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SYNTHESIS OF TRIMETHYLSILYL-μ-*S*,*S*′-ETHYLENEDITHIOLATOHEXACARBONYLDIIRON AND 1-METHYL-3-TRIMETHYLSILYL-2,5-DITHIACYCLOPENTANE BY REACTION OF TRIMETHYLVINYLSILANE WITH S_8 IN THE PRESENCE OF $Fe_3(CO)_{12}$

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Summary

Reaction of trimethylvinylsilane with S_8 in the presence of $Fe_3(CO)_{12}$ led to 1-trimethylsilyl-μ-*S*,*S*′-ethylenedithiolatohexacarbonyldiiron and 1-methyl-3-trimethylsilyl-2,5-dithiacyclopentane. An X-ray study was carried out on compound VI.

Introduction

We have described some results on the reaction of elemental sulfur with trimethylvinylsilane in the presence of iron carbonyls, leading to a mixture of ironsulfurous clusters and the products of sulfur insertion at an olefinic double bond [1]. Here we present additional data on this reaction, in particular the synthesis of 1-trimethylsilyl-μ-*S*,*S*′-ethylenedithiolatohexacarbonyldiiron (VI) and 1-methyl-3-trimethylsilyl-2,5-dithiacyclopentane (VII). An X-ray analysis was performed on VI. NMR study of compound VII identified two isomeric forms, probably *aa*- and *ae*-isomers.

Results and discussion

We found that trimethylvinylsilane reacts with elemental sulfur in the presence of $Fe_3(CO)_{12}$ under mild conditions (55°C) (see eq. 1).

Yield relative to initial sulfur: VI, 3%; VII, 20%.

Physical-chemical constants and structure of polysulfides III–V are reported in our previous work [1].

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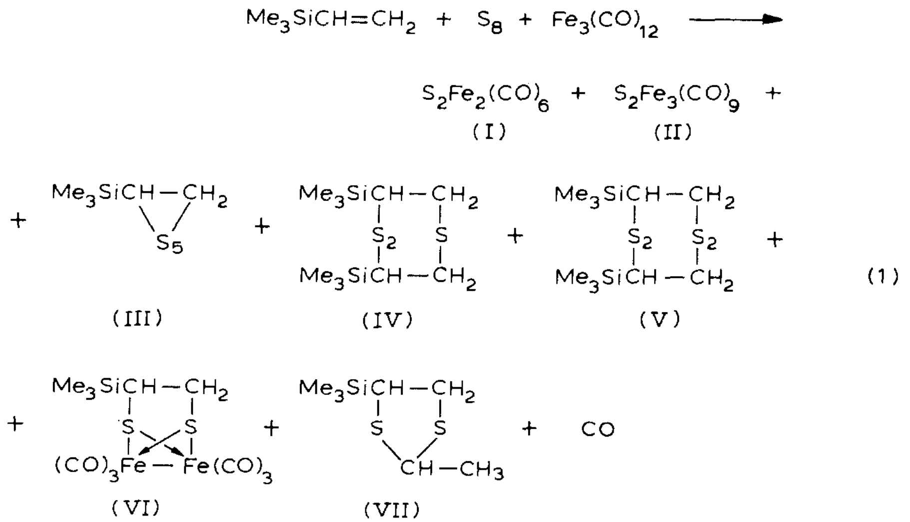
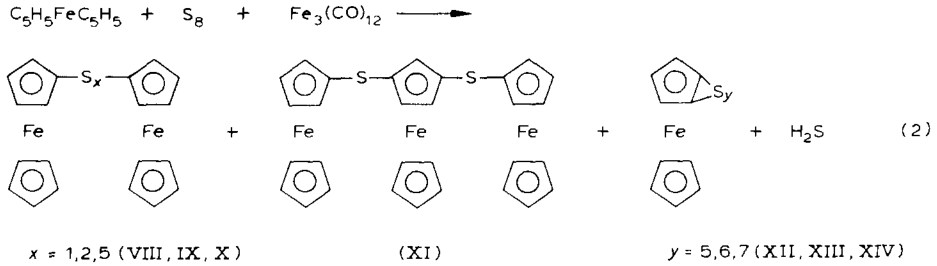


The conditions described afford no reaction of elemental sulfur with trimethylvinylsilane in the absence of $Fe_3(CO)_{12}$. We assume that the reaction involves electrophilic addition of sulfur at an olefinic double bond. The first reaction step may involve dissociation of $Fe_3(CO)_{12}$ to give coordinationally unsaturated $Fe(CO)_4$ species. This is supported by the fact that the presence of $Fe(CO)_5$ gives similar products but in lower yields than in the presence of $Fe_3(CO)_{12}$, which may be due to the greater dissociation of $Fe_3(CO)_{12}$ with respect to that of $Fe(CO)_5$.

