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Regio- and stereoselective a^4-umpolung reactions of α,β-unsaturated esters to 1,6-dicarbonyl compounds by addition of enantiopure nucleophiles to racemic tetracarbonyl(η^3-allyl)iron(1 +) complexes

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Abstract

The nucleophilic addition of various enantiopure d^2-carbon nucleophiles (chiral enamines **1** or metalated imines **2** and silylketon derivatives **3**) to racemic planar chiral electrophilic tetracarbonyl(η^3-allyl)iron(1 +) complexes **5** proceeds with complete γ-regioselectivity and with kinetic resolution of complex **5**. Subsequent oxidative demetalation provides access to enantiomerically enriched (*ee* < 5–> 92%) 1,6-dicarbonyl compounds **7** in moderate overall yields (14–53%, four steps or 5–21%, five steps) and with retention of the (*E*)-double bond geometry with respect to the starting material **4**.

Keywords: Iron; Tetracarbonyl(η^3-allyl)iron(1 +) complex; Planar chirality; Allylic substitution; a^4-Umpolung; 1,6-Dicarbonyl derivatives; Asymmetric synthesis; Kinetic resolution

1. Introduction

Among the various methods for allylic substitution reactions, transition metal promoted or catalysed procedures appear most suitable to achieve this goal with high chemo-, regio- and stereoselectivity. Accordingly, complexes containing allyl ligands which act as stabilised carbocation equivalents have been of particular synthetic interest owing to their enhanced reactivity towards nucleophiles [1–6]. Alkyl- and aryl-substituted tetracarbonyl(η^3-allyl)iron(1 +) complexes are known to undergo preferential regioselective nucleophilic attack at the less substituted allyl terminus by a variety of soft carbon and heteroatom nucleophiles [7]. In early studies directed towards the use of diastereo- and enantiomerically pure transition metal complexes in asymmetric synthesis we have shown that isolated acceptor-substituted (with acceptors such as CO_2R, $CONR_2$, COR, SO_2Ph, etc.) cationic (π-allyl)carbonyliron complexes in their diastereo- and enantiomerically pure form proved to be synthetically useful as intermediates in asymmetric and natural product synthesis [8]. Later, Green and coworkers [9] and Speckamp and coworkers [10] demonstrated likewise that in situ generated acceptor-substituted tetracarbonyl(η^3-allyl)iron(1 +) complexes undergo facile addition reactions with several soft nucleophiles, generally to provide allyl coupled products in a stereoselective (retention of double bond geometry) and exclusively γ-regioselective manner after oxidative removal of the stabilizing $Fe(CO)_4$ fragment. A general use of these iron complexes as a synthetic equivalent of a^4-synthons for the homologous (1,5)-Michael addition [11] is of interest both as a form of umpolung [12] of classical d^4-chemistry and as a synthetic method of considerable potential. Chiral 1,6-dicarbonyl compounds **A** can be disconnected retrosynthetically to the enantiopure carbon nucleophiles **B** (representing chiral d^2-synthons **D**) and to racemic ester substituted tetracarbonyl(η^3-allyl)iron complexes **C** rep-

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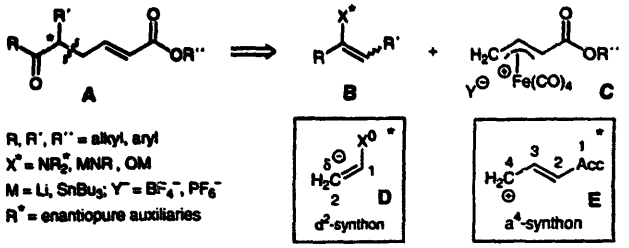
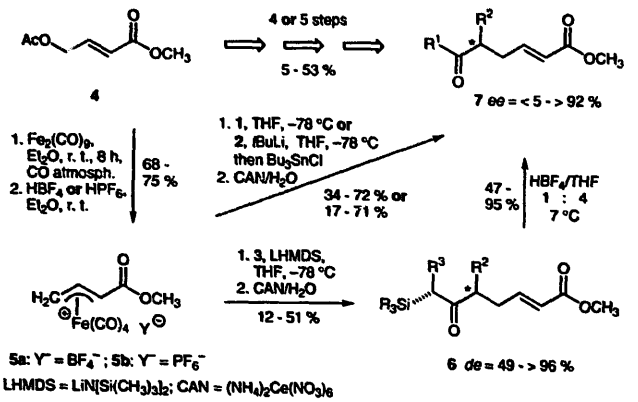


