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Reaction of Ethynylferrocene with Mercuric Acetate

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The reaction of ethynylferrocene with mercuric acetate has been investigated in methanol and other solvents. The reaction involves a number of mercurated intermediates and eventually leads to acetylferrocene. For comparison the behavior of ethynylbenzene with the same mercurating system has also been investigated. The reaction mechanism is discussed in the light of the mercurated and nonmercurated reaction intermediates.

Introduction

In recent years we have been interested in giving a quantitative basis to the generally accepted but still largely qualitative notion that the ferrocene system is very reactive toward electrophilic reagents, due to its strong electron-releasing ability.[1] Electrophilic ring substitution[2] and addition to the double bond[3] have been investigated with ferrocene derivatives, the choice of electrophilic species being limited by the easy oxidation of the iron atom.

We now wish to report on the reaction of ethynylferrocene with mercuric acetate. This reaction has been investigated for several reasons. Very little is known about the reactivity of a triple bond in the side chain of a ferrocenyl moiety, with the exception of polymerization reactions.[4] Moreover, the interaction of triple bonds with Hg(II) compounds is synthetically useful—for example, in the catalytic hydration of alkynes—but mechanistic details are scarce.[5] Mercuric acetate is a mild electrophilic reagent; the methoxymercuration of vinylferrocene has been investigated in some detail[3a] and so has the same reaction on styrene derivatives.[6] Finally, a comparison between the reactions with electrophilic species of alkenes and the corresponding alkynes can give useful information about the mechanism of the reaction[7] mainly with respect to the nature of the cationic intermediate.

By investigation of the ethynylferrocene reaction with mercuric acetate, our aim was to get a deeper insight into the interaction between alkynes and a mercuric species, in order to elucidate the behavior of ethynylferrocene under electrophilic conditions. When missing and necessary for a comparison, data have been obtained for ethynylbenzene under comparable reaction conditions.

Results and Discussion

Ethynylferrocene reacts with mercuric acetate in methanol under mild conditions to give a mixture of products, the composition of which is strongly dependent on the reaction time (see Experimental Section, Tables I and II). When the reaction is quenched immediately after the end of $Hg(OAc)_2$ addition, bis(ferrocenyl acetylide)mercury, $(FcC{\equiv}C)_2Hg$, is obtained quantitatively, as an orange solid that precipitates from the reacting mixture. If the reaction is allowed to proceed for 3 days at room temperature, the precipitated $(FcC{\equiv}C)_2Hg$ slowly dissolves and acetylferrocene, $FcCOCH_3$, forms quantitatively. With reaction times intermediate between the above limits, bis(ferrocenyl acetylide)mercury and acetylferrocene are not the only products, since the vinyl ether (α-methoxyvinyl)ferrocene, $FcC(OCH_3){=}CH_2$, has been isolated (Table II) and evidence for the existence of another mercurated species has been obtained by the iododemercuration of the reaction mixture (Table II, run 2). Iododemercuration is a well-known method to cause cleavage of carbon–mercury bonds, thus yielding soluble, easy to purify products.[8] After iododemercuration, the following compounds have been isolated: (iodoethynyl)-

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[1] Rosenblum, M. "Chemistry of Iron Group Metallocenes, Part One"; Wiley: New York, 1965.

[2] Floris, B.; Illuminati, G. *J. Organomet. Chem.* **1978**, *150*, 101.

[3] (a) Floris, B.; Illuminati, G. *J. Organomet. Chem.* **1979**, *168*, 203. (b) Floris, B. *Gazz. Chim. Ital.* **1982**, *112*, 489. (c) Floris, B.; Illuminati, G. *J. Organomet. Chem.* **1982**, *225*, 301.

[4] (a) Simionescu, C.; Lixandru, T.; Negulescu, I.; Mazilu, I.; Tataru, L. *Makromol. Chem.* **1973**, *63*, 59. (b) Korshak, V. V.; Dzhashi, L. V.; Antipova, B. A.; Sosin, S. L. *Dokl. Vses. Konf. Khim. Atsetilena, 4th* **1972**, *3*, 217; *Chem. Abstr.* **1974**, *81*, 26007. (c) Trevor, A. S.; Watts, W. E.*J. Organomet. Chem.* **1976**, *105*, C16. (d) Lixandru, T.; Chirvu, C.; Tataru, L.; Mazilu, I. *Bul. Inst. Politeh. Iasi, Sect. 2: Chim.* **1977**, *23*, 65.

[5] March, J. "Advanced Organic Chemistry: Reaction, Mechanisms, and Structure", 2nd ed.; McGraw-Hill: New York, 1977; p 698.

[6] Bassetti, M.; Floris, B.; Illuminati, G. *J. Organomet. Chem.* **1980**, *202*, 351.

[7] Melloni, G.; Modena, G.; Tonellato, U. *Acc. Chem. Res.* **1981**, *14*, 227.

[8] Chatt, J. *Chem. Rev.* **1951**, *48*, 7.

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ferrocene, FC≡CI, (β-iodoacetyl)ferrocene, $FcCOCH_2I$, and acetylferrocene, according to eq 1. Apparently, two different mercurated species are formed in the reaction, leading after iododemercuration to (iodoethynyl)ferrocene and (β-iodoacetyl)ferrocene, respectively.

$$FcC{\equiv}CH \xrightarrow[(2)\ I_2,\ CH_3OH]{(1)\ Hg(OAc)_2,\ CH_3OH} FcC{\equiv}CI + FcCOCH_3 + FcCOCH_2I \quad (1)$$

