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Ferrocene Compounds. XVIII*. Synthesis of some 1,1'-Bis(ureidomethyl)ferrocene Derivatives

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Several 1,1'-ferrocenylenebiscarbinols (*2*) were prepared by reduction of the corresponding 1,1'-diacylferrocene (*1*; R = CH_3, C_6H_5, *p*-ClC_6H_4, and *m*-$CH_3C_6H_4$) with sodium borohydride. Condensations of the carbinols prepared with methyl isocyanate in boiling toluene gave α,α'-(1,1'-ferrocenylene)bis(*N*-ethyl-*N,N'*-dimethylurea) (*4a*) and α,α'-(1,1'-ferrocenylene)bis(*N*-arylmethyl-*N,N'*-dimethylureas) (*4b* – *4d*).

Addition of various hydroxylic compounds to alkyl or aryl isocyanates, giving the corresponding carbamates, is a well known reaction. Also, several ferrocenemethanol derivatives were converted by Lorkowsky and coworkers[1,2] into the expected ferrocenylmethyl *N*-alkyl/arylcarbamates.

However, we have already shown that the reactions of 1-ferrocenylethanol and α-arylferrocenemethanols with methyl isocyanate in boiling toluene gave exclusively *N*-(1-ferrocenylethyl)- and *N*-[aryl(ferrocenyl)methyl]-*N,N'*-dimethylureas.[3]

Depending on the reaction conditions, the conversion of 1,1'-ferrocenebismethanol with aryl isocyanates gave the corresponding biscarbamates, and a small amount of *N*-aryl-2-aza[3]ferrocenophane.[1] In the reaction of cyclohexyl isocyanate with the same carbinol, only the expected biscarbamate was produced.[2] Therefore, we have decided to investigate the interaction of methyl isocyanate with 1,1'-ferrocenylenebiscarbinols.

1,1'-Diacylferrocenes (*1*), which we prepared by Friedel-Crafts reactions of ferrocene, were reduced by sodium borohydride to biscarbinols *2a* – *2d*. Attempts to reduce

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* For Part XVII see ref. 3.

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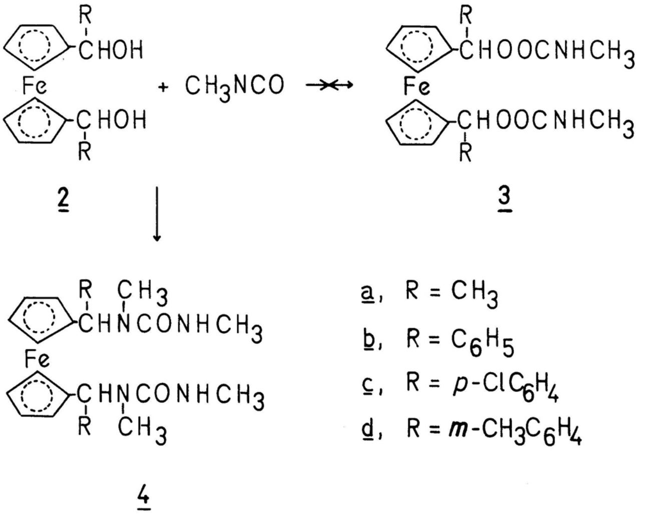
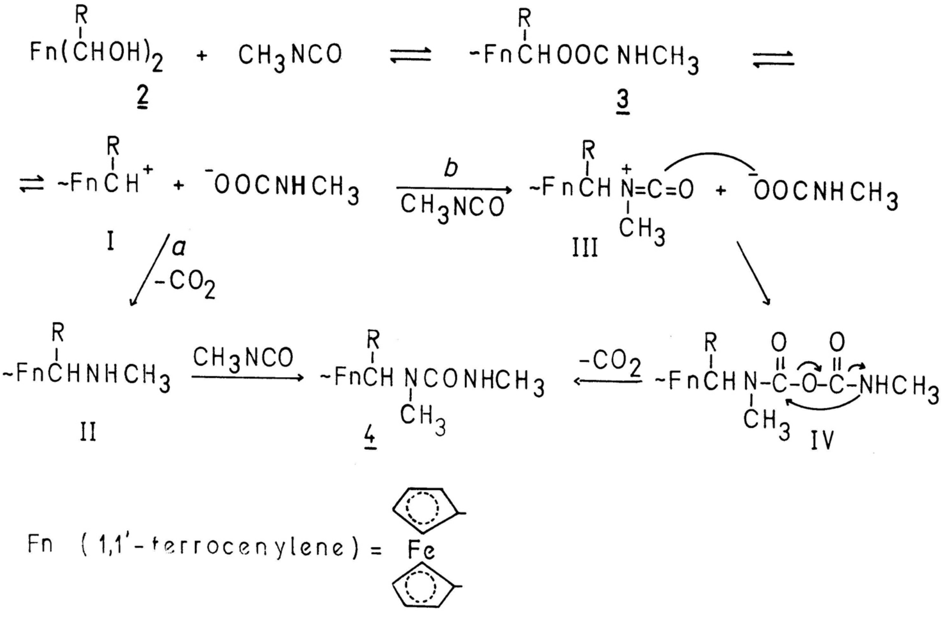
1b (see Table I) were unsuccessful, probably for sterical reasons. The reaction of *1e* with $NaBH_4$ gave dark decomposition products. Reactions of biscarbinols prepared with an excess of methyl isocyanate in boiling toluene gave 21–59% of substituted 1,1'-bis(ureidomethyl)ferrocenes (*4a–4d*). Under these conditions, no formation of biscarbamates *3* or of the corresponding 2-aza- or 2-oxa[3]ferrocenophane was observed. (TLC of the reaction mixtures showed, besides ureas *4* only dark peaks near the start line, representing the decomposition products, which couldn't be characterized by spectroscopic means).