Fig. 1. Retrosynthetic analysis of 1,6-dicarbonyl compounds.

resenting the synthetic equivalents of a^4-synthons E (Fig. 1).



Scheme 1.

2. Results and discussion

We now wish to report on the regio- and stereoselective synthesis of enantiomerically enriched 1,6-dicarbonyl compounds **7** by means of kinetic resolution of racemic methoxycarbonyl-substituted tetracarbonyl(η^3-allyl)iron(1 +) complexes **5**, easily prepared from the enoate **4**. The key step of the synthesis is the C–C connective γ-regioselective addition of various enantiopure d^2-carbon nucleophiles, such as enamines **1**, metalated imines **2** and metalated α-silyl ketones **3** (Fig. 2) to the complexes **5** (Scheme 1).

The enamines **1** are easily prepared by acid catalysed azeotropic condensation of cyclohexanone with the enantiopure (*S*)-proline based auxiliaries [SMP: (*S*)-2-methoxymethyl)pyrrolidine, SDP: (*S*)-2-(1'-methoxy-1'-methylethyl)pyrrolidine, SEP: (*S*)-2-(1'-methoxy-1'-ethylproyl)pyrrolidine, SPP: (*S*)-2-(1'-methoxy-1',1'-diphenyl)pyrrolidine] [13]. Accordingly, the Schiff bases **2** were obtained by condensation of the corresponding ketones with the enantiopure amine (4*S*, 5*S*)-(+)-5-amino-2,2-dimethyl-4-phenyl-[1,3]-dioxane [(4*S*, 5*S*)-ADPD], which has been proved to be a synthetically useful chiral auxiliary in various asymmetric syntheses [14]. Virtually enantiopure (*ee* > 98%) symmetrically and unsymmetrically α-silylated ketones **3** can be prepared in both enantiomeric forms employing our established SAMP-/RAMP-hydrazone method [15]. In order to examine the steric influence of the silyl group both α-tert-butyldimethylsilyl and α-iso-propyldimethylsilyl ketones **3** were prepared.

As illustrated in Scheme 1, the reaction of the ester **4** [16] with excess diironnonacarbonyl [$Fe_2(CO)_9$] under an atmosphere of carbon monoxide initially yields the neutral methoxycarbonyl-substituted tetracarbonyl(η^2-olefine) iron complex [17], which is directly converted without isolation to the corresponding tetracarbonyl (η^3-allyl)iron(1 +) salts **5a** and **5b** by treatment with excess anhydrous tetrafluoroboric acid (→ **5a**) or anhydrous hexafluorophosporic acid (→ **5b**) in diethylether (68–75%) respectively [18]. The complexes were isolated as pale yellow powders, which were moderately stable to air and moisture and could be used without further purification [19]. The nucleophilic additions were carried out by adding between 1.0 and 2.0 equivalents of the appropriate nucleophilic species to a suspension of 1.0 equivalent of the complexes **5a** or **b** in THF at −78°C and warming the reaction mixture to room temperature. Oxidative cleavage of the ironcarbonyl fragment with excess aqueous ceric ammonium nitrate solution afforded, after work up and purification by column chromatography on silica gel, the 1,6-dicarbonyl compounds **6** or **7** as pale yellow to colourless liquids [20].

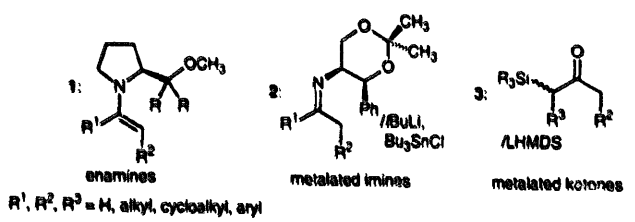


Fig. 2. Chiral nucleophiles.