An effort has been made to isolate and identify the mercurated products. Mercuric acetate in methanol has been added to ethynylferrocene (Experimental Section, Table I, run 3), and the precipitation of the orange $(FcC{\equiv}C)_2Hg$ started immediately. By gas chromatographic analysis (mercurated species being not detectable by this method) the solution after 20 min reaction consisted of 18% unreacted ethynylferrocene, 72% acetylferrocene, and 10% (α-methoxyvinyl)ferrocene. The gas chromatographic analysis was repeated after an additional 55 min, showing the disappearance of the starting material, the increase of acetylferrocene to 95%, and the decrease of (α-methoxyvinyl)ferrocene to 5%. Apparently, (α-methoxyvinyl)ferrocene is not a final product but an intermediate, which converts to acetylferrocene. This is confirmed by the observation that a sample of the vinyl ether was completely transformed into acetylferrocene after standing some days in the air. Bis(ferrocenyl acetylide)mercury was recovered by filtration, and from the filtered solution after 48 h a brown solid precipitated, which was transformed into (β-iodoacetyl)ferrocene by treatment with iodine in methanol, thus indicating a structure of the type $FcCOCH_2HgX$. X appeared to contain another mercury atom (see Experimental Section), on the basis of the elemental analysis. Quantitative product analysis of the reaction between ethynylferrocene and mercuric acetate under the above conditions (reaction time, 75 min) can be summarized according to eq 2.

$$\begin{aligned} &FcC{\equiv}CH + Hg(OAc)_2 \xrightarrow{CH_3OH} \\ &\underset{52\%}{(FcC{\equiv}C)_2Hg} + \underset{21\%}{FcCOCH_2HgX} + \underset{1\%}{FcC(OCH_3){=}CH_2} + \\ &\qquad \underset{22\%}{FcCOCH_3}\ \text{(overall yield 96\%)} \quad (2) \end{aligned}$$

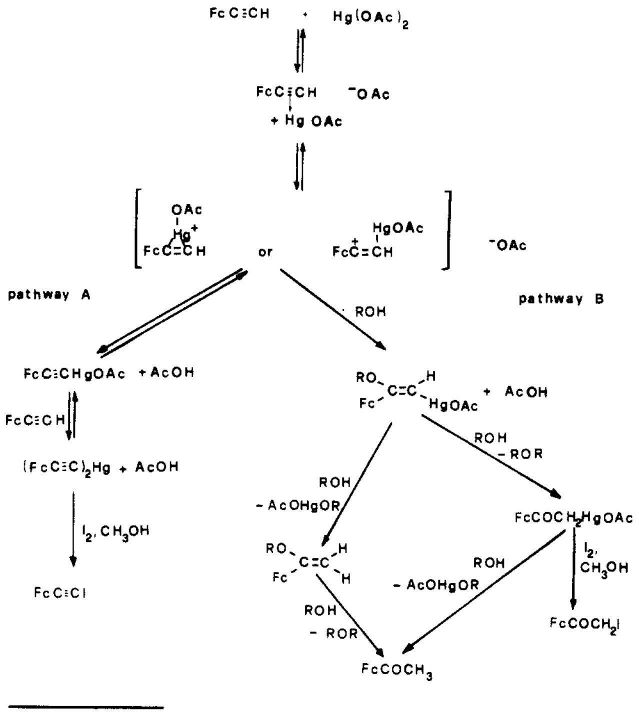
The results obtained by reacting ethynylferrocene and mercuric acetate in methanol lead to a series of considerations that can be summarized as follows.

(i) Ethynylferrocene reacts with mercuric acetate by two pathways, depending on whether the acidic hydrogen (pathway A) or the nucleophilic triple bond (pathway B) is involved. These two pathways should derive from a common intermediate, i.e., a cationic species directly formed by the interaction between the substrate and the electrophilic reagent.

(ii) $(FcC{\equiv}C)_2Hg$ forms immediately and nearly quantitatively: 91.8% yield is obtained by filtering the reaction mixture at the end of $Hg(OAc)_2$ addition. The amount of bis(ferrocenyl acetylide)mercury decreases with time (see Tables I and II). When the reaction mixture is allowed to stand long enough, $(FcC{\equiv}C)_2Hg$ eventually disappears. This behavior indicated that the primary reaction is kinetically controlled and is reversible. The reaction more slowly reverts from pathway A to pathway B irreversibly leading to acetylferrocene as a final product.

(iii) $(FcC{\equiv}C)_2Hg$ has been suspended in methanol and quantitatively recovered unchanged after 6 days of stirring (see Experimental Section). When $(FcC{\equiv}C)_2Hg$ has been treated with methanol containing 0.1% v/v acetic acid, acetylferrocene was obtained together with unreacted bis(ferrocenyl acetylide)mercury. The formation of acetylferrocene under these conditions is much slower than that observed under the mercuration conditions, which may be due to the low concentration of the mercurating reagent, since the only source of mercurating species is $(FcC{\equiv}C)_2Hg$.

Scheme I



R = CH_3, Ac

(iv) With an excess of the mercurating reagent, acetylferrocene is obtained together with a mercurated species of the type $FcC{\equiv}CHgX$, containing a single ferrocenyl moiety for every three mercury atoms (see Experimental Section). This seems to indicate that $(FcC{\equiv}C)_2Hg$ forms in subsequent steps, when excess ethynylferrocene is available.

(v) (α-Methoxyvinyl)ferrocene is obtained when water is added to the reaction mixture (Table II, run 1). However, it is also present in the absence of water (Table II, runs 3–6). On standing, the vinyl ether converts to acetylferrocene, thus indicating it is an intermediate. This behavior may be compared with the hydrolysis of vinyl ethers investigated by Kresge,[9] that is suggested to occur via carbocation, as an acid-catalyzed addition of the protic solvent. The same mechanism might work in our case, being favored by the well-known stability of α-ferrocenyl carbocations,[10] with methanol playing the same role as water. Support for this hypothesis comes from the easy formation of ferrocenylvinyl cations, $FcC^+{=}CHR$,[11,12] which are reported to undergo addition by nucleophilic solvents and subsequent hydrolysis to ketones.[11,12]

Alternatively, with the data at hand, it is not possible to exclude that the methoxy group is transformed into an enolic hydroxyl group, that immediately tautomerizes.

(vi) A derivative of acetylferrocene containing a mercuric atom in the β-position of the side chain has been isolated and transformed into (β-iodoacetyl)ferrocene. This mer-

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[9] Kresge, A. J.; Jerry, A. *J. Am. Chem. Soc.* **1971**, *93*, 413.

[10] Watts, W. E. *J. Organomet. Chem. Lib.* **1979**, *7*, 399 and reference therein.

[11] Abram, T. S.; Watts, W. E. *J. Chem. Soc., Chem. Commun.* **1974**, 857.

