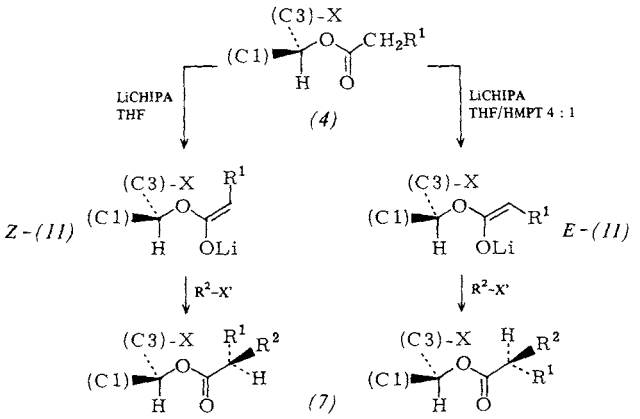

Scheme 1. Configurations of educt, intermediates and products in the asymmetric alkylation of the esters *(4)*.

The configurational relationships can all be explained on the basis of the following *hypotheses* (cf. Scheme 1):

1) According to *Ireland* and *Willard* the esters Alkyl-CH_2—COOR are deprotonated with lithium amides in THF preferably to *Z*-, in THF-HMPT (4:1) preferably to *E*-enolates (selectivity in each case $\geq 4:1$)[10]; thus, *Z*- or *E*-*(11)* can be generated selectively from *(4)*.

2) The conformation of the H—C—O—C—OLi group parallels that of the corresponding H—C—O—C=O group of esters[11] (torsional angle about the bold bonds $\cong 0°$).

3) Attack of the electrophile R^2—X at the enolate is blocked by the group X; that is in the case of *(11)* it takes place from the front side. Under otherwise equal conditions, therefore, *Z*- and *E*-enolates are alkylated to inversely configurated products.

4) The esters *(4)* and *(5)* as well as *(4)* and *(6)* are heterochiral[12] with respect to the X—C—$\dot{C}$H—O group ($\dot{C}$ = C-2 or C-3), and therefore under the same conditions give products with inverse configuration of the acyl group.

5) Inversely configurated products are also formed in the reactions of *(4)*—*(6)* with R^2—X' when $R^1 = R^a$, $R^2 = R^b$ and $R^1 = R^b$, $R^2 = R^a$ (cf. references cited in[9a]).

Other than in the case of the systems described in[9], complexation of the lithium by X in *(4)*—*(6)* does not seem to play an important role. This is supported by results obtained with esters of 2-aminoalcohols [*(1)*, X = *N*(alkyl)aryl; *N*-alkylephedrine] and 1,2-diols and their derivatives [*(1)*, *(2)*, X = *O*-alkyl and $O(CH_2)_2OCH_3$, 2,2'-binaphthol, *trans*-1,2-cyclohexandiol][13].

