

SYNTHESIS OF MONO- AND DIACETYLENIC DERIVATIVES OF SILYLFERROCENE

Abdel GHANI Ali EL-AGAMEY^a and Levan P. ASATIANI^b

^a Faculty of Education, Damiatta, Mansoura University, Egypt and

^b Faculty of Chemistry, Tbilissi University, Tbilissi, USSR

Received September 19th, 1983

1-Ferrocenyl(methyl)phenylsilane (*I*) was prepared by silylation of ferrocene at low temperature. Mono- and diacetylenic compounds of silylferrocene were prepared by the interaction of chloroferrocenylsilane with mono- and dilithium acetylenic derivatives, respectively. It has been found that, catalytic hydrogenation of the prepared acetylenic compounds seem to be totally determined by steric considerations.

Ferrocenylsilane derivatives have recently become of increasing importance owing to its higher antiknock properties¹. Keludza² had reported that 1-ferrocenyl(methyl)phenylsilane (*I*) increases the octane number. As a part of our program^{3,4} directed for synthesis of ferrocene derivatives, we report here some chemical reactions of *I*. Now, compound *I* was prepared in a modified method, as a sole product without the production of 1,1'-differrocenylsilane², using ferrocene and butyllithium in molar ratio (1 :) at room temperature in hexane, and chloro(methyl)phenylsilane was added to the reaction mixture at -40 to -45°C .

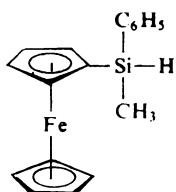
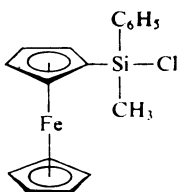
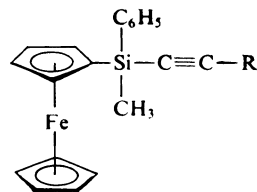
The IR spectrum^{5,6} of *I* shows bands at $2\ 140\ \text{cm}^{-1}$ (Si—H); $3\ 110\ \text{cm}^{-1}$ (C—H ferrocene); $1\ 430$, $1\ 260$ and $740\ \text{cm}^{-1}$ (Si—Alk/Ar).

Chloro(ferrocenyl)(methyl)phenylsilane (*II*) was prepared by the action of PdCl_2 on *I* according to Corriu⁷. The chlorosilane *II* is sensitive to air oxidation, and was purified by column chromatography under helium using benzene as eluant.

Compound *II* reacted smoothly with lithium derivatives of phenyl-, triethylsilyl- and triphenylsilylacetylenes in tetrahydrofuran to give the corresponding disubstituted acetylenes *III*, *IV* and *V*, respectively. Condensation of two mol of *II* with one mol of dilithium diacetylenic derivatives of diphenylsilane in tetrahydrofuran gave the corresponding (diphenyl) di[2-ferrocenyl(methyl)(phenyl)silylethynyl]silane (*VI*), as a solid product, in 43% yield. The IR spectra of *III*–*VI* show absorption peaks at $1\ 430$, $1\ 250$, $740\ \text{cm}^{-1}$ (Si—Alk/Ar); $2\ 030$ – $2\ 060\ \text{cm}^{-1}$ ($\text{C}\equiv\text{C}$) and $3\ 100\ \text{cm}^{-1}$ (C—H ferrocene).

Condensation of *II* with dilithium diacetylenic derivative of diethylsilane gives a mixture of *VII* and *VIII*. Compound *VIII* could be received in pure form by fractional crystallization, whilst *VII* remains always contaminated with some *VIII*.

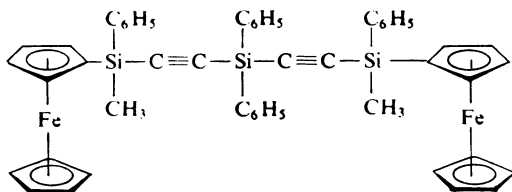
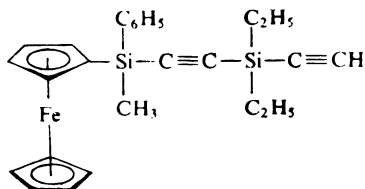
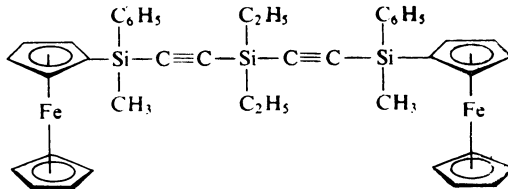
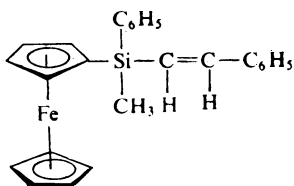
The two products were successfully isolated by TLC using octane. The IR spectrum^{5,6} of compound *VIII* showed absorption bands at 1 445, 1 260, 740 cm^{-1} (Si—Alk/Ar); 2 030–2 060 cm^{-1} ($\text{C}\equiv\text{C}$) and 3 100 cm^{-1} (C—H ferrocene). In addition to the bands mentioned above, compound *VII* have also bands at 2 040 and

*I**II*

III, R = C₆H₅

IV, R = (C₂H₅)₃Si

V, R = (C₆H₅)₃Si

*VI**VII**VIII**IX*

3 290 cm^{-1} corresponding to ($-\text{C}\equiv\text{C}-$) and ($\text{C}-\text{H}$) which suggested that the terminal group is $\text{C}\equiv\text{C}-\text{H}$ and *VII* is a condensation product of one acetylenic group only.