[12] Abram, T. S.; Watts, W. E. *J. Chem. Soc., Perkin Trans. 1* **1977**, 1522.

curated species, of the type $FcCOCH_2HgX$, may come from the corresponding vinyl ether (not detected) (β-(acetoxymercurio)-α-methoxyvinyl)ferrocene through a ferrocenylvinyl cation, as indicated above.

From the above considerations a mechanistic scheme is proposed that may be represented as in Scheme I.

For a check on the reliability of the hypotheses made, the reaction was performed in a nonprotic solvent. When ethynylferrocene was treated with mercuric acetate in anhydrous tetrahydrofuran, a very slow reaction occurs. The orange precipitate appears only after 2–3 h of stirring, and after an additional 2 h bis(ferrocenyl acetylide)mercury was obtained in a 50% yield. Furthermore very little acetylferrocene is obtained (ca. 2%). The slowing down of the reaction is presumably due to a decreased electrophilic reactivity of mercuric acetate in THF, but the essential inhibition of the formation of acetylferrocene is due to the fact that, in agreement with the proposed mechanism, pathway B requires a protic reagent. In anhydrous THF only the small amount of acetic acid formed in pathway A is available for the system undergoing transformation toward acetylferrocene.

The reaction has been further investigated in a different protic solvent, such as acetic acid. Mercuric acetate in AcOH was added under nitrogen to ethynylferrocene in the same solvent, and the reaction mixture was stirred at room temperature, with the orange precipitate starting to appear after a few minutes. Bis(ferrocenyl acetylide)mercury was recovered by filtration, and the filtered solution resulted to contain 67% acetylferrocene and 32% (α-acetoxyvinyl)ferrocene.

Therefore, the reaction in acetic acid can be summarized according to eq 3.

$$\begin{array}{ccccccc} FcC{\equiv}CH & \xrightarrow[AcOH]{Hg(OAc)_2} & (FcC{\equiv}C)_2Hg & + & FcCOCH_3 & + & FcC(OAc){=}CH_2 \\ & & 19\% & & 58\% & & 23\% \\ & & \Big\downarrow{\scriptstyle I_2,\ CH_3OH} & & & & \\ & & FcC{\equiv}CI & & & & \end{array} \qquad (3)$$

The results are consistent with the proposed mechanistic scheme (R = Ac). α-Acetoxyvinyl derivatives are known to undergo solvolysis in acetic acid.[14] The percentage of bis(ferrocenyl acetylide)mercury is lower than that obtained in methanol with the same reaction time, which may be explained on the basis of a decreased acidity of the acetylenic proton in the substrate, due to the decreased basicity of the solvent.

In order to have a comparison with the corresponding benzene system, ethynylbenzene was made to react with mercuric acetate in methanol. Ethynylbenzene with $Hg(OAc)_2$ in acetic acid is reported to yield bis(phenyl acetylide)mercury quantitatively.[15]

When ethynylbenzene and mercuric acetate are allowed to react for a long time, acetophenone is quantitatively obtained (see Experimental Section) by a reaction similar to that of ethynylferrocene. The behavior of ethynylbenzene can be followed with the aid of Figures 1 and 2. Bis(phenyl acetylide)mercury is not formed quantitatively, but its amount is high in the early stage of the reaction and decreases with time. The results from the various runs performed (see Experimental Section) may be summarized according to eq 4. Bis(phenyl acetylide)mercury or PhC≡CHgOAc, β-(acetoxymercurio)-α-methoxystyrene, and β-(acetoxymercurio)acetophenone form immediately. The decrease of these species is accompanied by the formation of nonmercurated species, i.e., α-methoxystyrene and acetophenone.

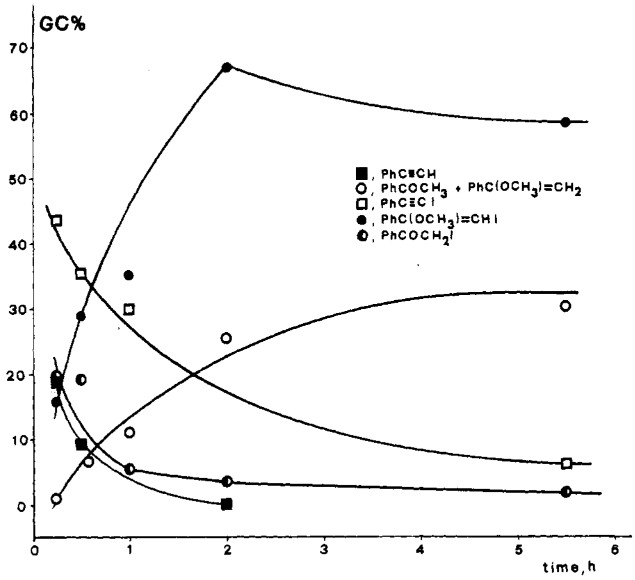

Figure 1. Gas chromatographic percentages vs. time of products from the reaction between ethynylbenzene and $Hg(OAc)_2$ in methanol.

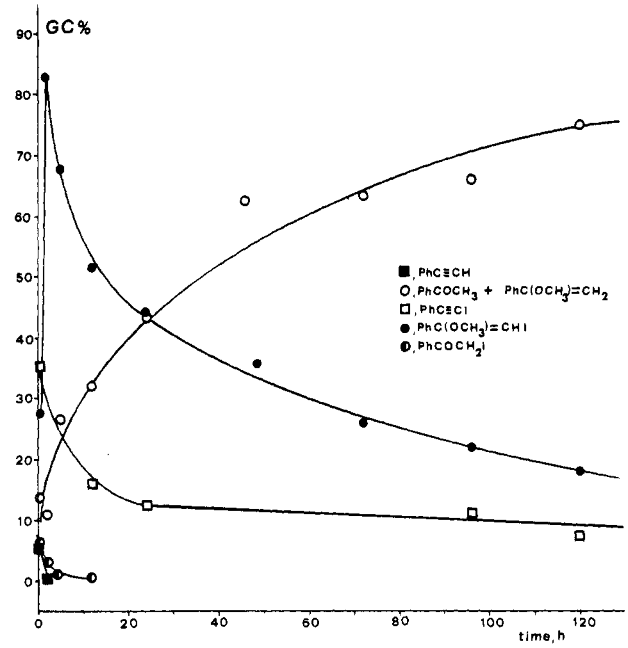

Figure 2. Gas chromatographic percentages vs. time of products from the reaction between ethynylbenzene and $Hg(OAc)_2$ in methanol.