SCHEME I

This course of reaction may be interpreted by one of the processes depicted in Scheme 2. Formation of amines *II*, which are intermediates for ureas *4*, is possible only *via* the α-ferrocenylcarbonium ions *I*, but such species can be formed from ferrocenylcarbinols only in the presence of an acid.[4] Since the reactions of carbinols with methyl isocyanate were performed in pure toluene, we suggest that there was an initial formation of carbamates *3*, which could be heterolytically cleaved in an uncatalyzed reaction to give carbonium ion *I*, and carbamate anion. This anion could undergo decarboxylation and the amine ions formed would then react with *I* to give the secondary amines *II*, which would finally give ureas *4* (route *a*). In an alternative pathway *b*, *I* could react with isocyanate to give *III* which would add carbamate anion to give mixed anhydrides *IV*, which could then be decarboxylated to give ureas *4*.

Consequently the stability of α-ferrocenylcarbonium ions, further enhanced by the presence of α-aryl/alkyl substituents, enables cleavage of the initially formed carbamates, so that the reaction is driven towards formation of ureas. The tendency to this heterolytical cleavage is so great, that even by using the starting reactants in ratio 1:2, which ought to result in formation of biscarbamates *3*, ureas *4* could be isolated, though in lower yields, as unique products.



SCHEME II

TABLE I

Physical constants and spectral data for $1,1'\text{-}C_{10}H_8Fe(COR)_2$ (1)

Compd.	R	*m.p.*	Yield	^{1}H NMR spectra					IR spectra
		°C	%	Aromatic protons			Ferrocene protons		$\bar{\nu}$(C=O)/cm^{-1}
1a[5]	C_6H_5	97–101	72	7.73 (4,m)		7.47 (6,m)	4.90 (4,m)	4.56 (4,m)	1630 s
1b[6]	*o*-ClC_6H_4	150–153	76		7.39 (8,m)		4.82 (4,t)	4.69 (4,t)	1640 s
1c[7]	*p*-ClC_6H_4	172–175	68	7.77 (4,d)		7.51 (4,d)	4.86 (4,m)	4.76 (4,m)	1620 s
*1d**	*m*-$CH_3C_6H_4$	83–84	69	7.73 (4,m)		7.52 (4,m)	5.00 (4,t)	4.76 (4,t)	1625 s
*1e***	α-furyl	122–124	44	7.55 (2,m)	7.26 (2,d)	6.53 (2,d)	5.16 (4,m)	4.57 (4,m)	1615 s

**Anal.* for $C_{26}H_{22}FeO_2$ (M_r = 422.3): C 73.94, H 4.77%; found C 73.61, H 4.72%, CH_3 protons in ^{1}H NMR at 2.52 ppm (6,s).

