droperoxides or 1,3 dibromides may possibly act as precursors for authentic PGG or PGH or for other biologically active analogues.[19]

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(8) The chromatographic scheme was successive elution with 400 mL each of hexane and 1, 2, 3, and 4% ether in hexane. **2** eluted primarily with the 3% ether fractions, **3** with the 4% ether fractions.

(9) **2** ^{1}H NMR (CCl_4) δ 1.8–2.3 (4 H, m), 2.3–2.5 (2 H, t), 4.2–4.9 (2 H, m), 8.65 (1 H, s); **2** ^{13}C NMR ($CDCl_3$) δ 29.09, 36.01, 43.05, 50.13, 86.10; **3** ^{1}H NMR (CCl_4) δ 1.8–2.3 (4 H, m), 2.3–2.7 (2 H, m), 4.1–4.5 (1 H, pentet), 4.6–4.8 (1 H, sextet), 8.9–9.2 (1 H, s); **3** ^{13}C NMR ($CDCl_3$) δ 29.91, 36.21, 42.11, 47.65, 85.70.

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(19) **1** was found to inhibit arachidonic acid initiated human blood platelet aggregation at concentrations as low as 15 μM with I_{50} = 50 μM. We thank J. R. Nixon, J. H. Roycroft, and D. B. Menzel for conducting this study.

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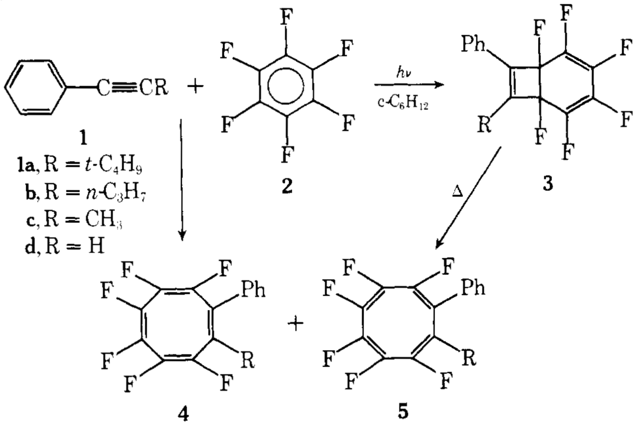
[2 + 2] Photoaddition of Acetylenes to Hexafluorobenzene. Isolation of Bicyclo[4.2.0]octatriene Derivatives

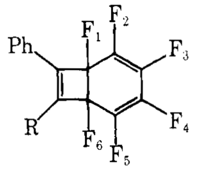
Sir:

Benzene and substituted benzenes undergo several types of cycloaddition reactions with olefins.[1] Photoaddition of acetylenes to benzene results in the formation of a cyclooctatetraene derivative via the bicyclo[4.2.0]octatriene derivative.[2] However, such an intermediate has never been isolated in photoaddition reactions. Recently, we have found that photoaddition of indene or 1,2-dihydronaphthalene to hexafluorobenzene results in the formation of cis-syn-cis[2 + 2] cycloadducts.[3] We now report that under photochemical conditions, hexafluorobenzene (**2**) readily reacts with phenyl-substituted acetylenes (**1**) to form the corresponding phenyl-substituted hexafluorobicyclo[4.2.0]octatrienes (**3**) in high yield.

Scheme I



NMR data[a] for **3**:



Compd	δF_3, δF_4	δF_1, δF_6	δF_2, δF_5	δR
3a	−162.75, −161.6	−159.0, −154.9	−153.4, −151.1	1.4
3b	−155.3	−152.6, −151.5	−148.1, −143.6	1.0, 1.8, 2.6
3c	−162, −160.5		−156.4, −150.4	2.1

[a] CCl_4 solvent, $CClF_3$ as internal standard.