$$\begin{aligned} PhC{\equiv}CH + Hg(OAc)_2 &\xrightarrow{CH_3OH} (PhC{\equiv}C)_2Hg + \\ &PhCOCH_2HgOAc + PhC(OCH_3){=}CHHgOAc + \\ &PhCOCH_3 + PhC(OCH_3){=}CH_2 \xrightarrow{I_2,\ CH_3OH} \\ &PhC{\equiv}CI + PhCOCH_2I + PhC(OCH_3){=}CHI \end{aligned} \qquad (4)$$

This behavior is completely analogous to the one corresponding to the proposed mechanistic scheme for the reaction of ethynylferrocene. It is worth noting the identification of β-(acetoxymercurio)-α-methoxystyrene through its iodo derivative, since we have no direct evi-

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[13] In this scheme the initial π complex is included, since its formation is commonly accepted (Baciocchi, E.; Marino, G. "Meccanismi delle Reazioni Organiche; USES: Firenze, 1982; p 380). We have no evidence either in favor or against π-interaction. Moreover, the nature of the cationic intermediate cannot be undoubtedly indicated.

[14] Fahey, R. C.; Lee, D. J. *J. Am. Chem. Soc.* **1968**, *90*, 2124.

[15] Uemura, S.; Miyoshi, H.; Sohma, K.; Okano, M. *J. Chem. Soc., Chem. Commun.*, **1975**, 548.

dence for the corresponding ferrocenyl compound $\mathrm{FcC(OCH_3){=}CHHgOAc}$. This might be understood in terms of a higher reactivity of (β-(acetoxymercurio)-α-methoxyvinyl)ferrocene with respect of $\mathrm{PhC(OCH_3){=}CHHgOAc}$, due to the higher stability of the carbocation presumably formed in the course of the subsequent reaction.

In conclusion, the reaction of ethynylferrocene with mercuric acetate, as well as the corresponding reaction of ethynylbenzene, is a complex one, because the product of electrophilic addition evolves to a variety of derivatives through different pathways. The overall result in anhydrous protic solvents is a formal Markownikov addition of water to produce ketones.

Further work is in progress to verify the scope of the reaction with other alkynes.

Experimental Section

^{1}H NMR spectra have been recorded on a Brucker WP-80 and a Varian EM-360 spectrometers, with $\mathrm{CDCl_3}$ or $\mathrm{CCl_4}$ as solvents and $\mathrm{Me_4Si}$ as the internal standard.

Infrared spectra have been obtained with Perkin-Elmer 257 and 298 spectrophotometers, as $\mathrm{CCl_4}$ or $\mathrm{CHCl_3}$ solutions in sodium chloride cells (l = 0.1 cm).

Gas chromatographic analyses have been performed with a Hewlett-Packard Model 5830A, equipped with a 1-m 2% OV 17 Chromosorb GAW-DMCS column, or with a Varian VISTA 6000, equipped with a 0.5 m 5% OV 101 Chromosorb GHP 100-120 column, apparatus. Mercurated products are not revealed under the used conditions. Gas-mass spectroscopy analyses have been performed with a Kratos MS 80 spectrometer.

Microanalyses were obtained from Microanalysis Service of the C.N.R. "Area di Ricerca" (Montelibretti, Roma).

Mercury content has been determined by titration, according to the method by Kolthoff.[16] Mercurated compounds decomposed without melting.

Materials. Ethynylferrocene was prepared by the method of Rosenblum.[17] Ethynylbenzene, mercuric acetate, and iodine were commercially available products and were used without further purification. Spectrograde solvents were used for all spectroscopic measurements. Mercuric acetate solutions in methanol contained 0.1% AcOH, in order to avoid decomposition.[6]

Product Analysis. Mercurated products have been identified as iodo derivatives. The following general procedure was used for the iododemercuration reaction.[15] An excess of iodine in either methanol or dichloromethane saturated solutions was added to a stirred solution or suspension of the mercurated compound in the same solvent. Stirring was maintained until the starting material dissolved, and the iodine color was persistent. The mixture was poured into water and $\mathrm{CCl_4}$; the organic phase, separated, was treated twice with 10% aqueous sodium thiosulfate, washed with water, dried over anhydrous $\mathrm{Na_2SO_4}$, and analyzed on the gas chromatograph. Removing the excess iodine was necessary before GC analysis, in order to completely reveal the presence of unsaturated compounds. The organic phase was evaporated, and the residue was chromatographed over a silica gel column, in order to isolate the products.

Blank experiments performed by treating ethynylferrocene and ethynylbenzene with iodine excess in methanol gave none of the iodo derivatives observed in the iododemercuration reaction.

(a) Reaction of Ethynylferrocene with Mercuric Acetate in Methanol. In a typical experiment, mercuric acetate in 10–15 mL of anhydrous methanol was added dropwise (generally in 10–15 min) to a stirred solution of ethynylferrocene in 10–15 mL of the same solvent, at room temperature and under nitrogen atmosphere. An orange solid began to precipitate immediately.

Different runs have been performed by changing reaction parameters, such as reaction time, molar ratio of reagents, and workup of the mixture.

Table I. Conditions for the Reaction of Ethynylferrocene with Mercuric Acetate in Methanol

run	reactn time[a]	$\mathrm{FcC{\equiv}CH}$, mmol	$\mathrm{Hg(OAc)_2}$, mmol	method of workup	overall yield, %
1	2 h	1.14	1.03	II[b]	61.6
2	1 h	3.30	3.10	I[c]	93.7
3	75 min	0.70	0.40	III[d]	96.0
4	0 min	0.48	0.22	II	97.7
5	7 h	0.48	0.44	II	77.1
6	12 h	0.48	0.44	II	69.8
7	72 h	0.48	0.44	I	99.5
8	10 h	2.00	2.50	II	44.8
9	10 h	2.00	4.00	II	59.9
10	16 h	1.00	1.25	I	82.4
11	16 h	1.00	2.00	I	80.1

[a] Measured from the end of $\mathrm{Hg(OAc)_2}$ addition. [b] Filtration of the precipitate and chromatography of the filtrate. [c] Direct iodomercuration. [d] Subsequent filtration of two different precipitates and chromatography of the filtrate.