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CAS Registry numbers:
(4a) ($R' = CH_2Ph$), 76529-52-7; *(4a)* ($R' = CH_3$), 75817-71-9; *(4a)* ($R' = CH_2CHCH_2$), 76529-53-8; *(4a)* ($R' = nC_4H_9$), 76529-54-9; *(4a)* ($R' = nC_{16}H_{33}$), 76529-55-0; *(5a)* ($R' = CH_2Ph$), 76529-56-1; *(5a)* ($R' = CH_3$), 76529-57-2; *(5a)* ($R' = nC_{16}H_{33}$), 76529-58-3; *(4b)* ($R' = CH_3$), 76529-59-4; *(6b)* ($R' = CH_3$), 76529-60-7; *(R)-(7a)* ($R' = CH_2Ph$, $R^2 = CH_3$), 76529-61-8; *(S)-(7a)* ($R' = CH_3$, $R^2 = PhCH_2$), 76582-32-6; *(R)-(7a)* ($R' = CH_2Ph$, $R^2 = CH_2CHCH_2$), 76529-62-9; *(S)-(7a)* ($R' = CH_2CHCH_2$, $R^2 = PhCH_2$), 76582-33-7; *(R)-(7a)* ($R' = CH_2Ph$, $R^2 = nC_4H_9$), 76529-63-0; *(S)-(7a)* ($R' = nC_4H_9$, $R^2 = PhCH_2$), 76582-34-8; *(R)-(7a)* ($R' = CH_2CHCH_2$, $R^2 = CH_3$), 76529-64-1; *(S)-(7a)* ($R' = CH_3$, $R^2 = CH_2CHCH_2$), 76582-35-9; *(S)-(7a)* ($R' = CH_3$, $R^2 = iC_4H_9$), 76529-65-2; *(R)-(7a)* ($R' = nC_{16}H_{33}$, $R^2 = CH_3$), 75879-21-9; *(S)-(7a)* ($R' = CH_3$, $R^2 = nC_{16}H_{33}$), 75817-73-1; *(R)-(7a)* ($R' = CH_3$, $R^2 = iC_4H_9$), 76582-36-0; *(S)-(8a)* ($R' = CH_2Ph$, $R^2 = CH_3$), 76529-66-3; *(R)-(8a)* ($R' = CH_3$, $R^2 = PhCH_2$), 76582-84-8; *(S)-(8a)* ($R' = nC_{16}H_{33}$, $R^2 = CH_3$), 76529-67-4; *(R)-(8a)* ($R' = CH_3$, $R^2 = nC_{16}H_{33}$), 76582-37-1; *(S)-(7b)* ($R' = CH_3$, $R^2 = C_{14}H_{29}$), 76529-68-5; *(R)-(7b)* ($R' = CH_3$, $R^2 = nC_{14}H_{29}$), 76582-38-2; *(R)-(9b)* ($R' = CH_3$, $R^2 = nC_{14}H_{29}$), 76582-85-9; *(S)-(9b)* ($R' = CH_3$, $R^2 = nC_{14}H_{29}$), 76582-39-3

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[3] a) Preparation of the esters *(4a)* and *(5a)*: *R. Schmierer*, Dissertation, Universität Stuttgart 1980; b) preparation of the esters *(4b)* and *(6b)*: *G. Helmchen, G. Grotemeier, A. Selim*, unpublished.
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[6] a) Ethanol (95%), 0 °C, only applicable in the case of *(8a)*; b) the urethanes *(7a)* and *(8a)* yield 2,3-bornanediol; in the case of the sulfonamides *(7b)* and *(9b)*, *(1b)* and *(3b)* are reobtained.
[7] All the new compounds gave correct analyses and characteristic spectra.
[8] An example: *E. Ade, G. Helmchen, G. Heiligenmann*, Tetrahedron Lett. *1980*, 1137.
[9] a) *A. I. Meyers, E. S. Snyder, J. J. H. Ackerman*, J. Am. Chem. Soc. *100*, 8186 (1978); b) *K. G. Davenport, H. Eichenauer, D. Enders, M. Newcomb, D. E. Bergbreiter*, J. Am. Chem. Soc. *101*, 5654 (1979).
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[11] Cf. *G. Helmchen*, Tetrahedron Lett. *1974*, 1527; *L. Golka*, Dissertation, Universität Stuttgart 1980.
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[13] *G. Helmchen et al.*, unpublished results.

Selective Reduction of the Nitro to the Amino Functional Group by means of the Phthalocyaninecobalt (I) Anion; Synthesis of N-Heterocycles and Alkaloids

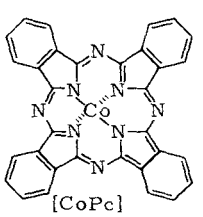
By *Heiner Eckert*[*]

The directed transformation of functional groups, while other functionalties with similar reaction specifity are retained intact, is one of the most frequently encountered problems in synthetic organic chemistry. The reduction of nitro to amino groups is the best route to the important aromatic amine class of compounds; it is however well known[1a] that this is often accompanied by reactions of other functional groups (C=C, >C=O, —C≡N, aryl halides)[1]. Under basic reaction conditions rearrangement products and products arising from *N*-coupling are often produced in considerable amounts[1a,2]. The reduction of unsaturated compounds in the presence of metallic macrocycles of the vitamin B_{12} structure type, although not with stable phthalocyaninemetal anions, has already been described[3].