A heterolytic cleavage of the cyclooctasulfane molecule may then occur in the presence of a coordinationally unsaturated $Fe(CO)_4$ giving rise to a zwitter ion:

$S_8 + Fe(CO)_4 \rightarrow \overset{+}{S}\text{–}S_6\text{–}\overset{-}{S}Fe(CO)_4$

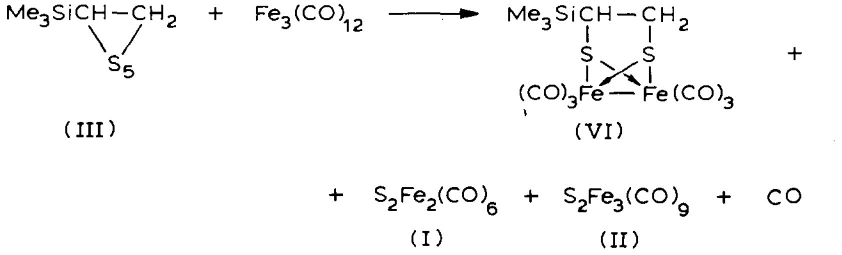
The zwitter-ion may then react with $Fe(CO)_4$ giving compounds I and II as well as with the double bond of trimethylvinylsilane, producing polysulfide III. This has been confirmed recently by reaction of ferrocene with S_8 in the presence of $Fe_3(CO)_{12}$ [2]:



The reaction proceeds with evolution of H_2S and formation of ferrocene-containing sulfides (VIII, XI), disulfides (IX) and polysulfides (X, XII–XIV) with a total number of sulfur atoms of up to 7. This is a result of reaction of the zwitter ion and its decomposition products with ferrocene; this reaction is generally electrophilic.

Varying the $S_8/Fe_3(CO)_{12}$ ratio causes no increase in the yields of polysulfides III–V and the respective dithiolanediiron hexacarbonyl complex (VI), which may be explained by the greater reactivity of S_8 towards $Fe_3(CO)_{12}$ with respect to that of the zwitter ion with the olefin double bond.

Separate experiments (C_6H_6, 50°C, 2 hours) show that the formation of VI occurs on treatment of $Fe_3(CO)_{12}$ with III, also giving rise to a mixture of I and II.



(3)

Experiments on the reaction of IV and V with $Fe_3(CO)_{12}$ (C_6H_6, 80°C, 8 h) demonstrate that these sulfides react with $Fe_3(CO)_{12}$ at a very low rate. We failed to isolate the respective iron carbonyl complexes.

It is not excluded that the formation of VI follows not only eq. 3 but also involves reaction of $Fe_3(CO)_{12}$ with cyclic polysulfides having other numbers of sulfur atoms. These could not be isolated because of the higher reactivity of such sulfides towards $Fe_3(CO)_{12}$ with respect to III.

It should be pointed out that if necessary the reaction of trimethylvinylsilane with S_8 in the presence of $Fe_3(CO)_{12}$ could be guided towards generation of the dithiolanediiron hexacarbonyl complex VI. An increase of temperature of the reaction mixture to 80°C gives generally II and VI with the yield of the latter increasing slightly (to 7%).

The molecular structure of VI, its bond lengths and angles are shown in Fig. 1. The Fe atom coordination and the geometric parameters with participation of bridged S atoms are close to those detected in the structurally investigated complexes $(EtS)_2Fe_2(CO)_6$ [3], $[PhCSFe(CO)_3]_2$ [4], $[CH_3SFe_2(CO)_6]S$ [5] and $S_2Fe_2(CO)_6$ [6]. Analogously to these structures, each Fe atom in the square pyramid is coordinated to two sulfur atoms and three carbonyl groups. The atoms C(8) and C(11) are at Fe(1) and Fe(2) atoms at the pyramide vertices, respectively. Let us consider only the $S_2Fe_2(CO)_6$ fragment: it has approximate *mm* symmetry, with one symmetry plane *m* including the Fe(1)–Fe(2) bond and the carbonyl groups C(11)–O(6) and C(8)–O(3) and the other perpendicular to the Fe(1)–Fe(2) bond passing through its center.

