May, 1985] © *1985 The Chemical Society of Japan* NOTES *Bull. Chem. Soc. Jpn., 58, 1615—1616 (1985)* 1615

Syntheses of Diferrocenyl Trithiocarbonate and a Tetrathio-substituted Ethylene Derivatives of Ferrocene

Masaru SATO* and Sadatoshi AKABORI†
Chemical Analysis Center, Saitama University, Urawa, Saitama 338
†*Department of Chemistry, Faculty of Science, Toho University, Funabashi, Chiba 274*

(Received December 14, 1984)

Synopsis. Diferrocenyl trithiocarbonate, 1,3-dithia[3]ferrocenophane-2-thione, and 2,2′-bi(1,3-dithia[3]-ferrocenophan-2-ylidene) were prepared.

Electron-rich olefins,[1] in which all substituents are electron-donating groups, are interesting from the viewpoints of both their chemical reactivities and their physical properties. Tetrathio-substituted ethylene derivatives attract much attention in connection with tetrathiafulvalene which forms high-conducting complexes with DDQ,[2] but only a few derivatives have been prepared.[3] We now report the synthesis of tetrathio-substituted ethylene derivatives of ferrocene through 1,1′-ferrocenediyl trithiocarbonate.

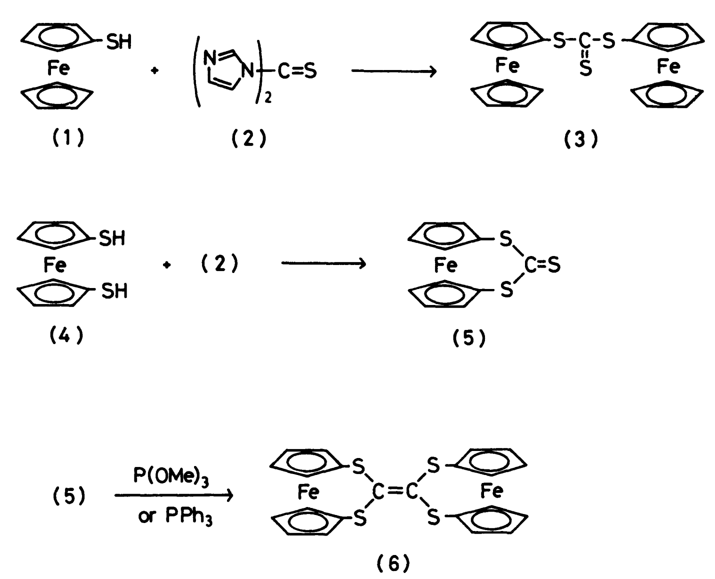
Ferrocenethiol (**1**) reacted with 1,1′-thiocarbonyldiimidazole (**2**) in tetrahydrofuran (THF) at room temperature to give diferrocenyl trithiocarbonate (**3**) in good yield. Similarly, the reaction of 1,1′-ferrocenedithiol (**4**) with **2** gave 1,3-dithia[3]ferrocenophane-2-thione (**5**) in a 78% yield. The structure of these compounds was confirmed by elemental analysis, mass- and ^{1}H-NMR spectra. For example, ^{1}H-NMR spectrum (CDCl$_3$) of **2** showed only two signals at δ 4.21 (s, 10H) and 4.43 (m, 8H), due to the cyclopentadienyl ring protons of a ferrocene nucleus. The comparison of the IR and electronic spectra of **5** and **3** is interesting. The stretching frequency of the thiocarbonyl group in **5** (975 cm^{-1}) appeared at lower frequency than that of **3** (1043 cm^{-1}). In the electronic spectrum, the absorption band of **5** (424 nm) showed a large bathochromic shift compared with that of **3** (406 nm). These results suggest that there is some interaction between the nonbonding d (e_{2g}) orbital of the ferrocene nucleus and the antibonding orbital of the thiocarbonyl double bond.

The compound **5** was refluxed for 24 h with triphenylphosphine to give 2,2′-bi(1,3-dithia[3]ferrocenophan-2-ylidene) (**6**) in good yield. A similar reaction of **5** with trimethyl phosphite gave **6** in a 44% yield. However, the reaction of **3** with triphenylphosphine or trimethyl phosphite affords no ethylenic compound. The compound **6** was insoluble in almost all common organic solvents, but slightly soluble in chloroform. The structure of **6** was determined by elemental analysis, mass (M$^+$ m/z 520) and ^{1}H-NMR spectra [δ 4.36 (t, 8H) and 4.19 (t, 8H)]. Attempt to prepare the charge-transfer complex with tetracyanoquinodimethane or tetracyanoethylene and oxidation with silver tetrafluoroborate in chloroform were unsuccessful.

