products from the cold finger were then pumped through an ice-salt cooled trap, and the solids were scraped out of the reactor and the ice-cooled trap in an inert atmosphere. The solids were extracted with about 10 mL of freshly dried and degassed acetonitrile. The insoluble portion was removed in a centrifuge, and the acetonitrile was removed by vacuum distillation to give a light yellow solid. The mixture was then sublimed to give 730 mg of $Hg(SiF_3)_2$ (26% yield) (mp 205 °C). $Hg(SiF_3)_2$ is a white, crystalline solid which is soluble in many organic solvents. Infrared analysis of a KBr disk gave bands at 880 (vs), 825 (s), 800 (vs), 445 (s), and 305 cm^{-1} (w). The ^{19}F NMR spectrum in CH_3CN solution showed a singlet at +29 ppm from external CF_3COOH with $J(^{199}Hg–F)$ = 1160 Hz. Mass spectral analysis gave a base peak of m/e 85 (SiF_3^+) (100%) and the following comparative abundances of ^{198}Hg isotopes (each envelope possessed the expected peak ratios for mercury and silicon isotopes): Hg^+, 21%; SiF_2Hg^+, 1.7%; SiF_3Hg^+, 1.4%; $Si_2F_5Hg^+$, 0.4%; $Si_2F_6Hg^+$, 0.8%. The identity of the parent was confirmed by high-resolution mass spectroscopy. Reaction of $Hg(SiF_3)_2$ with elemental fluorine in a passivated Kel-F and stainless steel system gave SiF_4. $Hg(SiF_3)_2$ is easily hydrolyzed but can be kept for long periods of time in an inert atmosphere. Anal. Calcd for $Hg(SiF_3)_2$: Hg, 54.1; Si, 15.15; F, 30.75. Found: Hg, 52.1; Si, 14.5; F, 30.1.

Synthesis of $Bi(SiF_3)_3$. Bismuth (1.5 g) was evaporated over a 3-h period with a hexafluorodisilane glow discharge. The volatile products were removed from the cold finger and were collected in a −63 °C trap. Vacuum distillation on a Dobson low-temperature distillation apparatus at −40 °C gave 630 mg of tris(trifluorosilyl)bismuth (21% yield based on metal vaporized). The compound was difficult to obtain in high purity due to its low thermal stability. On the basis of its ^{19}F NMR spectrum, the compound was obtained in greater than 95% purity, with some volatile decomposition products such as SiF_4 and Si_2F_6 also being present. Tris(trifluorosilyl)bismuth is a volatile crystalline solid which reacts with oxygen, water, and many polar organic solvents such as diethyl ether and tetrahydrofuran. The ^{19}F NMR spectrum at −30 °C gave a singlet at +90.4 ppm from external $CFCl_3$ when dichloromethane was used as a solvent. Upon warming the sample to +15 °C, the height of the peak decreased dramatically while the line width broadened, suggesting that decomposition was occurring. Mass spectral analysis gave a base peak of m/e 85 (SiF_3^+) (100%), and the following bismuth-containing species were observed (each occurred in an envelope having the correct isotope distribution for silicon): Bi^+, 77%; SiF_2Bi^+, 22.4%; $(SiF_3)_2Bi^+$, 0.2%; $Si_3F_8Bi^+$, 2.4%; $(SiF_3)_3Bi^+$, 0.1%. The identity of the parent ion was confirmed by high-resolution mass spectroscopy.

Synthesis of $Te(SiF_3)_2$. Tellurium (1.5 g) was evaporated over a 3-h period with a hexafluorodisilane glow discharge. The volatile products were removed from the cold finger and were collected in a −63 °C trap. Low-temperature sublimation of the product mixture at −50 °C gave 773 mg of the dark yellow liquid bis(trifluorosilyl)tellurium (25% yield). Bis(trifluorosilyl)tellurium is a volatile liquid soluble in most organic solvents and, like the bismuth product, reacts with water and polar organic solvents. ^{19}F NMR spectrum at −45 °C gave a singlet at 102.0 ppm from $CFCl_3$ with $J(^{125}Te–F)$ = 210 Hz. The compound is sufficiently stable to be vaporized at −30 °C in vacuo with minimal decomposition. Mass spectral analysis gave a base peak of m/e 85 (SiF_3^+) (100%) along with the following tellurium species (each envelope had the isotopically correct pattern for silicon and tellurium): Te^+, 7.0%; $SiFTe^+$, 1.0%; SiF_2Te^+, 4.5%; SiF_3Te^+, 1.4%; $Si_2F_5Te^+$, 0.4%; $Si_2F_6Te^+$, 0.2%. The identity of the parent ion was also confirmed by high-resolution mass spectroscopy. Elemental analyses for bis(trifluorosilyl)tellurium and tris(trifluorosilyl)bismuth were not sought because they are unstable at room temperature.

Currently, work under way has produced preliminary evidence for trifluorosilyl compounds such as $Sn(SiF_3)_4$, $Ge(SiF_3)_4$, $Pd(SiF_3)_2(PPh_3)_2$, and $Pt(SiF_3)_2(PPh_3)_2$.