The first test series was carried out by the addition of the enantiopure enamines **1** to the complexes **5** (Table 1). As expected and rationalised from the sign of optical rotation of the addition product **7a**, in all cases the newly generated stereogenic centre possesses the same absolute configuration independent of the chiral auxiliary. The enantiomeric excesses of the reaction products **7a** are in line with the steric bulk of the substituents of the pyrrolidine ring in **1** increasing in the order R = H (*ee* = 34%), R = Me (*ee* = 64%), R = Et (*ee* = 72%). However, no product could be obtained from the reaction of nucleophile **1d** (R = Ph) with the complexes **5**. Table 1 summarizes the results of the reaction of the (*S*)-proline derived enamines of cyclohexanone **1** with the electrophilic cation complexes **5**.

In addition, the reaction of various metalated Schiff bases **2a–d** was examined. The usual optimisation tests

Table 1
Addition of proline based chiral enamines **1a–d**

Nucleophile	R	Product	R^1	R^2	Yield[%] [a]	*ee*[%] [b]
(*S*)-**1a**	H	**7a**	$-(CH_2)_4-$		65	34
(*S*)-**1b**	Me	**7a**	$-(CH_2)_4-$		64	64
(*S*)-**1c**	Et	**7a**	$-(CH_2)_4-$		41	72
(*S*)-**1d**	Ph	**7a**	$-(CH_2)_4-$		— [c]	—

[a] Based on isolated material after column chromatography (GC > 97%). All products gave satisfactory spectroscopic data. [b] Determined by ^1H NMR shift experiment with [Eu(hfc)$_3$] (300 MHz). [c] No product could be isolated.

showed that best results were obtained when the imines were lithiated with ^{t}BuLi and the reaction was carried out in THF at −78°C (17–71%, *ee* = 40–67%). The yields and enantiomeric excesses could be improved by transmetalation with Bu_3SnCl to the corresponding stannylated imines. Other metals (M = Li, K, Bu_2B, 9-BBN, Me_3Si, Ph_3Si, Me_3Sn) or the Bu_4N^+ gegen ion, as well as chelating additives (HMPA, DMPU), proved to be synthetically less efficient. Variations of the ester functionality (CO_2R, R = ^{t}Bu, 1-naphthyl, 2-napthyl) of the complexes of type **5** showed no significant influence on chemical and optical yields of the addition reaction of the chiral Schiff base **2**. Table 2 summarizes the essential results of the reaction of different enantiopure metalated imines **2** with the electrophilic cation complexes **5**.

Lithiation of the acyclic α-silylated ketones **3b–f** with lithium hexamethyldisilazide (LHMDS) in THF at low temperatures yielded the appropriate lithium enolates as predominately (*Z*)-isomers [(*E*):(*Z*) < 4: > 96] as could be deduced from trapping experiments with trimethyl chlorosilane, while the lithium enolate of α-silylated cyclohexanone **3a** naturally possesses exclusively (*E*)-geometry. The addition of the enolates furnished diastereomeric mixtures (*de* = 49–> 96%) of α-silyl α-allylated ketone derivatives **6** in 15–51% yield after removal of the iron carbonyl group with ceric ammonium nitrate (Scheme 1, Table 3). The diastereomeric excesses could easily be determined by ^{13}C NMR spectroscopy. Fluoride induced desilylation of **6** to the 1,6-dicarbonyl compounds **7** under various conditions, e.g., TBAF/THF/H_2O [21], HF/CH_3CN [22], proved to be synthetically unattractive and gave rise to side reactions. Best results were obtained by desilyla-

