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LETTERS

Ureas: New Efficient Lewis Base Catalysts for the Allylation of Aldehydes

Isabelle Chataigner,[a] Umberto Piarulli,[b] Cesare Gennari*[a,1]

a) Dipartimento di Chimica Organica ed industriale, Universita' degli Studi di Miano, Centro CNR (Sost. Org. Nat.),
via Venezian 21, 20133 Milano, Italy

b) Dipartimento di Scienze Chimiche, Fis. Mat., Universita' degli Studi dell'Insubria, via Lucini 3, 22100 Como, Italy

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Abstract : *Catalytic amounts of ureas in the presence of silver salts readily promote the reaction of allyltrichlorosilanes with aldehydes.* © 1999 Elsevier Science Ltd. All rights reserved.

The addition of allylmetal reagents to aldehydes has proven to be a very effective method for synthesizing homoallylic alcohols [1]. The allylation reaction using allyltrichlorosilanes has been shown to be promoted by Lewis bases such as phosphine oxides [2], phosphoramides [3], *N*-oxides [4], and formamides [2,5]. This reaction can be rendered catalytic in Lewis base since, in an appropriate solvent (e.g. dichloromethane or toluene), the non-catalysed background reaction is negligible. In this case, the mechanistic profile probably proceeds *via* a cyclic chair-like transition state [2,4], thus giving access to *syn* or *anti* diastereoisomers from (*Z*)- or (*E*)-crotyltrichlorosilanes respectively.

Considering the Lewis base properties of ureas [6] and their versatility as chiral auxiliaries, we were intrigued by the feasibility of this catalytic process based on the most commonly used urea, i.e. 1,3-dimethyl-3,4,5,6-tetrahydro-2(1H)-pyrimidone (DMPU, **3**). Herein we report our preliminary results on this unprecedented type of Lewis base catalysis in the allylation reactions.

The allylation reaction appeared to be effectively promoted by stoichiometric amounts of DMPU (Table 1, entry 1), but its rate was too slow to permit the use of substoichiometric quantities. Based on the premiss that sequestering the halide might enhance the reactivity [2], we investigated the reaction promoted by DMPU in the presence of silver triflate. Stoichiometric amounts of AgOTf allowed completion of the reaction in a few minutes (entry 2). However, decreasing the amount of urea caused decomposition of the reaction mixture (entry 3), while the use of substoichiometric amounts of silver triflate caused limited conversion (entry 4). Accordingly, the less active silver tosylate was screened and found to be the best additive, allowing the allylation reaction to proceed quantitatively at low temperature in a few hours using catalytic amounts of DMPU (entries 5-8) [7]. Control reactions with silver tosylate as the only promoter revealed that allylations still require the presence of the urea (entry 9).

The rate of crotylation is also enhanced to a similar degree and significantly the intrinsic diastereoselectivity is unaffected by the presence of the silver salt: A 80/20 mixture of (*E*)/(*Z*)-crotyltrichlorosilanes affords a 80/20 mixture of *anti/syn* homoallylic alcohols (entry 10). This stereospecific process suggests that the reaction proceeds through a cyclic chair-like transition state involving a hypervalent silicate species where the ligand occupies an axial position [2,4].

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[1] E-mail address : cesare@iumchx.chimorg.unimi.it

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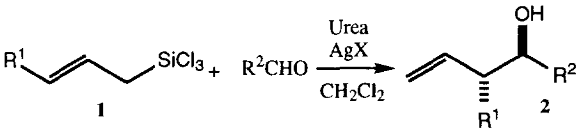

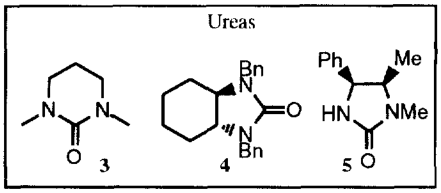

Table 1 : Allylation reactions.

Entry	R^1	R^2	urea (mol%)	AgX (mol%)	Temp (°C)	Time (h)	Yield[a] (%)	e.r.[b]
1	H	Ph	**3** (120)	-	25	96	81	-
2	H	Ph	**3** (120)	AgOTf (120)	0	0.25	85	-
3	H	Ph	**3** (20)	AgOTf (120)	25	36	28	-
4	H	Ph	**3** (20)	AgOTf (20)	0	3	40	-
5	H	Ph	**3** (20)	AgOTs (120)	0	2	99	-
6	H	Ph	**3** (20)	AgOTs (120)	-78	8	73	-
7	H	Ph	**3** (10)	AgOTs (120)	0	4	99	-
8	H	cyclohexyl	**3** (10)	AgOTs (120)	0	4	78	-
9	H	Ph	-	AgOTs (120)	25	96	0	-
10	CH_3[c]	Ph	**3** (10)	AgOTs (120)	0	4	99[d]	-
11	H	Ph	**4** (20)	AgOTs (120)	-78	6	81	46:54
12	H	Ph	**5** (20)	AgOTs (120)	-78	10	87	58:42

a) Isolated yields. b) Determined by GC analysis of the silylated compounds on a chiral column (megadex DMP β). c) (E)/(Z) 80/20. d) *anti/syn* 80/20.

A chiral version of this new type of Lewis-base catalysis was then examined, but the enantiomeric ratios (e.r.) observed were low (entries 11-12). Further studies to improve the enantioselectivities are in progress.

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References and notes

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[7] General procedure : To a suspension of AgOTs (1.2 mmol) and DMPU (0.1 mmol) in CH_2Cl_2 (1.0 ml), was added at 0 °C the allyltrichlorosilane (1.2 mmol) and then the aldehyde (1.0 mmol). The mixture was stirred for 4 hours, diluted with CH_2Cl_2, quenched with a KF aqueous solution and filtered on celite to remove the silver salts. After extraction, the organic phase was washed with water and brine. The reaction products were purified by flash chromatography on silica gel.