The formation of VII is rather complicated, including detrimethylsilylation and CH_2-group protonation steps, probably via an unstable intermediate carbonyl complex.

The structure of VII is confirmed by the data from mass, IR and UV spectra. The PMR spectrum of compound VII exhibits two spin systems A_3K, spin system ABC and a singlet of $SiMe_3$ group protons which is evidence for two isomeric forms of this compound. ^1H NMR spectrum of VII: CH (K-part of A_3K system) 4.63 and 4.53 ppm (two quartets with $^3J(HH) = 6$ Hz); CH–CH_2 (ABC system) multiplet centered at 2.89 ppm (3H); (A-part of A_3K system) 1.48 and 1.47 ppm (two doublets with $^3J(HH) = 6$ Hz); $SiMe_3$ -0.03 ppm (9H). The double $H\{^1H\}$ resonance shows that the spin systems (ABC and A_3K) possess no bonding transitions.

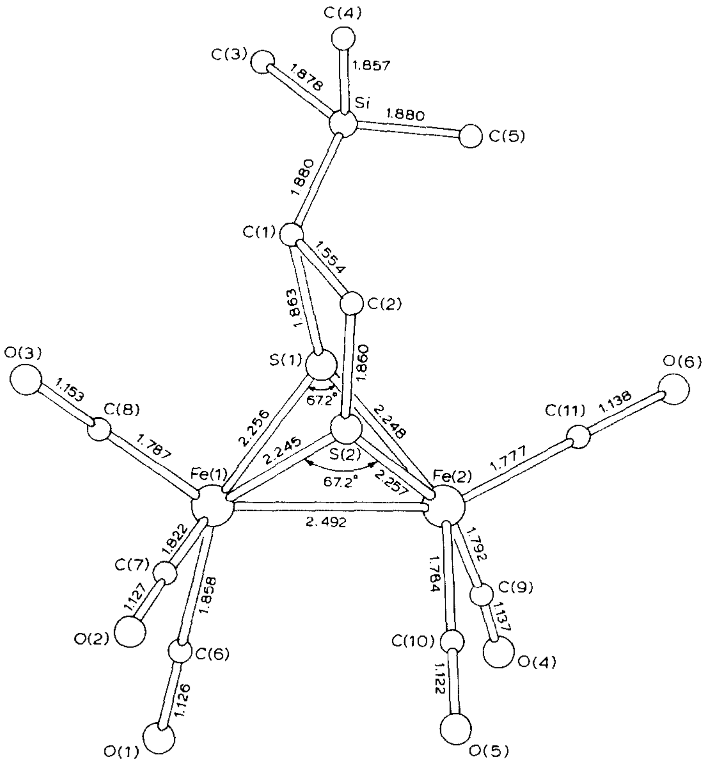


Fig. 1. Structure of compound VI.

To investigate the isomerism of compound VII in more detail we measured its ^{13}C NMR spectrum. This spectrum contains two groups of signals which may correspond to two isomeric forms of VII. For unequivocal signal assignment the ^{13}C NMR spectrum was recorded under "gated decoupling" which retains the $^{1}J(CH)$ spin coupling constants. The data of the ^{13}C NMR spectrum of VII are listed in Table 1.

The equal values of ^{1}J (CH) for each carbon nucleus and the practically equivalent signal intensities in each pair suggest *aa* and *ae* isomeric forms for VII.

TABLE 1

^{13}C NMR SPECTRUM OF VII ($\delta(^{13}C)$, ppm)

First group of signals	Second group of signals
50.65 (CH, $^{1}J = 153.5$ Hz)	50.09 (CH, $^{1}J = 153.5$ Hz)
44.05 (CH_2, $^{1}J = 140$ Hz)	41.28 (CH_2, $^{1}J = 140$ Hz)
45.06 (CH, $^{1}J = 135$ Hz)	40.91 (CH, $^{1}J = 135$ Hz)
24.80 (CH_3, $^{1}J = 129$ Hz)	26.42 (CH_3, $^{1}J = 129$ Hz)
−2.10 ($SiCH_3$, $^{1}J = 120$ Hz)	−2.21 ($SiCH_3$, $^{1}J = 120$ Hz)