Aromatic and aliphatic nitro compounds *(1)* can be reduced to primary amines *(2)* at room temperature using weakly basic conditions in protic solvents *e. g.* alcohols, in the presence of the phthalocyaninecobalt (I) anion $[Co^{I}Pc]^{\ominus}$. The reaction proceeds cleanly and selectively: the following functional groups do not react; arenes and aryl halides, C=C double bonds even when activated, cyanides and isocyanides, aldehydes and ketones, carboxylic acid esters and am-

$$O_2N\text{-}R\text{-}X \xrightarrow[MeOH]{6\,[Co^{I}Pc]^{\ominus}} H_2N\text{-}R\text{-}X$$

(1) *(2)*



$NC\text{-}(CH_2)_4\text{-}CN$ *(3)* $Ph\text{-}CH{=}CH\text{-}CO_2Et$ *(4)*

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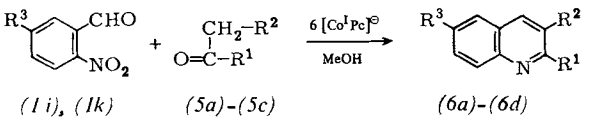
ides (see Table 1). The high yields, in particular with *(1g)* and *(1i)* which have a strong tendency to form side products, indicate the extremely high selectivity[4a] of the stable phthalocyaninecobalt (I) anion. Apart from its role in reduction reactions $[Co^{I}Pc]^{\ominus}$ only participates in substitution reactions[4a] with alkyl[4b] or acyl halides[4a]. Control experiments indicated that even at long reaction times, hexanedinitrile *(3)* and ethyl cinnamate *(4)* were not attacked by $[Co^{I}Pc]^{\ominus}$; only the transesterification of *(4)* was observed. Both the characteristic selectivity and reactivity parameter "supernucleophilicity relative to alkyl halides" ($n_{CH_3I} = 10.8$)[5a] and low reduction potential (−0.37 V)[5b] of the phthalocyaninecobalt(I)anion, have been determined in preliminary investigations of its mechanism of action[6] and for reduction processes.

Table 1. Selective reduction of nitro compounds *(1)*, which contain other reactive functional groups, to amines *(2)* by means of $[Co^{I}Pc]^{\ominus}$ at 20–25 °C in methanol.

	R	X	*t* [h]	Yield [%]
a		nC_3H_7	95	66
b		α-Naphthyl	48	70
c	C_6H_4	*p*-Cl	80	91
d	C_6H_4	*p*-F	26	63
e	C_6H_4	*p*-CH_2—CN	62	95
f	C_6H_4	*p*-NC	72	76
g	C_6H_4	*p*-CH=CH—CO_2Et	65 [a]	82
h	C_6H_4	*p*-CO—CH_3	90	78
i	C_6H_4	*o*-CHO	90	96

[a] EtOH as Solvent.

As a result of its high selectivity and mild conditions of reaction, this reduction method is highly suitable for use in the synthesis of *N*-heterocycles by the Friedländer reaction[7]. The nitroaldehydes *(1i)* or *(1k)* were reduced in this way in a one-pot reaction and, without being isolated, the sensitive aldehydes produced were condensed with the ketones *(5)*; it was therefore unnecessary to protect the reactive functional groups in the intermediates (Table 2). The synthesis of the alkaloid comptothecine *(9)* and its derivatives[8], which are powerful antitumor agents, was successfully carried out by condensing *(1i)* or *(1k)* with *(7)* to give the tetracyclic systems *(8a)* or *(8b)* respectively (A-B-C-D) with yields of 62 and 51% respectively; it is particularly noteworthy that *(7)* contains groups which can be further reduced. The classic, base catalyzed Friedländer reaction using freshly prepared *(2i)* and *(7)* proceeds in only 20% yield and leads to the formation of side products which are difficult to separate[8a].