Trifluorosilyl metal compounds undergo thermolysis and should provide an excellent liquid-phase source of the reactive SiF_2: species which has previously been shown by Margrave and co-workers to be an intriguing reactant in the gas phase.[4] Trifluorosilyl metal compounds such as bis(trifluorosilyl)mercury are very soluble in most organic solvents, and a study of the trapping reaction is under way

$$M(SiF_3)_n \xrightarrow{\Delta} MF_n + n(SiF_2{:})$$

to determine differences and similarities of the solution-phase reaction of SiF_2 with the gas-phase reagent which has been previously studied.[4]

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1-Deoxy-D-*threo*-2-pentulose: the Precursor of the Five-Carbon Chain of the Thiazole of Thiamine

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Thiamine pyrophosphate is one of the key coenzymes in metabolism and must be present in all living cells. Thiamine **1**, discovered in 1926, is the oldest known vitamin. Nevertheless, many important steps in its biosynthesis are still obscure. It is known that in *Enterobacteria* carbon-2 of the thiazole part, HET (**2**), comes from C-2 of tyrosine,[1] which also gives its nitrogen.[2] The fate of the carboxyl is unknown, although it was found in a stray metabolite (**3**) of obscure significance,[3] while the rest of the tyrosine molecule is excreted as 4-hydroxybenzyl alcohol.[4] In 1978, the presence of glycol **4** in *E. coli* culture media[5] suggested that a pentose sugar might be the precursor of the five-carbon chain in HET,[6] while independent experiments on the incorporation of labeled precursors led R. H. White et al.[7] to postulate the intermediacy of a pentulose derivative, arising by the following mechanism:

$$CH_3COCO_2^- + CHO–CHOH–CH_2–O–PO_3H_2 \rightarrow CH_3–CO–CHOH–CHOH–CH_2–O–PO_3H_2 + CO_2$$

We have found since[8] that the methyl of 1-deoxy-D-*threo*-2-[1-$^2H_3$]pentulose (not that of the erythro isomer) was a precursor of the methyl of HET. However, the possibility remained that this pentulose was cleaved before incorporation. Besides, R. L. White et al.[9] interpreted their experiments in yeast as an indication that a pentulose, rather than a deoxypentulose phosphate was the true precursor. The experiments now reported are a strong in-

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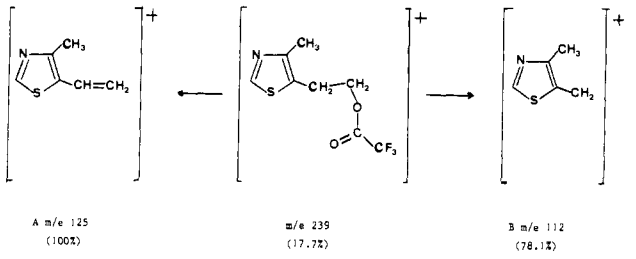
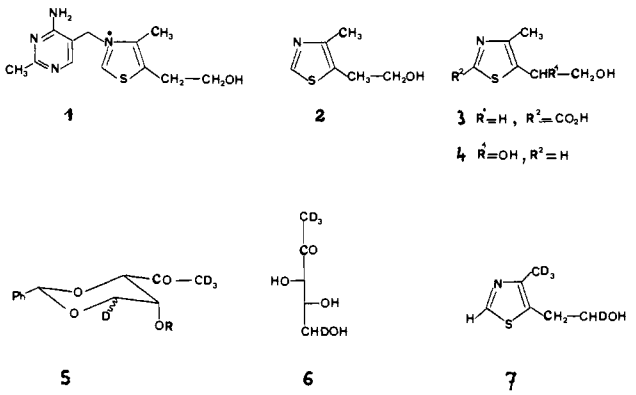
Scheme I



dication of incorporation of 1-deoxy-D-*threo*-pentulose without carbon–carbon bond cleavage.



1 2 3 R¹=H, R²=CO₂H 4 R¹=OH, R²=H

5 6 7

The labeled precursor utilized in the present investigation, 1-deoxy-D-*threo*-[1-$^2H_3$,5-$^2H_1$]pentulose (**6**) was synthesized from 2,4-*O*-benzylidene-D-[4-$^2H_1$]threose, which is available from D-[1-$^2H_1$]arabinitol by standard methods.[10,11] Reaction of the threose derivative with trideuteriomethylmagnesium iodide in ether then gave a mixture of protected, epimeric pentane tetrols, which was oxidized by the stannylene procedure[12] to 3,5-*O*-benzylidene-1-deoxy-D-*threo*-2-[1-$^2H_3$,5-$^2H_1$]pentulose **5**.[13] The labile, free pentulose **6** was prepared just before use by mild, acidic hydrolysis of **5** (4:1 water–acetic acid, 45 min at 80 °C).[14]

