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POLYLITHIATION OF FERROCENE*

A. F. HALASA AND D. P. TATE
Central Research Laboratory of The Firestone Tire & Rubber Company, Akron, Ohio (U.S.A.)

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SUMMARY

Ferrocene was metalated with n-butyllithium in hexane and in benzene to produce a mixture of polylithiated products. This mixture contained compounds with 1 to 7 lithium atoms per ferrocene molecule. The subsequent addition of chlorotrimethylsilane or deuterium oxide to these lithiated compounds resulted in products with as many as seven substituents on the ferrocene rings. A tetrasilylated ferrocene was isolated.

INTRODUCTION

The metalation of ferrocene with n-butyllithium in ether/hexane solvent has been previously reported[1]. Butane is evolved due to lithium–hydrogen exchange with the ferrocene ring. This system has been studied by Nesmeyanov[2], Rausch[3], Goldberg[4], and Benkeser[1]. Low yields of monometalated ferrocene were reported when the reaction was carried out using equimolar amounts of n-butyllithium and ferrocene. If, however, a large excess of n-butyllithium was used in 1/1 tetrahydrofuran/ether, 63% yields of a mixture containing mono and dilithio species were produced[3]. The reaction products generally were isolated and identified as derivatives by reaction with CO_2, chlorotrimethylsilane or ketones.

Benkeser and co-workers[5] have reported a higher metalation product of ferrocene using amylsodium in hydrocarbon solvent. They used equimolar amounts of amylsodium and ferrocene followed by derivatization with chlorotriethylsilane. They have also reported 8% mono-, 12% di- and 2% trimetalation at $-10°$.

RESULTS AND DISCUSSION

We have found that when ferrocene is metalated at elevated temperatures in the absence of ethers, or in the presence of chelating diamine, products of more extensive metalation are obtained. Treatment of ferrocene with 4 to 8 equivalents of n-butyllithium in hexane or benzene at 70° for 100 h under nitrogen gave a dark brown, pyrophoric precipitate. The brown precipitate of lithiated ferrocene was hydrolyzed with deuterium oxide at $-20°$ to give a total yield of deuterated ferro-

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cenes of 58%. It was found by GLC analysis of the hydrolyzed products that all of the n-butyllithium was consumed either by metalation or decomposition. This rules out the possibility that n-butyllithium may be occluded or associated with the insoluble products, since hydrolysis of the precipitated lithium derivatives showed no formation of butane gas.

Examination of the deuterated ferrocene in the mass spectrometer revealed products of mass numbers ranging from the 186 parent peak up to 194 (Table 1). It is clear from the table that there are large amounts of 2, 3 and 4 deuterio products with measurable amounts of 5, 6 and 7. The relative amounts of each deuterated species reported has been determined by peak height from the mass spectral chart after correction for naturally occurring iron and carbon isotopes.

TABLE 1

DEGREE OF METALATION ($FeC_{10}H_{10-x}Li_x$)

x	Without TMEDA		With TMEDA		
	% by deuteration	% by trimethylsilylation[a]	% by deuteration		% by trimethylsilylation
			0.5 h	5 h	
0	1.3		1.3	0.3	
1	4.2	0.5	1.3	0.7	0.40
2	25.6	1.9	10.7	2.4	2.2
3	28.3	10.7	23.6	5.9	13.5
4	30.8	48.0	43.6	23.0	45.6
5	7.4	28.4	43.1	26.0	30.5
6	1.5	10.4	3.7	29.0	9.4
7	0.3	0.2	0.73	9.6	0.10
8	0.1			3.2	

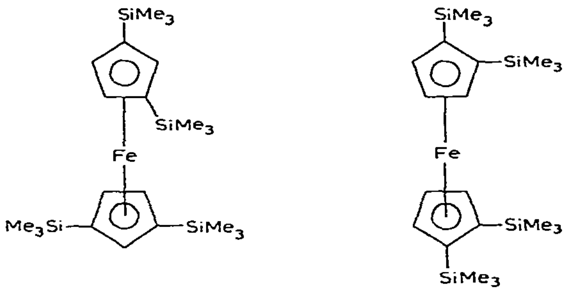
[a] TMEDA added after metalation followed by chlorotrimethylsilane.