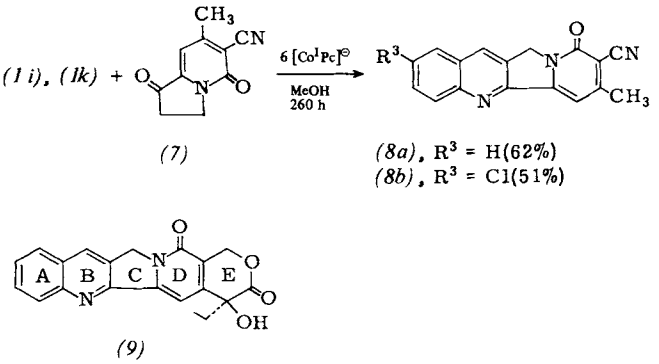


(1i), (1k) *(5a)-(5c)* *(6a)-(6d)*

Table 2. Synthesis of N-heterocycles *(6)* from nitro compounds using the onepot procedure in methanol at 20–25 °C.

Educts	R^1	R^2	R^3	*t* [h]	Products	Yield [%]
(1i) + *(5a)*	CH_3	H	H	63	*(6a)*	77
(1k) + *(5a)*	CH_3	H	Cl	160	*(6b)*	87
(1i) + *(5b)*	CH_3	CH_3	H	49	*(6c)*	71 [a]
(1i) + *(5c)*	C_6H_5	H	H	96	*(6d)*	88

[a] No isomeric 2-Ethylquinoline.



(7)

(8a), R^3 = H(62%)
(8b), R^3 = Cl(51%)

(9)

Procedure

(2): Under a nitrogen atmosphere, Li[CoPc]·4.5 tetrahydrofuran (THF)[9] (17–18 g, 19–20 mmol) is dissolved in 100 cm³ N_2-saturated methanol. The deep green solution is treated with 3.0 mmol *(1)* and stirred at 20–25 °C (Table 1). 10 cm³ H_2O is then poured into the reaction mixture, CO_2 and air passed in for 5 min and the mixture centrifuged to separate the deep blue precipitate (5 min; 3000 rpm) which is then washed twice with methanol. The combined centrifugates are then concentrated and the residue distributed between ether and water. The organic phase is dried over Na_2SO_4 and the solvent evaporated; compound *(2)* remains. For compound *(2a)* the mixture is not treated with H_2O, but with 50 cm³ of 1 N hydrochloric acid and centrifuged. The centrifugate is then made alkaline with NaOH and extracted with ether. The ether phase is extracted with 10 cm³ of 1 N hydrochloric acid and water and the combined aqueous extracts concentrated, by means of which *(2a)*·HCl remains.

(6): Under a N_2 atmosphere, Li[CoPc]·4.5 THF[9] (12–13 g, 13–14 mmol) is dissolved in 70 cm³ N_2-saturated methanol. The deep green solution is treated with an excess of *(6)* (*ca.* 50 mmol), 2.0 mmol *(1i)* or *(1k)* and stirred at 20–25 °C (see Table 2). Following this, 5 cm³ of H_2O is added to the green reaction mixture, CO_2 and air passed into the mixture for 5 min, before being centrifuged (5 min; 3000 rpm) from the deep blue precipitate, which is then washed once with ethanol and twice with ether. The combined centrifugates are concentrated, the still damp residue distributed between 0.5 N hydrochloric acid and hexane, and the hexane phase extracted twice with water. The combined aqueous phases are washed with hexane, neutralized with 5 N NaOH and extracted with ether. The ether extract is dried over KOH and concentrated; *(6)* remains behind.

(8a): Under a nitrogen atmosphere, Li[CoPc]·4.5 THF[9] (11.9 g, 13.2 mmol) is dissolved in 70 cm³ methanol which had been saturated with N_2. The deep green solution is treated with *(1i)* (302 mg, 2.0 mmol) and *(7)* (376 mg, 2.0 mmol)[8a] and stirred at 20–22 °C for 260 h. Following this, 5 cm³ H_2O is added to the reaction mixture, CO_2 and air passed in for 5 mins and the mixture then centrifuged (5 min, 3000 rpm) from the deep blue precipitate; the latter is washed with warm (50 °C) nitrobenzene (5 × 40 cm³). Further washing with methanol (3 × 40 cm³) and ether (2 × 40 cm³) and drying at 60 °C yields $Co^{II}Pc$ (7.35 g, 98%). Solvent is removed from the combined nitrobenzene centrifugates and the residue triturated in methanol and filtered. Yield 340 mg (62%) *(8a)*. M.p. = 340 °C (decomp.).

