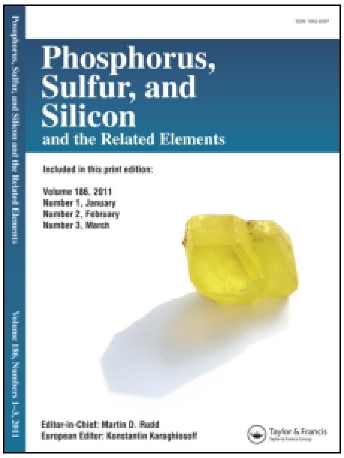

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Communication

NONCONVENTIONAL FRIEDEL-CRAFTS CHEMISTRY IV. ON THE REACTION OF 1,3-OXATHIOLAN-5-ONE-2-SPIRO-1′-CYCLOALKANES WITH FERROCENE IN THE PRESENCE OF $AlCl_3$ CATALYLST

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The reaction of ferrocene with 1-oxa-4-thiaspiro[4,4]nonan-2-one (**1**) and/or 1-oxa-4-thiaspiro[4,5]-decan-2-one (**2**) in the presence of aluminum chloride catalyst afforded the spiroferrocene derivatives **4**, **6**, **5** and **7**, respectively. The mechanism of these reactions is discussed.

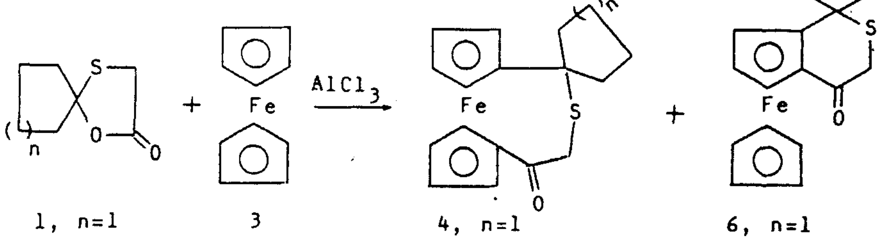
Key words: Friedel-Crafts reactions; ferrocene chemistry.

INTRODUCTION

The use of ferrocene in Friedel-Crafts[1-7] chemistry, combined with our interest in this field,[8,9] in addition to the importance of spiro compounds,[9,10] this work describes the reaction of some 1,3-oxathiolan-5-one-2-spiro-1′-cycloalkanes with ferrocene in the presence of aluminum chloride with the aim to find a facile rout for the synthesis of some spirosulfur derivatives incorporated with ferrocene moiety.

RESULTS AND DISCUSSION

In conjunction to our study of the interaction of the reagents **1** and/or **2** with arenes,[9] we explored the reaction of **1** and/or **2** with ferrocene (**3**) in the presence of $AlCl_3$ catalyst (Equation 1).



1, n=1
2, n=2

3

4, n=1
5, n=2

6, n=1
7, n=2

(1)

TABLE I

Reactions of 1,3-oxathiolan-5-one-2-spiro-1'-cycloalkanes with ferrocene in the presence of $AlCl_3$ catalyst

	Reaction Conditions[a]	
Entry	1-0/Ferrocene/Catalyst[b]	Observed Products[c] (%)
1	0.01/0.01/0.044	1,1'-[cyclopentylidenethio(2-oxoethylene)]ferrocene (55), η^5-cyclopentadienyl(4',7'-dihydro-4'-oxa-η-4'a-7'a-spiro[cyclopentane-1,1'(3'H)-cyclopenta[c]thiopyran]yl) iron (10), cyclopentyl mercaptane (5), dicyclopentyl disulfide (4).
2	0.01/0.03[d]/0.044	1,1'-[cyclopentylidenethio(2-oxoethylene)]ferrocene (70), η^5-cyclopentadienyl(4',7'-dihydro-4'a-7'a-spiro[cyclopentane-1,1'(3'H)-cyclopenta[c]thiopyran]yl) iron (7), cyclopentyl mercaptane (2), dicyclopentyl disulfide (3).
3	0.01/0.01/0.044	1,1'-[cyclohexylidenethio(2-oxoethylene)]ferrocene (70), η^5-cyclopentadienyl(4',7'-dihydro-4'-oxo-η-4'a-7'a-spiro[cyclohexane-1,1'(3'H)-cyclopenta[c]thiopyran]yl) iron (8), cyclohexyl mercaptane (2), dicyclohexyl disulfide (2).
4	0.01/0.03/0.044	1,1'-[cyclohexylidenethio(2-oxoethylene)]ferrocene (80), η^5-cyclopentadienyl(4',7'-dihydro-4'-oxo-η-4'a-7'a-spiro[cyclohexane-1,1'(3'H)-cyclopenta[c]thiopyran]yl) iron (5), cyclohexyl mercaptane (2), dicyclohexyl disulfide (2).

