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DIRECT α-ALLYLATION OF KETONES WITH O-ALLYLISOUREA CATALYZED BY PALLADIUM(0)

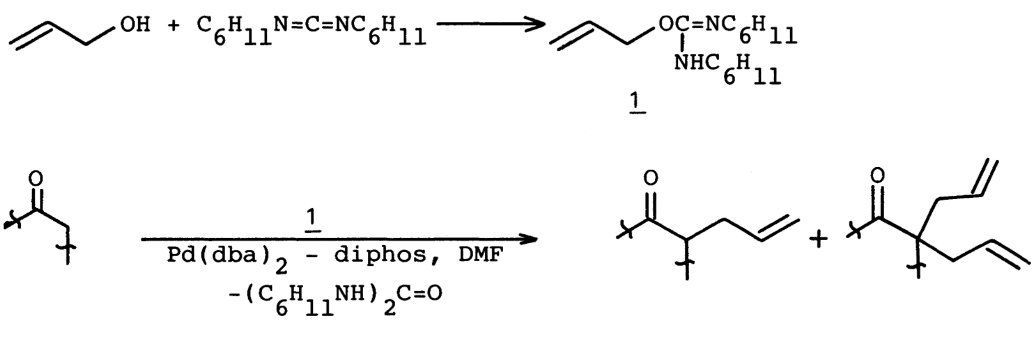
Yoshio INOUE,* Masanori TOYOFUKU, and Harukichi HASHIMOTO
Department of Applied Chemistry, Faculty of Engineering,
Tohoku University, Aoba, Aramaki, Sendai 980

Direct α-allylation of ketones catalyzed by a palladium(0)-diphosphine system took place employing O-allylisourea as the allylating reagent under neutral conditions at room temperature in DMF.

The palladium-catalyzed allylation reaction is a useful method for carbon-carbon bond formation. Stabilized carbanions (from the conjugated acids of pKa ca. 10-17) react smoothly. In these reactions, a stoichiometric amount of base is usually used for the generation of the carbanion to promote the reaction smoothly. However the direct allylation on the α-position of ketones is rather difficult.$^{1)}$ Recently the procedures via lithium,$^{2)}$ tin,$^{3)}$ boron,$^{4)}$ and silicon$^{5)}$ enolates of ketones have been developed to yield α-allyl ketones. Decarboxylative allylation of ketones catalyzed by palladium under neutral conditions has also been exploited.$^{6)}$

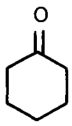
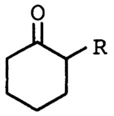
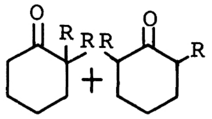
We have found that direct α-allylation of simple ketones occurs successfully in the presence of a catalytic amount of palladium(0) complex by the utilization of N,N'-dicyclohexyl-O-allylisourea (1), formed by treating allyl alcohol with N,N'-dicyclohexylcarbodiimide.$^{7)}$ This reaction is really catalyzed by palladium because the reaction does not occur in the absence of palladium.

Typically, the reaction was carried out in DMF at room temperature under nitrogen atmosphere employing ketone (1 equiv.), O-allylisourea 1 (1 equiv.), $Pd(dba)_2$ (2 mol%) [dba=dibenzylideneacetone], and a diphosphine (2 mol%). The progress of the reaction was conveniently informed by the deposition of N,N'-dicyclohexylurea formed.



The preliminary results are shown in Table 1. The diphosphines, $Ph_2P(CH_2)_nPPh_2$[n=2 (dppe), n=3 (dppp), n=4 (dppb)] and $Me_2P(CH_2)_2PMe_2$ (dmpe) were superior to PPh_3 or the diarsine, $Ph_2As(CH_2)_2AsPh_2$ (dpae), as the ligand for this reaction. The reaction proceeded efficiently in DMF, whereas in acetonitrile or THF the reaction was rather sluggish. As a rule, the dialkylation on the α-carbon of ketone was major in this system.

Table 1. α-Allylation of ketone$^{a)}$

Ketone	Catalyst	Solvent	Reaction time/h	Product,			Yield$^{b)}$/%
$PhCOCH_3$	$Pd(PPh_3)_3$	THF	5	$PhCOCH_2R$	20	$PhCOCHR_2$	7
		DMF	5		25		56
	$Pd(dba)_2$-dppe	DMF	3		4		96
	-dppp	DMF	3		3		89
	-dppb	DMF	3		8		90
$PhCOCH_2CH_3$	$Pd(dba)_2$-dppe	DMF	1	$PhCOCHRCH_3$	90	$PhCOCR_2CH_3$	0
$CH_3COCH_2CH_3$	$Pd(dba)_2$-dppe	DMF	3	$CH_3COCHRCH_3$	51	$CH_3COCR_2CH_3$	33
						$RCH_2COCHRCH_3$	7
$(CH_3CH_2)_2CO$	$Pd(dba)_2$-dppe	DMF	1	$CH_3CH_2COCHRCH_3$	37	$(CH_3CHR)_2CO$	41
	$Pd(dba)_2$-dppe	DMF	1		67		32
		DMF	$5^{c)}$		61		30
		THF	20		1		0
		CH_3CN	3		15		0
	-dpae	DMF	$4^{d)}$		15		0
	-dmpe	DMF	15 (min)		20		40
	$Pd(PPh_3)_3$	DMF	15		40		6
		THF	48		20		0
		CH_3CN	$5^{d)}$		37		10

a) Ketone (5 mmol), 1 (5 mmol), $Pd(PPh_3)_3$ (0.1 mmol), $Pd(dba)_2$ (0.1 mmol), dppe, dppp, dppb, dpae, dmpe (0.1 mmol), solvent (10 cm^3); room temperature. b) Based on 1 (by GLC). R=allyl. c) 0 °C. d) 60 °C.

References

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