The following procedures have been used for the reaction workup. (I) Iododemercuration has been performed without isolating the solid mercurated species, by adding the iodine solution directly into the reaction mixture. This method allows to deal with soluble and easily separable compounds, but identification of mercurated species is indirect. (II) The precipitate has been filtered off and the filtrate evaporated. The resulting residue has been either chromatographed over silica gel column (40–70 °C petroleum ether and diethyl ether as eluants) or dissolved with $\mathrm{CH_2Cl_2}$, washed with water, dried over anhydrous $\mathrm{Na_2SO_4}$, concentrated, and chromatographed over a silica gel column. (III) The precipitate has been filtered, and the filtrate has been allowed to slowly evaporate for a day, thus yielding a dark brown solid, that has been recovered by filtration. The filtrate has been concentrated and chromatographed over a silica gel column. In all procedures described, gas chromatographic analysis has been extensively used.

Experimental details for the different runs are reported in Table I and the results are reported in Table II, in terms of reaction products and yields.

The low overall yield in runs 1, 8, and 9 has to be attributed to the procedure for the workup, since $\mathrm{FcCOCH_2HgX}$ remains absorbed on the silica gel. An attempt of iododemercuration performed on absorbed $\mathrm{FcCOCH_2HgX}$ (runs 5 and 6) increased the overall yield, but heterogeneous iododemercuration resulted to be nonquantitative.

The formation of $\mathrm{FcC{\equiv}CHgX}$ in runs 8–11 instead of $\mathrm{(FcC{\equiv}C)_2Hg}$ is due to the excess of the mercurating reagent used in these cases.

The absence of $\mathrm{(FcC{\equiv}C)_2Hg}$ in runs 5–7 is due to the prolonged reaction time. The orange precipitate was observed at the beginning and gradually disappeared to give a clear solution.

A sample of 60 mg (0.1 mmol) of $\mathrm{(FcC{\equiv}C)_2Hg}$ in methanol remained insoluble and was recovered quantitatively and unchanged after 8 days. A sample of 60 mg (0.1 mmol) of $\mathrm{(FcC{\equiv}C)_2Hg}$ in methanol containing 0.1% acetic acid slowly gave a colored solution, from which 25 mg (0.11 mmol, 54.8% yield) of acetylferrocene was obtained after 8 days. Unreacted bis(ferrocenyl acetylide)mercury was recovered (21 mg, 35%).

Characterization of the Reaction Products. $\mathrm{(FcC{\equiv}C)_2Hg}$ (bis(ferrocenyl acetylide)mercury): ^{1}H NMR ($\mathrm{Me_2SO}$-d_6) δ 4.32 (t, 2 H, α-protons of the substituted cyclopentadienyl ring), δ 4.10 (singlet with a broad base, 7 H, superposition of the unsubstituted Cp ring protons and β-protons of the substituted Cp ring). Anal. Calcd for $\mathrm{C_{24}H_{18}Fe_2Hg}$: C, 46.64; H, 2.93; Hg, 32.5. Found: C, 46.63; H, 3.00; Hg, 31.6.

Iododemercuration (4 h), as carried out with a 65-mg sample (0.10 mmol) of bis(ferrocenyl acetylide)mercury, gave 60 mg of a dark orange solid, which was identified as (iodoethynyl)ferrocene (0.18 mmol; 89% yield), on the basis of the IR and ^{1}H NMR spectra in $\mathrm{CCl_4}$ (see below). **$\mathrm{FcC{\equiv}CHgX}$.** This compound is transformed into (iodoethynyl)ferrocene by iododemercuration and into bis(ferrocenyl acetylide)mercury by reaction with ethynylferrocene. From the elemental analysis a tentative structure might be written as $\mathrm{FcC{\equiv}CHgOHgOAc{\cdot}Hg(OAc)_2}$. (Anal. (Calcd

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(16) Kolthoff, I. M.; Lingane, J. J. *J. Am. Chem. Soc.* **1935**, *57*, 2377.

(17) Rosenblum, M.; Brawn, N.; Papenmeier, J.; Applebaum, M. *J. Organomet. Chem.* **1966**, *6*, 173.

Table II. Products of the Reaction between Ethynylferrocene and Mercuric Acetate in Methanol

	$(FcC{\equiv}C)_2Hg$ or $FcC{\equiv}CI$[a]		$FcC{\equiv}CHgX$ or $FcC{\equiv}CI$[a]		$FcC(OCH_3){=}CH_2$		$FcCOCH_3$		$FcCOCH_2HgX$ or $FcCOCH_2I$[a]	
run	mmol	yield, %	mmol	yield, %	mmol	yield, %	mmol	yield, %	mmol	yield, %
1	0.53	51.4			0.008	0.8	0.10	9.4	. . .	
2	0.80	50.0			. . .		0.40	25.0	0.30	18.7
3	0.21	52.0				1.0	0.09	22.0	0.085	21.0
4	0.20	91.8			0.007	3.1	0.006	2.8	. . .	
5	. . .				0.007	1.7	0.019	43.2	0.141	32.2
6	. . .				0.003	0.6	0.247	56.3	0.057	12.9
7	. . .				. . .		0.433	98.7	0.003	0.8
8			0.46	22.9	. . .		0.434	21.9	. . .	
9			0.41	20.4	. . .		0.789	39.5	. . .	
10			0.014	1.4	. . .		0.767	76.7	0.043	4.3
11			0.068	6.8	. . .		0.653	65.3	0.080	8.0

[a] Depending on whether the mercurated species or the product from iododemercuration has been isolated.

for $C_{18}H_{18}FeHg_3O_7$: C, 21.53; H, 1.80; Hg, 59.94.) Found: C, 21.25; H, 1.62; Hg, 62.9.)

