give an $-Si(OMe)_3$ grouping.



(45% glc isolated yield)

(72% glc isolated yield)

Photolyses were carried out in a Rayonet photochemical reactor equipped with 16 RPP 2537-Å lamps. Irradiations varied from ~10 to 24 h and were carried out on samples in quartz tubes.

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(4) The greater polarity of $\equiv Si^{\delta+}$—$OEt^{\delta-}$ compared with $\equiv Si^{\delta+}$—$H^{\delta-}$ is no doubt responsible, in part at least, for this difference. An example is the fact that ≡Si—OEt reacts readily with RMgX to give ≡Si—R, whereas ≡Si—H reacts slowly or not at all with RMgX. See C. Eaborn, "Organosilicon Compounds", Butterworths, London, 1960, Chapters 2 and 6; A. G. MacDiarmid, "The Synthesis and Reactions of the Silicon–Carbon Bond", C. Eaborn and R. W. Bott, Ed., Marcel Dekker, New York, 1968, Part 1, Chapter 2.

(5) See Chapter 6 in C. Eaborn publication[4] for the high reactivity of Si—H in homolytic (free-radical) reactions.

(6) For a listing, with references, of almost 300 hydrosilylation reactions involving radical initiated addition of Si—H across carbon—carbon double bonds, see pp 148–171 in Table 4 of "Organic Insertion Reactions of Group IV Elements" by E. Y. Lukevits and M. G. Voronkov, translated from Russian by M. J. Newlands, Consultants Bureau, New York, 1966.

(7) For listings in ref 6 *specifically* dealing with radical initiated hydrosilylations of $(EtO)_3SiH$ with alkenes, see Table 4, ref 6, reactions 585, 586, 632, 650, 678, and 696. *No additions of ≡Si—OEt were observed!*

(8) We have corroborated the conclusion from ref 5–7 by demonstrating hydrogen–chlorine exchange between $(EtO)_3SiH$ and CCl_4 to give $(EtO)_3SiCl$ and $HCCl_3$ using both a radical initiator and 2537-Å light. This type of free-radical reaction of –Si—H has been well documented; see H. Sakurai, M. Murakami and M. Kumada, *J. Am. Chem. Soc.*, **91**, 519 (1969), for an interesting paper on the pyramidal, configurational stability of the $R_3Si\cdot$ radical and references to earlier silicon free-radical work involving radical exchange between ≡Si—H and ≡C—Cl.

(9) For a detailed and convincing theoretical treatment of $CH_2{=}SiH_2$ which showed the ground-state singlet, π-bonded species to be more stable than the lowest triplet diradical by ~28 kcal/mol, the bond strength of the $2p_\pi$–$3p_\pi$ bond to be ~46 kcal/mol, and also showed the silicon–carbon double bond to have considerable polarity: $C^{-0.4}\overline{\cdots}Si^{+0.5}$. See R. Ahlrichs and R. Heinzman, *J. Am. Chem. Soc.*, **99**, 7452 (1977).

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A Spirocyclophosphazene with Iron-Phosphorus Bonds and a P-Fe-Fe Three-Membered Ring

Sir:

We report here the synthesis and structure proof of an unusual new spirocyclophosphazene compound that contains

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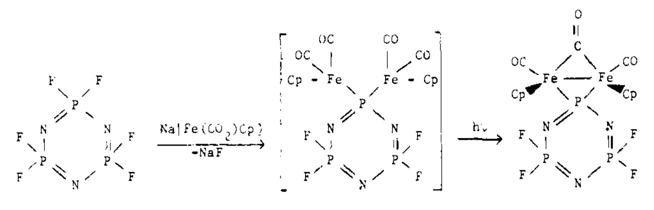

I II III

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 $C{\equiv}O$ 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 $C{\equiv}O$ 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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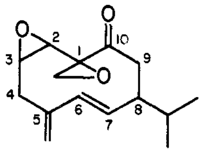
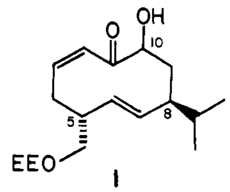
(±)-Periplanone-B. Total Synthesis and Structure of the Sex Excitant Pheromone of the American Cockroach[1]

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 ($\ll 1$ 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



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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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