Further, we have examined the reactivity of the triple bonds of the prepared compounds. Partial catalytic hydrogenation of the triple bond to the corresponding olefinic derivatives using Lindlar catalyst was carried out. The catalytic hydrogenation of compound *III* in the presence of ($\text{Pd}-\text{CaCO}_3$) successfully underwent to the corresponding olefinic derivative with *cis*-configuration *IX*. The catalytic hydrogenation of the other compounds was found to be failure, due to the steric factors of bulky ferrocenyl and methylphenylsilyl groups. The structure of *IX* has been established, apart from the analytical data, as follows: a) IR spectrum exhibited absorption bands at 1 420, 1 260, 790 cm^{-1} ($\text{Si}-\text{CH}_3/\text{C}_6\text{H}_5$), 3 100 cm^{-1} ($\text{C}-\text{H}$ ferrocene) and 1 625 cm^{-1} ($\text{C}=\text{C}$). b) The NMR spectrum shows two doubles, τ 3.90 and τ 3.46 ppm with $J_{\text{AB}} = 13.5$ Hz which confirmed the *cis*-configuration of *IX*. c) The *gem*- and *trans*-forms of *IX* were previously prepared³ by addition of *I* to phenylacetylene in the presence of Speier's catalyst.

EXPERIMENTAL

All melting points are uncorrected. R_F was determined using a chromatoplate ($21 \times 31 \times 0.2$ cm) coated with a thin uniform layer of adsorbent ($\text{Al}_2\text{O}_3 - 1.5$ mm). The reactions were carried out under helium. Purification and separation of products was done by TLC using Al_2O_3 of 1.2 mm thickness. Recorded yields correspond to the pure products. IR and NMR spectra were measured on UR-20 and Perkin-Elmer R-12, respectively. The acetylenes used were prepared according to known procedures⁸⁻¹⁰.

1-Ferrocenyl(methyl)phenylsilane (*I*)

To an ethereal solution of ferrocene 13 g (0.07 mol) in 250 ml ether was added 50 ml (1.4 mol l^{-1}) solution of *n*-butyllithium (0.07 mol) in hexane. The mixture was stirred at room temperature for 3 h, then left overnight. To the cold mixture at -40°C to -45°C , a solution of freshly distilled chloro (methyl)phenylsilane 30 g (0.19 mol) in 50 ml of ether was added dropwise while stirring. The mixture was stirred for another one hour at -45°C and set aside overnight, then poured in cold water and extracted with ether. The extract was dried over anhydrous sodium sulphate, the ether was evaporated and the residue was distilled as a sticky red oil with b.p. $177-178^\circ\text{C} / 0.13 \text{ kPa}$, yield 12.45 g (59%) $n_D^{20} = 1.6215$. For $\text{C}_{17}\text{H}_{18}\text{FeSi}$ (306.3) calculated: 66.67% C, 5.92% H, 0.34% Si-H; found: 66.63% C, 5.67% H, 0.35% Si-H.

1-Phenyl-2-[ferrocenyl(methyl)(phenyl)silyl]ethyne (*III*)

To a solution of 1.5 g (0.014 mol) of lithium phenylacetylide (prepared from 1.5 g (0.014 mol) of phenylacetylene and 0.11 g (0.016 mol) of lithium metal in 50 ml of tetrahydrofuran) a solution of 4.8 g (0.014 mol) of *II* (prepared from 4.2 g (0.014 mol) of *I* and 3 g (0.017 mol) of PdCl_2 in 100 ml of benzene) was added with stirring. The mixture was heated at $45-60^\circ\text{C}$ for 3 h, poured in cold water, extracted with ether and dried over Na_2SO_4 anhydrous, then evaporated.

The obtained residue was purified by TLC using pentane to give *III* as oil with $R_F = 0.58$ (pentane), yield 4 g (74%). For $C_{25}H_{22}FeSi$ (406.4) calculated: 73.89% C, 5.46% H; found: 73.95% C, 5.43% H.

1-Triethylsilyl-2-[ferrocenyl(methyl)(phenyl)silyl]ethyne (*IV*)

To a solution of n-butyllithium (0.015 mol) (prepared from 0.2 g (0.03 mol) of lithium and 1.4 g (0.015 mol) of butyl chloride) in 30 ml of hexane, a solution of 2.1 g (0.015 mol) of triethyl(ethynyl)silane in 40 ml of tetrahydrofuran was added. The mixture was stirred at room temperature for 2 h and then a solution of 5.1 g (0.015 mol) of *II* in 100 ml of benzene was added portionwise during a period of 30 min. The mixture was poured in cold water, extracted with ether, dried over Na_2SO_4 anhydrous. The oily product obtained after distilling off the ether was purified by TLC using light petroleum (b.p. 40–60°C) to give yellowish brown oil of *IV* with $R_F = 0.48$ (light petroleum–benzene 5 : 1), yield 4.46 g (77%). For $C_{25}H_{32}FeSi_2$ (444.5) calculated: 67.55% C, 7.26% H; found: 68.11% C, 7.49% H.