Table 2
Addition of (4*S*, 5*S*)-ADPD based metalated chiral imines **2a–d**

Nucleophile	M	Product	R^1	R^2	Yield[%] [a]	*ee*[%] [b]
(4*S*, 5*S*)-**2a**	Bu_3Sn	**7a**	$-(CH_2)_4-$		59	62
(4*S*, 5*S*)-**2b**	Li [c]	**7b**	$-(CH_2)_5-$		17	67
(4*S*, 5*S*)-**2b**	Bu_3Sn	**7b**	$-(CH_2)_5-$		71	62
(4*S*, 5*S*)-**2c**	Bu_3Sn	**7c**	^{n}Pr	Et	40	66
(4*S*, 5*S*)-**2d**	Bu_3Sn	**7d**	Ph	Me	20	40

[a] Based on isolated material after column chromatography (GC > 97%). All products gave satisfactory spectroscopic data. [b] Determined by ^1H NMR shift experiment with [Eu(hfc)$_3$] (300 MHz) or correlation of optical rotation. [c] Lithiated imine **2b** was not transmetalated with Bu_3SnCl.

Table 3
Addition of α-silylated α′-lithiated chiral enolates **3a–f**

Nucleophile	Product	R_3Si	R^3	R^2	Yield [%] [a]	*de* [%] [b]	Product	R^1	R^2	Yield [%] [a]	*ee* [%] [c]
(*R*)-**3a**	**6a** [d]	^{t}BuMe$_2$	$-(CH_2)_3-$		51	> 96	**7a**	$-(CH_2)_4-$		43	< 5 [e]
(*R*)-**3b**	**6b**	^{t}BuMe$_2$	Et	Et	31	84	**7c**	^{n}Pr	Et	47	92
(*S*)-**3c**	**6c**	^{t}BuMe$_2$	^{n}Bu	Et	15	60	**7e**	Pent	Et	52	53
(*S*)-**3d**	**6d**	^{t}BuMe$_2$	Bn	Et	26	84	**7f**	$BnCH_2$	Et	35	78 [e]
(*S*)-**3e**	**6e**	^{i}PrMe$_2$	Bn	Et	29	49	**7f**	$BnCH_2$	Et	95	47
(*S*)-**3f**	**6f**	^{i}PrMe$_2$	Bn	^{i}Pr	12 [f]	65	**7g**	$BnCH_2$	^{i}Pr	92	66

[a] Based on isolated material after column chromatography (GC > 97%). All products gave satisfactory spectroscopic data. [b] Determined by ^{13}C NMR spectroscopy (75 MHz). [c] Determined by ^1H NMR shift experiments with [Eu(hfc)$_3$] (300 MHz) or correlation of the optical rotations. [d] Absolute configuration could be assigned as (5*S*, 7*R*). [e] Complete racemisation occurs during prolonged desilylation. [f] Accompanied by desilylated product **7g** (19%).

tion with a HBF_4/THF mixture (1 : 4). Unfortunately, the TBDMS derivatives **6a–d** do not only suffer from significant racemisation ($ee < 5 -> 92\%$) during the desilylation reaction but also from poor chemical yields (35–52%) [23]. The DMIPS-ketones **6e,f** ($de = 49$, 65%) are readily desilylated (92–95%, Table 3) to **7f,g** without remarkable loss of stereochemical purity ($ee =$ 47, 66%). In summary, the resulting enantiomeric excesses of **7** are only slightly higher than those obtained by the alternative route employing the enamines **1** or metalated imines **2**. Table 3 summarizes the results obtained for the addition of lithiated α-silylketones **3**.

The enantiomeric excesses of the reaction products **7** thus obtained are generally in line with the increase in steric bulk of the nucleophile, e.g. the enamines **1** (Table 1). In contrast, the chemical yields of 1,6-dicarbonyl compounds **7** conflict with increasing enantiomeric excesses. The results presented support the assumption that the planar chiral tetracarbonyl(η^3-allyl)iron(1 +) complexes **5** are effectively kinetically resolved by the predominant reaction of the enantiopure carbon nucleophiles **1–3** with one of the enantiomers of the iron complexes **5**, as has previously been reported in the literature for similar systems [24]. Extensive NMR studies (NOE, COSY, HETCOR experiments and conformational analysis of the cyclohexanone ring system) of the addition product **6a** demonstrated a *trans* relative configuration with respect to the silyl group, where the silyl group occupies an axial and the butenoic acid ester fragment an equatorial position. In addition, the known (*R*)-configuration of the stereogenic centre bearing the silyl group allowed the assignment of the absolute configuration of the newly generated stereogenic centre to be (*S*), which is in full accord with the proposed reaction mechanism. The nucleophilic attack occurs *anti* to the $Fe(CO)_4$ fragment of **5** and *trans* relative to the sterically shielding silyl group of the enolate **3a** (Fig. 3).