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CAS Registry numbers:
(1a), 108-03-2; *(1b)*, 86-57-7; *(1c)*, 100-00-5; *(1d)*, 350-46-9; *(1e)*, 555-21-5; *(1f)*, 619-72-7; *(1g)*, 953-26-4; *(1h)*, 100-19-6; *(1i)*, 552-89-6; *(1k)*, 6628-86-0; *(2a)*, 107-10-8; *(2b)*, 134-32-7; *(2c)*, 106-47-8; *(2d)*, 371-40-4; *(2e)*, 3544-25-0; *(2f)*, 873-74-5; *(2g)*, 5048-82-8; *(2h)*, 99-92-3; *(2i)*, 556-18-3; *(5a)*, 67-64-1; *(5b)*, 78-93-3; *(5c)*, 98-86-2; *(6a)*, 91-63-4; *(6b)*, 92-46-6; *(6c)*, 1721-89-7; *(6d)*, 612-96-4; *(7)*, 58610-63-2; *(8a)*, 66911-21-3; *(8b)*, 76529-26-5; Li[CoPc], 14516-90-6

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"Magnetochemical Series" for Lanthanoid Compounds[**]

By *Werner Urland*[*]

Dedicated to Professor Wilhelm Klemm on the occasion of his 85th birthday

Klemm was the first to make use of magnetic measurements to determine the "valence" of rare earth elements in compounds where this was not immediately apparent from their composition (*e.g.* $Ce^{IV}O_2$, $Ce^{III}S_2$)[1]. In this article it will be shown that magnetochemistry also enables statements to be made about the chemical bonding in lanthanoid compounds.

Powdered samples of NT-$CsTmO_2$[2a] (NT ≙ low temperature form), NT-$CsYbO_2$[2b], $CsAPrF_6$ (A = K, Rb)[2c], Cs_2AHoF_6 (A = Na,K, Rb)[2d], Cs_2LiTmX_6 (X = Cl, Br, I)[2e], Cs_2NaTmI_6[2e], Cs_2KTmX_6 (X = Cl, Br)[2f], $CsATmF_6$ (A = Na, K, Rb)[2f], Cs_2AYbF_6 (A = Na, K, Rb)[2g] and $Cs_2NaYbBr_6$[2g] were studied over the temperature range of 3–250 K using the Faraday method. Their magnetic behaviour could be explained applying a model of paramagnetism[3a] in which the influence of the crystal field was treated by the Angular Overlap (AO) model[3b]. The conventional crystal field parameters can be expressed in terms of the AO parameters, $e_\sigma(R)$ and $e_\pi(R)$, which are directly related to the σ- and π-covalent contribution to the chemical bonding and should be proportional to the square of the respective overlap integral[3b]. If it is assumed, on the basis of earlier investigations[4], that the value of the ratio, $e_\sigma(R)/e_\pi(R)$, lies between 2 and 6 for all the compounds considered here, then the values of $e_\sigma(R)$ for the alkali metal thulium halides can be determined unequivocally from measurements of the magnetic susceptibility. From these considerations, a ligand "magnetochemical series" can be drawn up. Table 1 shows values of $e_\sigma(R)$ compared with those of the overlap integrals $S_\sigma^2(R)$. The values of $S_\sigma^2(R)$ for the quaternary sodium compounds[2e,f] were calculated from[5] using the 4f-Er^{3+} and 4f-Yb^{3+} functions[6a] respectively, and the corresponding np-ligand function of X^-[6b] (for NT-$CsTmO_2$ of O^{2-}, 2p solution function for the +2 potential well[6c]) for the respective Tm^{3+}-ligand ion distance R. Then the average value was formed. Since the Hartree-Fock 5p-function for I^- could not be found in the literature, the calculation of the respective overlap integrals was not performed in this case.