Experimental

Materials. Ferrocenethiol,[4] 1,1′-ferrocenedithiol,[5] and 1,1′-thiocarbonyldiimidazole[6] were prepared according to the literature.

Diferrocenyl Trithiocarbonate (3). To a solution of ferrocenethiol (**1**) (0.40 g, 1.8 mmol) in N$_2$-saturated THF (10 cm^3) was added 1,1′-thiocarbonyldiimidazole (**2**) (0.19 g, 1.08 mmol). The solution was stirred for 2 h at room temperature. After evaporation, the residue was chromatographed on silica gel by elution with toluene to give diferrocenyl trithiocarbonate (**3**) (0.35 g, 81%) as orange crystals. Recrystallization from benzene-hexane gave an analytically pure sample as orange leaflets, mp 193—194 °C. Found: C, 52.90; H, 3.91%. Calcd for $C_{21}H_{18}S_3Fe_2$:



C, 52.74; H, 3.79%. MS (75 eV): *m/z* 476 (M^+, 100%). IR (KBr): 1043 cm^{-1}. UV-VIS (EtOH): λ_{max} 406 nm (log ε 3.09). ^{1}H-NMR ($CDCl_3$): δ=4.43 (m, 8H) and 4.21 (s, 10H).

1,3-Dithia[3]ferrocenophane-2-thione (5). To a solution of 1,1′-ferrocenedithiol (**4**) (1.74 g, 7 mmol) in N_2-saturated THF (100 cm^3) was added **2** (1.46 g, 8.2 mmol). The solution was stirred for 1 h at room temperature. After evaporation, the residue was chromatographed on silica gel; elution with dichloromethane gave the title compound **5** (1.59 g, 78%) as red orange crystals. Recrystallization from benzene gave an analytically pure sample as red plates, mp 195 °C (dec). Found: C, 45.18; H, 2.79%. Calcd for $C_{11}H_8S_3Fe$: C, 45.21; H, 2.76%. MS (75 eV): *m/z* 292 (M^+, 100%). IR (KBr): 975 cm^{-1}. UV-VIS (EtOH): λ_{max} 424 nm (log ε 3.18). ^{1}H-NMR ($CDCl_3$): δ=4.54 (t, 4H, J=1.8 Hz) and 4.36 (t, 4HJ=1.8 Hz).

2,2′-bi(1,3-dithia[3]ferrocenophan-2-ylidene) (6). A solution of 1,3-dithia[3]ferrocenophane-2-thione (**5**) (0.20 g, 0.7 mmol) and triphenylphosphine (0.23 g, 0.88 mmol) in anhydrous toluene (5 cm^3) was refluxed for 24 h under nitrogen. After keeping at room temperature overnight, the resulting crystals (123 mg, 68%) were filtered. The yellow crystals were recrystallized from a large volume of chloroform. mp 250 °C. Found: C, 50.97; H, 3.28%. Calcd for $C_{22}H_{16}S_4Fe_2$: C, 50,79; H, 3.10%. IR (KBr): 3070, 1410, 1164, 1025, 895, and 815 cm^{-1}. ^{1}H-NMR ($CDCl_3$): δ=4.36 (t, 8H, J=1.8 Hz) and 4.19 (t, 8H, J=1.8 Hz).

A solution of **5** (0.20 g, 0.7 mmol) and trimethyl phosphite (0.1 cm^3, 0.85 mmol) in anhydrous benzene (5 cm^3) was refluxed for 2 h. After a similar work-up described above, yellow crystals (80 mg, 44%) of **6** were obtained.

References

1) R. W. Hoffmann, *Angew. Chem., Int. Ed. Engl.*, **7**, 754 (1968).

2) J. H. Perlstein, *Angew. Chem., Int. Ed. Engl.*, **16**, 519 (1977).

3) D. L. Coffen, J. Q. Chambers, D. R. Williams, P. E. Garrett, and N. D. Canfield, *J. Am. Chem. Soc.*, **93**, 2258 (1971) and references therein.

4) G. P. Knox and P. L. Pauson, *J. Chem. Soc.*, **1958**, 692.

5) G. P. Knox, I. G. Morrison, and P. L. Pauson, *J. Chem. Soc. (C)*, **1967**, 1842.

6) H. A. Staab and G. Walther, *Liebigs Ann. Chem.*, **675**, 98 (1962): T. J. Pullukat and G. Urry, *Tetrahedron Lett.*, **1967**, 1953.