$FcC{\equiv}CI$ ((iododethynyl)ferrocene): IR (CCl_4) $\nu_{C\equiv C}$ 2180 cm^{-1}; ^1H NMR (CCl_4) δ 4.30 (t, 2 H, α-protons of the substituted cyclopentadienyl ring), 4.06 (s, 5 H, Cp), 4.00 (t, 2 H, β-protons of the unsubstituted Cp ring).

$FcC(OCH_3){=}CH_2$ ((α-methoxyvinyl)ferrocene): ^1H NMR ($CDCl_3$) δ 10.09 (d, J = 7.2 Hz, 1 H) and 6.39 (d, J = 7.2 Hz, 1 H, vinylic protons), 4.74 (2 H) and 4.55 (2 H, t, α- and β-protons of the substituted Cp ring), 4.24 (singlet with a broad base, 8 H, superposition of unsubstituted Cp and OCH_3 signals). In a different solvent (CCl_4) the OCH_3 singlet appears at δ 4.10, separated from the unsubstituted Cp signal (δ 4.00).

$FcCOCH_3$ (acetylferrocene): ^1H NMR δ 4.52 (t, 2 H) and 4.20 (t, 2 H, α- and β-protons, respectively, of the substituted cyclopentadienyl ring), 4.01 (s, 5 H, Cp), δ 2.22 (s, 3 H, CH_3). The IR carbonyl absorption was found at 1676 cm^{-1} (lit.[1] 1672 cm^{-1}).

$FcCOCH_2HgX$. The structure $FcCOCH_2HgOHgOCOCH_3$ is proposed for this mercurated species, on the basis of elemental analysis and of the subsequent transformation into $FcCOCH_2I$. Anal. Calcd for $C_{14}H_{14}FeHg_2O_4$: C, 24.50; H, 2.00; Hg, 57.1. Found: C, 24.53; H, 1.94; Hg, 58.4.

$FcCOCH_2I$ ((β-iodoacetyl)ferrocene): ^1H NMR δ 4.72 (t, 2 H, α-protons of the substituted Cp ring), 4.50 (t, 2 H, β-protons of the same Cp ring), 4.18 (s, 5 H, unsubstituted Cp ring), 4.06 (s, 2 H, methylene protons). The IR spectrum showed the carbonyl absorption at 1670 cm^{-1}.

(b) Reaction of Ethynylferrocene with Mercuric Acetate in Tetrahydrofuran. The solvent used in this experiment was distilled over $LiAlH_4$ directly into the reaction flask. Mercuric acetate (0.52 g, 1.6 mmol) was allowed to dissolve in 20 mL of freshly distilled THF with a drop of AcOH. The resulting solution was added dropwise to 0.68 g (3.2 mmol) of ethynylferrocene, stirred in 30 mL of the same solvent, at room temperature, under nitrogen atmosphere. No visible change occurred during the addition, and only 2 h later an orange solid began to precipitate. The mixture was kept under stirring 3 h, and then the solid material was filtered and washed with THF, to give 0.50 g of bis(ferrocenyl acetylide)mercury (0.8 mmol; 50% yield) that by iododemercuration afforded (iodoethynyl)ferrocene as the sole product. GC analysis of the filtrate revealed the presence of unreacted ethynylferrocene (49%) and traces of acetylferrocene (ca. 2%, on the basis of starting material).

(c) Reaction of Ethynylferrocene with Mercuric Acetate in Acetic Acid. Mercuric acetate (0.16 g, 2.0 mmol) in 20 mL of anhydrous acetic acid was added dropwise to a stirred solution of ethynylferrocene (0.55 g, 2.6 mmol) in 30 mL of the same solvent, at room temperature and nitrogen atmosphere. During the addition, immediate precipitation of an orange solid occurred. After 1.5 h of stirring, the solid material was filtered and washed with cold methanol, to give bis(ferrocenyl acetylide)mercury (0.24 g, 0.38 mmol; 19% yield). Iododemercuration afforded (iodoethynyl)ferrocene as the sole product.

The filtrate from the reaction mixture was poured into 200 mL of water and extracted with CH_2Cl_2. The organic extracts, washed with water, dried over anhydrous Na_2SO_4, and evaporated, gave 0.4 g of a red oil, the ^1H NMR spectrum of which in Me_2SO-d_6 revealed the presence both of acetylferrocene (67%; 58% yield) and (α-acetoxyvinyl)ferrocene (33%; 23% yield). The relative percentages were calculated by integration of isolated peaks from the two compounds in the mixture: δ 5.62 (s, 2 H, vinylic protons of $FcC(OAc){=}CH_2$), δ 2.20 (s, 3 H, methyl protons of the same compound), and 2.32 (s, 3 H, methyl protons of $FcCOCH_3$). The signals due to ferrocenyl groups are superimposed and appear as multiplets centered at δ 4.70 and 4.50 (substituted Cp ring) and a singlet at δ 4.18 (unsubstituted Cp ring). Upon standing for some days in the air, (α-acetoxyvinyl)ferrocene turned into acetylferrocene, as revealed by NMR analysis.

To verify whether aqueous workup was responsible for the formation of some of the observed products, mercuric acetate (0.11 g, 0.34 mmol) in 10 mL of anhydrous acetic acid was added dropwise to a stirred solution of ethynylferrocene (0.10 g, 0.47 mmol) in 10 mL of the same solvent. After 1.5 h of stirring, 55 mg of $(FcC{\equiv}C)_2Hg$ (0.09 mmol; 26% yield) was recovered by filtration. Gas chromatographic analysis of the solution revealed the presence of acetylferrocene. Acetic acid was completely removed under vacuum, and the residue was treated with diethyl ether and evaporated, leaving 60 mg of a red oil, consisting of 1.7% unreacted ethynylferrocene, 88.6% acetylferrocene (0.23 mmol; 68% yield), and 9% (α-acetoxyvinyl)ferrocene (0.02 mmol; 6% yield).