Table 1. AO parameters $e_\sigma(R)$, overlap integrals $S_\sigma^2(R)$ and Tm^{3+} ligand ion distances R, for NT-$CsTmO_2$ and Cs_2NaTmX_6 (X = F, Cl, Br, I).

Compound	$e_\sigma(R)$ [cm^{-1}]	$S_\sigma^2(R)\cdot 10^4$	R [pm]	Ref.
NT-$CsTmO_2$	450 [a]	2.47	219.8	[2a]
Cs_2NaTmF_6	450 ± 10	2.36	217 [b]	[2f]
$Cs_2NaTmCl_6$	215 ± 10 [c]	0.81	269 [d]	[2e,f]
$Cs_2NaTmBr_6$	145 ± 8 [c]	0.60	284 [d]	[2e,f]
Cs_2NaTmI_6	125 ± 5	—	308 [d]	[2e]

[a] Without determination of the errors involved. [b] cf. [7]. [c] Average value, including the values for lithium and potassium compounds. [d] Sum of the ionic radii of Tm^{3+} and ligand ion for the coordination number 6: *R. D. Shannon*, Acta Crystallogr. *A 32*, 751 (1976).

With the exception of NT-$CsYbO_2$[2b] the unequivocal determination of $e_\sigma(R)$ from magnetic studies of this type did not prove possible for the remaining compounds. As an approximation a value of $e_\sigma(R)/e_\pi(R) = 3$ can be used for the halides[4a]. The values of $e_\sigma(R)$ for the ratio $e_\sigma(R)/e_\pi(R) = 3$ also allow the ligands to be arranged in a "magnetochemical series" (Table 2).

Table 2. AO parameters $e_\sigma(R)$ for $e_\sigma(R)/e_\pi(R) = 3$, overlap integrals $S_\sigma^2(R)$, and Yb^{3+}-ligand ion distances R for NT-$CsYbO_2$ and Cs_2NaYbX_6 (X = F, Cl, Br).

Compound	$e_\sigma(R)$ [cm^{-1}]	$S_\sigma^2(R)\cdot 10^4$	R [pm]	Ref.
NT-$CsYbO_2$	360 ± 30	2.18	219	[2b]
Cs_2NaYbF_6	360 ± 30	2.11	216	[2g]
$Cs_2NaYbCl_6$	252 [a]	0.72	267 [b]	[2g,8]
$Cs_2NaYbBr_6$	160 ± 10	0.59	278	[2g]

[a] For $e_\sigma(R)/e_\pi(R) = 1.62$. [b] *G. Meyer*, personal communication.

When the ligands are ordered according to increasing $e_\sigma(R)$ values, (cf. Tables 1 and 2), the following "magnetochemical series" arises:

$$I^- < Br^- < Cl^- < F^- \approx O^{2-}$$

Table 3. AO parameters $e_\sigma(R)$ for $e_\sigma(R)/e_\pi(R) = 3$, overlap integrals $S_\sigma^2(R)$ and M^{3+}—F^- distances R for Cs_2AMF_6 (A = K, Rb; M = Pr, Ho, Tm, Yb).

Compound	$e_\sigma(R)$ [cm^{-1}]	$S_\sigma^2(R)\cdot 10^4$	R [pm]	Ref.
Cs_2KPrF_6	720 ± 30	6.90	227 [a]	[2c]
Cs_2RbPrF_6	690 ± 30			
Cs_2KHoF_6	420 ± 30	2.88 [b]	219	[2d]
Cs_2RbHoF_6				
Cs_2KTmF_6	420 ± 10	2.36	217 [a]	[2f]
Cs_2RbTmF_6	390 ± 10			
Cs_2KYbF_6	360 ± 30	2.11	216 [a]	[2g]
Cs_2RbYbF_6				

[a] Cf. [7]. [b] Average value including functions for 4f-Dy^{3+} and 4f-Er^{3+} [6a].

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