A cyclohexane solution of 1-phenyl-2-*tert*-butylacetylene (**1a,** 10 mmol) and hexafluorobenzene (**2,** 20 mmol) was irradiated at 253.7 nm for 60 h. The structure of the product (**3a**) formed in high yield (86%) was established on the basis of its spectroscopic data. X-ray analysis[4] of **3c,** also formed in high yield, shows that a bicyclo[4.2.0]octatriene derivative was formed. The mass spectrum of **3a** shows the following major fragments: *m/e* 344 (M^+, 80%), 158 (82, phenyl-*tert*-butylacetylene species), 144 (41), 143 (100), 129 (55), 57 (64). A ^{19}F NMR spectrum of crude reaction mixture showed six multiplets and by careful measurement of pure product **3a** the following multiplets were observed: δF_2, δF_5 −151.1 ppm, −153.4 ppm as ddtd; δF_1, δF_6 −154.9 ppm, −159.0 ppm as ddt, and δF_3, δF_4 −161.6 ppm, −162.75 ppm as tdd with coupling constants $^3J_{F_1,F_6}$ = 15 Hz, $^3J_{F_1,F_2} = {}^3J_{F_5,F_6}$ = 35 Hz, $^3J_{F_2,F_3} = {}^3J_{F_4,F_5} = {}^4J_{F_2,F_4} = {}^4J_{F_3,F_5}$ = 7 Hz, $^5J_{F_2,F_5}$ = 21 Hz, $^3J_{F_3,F_4}$ = 5 Hz, $^4J_{F_1,F_3} = {}^4J_{F_4,F_6} = {}^4J_{F_2,F_6} = {}^4J_{F_1,F_5}$ = 1.5 Hz. The observed coupling constants are very similar to those, observed by fluorocyclopentadiene derivates.[5] It is very interesting, that fluorine atoms bonded at the sp^3 carbon atom appear at lower field than fluorine atoms at an sp^2 carbon atom. On heating (T = 150 °C), product **3a** was quantitatively transformed into product **5a,** which shows in its ^{19}F NMR spectrum five signals at lower field than those of **3a** (δF: −144 (m, 2F), −136:5 (d, 1F), −134.6 (d, 1F), −133.1 (dd, 1F), −130.1 (dd, 1F)). The mass spectrum shows the following major fragments: *m/e* 344 (M^+, 5%), 283 (35), 268 (33), 61 (37), 57 (100).

Being interested in the effect of the magnitude of the group R on the products formed in the photocycloaddition reaction, we found it instructive to study the reactions of acetylenes with *n*-propyl (**1b**), methyl (**1c**), and hydrogen (**1d**) as substituents. Acetylenes **1b** and **1c** gave products **3b** and **3c,** while in the case of **1d** a mixture of two products (**4d**:**5d** = 1.75:1) was formed. The mixture was separated by preparative GLC or TLC. Minor product **5d** shows in its ^{19}F NMR spectrum six signals (δF −123.75 (m), −125.25 (m), −127.5 (dd, J = 39 and 24 Hz), −129 (m), −135.75 (m)) and in its ^{1}H spectrum a doublet signal at 6.3 ppm (J = 24 Hz). Its mass spectrum shows the following major fragments: 288 (M^+, 100%), 273 (32), 219 (30), 120 (42), 102 (22). Major product **4d** shows in its ^{19}F NMR spectrum three signals at lower field than those of **5d**

(δF −107.25 (m, 1F), −111.75 (m, 2F), −129.4 (m, 3F)) and in its ^{1}H spectrum a singlet at 6.1 ppm. Its mass spectrum shows the following major fragments: 288 (M$^+$, 88%), 237 (40), 219 (26), 120 (26), 102 (100). If we now examine the differences in mass spectra of products **4d** and **5d**, we observe that the fragment *m/e* 102 (corresponding to phenylacetylene species) occurs as the major peak for **4d**, while on the other hand, the fragment *m/e* 120 (corresponding to the phenylfluoroacetylene species) is more intense in the case of **5d**. Chemical shifts for fluorine atoms for **5d** are also very similar to those observed for **5a** (formed by heating of **3a**), while $J_{\text{F-H}}$ (24 Hz) for **5d** is characteristic of cis olefinic coupling constants.[6] On the basis of the above mentioned differences in mass fragments and NMR data, we have established that product **4d** is 1-phenyl-3,4,5,6,7,8-hexafluorocyclooctatetraene, formed in a cyclobutene ring opening reaction of the primarily formed product **3d** (which was not detected in the case of R = H), while product **5d** was found to be a bond shifted isomer of **3d**. The product **5a** is also a bond-shifted isomer of the primarily formed cyclooctatetraene **4a** (which was not detected by heating of **3a**). On heating (T = 150 °C), product **4d** was transformed into product **5d**.

The photoaddition of **1a** was completely quenched by piperylene and resulted in a complex mixture of piperylenehexafluorobenzene products. The reaction with diphenyl and diethoxycarbonylacetylene is very slow under the above mentioned conditions.

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Theoretical Studies of the Oxidized and Reduced States of a Model for the Active Site of Rubredoxin

Sir:

Although non-heme iron–sulfur proteins are ubiquitous among living systems, their role in biological processes is understood in only a few systems and even in these cases the details of the electron transfer and chemical processes they promote have not been elucidated.[1-5] The physical propertes are best understood for rubredoxin (Rd, hereafter), plant ferredoxin (Fd, hereafter), bacterial ferredoxin, and high potential iron-sulfur protein containing one, two, four, and eight irons, respectively, with each iron tetrahedrally coordinated to four sulfurs, and contained in clusters of one, two, or four irons.[1-4] In this initial study we use ab initio quality theoretical methods to examine the electronic properties of the active site of oxidized and reduced Rd for several geometries.

