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BASE-DEPENDENT STEREOSELECTIVITY IN REACTIONS OF ACYL LIGAND IN PHENYLACETYLIRON COMPLEX $(\eta^5\text{-}C_5H_5)Fe(CO)(PPh_3)(COCH_2Ph)$

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*Summary: Alkylation of the anion **4** is only little stereoselective and leads to mixtures of stereoisomeric products **5A,B-9A,B**. Proportion of stereoisomers depends strongly on the base employed. Condensation with acetaldehyde or benzaldehyde leads to four stereoisomeric products **11C-F** and **12C-F**, proportion of which depends also on the bases used.Decomplexation leads in the case of alkylated products to bromides **13**, and in the case of aldol product **11** to bromohydrin **14** and epoxides **15** and **16**.*

Since the first elaboration of the acetyl ligand in acetyliron $[(\eta^5\text{-}C_5H_5)Fe(CO)(PPH_3)(COCH_3)]$(1) *via* reactions of the anion **2** with many electrophiles[1,2], different kinds of acyl ligands, especially aliphatic acyl[3], α-alkoxyacetyl[4,5], and α,β-unsaturated acyl[6] attached to the $(\eta^5\text{-}C_5H_5)Fe(CO)(PPh_3)$ moiety were carefully studied. Up to now, no research has been reported on reactions of α-arylacyliron complexes. In view of interesting properties of aromatic substituents and because of importance of these ligands in synthetic organic chemistry we undertook the study phenylacetyliron complex $[(\eta^5\text{-}C_5H_5)Fe(CO)(PPh_3)(COCH_2Ph)]$(3)[7]. This research provided new results which substantially expand our knowledge on acyliron complexes.

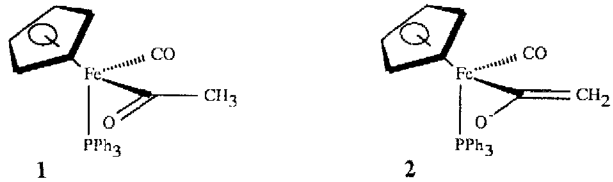
Complex *3* forms air-stable, well-shaped orange crystals. X-ray structural investigation of **3**[8] proved that the molecule adopts the typical pseudooctahedral arrangement[9].

Deprotonation of **3** with strong bases such as n-butyl lithium, t-butyl lithium, or lithium diisopropylamide (LDA)in THF solution at -78° led to a dark-red solution of the enolate **4** which could be deuterated with deuterium oxide or alkylated with alkyl halides in very good yields (75-97%). The ^{1}H NMR spectra of the products **5-9** obtained showed that both stereoisomers were formed with only little stereodiscrimination. The low stereoselectivity was surprizing because alkylation reactions of all monosubstituted acyliron complexes studied up to now were highly stereoselective[3-6].

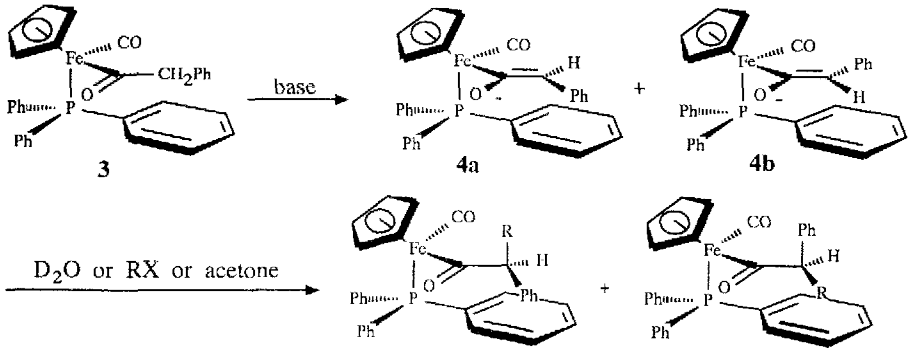
An another and even more interesting observation was that the diastereoisomeric proportions were determined by bases employed for deprotonation of **3** (Table 1). To the best of our knowledge this is the first report on the stereoselectivity induced just by different achiral bases.

The proportion of diastereoisomers was not influenced by the alkylating reagents used. This observation suggests that there is no equilibrium between E- and Z-enolates **4a** and **4b** at -78°. A similar result was also obtained from the reaction of the enolate with acetone (Table 1).

The reaction of the lithium enolate **4** with acetaldehyde or benzaldehyde at -78° led to all four



1 **2**



A **B**

5	R= -D
6	-Me
7	-Et
8	-All
9	-Bzl
10	$-CMe_2(OH)$

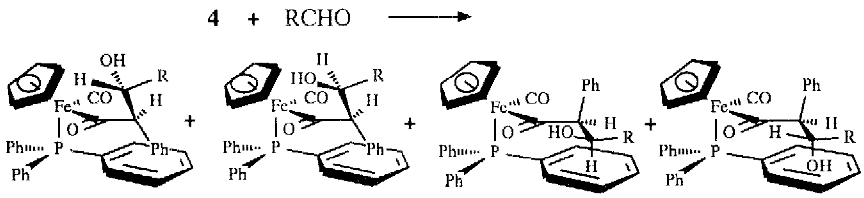
Table 1. Deuteration and alkylation product proportions in relation to bases used for deprotonation