[a] All experiments have been carried out in CS_2 at room temperature and magnetically stirred for 24 hrs.

[b] 1-0 = 1-oxa-4-thiaspiro[4,4]nonan-2-one and/or 1-oxa-4-thiaspiro[4,5]decan-2-one. Units of 1-0; ferrocene; catalyst are in moles.

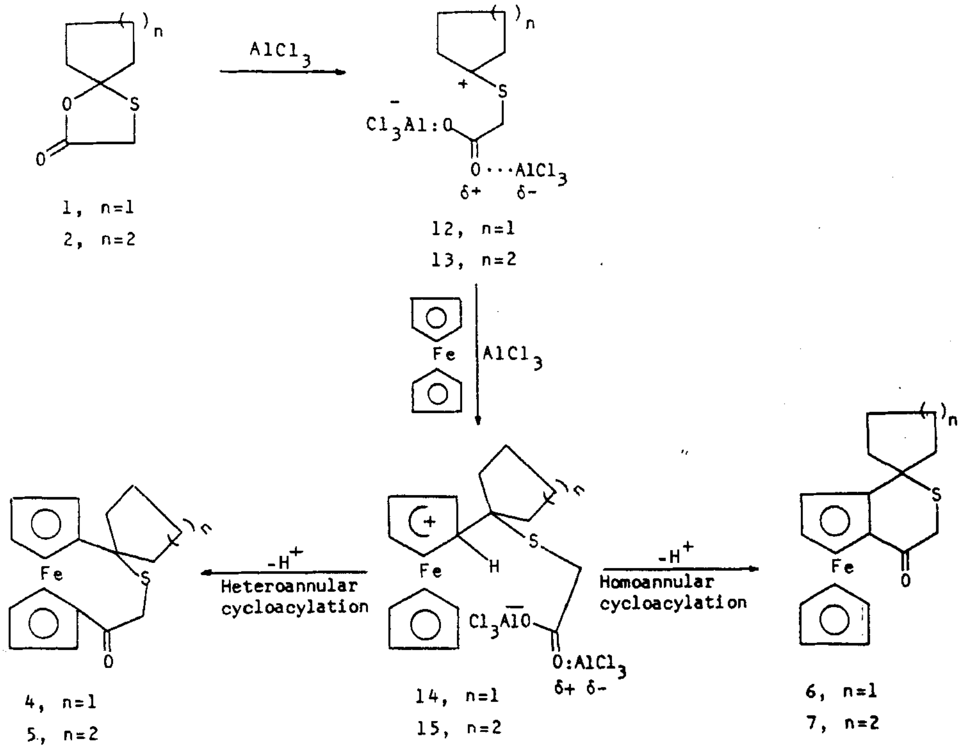
[c] The percentages of these products were calculated by HPLC; the separations of these products were achieved by preparative thin layer chromatography.

[d] The unreacted ferrocene was separated before the HPLC analysis.

Examination of the results depicted in Table I revealed that 1-oxa-4-thiaspiro[4,4]nonan-2-one (**1**) and/or 1-oxa-4-thiaspiro[4,5]decan-2-one (**2**) were reacted with ferrocene in the presence of $AlCl_3$ catalyst to yield a mixture of 1,1'-[cycloalkylidenethio(2-oxoethylene)]-ferrocene **4** and **5** and η^5-cyclopentadienyl(4',7'-dihydro-4'-oxo-η-4'a-7'a-spiro[cycloalkane-1,1'(3'H)-cyclopenta[c]thiopyran]yl)iron **6** and **7** (Equation 1).

