CsF-promoted Michael Addition in Heterogeneous Catalysis

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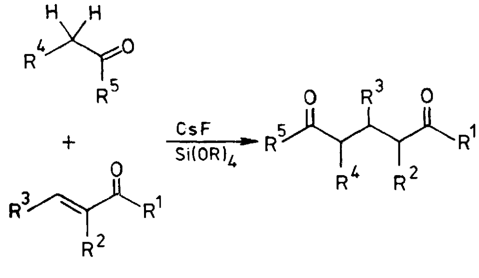
Summary CsF in the presence of $Si(OR)_4$ is found to be an efficient, simple catalyst for the Michael addition of monoketones; yields are satisfactory and side reactions are not observed.

The Michael addition is one of the most important methods available for carbon–carbon bond formation. Following our interest in heterogeneous catalysis by salts,[1] we have found a new procedure for performing both cross-aldol and Michael reactions by the activation of silyl enol ethers with CsF.[2]

We report now the direct reaction of monoketones with $\alpha\beta$-unsaturated ketones, esters, and nitriles. The heterogeneous reactions were carried out in the presence of $Si(OEt)_4$ or $Si(OMe)_4$ and CsF, without solvent [equation (1)].



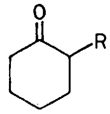
(1)

TABLE. Addition of electrophiles to carbonyl compounds catalysed by $Si(OR)_4$–CsF.[a]

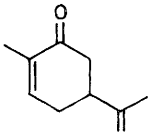
Carbonyl compound	Electrophile	Catalyst[b]	T/°C	t/h	Product	(% yield[c])
(**1a**)	Cyclohex-2-enone	(A)	25	6	(**4**)	(65)
"	PhCH=CHCOPh	"	60	2	(**5**)	(65)
(**1b**)	$MeCH=CHCO_2Et$	"	100	2	(**6**)	(55)
"	$PhCH=CHCO_2$-menthyl	"	80	5	(**7**)	(70)
PhCOMe	(**2**)	"	70	4	(**8**)	(60)
"	(**3**)	(B)	80	6	(**9**)	(65)
"	$MeCH=CHCO_2Et$	(A)	60	3	(**10**)	(80)
"	$Me_2C=CHCN$	(B)	80	3	(**11**)	(55)
$Bu^i{}_2CO$	$PhCH=CHCO_2Me$	"	"	48	(**12**)	(60)
$(PhCH_2)_2CO$	$PhCH=CHCO_2$-menthyl	(A)	"	2·5	(**13**)	(85)
"	PhCH=CHCN	"	25	3	(**14**)	(65)

[a] Reactions were carried out under nitrogen with equimolar amounts of the reagents, CsF, and $Si(OR)_4$. After hydrolysis (MeONa–MeOH–H_2O or 2M HCl–acetone) the products were isolated, purified by distillation and preparative chromatography (silica gel), and identified by n.m.r., i.r., and mass spectroscopy and elemental analysis. [b] (A), CsF + $Si(OEt)_4$; (B), CsF + $Si(OMe)_4$. [c] Yield of isolated purified product.

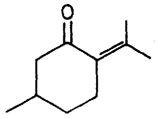
The results are summarized in the Table. The use of the $Si(OR)_4$ and CsF system allows the direct reaction of monoketones with different kinds of unsaturated ketones, esters, and nitriles, whereas generally the Michael reaction requires either a very active methylene compound (*e.g.* a β-dicarbonyl compound) or a very active Michael acceptor (*e.g.* methyl vinyl ketone or acrylonitrile).[3] Moreover, this procedure allowed us to avoid the isolation of silyl enol ethers, which are not always easy to prepare and are generally unstable. Furthermore it avoids undesirable side reactions which usually occur when Michael additions are catalysed by strong bases.



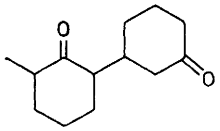
(1) a; R = Me
b; R = H



(2)



(3)



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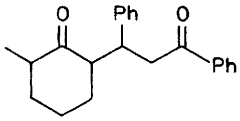

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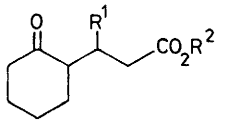
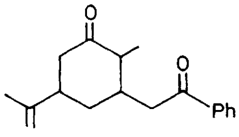
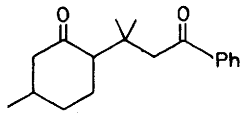


(6) R^1 = Me, R^2 = Et
(7) R^1 = Ph, R^2 = menthyl



(8)



(9)

$PhCOCH_2CHMeCH_2CO_2Et$ (**10**)

$NCCH_2CMe_2CH_2COPh$ (**11**)

$Bu^iCOCHPr^iCHPhCH_2CO_2Me$ (**12**)

$PhCH_2COCHPhCHPhCH_2CO_2$-menthyl (**13**)

$PhCH_2COCHPhCHPhCH_2CN$ (**14**)

Finally, the selectivity of this reaction with 2-methylcyclohexanone is noteworthy; we obtained only the product of addition on the less hindered carbon (corresponding to the product from the kinetically controlled enolate).

We think that $Si(OR)_4$ has two roles in the reaction: it generates the base at the surface of CsF, and traps the enolate giving a silyl enol ether which reacts immediately *in situ*. We propose this second step in order to explain the Michael-type reaction previously observed in the case of the activation of silyl enol ethers by CsF.[2]

(*Received*, 17*th October* 1980; *Com.* 1124.)

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[1] J. Boyer, R. J. P. Corriu, R. Perz, and C. Réyé, *J. Organomet. Chem.*, 1978, **148**, C1; 1978, **157**, 153; 1979, **172**, 243.

[2] J. Boyer, R. J. P. Corriu, R. Perz, and C. Réyé, *J. Organomet. Chem.*, 1980, **184**, 157.

[3] E. Bergmann, D. Ginsburg, and R. Pappo, *Org. React.*, 1959, **10**, 179; G. Krychtal, V. V. Kulganek, F. Kucherov, and L. A. Yanovskaya, *Synthesis*, 1979, 107; J. H. Nelson, P. N. Howells, G. C. Delullo, and G. L. Landen, *J. Org. Chem.*, 1980, **45**, 1247.