'Naked' Fluorid-ecatalysed Michael-Additions

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Summary Michael addition reactions can be efficiently catalysed, giving high yields, by KF in aprotic solvents containing 1,4,7,10,13,16-hexaoxacyclo-octadecane (18-crown-6).

THE ability of solubilized 'naked' fluoride ion to behave, in aprotic solvents, as a strong base and nucleophile was recently described.[1] There have been some reports regarding the ability of alkali metal fluorides to catalyse Michael additions,[2] but these were hampered by the low solubility of the fluorides in organic solvents. More recently catalysis by the more soluble tetra-alkylammonium fluorides was described.[3] We now report that in aprotic solvents containing 18-crown-6, KF is an efficient and powerful catalyst for Michael additions.[4] High yields are obtained in solvents such as benzene, dichloromethane, or acetonitrile using 0·03—0·05 equiv. of 18-crown-6, and *ca.* 0·2 equiv. of KF (Table).

TABLE. Reactions (1·5 h at 81 °C in MeCN unless otherwise stated) of active methylene compounds (A) with compounds (B) containing an activated double bond.

(A)	(B)	(A) : (B)	Product	% Yield[a]
$MeNO_2$	PhCH=CHCOPh	20 : 1[b]	$O_2NCH_2CH(Ph)CH_2COPh$	94
EtO_2CCH_2CN	PhCH=CHCOPh	1 : 2	$EtO_2CC(CN)(CHPhCH_2COPh)_2$[d]	83
$CH_2(CN)_2$	CH_2=CHCN	1 : 2	$(CN)_2C(CH_2CH_2CN)_2$[e]	69
$MeNO_2$	CH_2=CHCN	1 : 3	$O_2NC(CH_2CHCN)_3$[f]$_2$	72[g]

[a] Yields of crude isolated products are given. Recrystallized samples were compared with authentic specimens. [b] At lower ratios, mixtures of this compound and the 1 : 2 adduct $O_2NCH(CHPhCH_2COPh)_2$ were obtained. [c] M.p. 101 °C (lit., 101—102 °C: W. Davey and D. J. Tivey, *J. Chem. Soc.*, 1958, 2276). [d] M.p. 219—223 °C (lit., 220—225 °C: W. Davey and D. J. Tivey, *J. Chem. Soc.*, 1958, 2606). [e] M.p. 91 °C [lit., 89·5 °C: A. Kost, V. Kamernitskii, and S. M. Gurrich, *Vestnik Moskov. Univ.* 9, *No.-*9, *Ser. Fiz.-Mat. Estestven. Nauk*, 1954, **6**, 115, (*Chem. Abs.*, 1955, **49**, 15,856)]. [f] M.p. 113 °C (lit., 112—113 °C: J. M. Patterson and M. W. Barnes, *Bull. Chem. Soc. Japan*, 1967, **40**, 2715). [g] Yield after 2·5 h at 81 °C in MeCN. The same product is obtained from a 1 : 3 ratio of (A) : (B) in 68% yield after 18 h at 23 °C in CH_2Cl_2

A typical procedure is exemplified by the addition of nitromethane to chalcone. To a solution of 18-crown-6 (0·03 mmol) in dry MeCN (65 ml), dry KF (*ca.* 1 mmol) was added followed by $MeNO_2$ (0·1 mol) and chalcone (5 mmol). The mixture was stirred at 81 °C for 1·5 h. MeCN was removed *in vacuo*, CH_2Cl_2 was added, and the organic layer was washed with 2N HCl. Removal of CH_2Cl_2 left a solid which was recrystallized from EtOH. Comparable yields can be obtained using CH_2Cl_2 or benzene as solvent, but acetonitrile is preferable for a combination of high yields and short reaction times.

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