Nongrowing, washed cells of *Escherichia coli*, derepressed for the biosynthesis of thiamine, were incubated in the presence of the labeled pentulose **6** in a medium containing the pyrimidine of thiamine, L-tyrosine, and glucose. The thiamine was then extracted, and cleaved by bisulfite to give HET in the usual way. This was converted to the trifluoroacetic ester for MS examination.[15]

The relevant fragmentations of HET trifluoroacetate, according to ref 7 are given in Scheme I. In the present investigation, the observed incorporations[16] were as follows: species with four deuterium atoms were present to the extent of ca 19% in the molecular ion and 22% in fragment A. On the other hand, there was 21% of a species with three deuterium atoms in fragment B. Species with one to five deuterium atoms, other than those mentioned above, were only present to an insignificant extent in the molecular ion and fragments A and B. Now fragment A retains the hydrogen atoms of the CH_3 and CH_2OH groups of HET, while, in fragment B, the CH_2OH group is lost. Thus, this fragmentation shows the presence of species **7** in biosynthetic HET.

From an estimation of the total amount of HET biosynthesized during the incubation, one can calculate that ca. 25% originated from deoxypentulose **6**. The identity of the distributions of the label in the five-carbon chains of both the precursor **6** and the HET indicated incorporation without rupture. Otherwise, fragments of **6** would have mixed with the unlabeled precursors of the thrice as much abundant, unlabeled HET to give a completely different pattern. A Schiff base of tyrosine and **6** seems a probable intermediate.[17] The presence in cells of 1-deoxy-D-*threo*-pentulose or a phosphorylated derivative has not been recorded so far.

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(13) Crystals, mp 96–97 °C (cyclohexane–ethyl acetate), $[\alpha]^{20}_D$ −90° (*c* 2.2, methanol); ν_{max}^{film} 1715 (CO), 3400 cm^{-1} (OH); *m/e* (relative intensities) 225 (0.4, M − H), 181 (20), 180 (100, M − CD_3CO), 46 (64, CD_3CO^+); the validity of this interpretation was checked by comparison with the fragmentation of the undeuterated analogue. A satisfactory analysis was found, and the 250-MHz ^1H NMR spectrum was compatible with the conformation as in **5**. Compound **5** in its unlabeled form was further characterized by its *O*-acetate, mp 100 °C (ethyl acetate–cyclohexane), $[\alpha]^{20}_D$ −101° (*c* 2.2, methanol).
(14) ^1H NMR spectra show that **6** is a 3:2 mixture of pentuloses epimeric at C-5.
(15) A shikimate auxotroph mutant of *E. coli* (strain 83-1) was cultivated according to a described procedure[1] in the presence of adenosine. The cells were washed and resuspended in a minimal medium without glucose. This suspension (105 mL, dry weight of cells 2 mg/mL) was added to the labeled pentulose **6** (0.46 mmol) in water (5 mL), and then stirred for 5 min at 37 °C. The pyrimidine of thiamine (50 μg), tyrosine (2 × 10^{-4} M) and glucose (to a final concentration of 0.4%) were added, and the suspension was stirred again for 1 h at 37 °C. Thiamine was extracted, and HET was obtained as described before.[8] The crude thiazole was taken over in a mixture of carbon tetrachloride (50 μL) and trifluoroacetic anhydride (5 μL) and stirred for 5 min. Then phosphate buffer (0.5 M, pH 6; 0.5 mL) was added, the mixture was stirred, and the organic layer recovered with a syringe through the aqueous layer.
(16) A Ribermag R 10–10 gas chromatograph–mass spectrometer equiped with a 25-m × 0.34-mm Girdel capillary column packed with CPSIL 5 was used at 150°C. Volume of injections 1.5 μL.
(17) In purely chemical experiments, incubation of 1-deoxy-D-*threo*-pentulose, tyrosine, or glycine and hydrogen sulfide in DMF solution gave traces of thiazoles **2** and **4**, which could be detected by bioautography.

Sonochemistry and Sonocatalysis of Iron Carbonyls

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The chemical effects of high-intensity ultrasound have long been known to arise from cavitation: the creation, expansion, and adiabatic compression of gas vacuoles in solution during sonication.[1] The intense, but transient, local heating and compression produced during cavitation have been calculated[2,3] to reach as high as 10 000 °C and 10 000 atm, thus producing a variety of high-energy species in solution. The effects of high-intensity ultrasound on transition-metal and organometallic complexes have not been previously studied. We report herein the observed sonochemistry of the neutral iron carbonyls and the use of high-intensity ultrasound to initiate catalysis of olefin isomerization by these complexes. The iron carbonyls were chosen for our initial studies because of their well-studied thermal and photochemical reactivities.[4-6]

The thermolysis, ultraviolet photolysis, and multiphoton infrared photolysis of $Fe(CO)_5$ serve as a useful backdrop to this present work. Thermolysis[7] of $Fe(CO)_5$ above 100 °C gives pyrophoric, finely divided iron powder; ultraviolet photolysis[5] yields $Fe(CO)_4$,

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