

KETONE SYNTHESIS VIA PALLADIUM-CATALYZED CARBONYLATION
 OF ORGANOALUMINIUM COMPOUNDS

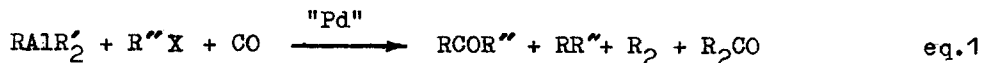
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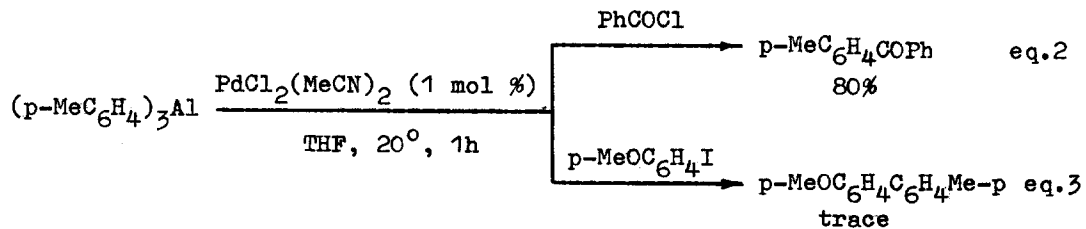
Summary: arylaluminium compounds react with aryl iodides and carbon monoxide in the presence of palladium complex to produce unsymmetrical ketones

The reaction of organometallic compounds with organic halides and carbon monoxide in the presence of transition metal complexes is a convenient route to unsymmetrical ketones. Up to now this reaction have been carried out with organic derivatives of magnesium¹, zinc² and tin³. Palladium-catalyzed carbonylation of organomercury compounds yielded symmetrical ketones⁴.

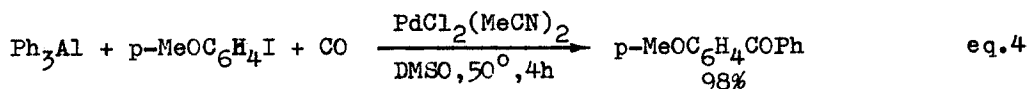
Easily available organoaluminium reactants are of much interest to undergo this type of carbonylation. Our studies have been aimed at synthesis of unsymmetrical diaryl ketones by carbonylation of the mixture of organoaluminium compounds and aryl iodides in the presence of palladium complex.



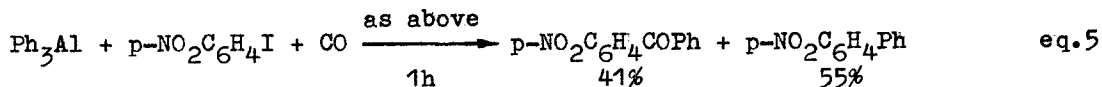
In preliminary experiments triarylaluminium reacted with benzoyl chloride in the presence of $PdCl_2(MeCN)_2$ in THF much faster than with p-iodoanisole.



Since carbon monoxide insertion into the Ar-Pd bond in the ArPdIL_2 complexes proceeds easily⁵ one should expect ketone to be the main product when $p\text{-MeOC}_6\text{H}_4\text{I}$ reacts with $(p\text{-MeC}_6\text{H}_4)_3\text{Al}$ in the presence of CO. However, the reaction of triphenylaluminum with p -iodoanisole and carbon monoxide in the presence of $\text{PdCl}_2(\text{MeCN})_2$ in THF at room temperature yielded only traces of p -methoxybenzophenone along with palladium black precipitation. When DMSO ($D_N=29.8$) was used instead of THF ($D_N=20.0$) the ketone was obtained quantitatively. Dimethyl sulfoxide ligand is likely to stabilize the acylpalladium complex. Under these conditions the temperature increase accelerates the reaction - the yield of p -methoxybenzophenone at 50°C is 98% in 4h (eq.4). For this reason DMSO was used for reactions of Ph_3Al with iodobenzene and 2-iodothiophene.



Quite different situation is observed when aryl iodides with electron-withdrawing substituents are used. In this case cross-coupling reactions compete with carbonylation (for example, eq.5).



However, with application of THF-HMPA mixture (of broad composition range) as a solvent nearly quantitative yields of ketones could be achieved for all substituted aryl iodides (Table 1).


Since only one organic group of Ar_3Al took part in the carbonylation, $(i\text{-Bu})_2\text{AlPh}$ obtained *in situ* from $(i\text{-Bu})_2\text{AlCl}$ and PhLi was tested as reactant instead of Ph_3Al . Under the reported conditions the yields of diaryl ketones are 80-97%. 2-Iodothiophene and p -nitrobenzyl bromide were also converted into corresponding ketones (Table 1).