To model the active site of Rd, we have replaced the four cysteine ligands of the Fe with (SH)$^-$ groups. The Fe–S bond length was set to the average distance of 2.21 Å from the crystal structure studies[6] (more recent results[7] do not confirm the large inequalities of the Fe–S bond lengths of the early structural work[6]) and the sulfur atoms placed tetrahedrally. The S–H bond distance was fixed at 1.33 Å (as in SH$_2$) and the H–S–Fe angle was chosen as the average value 107° of the C(β)–S–Fe angle from the crystal structure studies[6] (except for geometry A where the angle was taken as 92.2°). The spectrum of low excited states was examined for three different sets of S–Fe–S–H dihedral angles, as indicated in Figure 1. Geometry C most closely models the experimentally determined structure (oxidized Rd, we also find a lowest energy for this geometry).

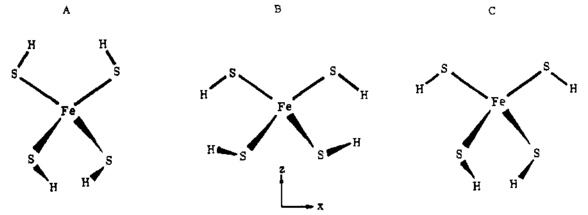

Figure 1. Geometries of Fe(SH)$_4$ model complexes.

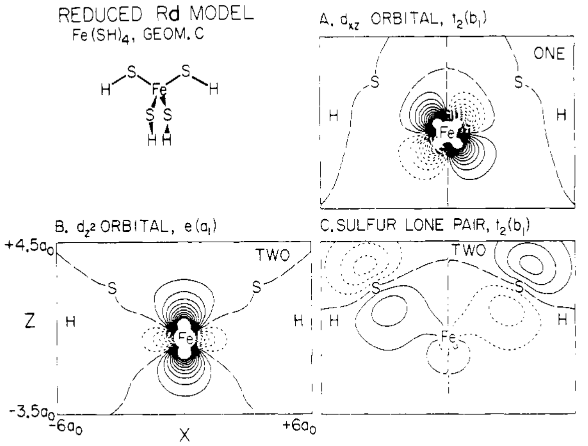

Figure 2. Amplitudes for the d orbitals for the quintet ground state of the reduced model, Fe(SH)$_4^{2-}$. Long dashes indicate zero amplitude, solid and dotted lines indicate positive and negative amplitude (separation of adjacent contours is 0.05 au). In this state four d orbitals are singly occupied while the d_{z^2} orbital is doubly occupied.

We carried out Hartree-Fock (HF)[8] calculations on a number of excited states as discussed below. The calculations are ab initio except that the argon core of the Fe atom[9] and the Ne core of each S atom[10] were replaced with ab initio effective potentials. This allows ab initio quality calculations using an extensive "double zeta" basis set.[11]

The oxidized complex may be considered as Fe$^{\text{III}}$(SH$^-$)$_4$ or [Fe(SH)$_4$]$^-$ and the reduced state as Fe$^{\text{II}}$(SH$^-$)$_4$ or [Fe(SH)$_4$]$^{2-}$. However, no restrictions were made on the shape or localization of the various orbitals; they were solved self-consistently for numerous states of both the oxidized and reduced forms.

In oxidized Rd, the Fe can be thought of as ferric d^5 and hence can lead to either high spin (S = $\frac{5}{2}$ or sextet), intermediate spin (S = $\frac{3}{2}$ or quartet), or low spin (S = $\frac{1}{2}$ or doublet). Magnetic susceptibility results[12] clearly indicate an S = $\frac{5}{2}$ ground state which is also consistent with ESR[13] and Mössbauer[14] experimental results. We considered the lower states of each spin and found (see Table I) that the ground state is clearly high spin with the lowest quartet state higher by over 1.5 eV and the lowest doublet state higher by over 3 eV. This result confirms experimental observation and indicates our methods are accurate enough to predict ground state spins.

A d^5 configuration leads to only one sextet state and consequently the lower excited states are found to result from spin-forbidden (sextet to quartet) d–d transitions, as indicated in Table I. In oxidized Rd, the charge transfer bands are found to start at ~2.2 eV;[15] however, there is a weak band observed at 1.66 eV[16] which, on the basis of these calculations, could be