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Regioselective α-arylation of *N*-vinylpyrroles by the Heck reaction

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N-Vinylpyrroles which became available from ketoximes and acetylene[1,2] have been used by as substrates in the Heck reaction (Scheme 1).

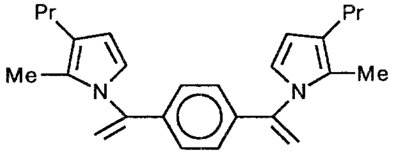
All of the experiments were carried out under conditions routinely used for Heck arylation (DMF as a solvent, NBu_3 as a base, $PdCl_2$ as a catalyst, 80 °C).

Unsubstituted *N*-vinylpyrrole was found to be the most reactive (Table 1, Entry *1*). As usual in the Heck reaction, β-*trans*-substitution (α/β = 30/70) dominates in this case. However, arylation of *N*-vinyl-2,3-dialkylpyrroles (see Table 1, Entries *2* to *7*) unexpectedly exhibits high regioselectivity toward the α-position of the vinyl group for different aryl iodides. This high percentage of α-arylation under the standard conditions of the Heck reaction has not been observed previously, and it was achieved in the arylation of vinyl ethers only when the halogen in the aryl halides was replaced by a triflate substituent.[3]

Table 1. *N*-Vinylpyrroles in the Heck reaction

Entry	R^1	R^2	Aryl halide	By-product	Rate, $w \cdot 10^{-3}$ /mol L^{-1} min^{-1}	α/β ratio*	Yield $\alpha+\beta$ (%)
1	H	H	PhI	Not found	9.4	30 : 70	100
2	Me	Me	PhI	Diphenyl	1.75	95 : 5	90
3	Me	Pr^i	PhI	Diphenyl	1.80	100 : 0	90
4	Me	Pr^n	PhI	Diphenyl	4.3	95 : 5	85.0
5	Me	Pr^n	p-C_6H_4IPh	Quaterphenyl	2.22	100 : 0	66.5
6	Me	Pr^n	p-$C_6H_4I_2$**	Not found	1.97	100 : 0	82
7	Ph	Pr^i	PhI	Diphenyl	1.23	100 : 0	83

* β-Products contained only the *trans*-isomer.

** 

This compound was obtained as the product.

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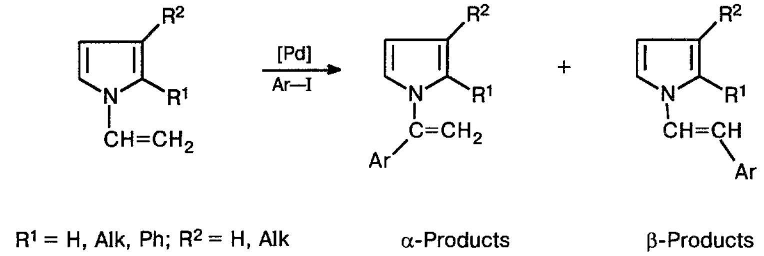
Scheme 1



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Metallomesogen with a large magnetic anisotropy

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The anisotropy of the electrical and magnetic features of liquid crystals determines their properties and behavior. The expected attractive features of metallomesogens of rare-earth elements are the large values of their magnetic moments, and, more important, their large magnetic anisotropy. Now we report the synthesis (analogous to that previously published[1]), measurements of static magnetic susceptibility in powders and solid melts, and the magnetic birefringence in solutions of mesogenic compounds $L(LH)_2M(NO_3)_2$, where LH is $C_7H_{15}O—C_6H_3(OH)—CH=N—C_{16}H_{33}$, and M is La^{3+}, Gd^{3+}, or Dy^{3+}. The composition was determined on the basis of elemental analysis. The following phase transition points (°C), mesophase types (determined using a polarization microscope and the DSC method), and magnetic susceptibilities (25 °C), (measured using the Faraday method) ($\chi_g \cdot 10^6$/cm^3 g^{-1}) are C 92 S_X 128 S_A 149 I (−0.7) for $L(LH)_2La(NO_3)_2$; C 128 S_A 146 I (15.9) for $L(LH)_2Gd(NO_3)_2$; C 140 S_A 142 I (29.6) for $L(LH)_2Dy(NO_3)_2$; where C is crystalline, S_A is smectic, and I is isotropic phase, respectively.

The magnetic susceptibilities of these compounds and their temperature dependences are typical of diamagnetic (La) and paramagnetic (Gd, Dy) lanthanides. Using the differences between the measured susceptibility (${}^c\chi_g \cdot {}^cm$) of the complexes and those expected[2] (${}^m\chi_g \cdot {}^mm$) for the metal ions (M) one can determine independently the number of ligands (n) in the $L_nM(NO_3)_2$ complex:

$${}^c\chi_g{}^cm = {}^m\chi_g{}^mm + n{}^L\chi_g{}^Lm,$$

where χ_g is the specific susceptibility, and m is its mass. The values $n \cong 3.1$ and 3.2 for Gd and Dy complexes, respectively, are in good agreement with the elemental analysis.

The measurements of magnetic birefringence of solutions of the complexes in CCl_4 demonstrates that this effect is not molecular (Cotton—Mouton effect) even for the minimum concentration of the complex (*ca.* $2 \cdot 10^{-4}$ *M*), but it results from the structurization of the solutions (formation of associates). Neglecting the pecu-

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