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PALLADIUM- AND NICKEL-CATALYZED ARYL- AND ACYL-DEMETALLATION OF ORGANOMETALLIC COMPOUNDS

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Summary

Various organometallic compounds obtained in situ from Grignard reagents or organolithiums were compared in reactions with aryl and acyl halides in the presence of transition metal complexes.

Transition metal-catalyzed cross coupling, discovered in 1972 in the reaction of Grignard reagents and organolithiums with aryl and vinyl halides [1], has subsequently been extended to include organic derivatives of zinc [2], aluminium [3], zirconium [4], tin [5], copper [6], mercury [7] and some other metals. In addition to cross-coupling products these reactions also involve homocoupling [6b,7]. It is interesting to compare the behaviour of various organometallic compounds under the same conditions when the metal, the organic group bonded to the metal, the electrophile and the catalyst are different. We carried out such a comparison for a number of organometallic compounds, RM (M = Li, Mg, Zn, Cd, Cu, B, Al, Sn, Hg, Ti) prepared in situ from Grignard reagents or organolithiums and the appropriate salts. *p*-Iodoanisole, benzoyl and *p*-nitrobenzoyl chlorides were used as electrophilic agents. Cross coupling was carried out in THF/ether at 0–20°C in the presence of $PdCl_2(PPh_3)_2$ or $PdCl_2(MeCN)_2$.

$$RM + R'X \xrightarrow{\text{"Pd"}} RR' + R_2 + R'_2 + MX \qquad (1)$$

To distinguish between cross- and homo-coupling products in equation 1 (R = Ph) *p*-iodoanisole was chosen. The reactions of p-$MeOC_6H_4I$ with the organometallic compounds under investigation, except PhZnCl and $AlPh_3$, show low selectivity, Table 1, and in addition to the cross-coupling product p-$MeOC_6H_4Ph$ give Ph_2 and $(p$-$MeOC_6H_4)_2$. The formation of the latter is likely to result from the exchange between RM and ArI. This exchange is catalyzed by transition metal complexes [8].

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TABLE 1

REACTIONS OF RM (0.55 mmol, R = Ph) WITH R′I (0.37 mmol, R′ = p-$MeOC_6H_4$) IN THE PRESENCE OF PALLADIUM CATALYST IN THF/ETHER 2/1 at 20°C

M	Catalyst [a]	Reaction time (min)	Yield (%) [b]			
			RR′	R_2 [c]	R'_2	R′I
Li	A	60	11	20	7	18
	B	60	7	15	6	17
MgCl	A	60	79	25	23	–
	B	60	51	47	47	–
ZnCl	A	5	96	16	3	–
	B	5	95	12	4	–
CdCl	A	15	74	21	24	–
	B	60	52	28	42	7
CuCl	–	60	–	26	–	100
	A	60	36	54	23	39
	A (0°C)	180	40	45	22	34
	B	60	12	39	13	62
$B(OMe)_2$	A(5%)	1080	13	4	–	87
	B(5%)	1080	26	20	21	53
$AlPh_2$	A [d]	20	95	7	trace	–
	A [e]	360	90	3	trace	–
	B [f](5%)	60	37	7	8	55
	B [g]	90	97	15	3	–
$SnMe_3$	A	60	–	7	5	90
	A [h]	90	39	54	16	44
	B	60	22	30	18	56
	B [h]	60	39	67	45	–
$TiCl_3$	A	60	–	–	–	97
	B	60	6	8	–	85

[a] A = $PdCl_2(PPh_3)_2$, B = $PdCl_2(MeCN)_2$. [b] Determined by TLC and UV spectroscopy. [c] Yield calculations based on organometallic compound. [d] In DMSO,50°C. [e] In THF,50°C. [f] Palladium black is formed. [g] In THF/HMPA = 2/1,55°C. [h] HMPA,50°C.

The selectivity in equation 1 depends on the nature of the catalyst and decreases sharply when complexes of palladium containing weak donating ligands, e.g., MeCN are being used. This is because the catalyst PdL_2 when L = MeCN is more active than when L = PPh_3. Earlier we named the former, "ligandless" palladium [9].

The reaction of PhZnCl leads mainly to a cross-coupling product. Triphenylaluminium reacts with p-iodoanisole in the presence of $PdCl_2(MeCN)_2$ under these conditions with low conversion and selectivity. However using DMSO at 50°C gives a high yield of p-$MeOC_6H_4Ph$ in the presence of $PdCl_2(PPh_3)_2$ or $PdCl_2(MeCN)_2$. Only one organic group takes part in Pd-catalyzed cross coupling.