The absolute configurations of the predominant enantiomers of the other addition products **7** could not be unambiguously assigned. Based on the assumption of a uniform reaction mechanism for the addition reaction and by comparison of the signs of optical rotation of the addition products **7**, we rationalized that the addition of the enamines **1** and metalated imines **2**, as well as the (*R*)-lithium enolates **3**, gave rise to (*S*)-configurated addition products, while (*S*)-lithium enolates would lead to the (*R*)-configuration at the newly generated stereogenic centre.

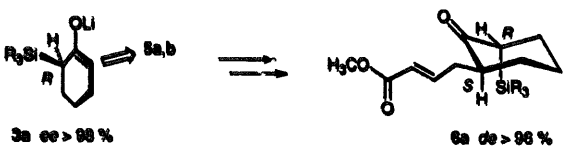


Fig. 3. Trajectory of the nucleophilic addition of **3a** to **5a** or **b** to yield **6a**.

In summary, we have shown that enantiomerically enriched 1,6-dicarbonyl compounds **7** can be prepared in moderate overall yields (5–53%) with enantiomeric excesses ranging from less than 5% to excellent (above 92%) by a kinetic resolution of the racemic planar chiral tetracarbonyl(η^3-allyl)iron(1 +) complexes **5** with enantiopure chiral d^2-carbon nucleophiles. More detailed investigations with regard to mechanistic aspects of this resolution process and extensions directed towards possible synthetic applications of this method are being investigated in our laboratories.

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[19] *Preparation of tetracarbonyl[(2-4-η^3-allyl)butenoic acid methylester]iron(1+) tetrafluoroborate* **5a** */ hexafluorophosphate* **5b**. According to literature procedures [17,18] 20 mmol (3.06 g) of the unsaturated 4-acetoxy methyl butenoate (**4**) [16] and 25 mmol (9.09 mg) diiron-nonacarbonyl [$Fe_2(CO)_9$] were placed under argon in a Schlenk flask and 200 ml anhydrous degassed diethyl ether was added. The suspension was saturated with carbon monoxide and the reaction mixture was stirred under an atmosphere of carbon monoxide with exclusion of light until the insoluble orange $Fe_2(CO)_9$ had been completely consumed (ca. 8 h). The resulting yellowish brown mixture was filtered over sea sand/Celite®. The residue was washed with diethyl ether until the filtrate was colourless. The clear yeliow filtrate was diluted with additional diethyl ether to give a total volume of 400 ml. A solution of 20 mmol anhydrous tetrafluoroboric acid (HBF_4) or alternatively hexafluorophosphoric acid (HPF_6) [freshly prepared by dehydration of 3.4 ml aqueous HBF_4 (48%) or 3.9 ml aqueous HPF_6 (60%) with 17 ml acetic anhydride at 0°C] was added dropwise with rapid stirring. The tetracarbonyl(π-ally)iron complex was obtained after precipitation, washing and drying in vacuo as a colourless moderately air stable solid (**5a**: 68%; **5b**: 75%). The complexes could be used without further purification. Analytically pure **5b** was obtained by fractional precipitation from a nitromethane solution with cold diethyl ether. Analytical data for **5b**. M.p.: 123°C (decomp.). ^{1}H NMR [200 MHz, CD_3NO_2, TMS(int)]: δ 3.73 (dd, $^3J(^1H-^1H) = 13.5$ Hz, $^2J(^1H-^1H) = 2.3$ Hz, 1H, C*H*H), 3.93 (s, 3H, OCH_3), 3.96 (d, superimposed, $J(^1H-^1H) = 10.5$ Hz, 1H, CO_2CH), 4.56 (dd, $^3J(^1H-^1H) = 7.5$ Hz, $^2J(^1H-^1H) = 2.3$ Hz, 1H, CH*H*), 6.49 (m, 1H, C*H*–CH_2) ppm. ^{13}C NMR [50 MHz, CD_3NO_2, TMS (int)]: δ 198.11, 197.61, 195.77, 195.46 (Fe–CO), 170.57 (CO_2), 102.46 (*C*H–CH_2), 60.69 (CH_2), 59.36 (CO_2CH), 54.55 (OCH_3) ppm. IR (CH_3NO_2, cm^{-1}): 2360, 2180, 2130, 2070, 2030 (Fe–CO), 1815, 1770, 1735 (CO_2), 1275, 1230, 1200, 1170, 1040, 960, 980, 860, 605, 575. Anal. Found: C, 26.07; H, 1.54. $C_9H_7F_6FeO_6P$ (M_r = 411.9) Calc.: C, 26.24; H, 1.71%.