It should be noted that only traces of homocoupling product R_2 (eq.1) were observed in all cases. However, with aryl iodides containing electron-donating groups formation of R_2CO in fairly large quantities is observed which is likely to result from palladium-catalyzed exchange processes.

Typical procedure. A. To a solution of 0.249g ($7.5 \cdot 10^{-4}$ mol) of Ph_3Al in Et_2O in DMSO (2 ml), 0.1245 g ($5 \cdot 10^{-4}$ mol) of $p\text{-NO}_2\text{C}_6\text{H}_4\text{I}$ were added and the mixture was stirred under carbon monoxide (1 atm) for 10 min. Then 1.3 mg ($5 \cdot 10^{-6}$ mol) of $\text{PdCl}_2(\text{MeCN})_2$ were added and the temperature was increased up to 50°C . The reaction was controlled by TLC. Product yield was determined by TLC and UV-spectroscopy. p -Nitrobenzophenone (41%) and p -nitrodiphenyl (55%) were formed in 1 hour.

B. To a solution of PhLi ($7.5 \cdot 10^{-4}$ mol) in THF (0.8 ml), 0.140 g of $(i\text{-Bu})_2\text{AlCl}$ ($8 \cdot 10^{-4}$ mol) were added and the mixture was stirred at 50° for

Table 1. Reactions of RAlR'_2 (0.75 mmol) with $\text{R}''\text{X}$ (0.5 mmol) and carbon monoxide (1 atm) in the presence of $\text{PdCl}_2(\text{MeCN})_2$ (0.05 mmol)

R	R'	R''X	Solvent ^a	T, °C	time h	Yield ^b , %		
						RCOR''	RR''	R ₂ CO
Ph	Ph	p-NO ₂ C ₆ H ₄ I	A	50	1	41	55	-
		p-CNC ₆ H ₄ I	B	50	2	96	3	trace
		p-ClC ₆ H ₄ I	A	50	1.5	57	40	-
		PhI	A	40	4	95	-	-
		p-MeOC ₆ H ₄ I	A	40	4	98	-	14
			A	55	3	99	-	5

Ph	i-Bu	p-NO ₂ C ₆ H ₄ I	C	50	40min	90	trace	-
		p-CNC ₆ H ₄ I	C	50	1	94	5	-
		p-ClC ₆ H ₄ I	D	40	2	97	-	16
		PhI	D	50	3	80	trace	-
		p-MeOC ₆ H ₄ I	B	50	3	84	-	34
		p-NO ₂ C ₆ H ₄ CH ₂ Br	C	40	40min	68 ^c	-	10
			D	50	1.5	82	-	13

CH ₂ =CH-	i-Bu	p-NO ₂ C ₆ H ₄ I	E	30	40min	45 ^c	-	-

^a A - DMSO; B - THF:HMPA=2:1; C - THF; D - THF:HMPA=5:1; E - THF:HMPA=1:2.

^b Yield of R₂CO is based on organoaluminium compound. ^c Tar-formation is observed.

20 min, then it was allowed to cool down to room temperature. The reaction flask was filled with carbon monoxide with intensive stirring. Then 0.1145 g ($5 \cdot 10^{-4}$ mol) of p-CNC₆H₄I and 1.3 mg ($5 \cdot 10^{-6}$ mol) of $\text{PdCl}_2(\text{MeCN})_2$ were added. The mixture was heated up to 50°C and stirred for another hour. Yield of p-CNC₆H₄COPh (94%) was determined by TLC and UV spectroscopy.

Till now our attempts to use the reaction (eq.1) for the synthesis of aryl vinyl ketones have failed. The formed ketone is consumed under the re-

action conditions (maybe through the reaction with organoaluminium compound). For example, $p\text{-NO}_2\text{C}_6\text{H}_4\text{COCH}=\text{CH}_2$ is consumed by $(i\text{-Bu})_2\text{AlCH}=\text{CH}_2$ in 30 min in THF at room temperature. Even the fastest reaction of $(i\text{-Bu})_2\text{AlCH}=\text{CH}_2$ with $p\text{-NO}_2\text{C}_6\text{H}_4\text{I}$ and CO gives $p\text{-NO}_2\text{C}_6\text{H}_4\text{COCH}=\text{CH}_2$ in only 45% yield. Nevertheless this reaction is of special interest due to availability of alkenylalanes, obtained via hydro- or carboalumination of alkynes and currently the work is in progress to improve its results.

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