In case of the reaction of ferrocene (**3**) with 1,1,1'-[cyclopentylidenethio(2-oxoethylene)]ferrocene (**4**, 55%); η^5-cyclopentadienyl(4',7'-dihydro-4'-oxa-η-4'a-7'a-spiro[cyclopentane-1,1'-(3'H)-cyclopenta[c]thiopyran]yl) iron (**6**, 10%), cyclopentyl mercaptane (**8**, 5%) and dicyclopentyl disulfide (**9**, 4%) (Table I, entry 1). Carrying the reaction of **1** with excess **3** afforded the same products **4**, **6**, **8** and **9** and the only difference is the increase of percentage of 4 to 70% (Table I, entry 2).

The interaction of **2** with ferrocene yielded 1,1'-[cyclohexylidenethio(2-oxoethylene)]ferrocene (**5**, 70%), η^5-cyclopentadienyl(4',7'-dihydro-4'-oxo-η-4'a-7'a-spiro[cyclohexane-1,1'(3'H)-cyclopenta[c]-thiopyran]yl) iron (**7**, 8%), cyclohexyl mercaptane (**10**, 2%) and dicyclohexyl disulfide (**11**, 2%). (Table I, entry 3). Again the increase of the ratio of 3 increases only the yield of 5 to 80% (Table I, entry 4).



SCHEME I

The sequence of these reactions could be explained as depicted[9,11] in Scheme I. From Scheme I it is obvious that compounds **1** and/or **2** were ionized under the effect of $AlCl_3$ catalyst to form the carbocations **12** and/or **13** which were reacted with ferrocene under the described reaction conditions to afford the intermediates **14** and/or **15**, respectively.[12]

The deprotonation of **14** and/or **15** followed by subsequent homoannular[13,14] cycloacylation yielded **6** and/or **7**, respectively, whereas heteroannular cycloacylation reactions gave **4** and **5**.

The formation of cycloalkyl mercaptions **8** and **10** and dicyloalkyl disulfides **9** and **11** could be explained as reported.[9,15,16] The failure to detect the cycloalkylferrecenylthioacetic acids could be argued to the reactivity of ferrocene toward Friedel-Crafts reactions.[7,17]

The structures of all spiroferrocene derivatives **4**, **5**, **6** and **7** were elaborated by IR, ^{1}H-NMR and microanalyses (Table II).

EXPERIMENTAL

Melting points are uncorrected. Elemental analyses were measured on a Perkin-Elmer 240C microanalyser. Nuclear magnetic spectra were recorded on EM-360 90 MHz spectrophotometer. Infrared spectra were recorded on a Pye-Unicam SP 200-G spectrophometer. Isolation of products was achieved on a 20 × 15 glass plate covered with thin silica gel film.

HPLC analyses were performed on a Hitachi apparatus (Japan) supplied with a variable wavelength monitor (190–600 nm), with a sulfonated silica gel type column, Nucleosil 55A, and methanol/water mixtures as a solvent.

TABLE II
Physical data of spiroferrocene derivatives

Compd. No.	Molecular formula[a] (Solvent of Crystallization)	m.p. °C	IR (KBr), cm^{-1}	^{1}H NMR (solvent), δ (TMS) ppm
4	$C_{17}H_{18}OSFe$ (ethanol)	73–75	700 (C—S), 1710 (C═O), 2800 (CH aliph.), 3100, 1480, 1390, 1290, 1120, 1050, 1000, 980, 900, 850, 830 (ferrocene moiety).	($CDCl_3$) 1.3–1.6 (4H, complex), 1.7–2 (4H, m), 3.3 (2H, s), 3.8–4.17 (8H, broad, ferrocene protons).
5	$C_{18}H_{20}OSFe$ (ethanol)	87–90	710 (C—S), 1715 (C═O), 2820–2800 (CH aliph.), 3100, 1480, 1390, 1290, 1120, 1050, 1000, 980, 900, 850, 830 (ferrocene moiety).	($CDCl_3$) 1.23–1.42 (6H, complex), 1.7–2.1 (4H, complex), 3.35 (2H, s), 3.67–4.10 (8H, broad, ferrocene protons).
6	$C_{17}H_{18}OSFe$ (ethanol)	78–80	715 (C—S), 1720 (C═O), 2800–2780 (CH aliph.), 3100, 1495, 1395, 1295, 1125, 1055, 1000, 985, 900, 850, 830 (ferrocene moiety).	($CDCl_3$) 1.4–1.7 (4H, m), 1.8–2.1 (4H, complex), 3.4 (2H, s), 3.85–4.15 (8H, broad, ferrocene protons).
7	$C_{18}H_{20}OSFe$ (ethanol)	90–92	710 (C—S), 1715 (C═O), 2830–2810 (CH aliph.), 3110, 1485, 1400, 1290, 1125, 1055, 1010, 985, 910, 850, 830 (ferrocene moiety).	($CDCl_3$) 1.4–1.7 (6H, complex), 1.8–2.2 (4H, m), 3.41 (2H, s), 3.9–4.2 (8H, broad, ferrocene protons).