We have attempted to derivatize the mixtures of lithiated ferrocene with CO_2 and chlorotrimethylsilane. Carbonation gave an intractable mixture of products from which pure compounds could not be conveniently isolated and identified. Similarly, trimethylsilylation reactions of the lithiated ferrocene in hexane were unsatisfactory as a derivatizing technique. This approach resulted in the formation of large amounts of insoluble materials, presumably polyferrocenylenes. This type of coupling reaction has been observed before, on treating ferrocenyllithium with organic halides[6].

In view of the recent findings of the great effect that *N,N,N′,N′*-tetramethylethylenediamine (TMEDA) has on the reactivity of n-butyllithium in metalation reactions, the above work was repeated using TMEDA[7]. The metalation of ferrocene in the presence of TMEDA gave a 95% yield of deuterated product upon hydrolysis with deuterium oxide. Mass spectral analysis of the deuterated ferrocene is also included in Table 1.

The use of TMEDA in the metalation reaction made it possible to obtain higher yields and to prepare trimethylsilyl derivatives without formation of insoluble polymeric material. This facet of the reaction has not been thoroughly studied, but it seems clear that the presence of TMEDA favors the displacement reaction over the coupling reaction. A dark reddish oil was obtained from the trimethylsilylation reaction from which red crystals were deposited. Recrystallization of these crystals from hexane gave a relatively pure material which was identified by NMR and mass spectral analysis as tetrakis(trimethylsilyl)ferrocene (I). The mass spectrum shows the parent ion as a cluster of peaks around *m/e* 474. There are small peaks around *m/e* 402 and 546, resulting from trace impurities having 3 and 5 trimethylsilyl groups on ferrocene rings.

The NMR spectrum of (I) showed a doublet and a triplet in ratio of 2/1 and a coupling constant *J* of 1.3 Hz for the ferrocene ring protons. This spectrum requires that each ring have two equivalent protons and one unique proton. The two possible structures that are in agreement with the NMR spectrum are the 1,2,1′,2′-tetrasubstituted ferrocene with the adjacent silicon atoms and the 1,3,1′,3′-tetrasubstituted ferrocene with a silicon separated by a unique proton on each ring. The coupling constant of 1.3 Hz favors the 1,3,1′,3′-structure (Ia) since most substituted ferrocenes that have been studied show coupling constants of 2.5 Hz between adjacent protons and 1.2–1.7 Hz for non-adjacent protons[8]. Further support for the tetrasubstituted structure is shown by the 6/1 ratio of methyl-to-ring hydrogens in the NMR spectrum.



(Ia)

(Ib)

Fig. 1. Tetrakis(trimethylsilyl)ferrocene.

The reddish oil from which the tetrasubstituted product was isolated contains a mixture of products. Mass spectral analysis of this crude product shows major peaks appearing around mass numbers 402, 474, 546, 618 and 690. This corresponds to 3, 4, 5, 6, and 7-trimethylsilyl groups on ferrocene. The relative amount of each compound, as determined from the mass spectrum chart, is listed in Table 1. The agreement between deuteration and trimethylsilylation techniques in establishing the distribution of products is not particularly good, due to the fact that the silylated derivatives, being of widely different volatility, behave differently in the mass spectrometer. That is, the volatile product is swept out at a faster rate even though it is the major component. This may account for the discrepancy between silylation and deuteration results. The exchange mechanism of deuterium for hydrogen in the mass spectrum was found to be of less importance and does not occur readily. This was confirmed when the metalated ferrocene was added to 100 fold excess of deuterium oxide and the mass spectrum was taken in the presence of deuterium oxide. The mass spectrum of the deuterated ferrocene isolated showed the same mass spectrum as that obtained by the direct hydrolysis method.

Based on these results, it is clear that ferrocene can be metalated in hexane or benzene at 70° with or without TMEDA to give a mixture of polylithiated products having from 1 to 7 lithium atoms per ferrocene molecule. They undergo typical organolithium reactions, such as reaction with chlorotrimethylsilane to give products having up to 7 substituents on the ferrocene rings. Further work to characterize the products is underway.