$PhSnMe_3$ obtained in situ in an ether/THF mixture at room temperature reacts with p-iodoanisole slowly and with low selectivity (Table 1). When HMPA was used instead of THF there was a high homocoupling product yield. However $RSnMe_3$ reacts with aryl iodides containing electron-withdrawing groups in HMPA at 20–70°C in the presence of "ligandless" palladium practically without homocoupling [5c].

Transition metal-catalyzed acyldemetallation of organometallic compounds is a convenient method of ketone synthesis [10]. Grignard reagents were the only

TABLE 2

REACTIONS OF RM (1.1 mmol) WITH R'COCl (1 mmol) IN THE PRESENCE OF CATALYST (0.01 mmol) IN THF/ETHER = 2/1 AT 0–20°. $R' = Ph(p\text{-}NO_2C_6H_4)$

M	R	Catalyst [a]	Reaction time (min)	Yield (%) [b]	
				RCOR'	R_2
MgBr	p-MeC_6H_4	–	4(1)	75 [c](22)	3(5)
		A	4(1)	87 [c](21)	7(12)
		B	4(1)	74 [c](21)	21(20)
ZnCl	p-MeC_6H_4	A	3(10)	98(69)	9(24)
		B	3(3)	74(49)	21(52)
		–	(15)	(43)	(54)
		C [d]	20	78	33
	Ph	B [e]	1	94	6
	n-Pr	A	45(7)	79(60)	–
		B	20(3)	81(66)	–
CdCl	p-MeC_6H_4	A	4(20)	96(56)	13(20)
		B	15(10)	10(20)	69(86)
	n-Pr	A	15	52 [f]	–
		B	10	74	–
Cu	p-MeC_6H_4	A	20	68	27
		B	30	60	22
$Al(p\text{-}MeC_6H_4)_2$	p-MeC_6H_4	A	240	46	3
		B	60	80	–
$SnMe_3$	p-MeC_6H_4	B	(120)	(70)	(17)
HgI [g]	p-MeC_6H_4	B	(10)	(72)	(18)
	Me	B	(5,40 [h])	(74,64 [h])	–
	n-Pr	B	(10,60 [h])	(90,87 [h])	–

[a] $A = PdCl_2(PPh_3)_2$. $B = PdCl_2(MeCN)_2$, $C = NiCl_2(PPh_3)_2$. [b] Determined by TLC and UV spectroscopy. [c] $R_2CR'(OH)$ is formed too. [d] −78–20°C. [e] PhZnCl from PhLi. [f] 50% of PhCHO is formed. [g] In acetone, NaI (4eqv). [h] In THF ether, Bu_4NI (4eqv.).

compounds to react, under these conditions, with acyl chlorides in the absence of a catalyst (Table 2). Besides ketones the reaction gives Ar_3COH. Catalyst addition does not increase the ketone yield. As for aryldemetallation, high selectivity in the reaction of acyldemetallation was obtained for organozinc and organoaluminium compounds, two organic groups of the latter type took part in the reaction. Organocadmium compounds gave ketones in high yield when palladium complexes were used. Alkyl derivatives (Alk = n-Pr) of zinc and cadmium turned out to be less active in the Pd-catalyzed cross coupling than aromatic substrates ($Ar = p\text{-}MeC_6H_4$). Therefore, the phosphine complex gives better results with aromatic, "ligandless" palladium – with alkyl derivatives of organometallic compounds. Yield of the by-product, R_2, decreased when phenyllithium was used to obtain PhZnCl instead of PhMgX. The presence of MgX_2 precipitate is likely to influence the state of "ligandless" palladium in the reaction mixture.

The study of organometallic compound reactions with $p\text{-}NO_2C_6H_4COCl$ has shown that organic derivatives of active metals (Mg, Zn, Cd) give low yield of the acyldemetallation product due to by-processes such as the reduction of NO_2 groups etc. The reaction of less active organometallic compounds ($ArSnMe_3$ or RHgX in the presence of Bu_4NI) obtained in situ gives $p\text{-}NO_2C_6H_4COR$ in ether/THF in high yield. When the solvent is replaced by acetone, sodium iodide can be used as the source of the iodide ion.

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