Under similar conditions, 1-triphenyl-2-[ferrocenyl(methyl)(phenyl)silyl]ethyne (*V*) was obtained as red oil after purification chromatographically using light petroleum–benzene, 3 : 1, $R_F = 0.36$ (light petroleum–benzene 5 : 1) yield 78%. For $C_{37}H_{32}FeSi_2$ (588.7) calculated: 75.49% C, 5.48% H; found: 75.44% C, 5.76% H.

(Diphenyl)bis[2-ferrocenyl(methyl)(phenyl)silylethynyl]silane (*VI*)

To a solution of n-butyllithium (0.02 ml) in 30 ml of hexane, a solution of 2.3 g (0.01 mol) diphenyldiacetylenylsilane in 50 ml of tetrahydrofuran was added. The mixture was stirred at room temperature for another 1 h, and then a solution of 6.8 g (0.02 mol) of *II* in 100 ml of benzene was added portionwise during a period of 30 min. The mixture was heated for 2 h at 50–60°C, and then cooled, poured in cold water, extracted with ether, dried over Na_2SO_4 anhydrous. The oily product obtained after distilling off the ether was crystallised from pentane to give yellowish brown crystals with m.p. 208–209°C, yield 3.9 g (43%). For $C_{50}H_{44}Fe_2Si_3$ (840.9) calculated: 71.42% C, 5.27% H; found: 71.35% C, 5.53% H.

Reaction of *II* with Dilithium Derivative of Diethyldiacetylenylsilane

To a solution of n-butyllithium (0.014 mol) in 30 ml of hexane, a solution of 1g (0.07 mol) of diethyldiacetylenylsilane in 50 ml of tetrahydrofuran was added. The mixture was stirred at room temperature for another 20 min, and then a solution of 4.8 g (0.014 mol) of *II* in 100 ml of benzene was added during a period of 20 min. The mixture was heated for 2 h at 50–60°C, poured in cold water, extracted with ether, dried over Na_2SO_4 anhydrous. The oil obtained after distilling off the ether was purified and then separated by TLC (eluant octane) into the two following products *VII* and *VIII*.

Diethyldiacetylenyl[2-ferrocenyl(methyl)(phenyl)silylethynyl]silane (*VII*) was obtained as a yellowish brown oil, with $R_F = 0.57$ (octane), yield 3.1 g (50%). For $C_{25}H_{28}FeSi_2$ (440.5) calculated: 68.16% C, 6.41% H; found: 68.51% C, 6.55% H.

Diethyldi[2-ferrocenyl(methyl)(phenyl)silylethynyl]silane (*VIII*) was obtained as yellowish crystals from octane with m.p. 213–215°C, yield 2.48 g (40%). For $C_{42}H_{44}Fe_2Si_3$ (744.8) calculated: 67.73% C, 5.95% H; found: 67.55% C, 5.76% H.

Catalytic Hydrogenation of *III*

A mixture of *III* 2.4 g (0.006 mol) in ethanol (50 ml) and 0.2 g Pd-CaCO₃ was shaken with hydrogen at room temperature and pressure (hydrogen absorbed 200 ml). The solution was filtered. The oil obtained after evaporating the ethanol, was distilled to give 2.3 g (96%) of 1-phenyl-2-[ferrocenyl(methyl)(phenyl)silyl]ethene (*IX*), b.p. 246–248°C/0.26 kPa. For C₂₅H₂₄FeSi (408.4) calculated: 73.52% C, 5.92% H; found: 73.79% C, 5.90% H.

REFERENCES

1. Gverdtsiteli I. M., Asatiani L. P., Keludza C. Kh.: Zh. Obshch. Khim. 46, 861 (1976).
2. Keludza C. Kh.: Thesis. Tbilissi University, Tbilissi 1978.
3. Asatiani L. P., El-Agamey A. A., Gverdtsiteli I. M.: Bull. Akad. Nauk GSSR. 1, 90, 172 (1978); 3, 90, 589 (1978).
4. Asatiani L. P., El-Agamey A. A., Diab M. A.: J. Polym. Sci., in press.
5. Bellamy L. G.: *The Infrared Spectra of Complex Molecules*. Wiley, New York 1970.
6. Wilkinson G., Bauson P. L., Cotton F. A.: J. Amer. Chem. Soc. 74, 6146 (1952).
7. Corriu R., Larcher F., Royo G.: J. Organometal. Chem. 16, 11 (1976).
8. Schlögl K., Strewer W.: Monatsh. Chem. 96, 1520 (1965).
9. Rosenblum M., Braun N., Papenmeier J.: J. Organometal. Chem. 6, 173 (1966).
10. Novikova O. A., Kaznetsova F. P., Korneva K. A.: Zh. Obshch. Khim. 38, 178 (1968).