This reaction has been applied successfully to the metalation of mono- and polynuclear aromatic compounds. The results and the data will be published at a later data.

EXPERIMENTAL

General procedure for metalation of ferrocene

A solution of ferrocene in hexane or benzene was metalated with 4 and 8 equivalents of n-butyllithium with or without the presence of chelating diamine, employing a solution of n-butyllithium in hexane. The metalation reaction was carried out as follows: Into a liter beverage bottle, which had already been swept with inert atmosphere, was placed a mole of ferrocene. The bottle was sealed with rubber lined crowned cap enclosure and the metalating agents were added by means of hypodermic syringes in a Vacuum Atmosphere Dry Box and the bottle was then placed in a constant 70° bath with agitation for the desired reaction time. The metalated ferrocene, which was insoluble in hexane, was then separated by decantation and washed several times with dry hexane in an inert atmosphere. The unreacted ferrocene was isolated from the combined washes and the mother liquor.

Deuterium derivatives of metalated ferrocene

Ferrocene 18.6 g (0.10 mole) was metalated in 200 cc of hexane by treatment with 250 ml (0.40 mole) n-butyllithium in hexane (14.98%) at 70° for four days. The bottle was cooled to room temperature and a brown solid settled to the bottom. The supernatant liquid gave upon evaporation 6.40 g (34.4%) of unreacted ferrocene, the dark brown pyrophoric precipitate was suspended in 200 ml hexane, cooled to −20° and treated with 10 increments of 1 cc of deuterium oxide. There was a rapid evolution of gas. The solvent was evaporated under vacuum at room temperature on a rotary evaporator. Deuterated ferrocenes (10.2 g, 83.6% yield based on reacted ferrocene) were recovered by sublimation. Metalation of ferrocene employing eight equivalents of n-butyllithium in the above reaction, gave essentially the same yield. Similar results were obtained when either hexane or benzene were used as solvents.

Metalation of ferrocene in the presence of chelating diamine N,N,N′,N′-tetramethylethylenediamine (TMEDA)

Ferrocene 18.6 g (0.10 mole) was metalated in 500 ml of hexane containing 1.0 mole of n-butyllithium and 0.75 mole of TMEDA at 70° for 5 h. The dark pyrophoric reaction mixture was cooled to −20° and hydrolyzed cautiously with incremental addition of deuteroacetic acid or deuterium oxide. The solvent was evaporated and deuterated ferrocene was recovered from the residue by sublimation; 17.50 g (93.50% yield). The deuterated ferrocene was examined by mass spectroscopy. The results are tabulated in Table 1.

Trimethylchlorosilane derivatives of metalated ferrocene

Metalated ferrocene prepared as above in the absence of TMEDA was treated with 135 cc of chlorotrimethylsilane at −20°, then warmed to 50° and kept at this temperature for 12 h. The resulting product was largely an intractable, insoluble polymer of ferrocene. Metalated ferrocene, prepared in the presence of 0.25 mole of TMEDA per mole of butyllithium, when treated in the same manner with chlorotrimethylsilane, was extracted with ether. The ether extract was evaporated to give 24 g of red oil from which red crystals deposited on standing. These red crystals (I), m.p. 164.5–165.0, were identified by mass spectrum, NMR and IR as tetrakis(trimethylsilyl)ferrocene. (Found: C, 55.52; H, 8.97; Fe, 11.58; Si, 23.3. $C_{22}H_{42}FeSi$ calcd.: C, 55.71; H, 8.86; Fe, 11.77; Si, 23.63%.) The IR spectrum showed absorption at 12.0 μ C–Si, and 3 medium bands between 10.7 and 10.9 μ (substituted ferrocene), consistent with the above structure. Examination of the crude red oil by mass spectroscopy indicated the presence of a mixture of substituted ferrocenes containing from 1 to 7 trimethylsilyl groups per ferrocene.

All mass spectra were obtained on an MS9, Electronics Industries, Ltd., High Resolution Spectrometer at the Mellon Institute. The NMR spectra were obtained on a DA501 Varian Spectrometer.

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