[20] *General procedure for the reaction of the tetracarbonyl(η^3-allyl)iron(1+) complexes* **5a** *or* **5b** *with chiral enamines* **1** *or metalated imines* **2** *and silyl keton derivatives* **3**. For the addition of the enamines **1** a Schlenk flask was charged under argon with 3.0 mmol of complex **5a** or **5b** and the complex was suspended in 20 ml of anhydrous THF at −78°C. To the stirred suspension was added 3.5 mmol of the appropriate enamine **1** and the reaction mixture was warmed to room temperature (ca. 8 h). ^{t}BuLi (3.0 mmol) was added dropwise to a solution of 3.0 mmol of the corresponding imine **2** in 30 ml anhydrous THF at −78°C under argon. After 1 h at −78°C, 3.3 mmol of the appropriate transmetalating agent (e.g. Bu_3SnCl) was added neat or as a solution in anhydrous THF and stirring was continued. After 4 h, 3.0 mmol of the complexes **5a** and **5b** were added at this temperature and the reaction mixture was allowed to warm to room temperature (ca. 8 h). The α-silyl ketones **3** (3.0 mmol) were metalated at −78°C with a solution of 3.0 mmol lithiumhexamethyldisilazide (LHMDS) [freshly prepared from 3.0 mmol ^{n}BuLi and 3.5 mmol $HN(SiMe_3)_2$ in 50 ml anhydrous THF]. After 5 h the addition reaction of the lithium enolate to the iron complexes **5** was performed as described for the metalated imines. For the oxidative decomplexation, the reaction mixture was diluted with water (10 ml) and treated at 0°C with an excess of solid $(NH_4)_2Ce(NO_3)_6$ (ca. 4 equivalents) until the evolution of carbon monoxide had stopped and the solution has turned yellowish red. After extraction with CH_2Cl_2 or Et_2O and separation of the organic extracts, Fe^{III} ions were removed from the latter by successive washing with saturated aqueous NH_4F solution and finally with pH 7 buffer. The organic phase was dried ($MgSO_4$), concentrated under reduced pressure and the residue purified by column chromatography on silica gel (Et_2O, petroleum ether mixtures) to afford compounds **6** or **7** in spectroscopically pure

form. Desilylation of the allylated silyl ketone derivatives 6 was accomplished by treatment of a solution of 1.0 mmol of the α-silyl ketone 6 in 2 ml THF with 0.5 ml of aqueous HBF_4 (64%) at 0°C. The reaction mixture was placed in a refrigerator at 4°C and the reaction was monitored by thin layer chromatography. Upon complete conversion the reaction mixture was diluted with diethyl ether (50 ml), washed until neutral with pH 7 buffer and dried (Na_2SO_4). After evaporation of the solvents under reduced pressure, the residue was purified on by column chromatography on silica gel (Et_2O, petroleum ether mixtures) to yield the 1,6-dicarboryl compounds 7 in spectroscopically pure form.

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