Electrophile	Products	Bases and product proportions		
Reaction temp. -78C°		LDA	t-BuLi	n-BuLi
D_2O	**5A : 5B**	1 .0 : 2 .4		5 .2 : 1 .0
MeI	**6A : 6B**	1 .0 : 2 .4	1 .6 : 1 .0	6 .3 : 1 .0
EtBr	**7A : 7B**	1 .0 : 2 .4	1 .6 : 1 .0	3 .5 : 1 .0
AllBr	**8A : 8B**	1 .0 : 1 .8		6 .4 : 1 .0
BzlBr	**9A : 9B**	1 .0 : 2 .3	1 .4 : 1 .0	8 .2 : 1 .0
Acetone	**10A : 10B**	1 .0 : 3 .2		6 .2 : 1 .0

diastereoisomeric products, **11C-11F** (70-93%) and **12C-12F** (81-92%), in proportions shown in Tables 2 and 3. It is evident that bases were again important in determining the product proportions. But the ratios of products having the same configuration at α-carbon atom, (C+D):(E+F), were different from those of the alkylation reaction (Tables 2 and 3). These results point at different stereoselectivities involved in alkylation and aldol condensation reactions of phenylacetyliron complex.

Treatment of a THF solution of the lithium enolate **4** with two equivalents of tin dichloride[10] or five equivalents of diethylaluminum chloride[11] for one hour at -78° resulted in transmetallation characterized by a significant lightening of the color of the solution. Addition of of the same aldehydes to the transmetallated enolates led to the predominant formation of one stereoisomer (Tables 4 and 5). The influence of countercations on the formation of products having the same α-carbon atom configuration was even more pronounced.

The stereochemistry of both alkylation and aldol condensation products **5-12** was deduced from their ^1H



	C	D	E	F
11	R=Me	Me	Me	Me
12	R=Ph	Ph	Ph	Ph

Table 2. Product proportions of reaction between lithium enolate **4** and acetaldehyde in relation to bases

Base	reaction temp.	11C	11D	11E	11F	(11C+11D):(11E+11F)
LDA	-78°C	1.0	4.4	5.4	10.8	1.0 : 3.0
t-BuLi	-78°C	1.0	16.1	7.6	10.6	1.0 : 1.1
n-BuLi	-78°C	1.0	12.4	4.4	2.3	2.0 : 1.0

Table 3. Product proportions of reaction between lithium enolate **4** and benzaldehyde in relation to bases

Base	reaction temp.	12C	12D	12E	12	(12C+12D):(12E+12F)
LDA	-78°C	1.3	1.0	5.5	2.4	1.0 : 3.5
t-BuLi	-78°C	1.0	2.4	4.3	1.4	1.0 : 1.7
n-BuLi	-78°C	1.0	3.3	2.7	1.1	1.2 : 1.0

Table 4. Product proportion of reaction between **4** and acetaldehyde in relation to bases and cations

Base + cation	11C	11D	11E	11F	(11C+11D):(11E+11F)	Major prod.
LDA + $SnCl_2$	5.2	1.0	2.4	1.2	1.7 : 1.0	**C**
n-BuLi + $SnCl_2$	20.6	7.1	1.0	1.8	9.9 : 1.0	**C**
LDA + Et_2AlCl	1.0	0.1	11.6	1.8	1.0 : 12.5	**E**
n-BuLi + Et_2AlCl	1.0	0.1	6.4	2.7	1.0 : 8.3	**E**

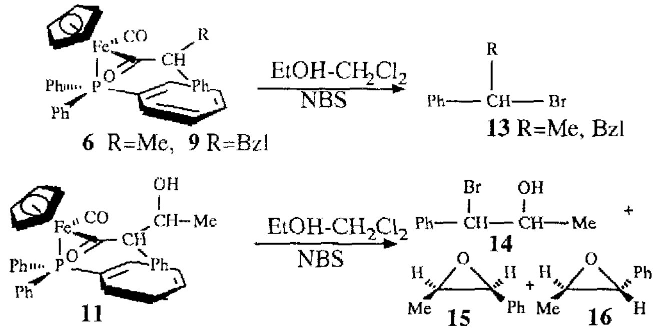
Table 5. Product proportion of reaction between **4** and benzaldehyde in relation to bases and cations

Base + cation	12C	12D	12E	12F	(12C+12D):(12E+12F)	Major prod.
LDA + $SnCl_2$	20.7	42.9	2.0	1.0	21.2 : 1.0	**D**
n-BuLi + $SnCl_2$	4.8	58.0	2.4	1.0	18.5 : 1.0	**D**
LDA + Et_2AlCl	1.0	-	30.0	2.3	1.0 : 32.3	**E**
n-BuLi + Et_2AlCl	1.0	-	16.0	6.1	1.0 : 22.1	**E**

NMR spectra and from X-ray determination made for **10A**[12] and **11C**[12].

Decomplexation of the alkylation products **5** and **8** with N-bromosuccinimide in dichloromethane-ethanol (1:1) solution was connected with decarbonylation and led to bromides **13** (R=Me, Bzl) as major products (50-60%). Similar decomplexation of **11C** yielded bromohydrine **14** and epoxides **15** and **16**. Here again, decarbonylation preceded further transformations. No products similar to those obtained from decomplexation of aliphatic acyl[3,4] or alkoxyacyl[5,6] complexes were observed by 500 MHz ^1H NMR spectra of the post-reaction mixtures.

The results reported in this paper demonstrated for the first time the dramatic influence of the type of



base employed for the deprotonation of the acyl ligand in an acyliron complex on the proportion of diastereoisomeric products, the influence of the phenyl group in α-position on stereoselectivity of the reactions and on the results of decomplexation of the products.

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