(d) Reaction of Ethynylbenzene with Mercuric Acetate in Methanol. Mercuric acetate (1.38 g, 4.0 mmol) in 40 mL of methanol was added dropwise (0.5 h) to a stirred solution of ethynylbenzene (0.8 g, 7.8 mmol) in 50 mL of the same solvent, at room temperature and under nitrogen atmosphere, with a white solid beginning to precipitate at the end of addition. After the mixture was stirred 1 h, 0.30 g of a white powder has been obtained by filtering and washing with cold methanol. Iododemercuration in methanol on 130 mg yielded 80 mg of an oil that revealed to be a mixture of (iodoethynyl)benzene and β-iodoacetophenone in similar percentages.

On removing the solvent from the filtrate of the mercuration reaction, 1.7 g of a viscous oil was obtained, which partially solidified 24 h later. The solid, filtered from the remaining oil and washed with 40–70 °C petroleum ether, was identified as β-(acetoxymercurio)acetophenone: ^1H NMR δ 7.8 and 7.3 (complex signals, 5 H, aromatic protons), 3.32 (s, 2 H, $-CH_2-$), 1.90 (s, 3 H, CH_3). The IR spectrum shows a carbonyl band at 1670 cm^{-1} and a band typical of the acetoxymercurio group at 1600 cm^{-1}, the same peak being shown by mercuric acetate.

Iodomercuration on 250 mg (0.6 mmol) of β-(acetoxymercurio)acetophenone yielded 0.13 g (0.5 mmol; 83% yield) of β-iodoacetophenone, identified by IR and NMR spectrum: δ 7.8 and 7.3 (m, 5 H, aromatic protons), δ 4.2 (s, 2 H, CH_2I). The IR carbonyl band is found at 1680 cm^{-1}.

The oil from the mercuration reaction revealed to be acetophenone, as confirmed by comparison with an authentic sample.

Because of the difficulties found in separating $(PhC{\equiv}C)_2Hg$ and $PhCOCH_2HgOAc$, to have a quantitative analysis, other runs of the reaction were performed, by direct treatment with iodine at different reaction times.

By reacting ethynylbenzene (0.80 g, 7.8 mmol) with $Hg(OAc)_2$ (1.28 g, 4.0 mmol) in methanol for 2.5 h at room temperature and adding subsequently iodine in methanol, an overall 84.4% yield of products has been obtained, consisting of 38% isolated β-(iodoethynyl)benzene (^1H NMR δ 7.2 (complex signal, aromatic protons)), 7.5% isolated acetophenone, and a number of other compounds (see below), the amount of which has been determined on the basis of GC analysis.

From the reaction of 0.21 g (2.0 mmol) of ethynylbenzene with 0.35 g (1.1 mmol) of $Hg(OAc)_2$ in methanol for 9 days at room temperature, an overall 99% product yield was obtained (1.05 mmol of isolated acetophenone, yield 95.9%, and 3.1% (β-iodoethynyl)benzene, on the basis of GC analysis).

Another run, performed with the same initial amounts and refluxed for 9 days, gave 99.0% acetophenone as the sole product.

When the reaction is quenched at shorter reaction times, a variety of compounds is observed after iododemercuration. According to increasing gas chromatographic retention times, the following compounds have been identified after iododemercuration and usual workup.

Acetophenone ($PhCOCH_3$): indicated by ^1H NMR spectrum and confirmed by comparison with an authentic sample.

α-Methoxystyrene ($PhC(OCH_3)=CH_2$): indicated by ^1H NMR spectrum (δ 7.1–7.3 (complex signal, 5 H, aromatic protons) 4.67 (s, $=CH_2$), 1.93 (s, OCH_3)) and confirmed by mass spectrometry (M^+, 134; mol wt, 134.18).

(β-Iodoethynyl)benzene ($PhC\equiv CI$) (^1H NMR δ 7.2 (complex signal aromatic protons)): indicated by mass spectrometry (M^+, 228; mol wt 228.03) and confirmed by comparison with a sample independently synthetized from cuprous phenylacetylide and iodine.

β-Iodo-α-methoxystyrene ($PhC(OCH_3)=CHI$) as indicated by mass spectrometry (M^+, 260; mol wt 260.07).

β-Iodoacetophenone ($PhCOCH_2I$): indicated by ^1H NMR spectrum (see above) and confirmed by comparison with a sample synthetized from freshly crystallized phenacyl bromide and potassium iodide in acetone.[18] Further support comes from mass spectrometry that gives M^+ 246 (mol wt 246.05).

Two additional compounds have been observed by GC analysis of reaction mixtures and have been identified with gas chromatography–mass spectrometry experiments.

The first compound has a retention time intermediate between those of $PhC\equiv CI$ and $PhC(OCH_3)=CHI$. A M^+ 202 value suggests it is the dimer $PhC\equiv CC\equiv CPh$ (mol wt 202.25), probably formed by coupling reaction from (β-iodoethynyl)benzene during the workup of the reaction.

The second compound has the highest retention time in the mixture and exhibits M^+ 278. The most likely structure seems to be $PhC(OH)(OCH_3)CH_2I$ (mol wt 278.09). Meaningful fragmentations are observed at 151 (M^+ – iodine) and 260 (M^+ – water). This compound might be formed by addition of water to β-iodo-α-methoxystyrene during the workup of the iododemercuration reaction.

Experimental conditions that lead to the above results were as follows: $PhC\equiv CH$, 1.57 mmol, $Hg(OAc)_2$, 0.80 mmol, reaction times, 0.25, 0.5, 1.0, 2.0, and 5.5 h [gas chromatographic percentages of the observed species are plotted vs. reaction times in Figure 1. $PhCOCH_3$ and $PhC(OCH_3)=CH_2$ have been plotted together, since their peaks are not completely resolved and therefore individual values for the corresponding area percent are not reliable]; $PhC\equiv CH$, 1.74 mmol, $Hg(OAc)_2$, 0.94 mmol, reaction times, 0.5, 2, 5, 12, 24, 48, 72, 96, and 120 h. [gas chromatographic percentages of the observed species vs. reaction times are shown in Figure 2].

Different ratios of starting materials have been used, and the reaction has been interrupted also within few seconds. Reaction conditions and gas chromatographic results are collected in Table III.