Experimental

The IR spectra were measured on a UR-20 spectrophotometer. The mass spectra were taken on an LKB 2091 instrument with direct inlet to the ion source at 50°C and ionization energy of 70 eV. The PMR spectra were recorded on a Varian T-60 (60 MHz) spectrometer with C_6H_6 as solvent and internal standard. The ^{13}C NMR spectrum was registered on a 'Bruker' WR-80 spectrometer at operating frequency on ^{13}C nuclei of 20.115 Hz. The spectrum of a 50% solution of VII was taken under standard conditions; chemical shifts were determined at ± 0.03 ppm accuracy. The UV spectra were taken on a Specord UV-Vis instrument in hexane. The X-ray analysis was performed on an automatic Nicolet R-3m diffractometer (λ(Mo), graphite monochromator). The crystals are triclinic, $a = 9.304(3)$, $b = 9.418$, $c = 11.646(3)$ Å, $\alpha = 114.28(3)$, $\beta = 92.21(2)$, $\gamma = 101.75(2)°$, $d_{calc.} = 1.28$ g/cm^3, $Z = 2$, space group $P\bar{1}$. The structure was decoded and iterated by the least squares method using full matrix anisotropic approximation to $R = 0.054$ with 1528 reflections and $J > 3\sigma(J)$. All computations were performed on a 'Nova-3' computer using the XTL program.

Synthesis of VI and VII

A mixture of 19.2 g (0.075 mol) of S_8, 50 g (0.099 mol) of $Fe_3(CO)_{12}$ and 50 cm^3 (0.34 mol) of trimethylvinylsilane in 200 cm^3 of benzene was stirred at 55°C for 8 hours. Silane and benzene excesses were removed in vacuo, and the residue Soxhlet extracted with pentane. After removal of pentane the residue was chromatographed on a silica gel column (hexane eluent). VI was isolated from the mixture of II, III and V. The mixture was dissolved in 50 ml of benzene and refluxed with stirring for 4 hours until complete decomposition of cluster II. The solution was evaporated, VI was purified by multiple crystallization of compounds III and V from ethanol. The pure compound VI was isolated by recrystallization from hexane. Compound VII was eluted from the column with benzene and distilled in vacuo to yield a small quantity of IV. For VI: m.p. 58°C (hexane). Mass spectrum (m/e): 444 (M^+), 416 ($M^+ - CO$), 388 ($M^+ - 2CO$), 360($M^+ - 3CO$), 332 ($M^+ - 4CO$), 304($M^+ - 5CO$), 276($M^+ - 6CO$), 176($Fe_2S_2^+$), 144 (Fe_2S^+), 56(Fe^+). IR spectrum (ν, cm^{-1}, KBr): 2980, 2938, 2900, 2840 (C–H), 2108, 2075, 2039, 2000, 1988, 1955 (C≡O), 860, 850, 753 (Si–C), 620 (C–S). IR spectrum (ν, cm^{-1}, C_6H_{14}): 2080, 2039, 2010, 1993, 1982 (C≡O). PMR specrtum (δ, ppm): 0.15 s ($3CH_3$); 1.28 m (CH); 1.92 m (CH_2); 2.75 m (CH_2). Found: C, 29,91; H, 2.70. $C_{11}H_{12}SiS_2Fe_2O_6$ calcd.: C, 29,75; H, 2.70%. For VII: m.p. 62–63°C/1 mmHg, $n_D^{20} = 1.5150$. Mass spectrum (m/e): 192 (M^+), 132 ($[Me_3SiC_2H_3S]^+$), 117 ($[Me_2SiC_2H_3S]^+$), 90 ($[Me_2SiS]^+$), 73 ($[Me_3Si]^+$), 60 ($[CH_3CHS]^+$), 59 ($[CHCH_2S]^+$). IR spectrum (ν, cm^{-1}): 2962, 2922, 2870 (C–H), 868, 848, 760, 750 (Si–C), 695, 644 (C–S). UV-spectrum (λ, nm,(log ε)): 241 (2.43). Found: C, 43.60; H, 8.27; Si, 15.00. $C_7H_{16}SiS_2$ calcd.: C,43.70; H,8.38; Si, 14.59%.

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