[a] Compounds **4**, **5**, **6** and **7** gave satisfactory elemental analysis.

Reaction of 1,3-oxathiolan-5-one-2-spiro-1′-cycloalkanes with ferrocene in the presence of $AlCl_3$ catalyst.

General Procedure.

A 0.044 mole of $AlCl_3$ was added portionwise to a solution of 0.01 mole of **1** and/or **2** in 25 ml CS_2 in a 100 ml two-necked flask equipped with a reflux condenser capped with calcium chloride tube, a magnetic stirrer and a dropping funnel. To this mixture there was added dropwise a 0.01 and/or 0.03 mol of ferrocene dissolved in 10 ml CS_2. The reaction mixture was stirred for 24 hr at room temperature, decomposed with 10% HCl solution, extracted with chloroform and methylene chloride; the combined extracts were washed with water, 10% sodium carbonate solution and again with water then dried over magnesium sulfate. The solvents were removed by distillation under reduced pressure using a rotatory evaporator, and the residue was subjected for HPLC analyses and for separation, purification by preparative thin layer chromatography. Products were identified as described under each individual run. Results are found in Table I and the physical data of products **4**, **5**, **6** and **7** are described in Table II.

REFERENCES

1. A. N. Nesmeyanov, N. A. Volkenau and V. D. Vil' Chovskaya, *Doklady A Kad. Nauk, S.S.S.R.*, **118,** 512 (1958).
2. R. Vladimir and K. Lidija, *J. Organomet. Chem.*, **260(2),** 219 -26 (1984).
3. M. Salisova, S. Toma and E. Solcaniova, *J. Organomet. Chem.*, **327(1),** 77–83 (1987).
4. S. Toma and M. Salisova, *Collect. Czech. Chem. Commun.*, **52(6),** 1136 (1987).

5. S. Kaluz and S. Toma, *Gazz. Chim. Ital.*, 529–31, (1987).
6. D. Eliane and M. Francois, *J. Organomet. Chem.*, **332(1–2)**, 141–52 (1987).
7. M. F. El-Zohry, *Bull. Soc. Chem. Fr.*, 1991 (accepted).
8. M. F. El-Zohry and A. M. El-Kawaga, *J. Org. Chem.*, **55**, 4036 (1990).
9. M. F. El-Zohry, *Phosphorus and Sulfur*, **61**, 373 (1991).
10. G. W. Morrow, S. Wang and J. S. Swenton, *Tetrahedron Lett.*, **29(28)**, 3441 (1988) and references therein.
11. R. M. Roberts and A. A. Khalaf, Friedel-Crafts Alkylation Chemistry; Marcel Dekker; New York, 376 (1984).
12. K. Plesske, *Angew. Chem. Int.* Ed(Eng). **1**, 312–327, 394–399 (1962).
13. V. Rapic and L. Korontos, *J., Organomet. Chemi*, **260(2)**, 219–226 (1984).
14. K. L. Rinehart, Jr., R. J. Curby, Jr. and P. E. Sokol, *J. Amer.* **79**, 3420 (1957).
15. A. M. El-Khawaga, M. F. El-Zohry, M. T. Ismail; A. A. Abdel-Wahab and A. A. Khalaf, *Phosphorus and Sulfur*, **29**, 256 (1987).
16. C. H. Han and W. E. McEwen, *Tetrahedron Lett.*, **30**, 2629 (1970).
17. B. E. Maryanoff, *J. Org. Chem.*, **46**, 70–74 (1981) and references therein.