***Anal.* for $C_{20}H_{14}FeO_4$ (M_r = 374.2): C 64.20, H 3.77%; found C 63.96, H 3.96%.

EXPERIMENTAL

The m.p.'s were determined with a Büchi apparatus and are uncorrected. The IR spectra ($\tilde{\nu}$/cm^{-1}) were recorded as KBr pellets with a Perkin-Elmer 257 grating Infrared Spectrophotometer. The ^{1}H NMR spectra of hexadeuterioacetone solutions, given in δ-values, were recorded on a Varian EM 360 Spectrometer with tetramethylsilane as internal standard.

All experiments were performed under argon.

1,1'-Diaroylferrocenes (*1a-1e*) were prepared by acylation of ferrocene using the standard methods[5,6] (Table I).

α,α'-(1,1'-Ferrocenylene)bisethanol (*2a*) and *α,α*'-(1,1'-ferrocenylene)bis(arylmethanols) (*2b-2d*) were obtained by reduction of diacylferrocenes (*1*) with NaBH$_4$ in boiling 2-propanol[8] (Table II).

α,α'-(1,1'-Ferrocenylene)bis(*N*-ethyl-*N,N'*-dimethylurea) (*4a*) and *α,α*'-(1,1'-ferrocenylene) bis-(*N*-arylmethyl-*N,N'*-dimethylureas) (*4b-4d*) were prepared as follows.

TABLE II

Physical constant and spectral data for 1,1'-$C_{10}H_8Fe(CHROH))_2$ (2)

Compd.	R	m.p.	Yield	^{1}H NMR spectra					IR spectra	
		°C	%	Aromatic protons	CHO	OH	Ferrocene protons	CH$_3$	$\tilde{\nu}$(OH) cm^{-1}	$\tilde{\nu}$(C–O) cm^{-1}
2a[8]	CH$_3$	105–106	72	—	4.54 (2,m)	3.81 (2,m)	4.13 (8,m)	1.37 (6,t)	3250 br	1217 m
2b[5]	C$_6$H$_5$	133–136	78	7.19 (10,m)	5.57 (2,s)	5.28 (2,d)	4.23 (8,m)	—	3275 br	1219 m
*2c**	*p*-ClC$_6$H$_4$	146–148	46	7.37 (8,m)	5.62 (2,d)	5.40 (2,t)	4.25 (8,m)	—	3240 br	1215 m
*2d***	m-CH$_3$C$_6$H$_4$	136–137	72	7.19 7.00 (6,m) (2,t)	5.58 (2,s)	5.28 (2,d)	4.22 (8,m)	2.29 (6,s)	3270 br	1216 m

* *Anal.* for $C_{24}H_{20}Cl_2FeO_2$ (M_r = 467.2): C 61.70, H 4.32%; found C 61.95, H 4.31%
***Anal.* for $C_{26}H_{26}FeO_2$ (M_r = 426.2): C 73.25, H 6.15%; found C 73.05, H 5.98%

TABLE III

Yields, analyses and melting points of 1,1'-$C_{10}H_8Fe(CHR\text{-}NCH_3\text{-}CONHCH_3)_2$ (4)

Compd.	R	Formula (M_r)	m.p.	Yield	Analysis [calc'd. (found)/%]		
			°C	%	C	H	N
4a	CH$_3$	$C_{20}H_{30}FeN_4O_2$ (414.3)	78–80	21	57.95 (57.58)	7.30 (7.42)	13.52 (13.90)
4b	C$_6$H$_5$	$C_{30}H_{34}FeN_4O_2$ (538.5)	206–207	43	66.91 (67.30)	6.37 (6.22)	10.41 (11.89)
*4c**	*p*-ClC$_6$H$_4$	$C_{30}H_{32}Cl_2FeN_4O_2$ (607.4)	211–213	59	59.32 (59.11)	5.31 (5.48)	9.32 (9.42)
4d	*m*-CH$_3$C$_6$H$_4$	$C_{32}H_{38}FeN_4O_2$ (566.5)	172–174	39	67.84 (67.32)	6.76 (6.49)	9.89 (10.31)