In blank experiments, ethynylbenzene remained unchanged for at least 24 h in methanol solutions containing 1% acetic acid and 1% p-toluenesulfonic acid, respectively.

Table III. Conditions for the Reaction of Ethynylbenzene with Mercuric Acetate in Methanol and Gas Chromatographic Percentages of the Products

	reaction conditions				gas chromatographic results							
run	reactn[a] time	$PhC\equiv CH$, mmol	$Hg(OAc)_2$, mmol	$PhC\equiv CH/Hg(OAc)_2$	$PhC\equiv CH$	$PhCOCH_3$	$PhC(OCH_3)=CH_2$	$PhC\equiv CI$	dimer	$PhC(OCH_3)=CHI$	$PhCOCH_2I$	$PhC(OCH_3)(OH)CH_2I$
1	10 s	0.50	0.58	0.87	28.5			16.4	8.0	7.9	37.9	1.4
2	19 min	0.50	0.58	0.87			10.2	1.8		70.6	12.8	4.5
3	45 min	0.50	0.58	0.87			2.2	2.6		87.8	4.7	2.7
4	19 h	0.50	0.58	0.87		26.9	10.9	1.2		58.1		2.9
5	10 s	0.50	0.19	2.60	78.3			13.0	0.6	1.4	3.3	3.4
6	18.4 h	0.50	0.19	2.60		49.1	11.6			39.3		
7	10 s	0.50	0.96	0.35	6.2			1.0		19.9	54.7	18.2

[a] Measured from the end of $Hg(OAc)_2$ addition.

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Registry No. $FcC{\equiv}CH$, 1271-47-2; $Hg(OAc)_2$, 1600-27-7; $(FcC{\equiv}C)_2Hg$, 94619-64-4; $FcCOCH_3$, 1271-55-2; $FcC{\equiv}CI$, 94598-10-4; $FcC{\equiv}CHgOHgOAc$, 94598-11-5; $FcC(OAc){=}CH_2$, 60732-82-3; $FcC(OCH_3){=}CH_2$, 94598-12-6; $PhC{\equiv}CH$, 536-74-3; $PhC{\equiv}CI$, 932-88-7; ICH_2COPh, 4636-16-2; $AcOHgCH_2COPh$, 5653-24-7; $PhCOCH_3$, 98-86-2; $PhC(OCH_3){=}CH_2$, 4747-13-1; $PhC(OCH_3){=}CHI$, 94598-14-8; $PHC{\equiv}CC{\equiv}CPh$, 886-66-8; $PhC(OH)(OCH_3)CH_2I$, 94598-15-9; $FcCOCH_2I$, 54804-01-2; $FcCOCH_2HgOHgOCOCH_3$, 94598-13-7.

Silyliron Carbonyl Complexes in Organic Synthesis: Selective Conversion of Nitriles into *N*,*N*-Bis(silyl) Enamines

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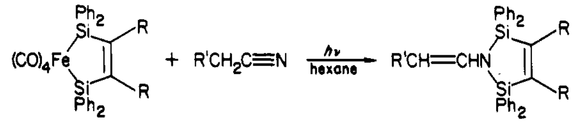
The readily available chelated bis(silyl)iron complex $(CO)_4\overline{FeSi(CH_3)_2\text{-}o\text{-}C_6H_4Si}(CH_3)_2$ reacts photochemically with nitriles, RCH_2CN, to give *N*,*N*-bis(silyl) enamines $RCH{=}CH\overline{NSi(CH_3)_2\text{-}o\text{-}C_6H_4Si}(CH_3)_2$. The scope of this new transformation of nitriles into enamines has been studied. Aliphatic and benzylic nitriles give high yields of a *Z* and *E* mixture of enamines. With dinitriles, the reaction occurs only with the cyano which has an α-hydrogen atom. Halonitriles, methoxyacetonitrile, and ethyl cyanoacetate also undergo a selective reaction affording good yields of functional enamines. In contrast, ketonitriles require protection of the carbonyl group. The reaction of allylic cyanides gives rise to *N*,*N*-bis(silyl) dienamines and to new $\{\eta^4$-[*N*,*N*-bis(silyl)amino]dienyl$\}$iron carbonyl complexes. The *N*,*N*-bis(silyl) enamines obtained give aldehydes upon hydrolysis with dilute acid. They are stable in the presence of electrophiles and nucleophiles and can be used as protected aldehydes. The reaction of the iron complex with nitriles that involve a transfer of the silyl ligand from the iron to the nitrogen atom and migration of one hydrogen atom α to the cyano group is interpreted as proceeding via an intermediate iron carbonyl carbene complex.

Introduction

Organosilicon compounds now constitute a well recognized class of reagents and intermediates in organic synthesis.[1] Our search for new silyl reagents for organic synthesis led us to study the possibilities offered by organosilyl transition-metal complexes.[2] The peculiar behavior of the silyl ligand has allowed to find new reactions affording new access to organometallic compounds[3,4] and novel chemical transformations of some organic functional groups.[5,7] This paper gives a detailed account of our studies of the reactions of a chelated bis(silyl)iron carbonyl complex with nitriles.

A preliminary study on the reactivity of bis(silyl)iron carbonyl complexes revealed that their photochemical reactions with nitriles produce *N*,*N*-bis(silyl) enamines[4a] (eq 1). The silyliron complexes are stoichiometric reagents for the conversion of nitriles into silylenamines. We report here that a readily available iron carbonyl complex can achieve this new chemical transformation of nitriles. The scope of the reaction has been examined. It provides easy access to a variety of *N*,*N*-bis(silyl) enamines[8-10] which were recently shown to be precursors of substituted 2-aza-1,3-butadienes.[11] A portion of this study has already been communicated.[6]



(1)

R = Et, R' = H, 84%; R = Et, R' = Ph, 75%, *E*/*Z* = 45/55; R = R' = Me, 71%, *E*/*Z* = 42/58

Results

A readily available chelated bis(silyl)iron carbonyl complex is **1** first reported by Fink.[12] It is obtained in two steps from *o*-dibromo- or *o*-dichlorobenzene according to a slight modification of the method described by Fink. 1,2-Bis(dimethylsilyl)benzene was easily prepared by use

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