**Anal.* for Cl: Calc'd. 11.68; found 11.39%

A solution of 1 mmol of the appropriate biscarbinol *2* and 4–5 mmol of methyl isocyanate in 5–10 mol of toluene abs. was refluxed for 2 hours, the progress of the reaction being monitored by thin layer chromatography. The mixture was left aside for 48 hours then either crystals, which had separated, were filtered off or the reaction mixture was evaporated to dryness (recrystallization from hexane or purification by TLC) (Tables III, IV).

TABLE IV

The spectral data of $1,1'$-$C_{10}H_8Fe(CHR$-NCH_3-$CONHCH_3)_2$ (4)

Compound.*	^{1}H NMR spectra							IR spectra		
	Aromatic protons	CH	NH	Ferrocene protons	$NHCH_3$	NCH3	CCH_3	$\bar{\nu}$(N–H) cm^{-1}	$\bar{\nu}$(C–H) cm^{-1}	$\bar{\nu}$(C=O) cm^{-1}
4a	–	5.67 (2,q)	6.10 (2,bm)	4.16 (8,m)	2.72 (6,d)	2.89 (6,s)	1.48 (6,d)	3300 s	2970 w 2930 w	1673 s
4b	7.23 (10,m)	6.75 (2,q)	5.87 (2,bm)	4.26 (8,m)	2.75 (6,d)	2.69 (6,s)	–	3340 m	2920 m 2880 m	1625 s
4c	7.18 (8,m)	6.75 (2.s)	5.81 (2,m)	4.25 (8,m)	2.75 (6,d)	2.69 (6,s)	–	3310 m	2915 w	1620 s
4d	7.01 (8,m)	6.68 (2,d)	5.85 (2,m)	4.21 (8,m)	2.72 (6,d)	2.67 (6,s)	2.23 (6,d)	3340 s	2910 m 2850 m	1620 s

* The structures of the ureas prepared are presented in Table II.

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REFERENCES

1. H.-J. Lorkowski and P. Kieselack, *Chem. Ber.* **99** (1966) 3619.
2. P. Kieselack and H.-J. Lorkowski, *J. Prakt. Chem.* **312** (1970) 989.
3. S. Kovač and V. Rapić, *J. Organomet. Chem.* **384** (1990) 147.
4. M. Cais, *J. Organomet. Chem.* **1** (1966) 435.
5. M. Rausch, M. Vogel, and H. Rosenberg, *J. Org. Chem.* **22** (1957) 903.
6. V. Rapić, K. Schlögel, and B. Steinitz, *J. Organomet. Chem.* **94** (1975) 87.
7. R. Riemschneider and D. Helm, *Liebigs Ann. Chem.* **646** (1961) 646.
8. E. C. Winslow and W. Brewster, *J. Org. Chem.* **26** (1961) 2982.

SAŽETAK

Priprava nekih derivata 1,1'-bis(ureidometil)ferocena

Spomenka Kovač i Vladimir Rapić

Redukcijom 1,1'-diacilferocena (*1*; R = CH_3, C_6H_5, *p*-ClC_6H_4 i *m*-$CH_3C_6H_4$) natrij-bor-hidridom pripravljeni su odgovarajući 1,1'-ferocenilenbiskarbinoli (*2*). Kondenzacijom dobivenih karbinola s metil-izocijanatom u vrijućem toluenu nastaju α,α'-(1,1'-ferocenilen)bis(*N*-etil-*N,N'*-dimetilurea) (*4a*) i α,α'-(1,1'-ferocenilen)bis(*N*-arilmetil-*N,N'*-dimetilureje) (*4b-4d*). Razmotren je mehanizam nastajanja tih urea.