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DABCO CATALYZED COUPLING OF α-KETO ESTERS WITH ACRYLONITRILE AND METHYL ACRYLATE

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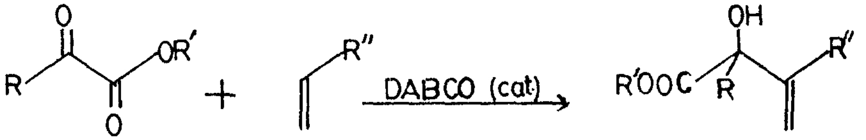
Summary: Coupling of acrylonitrile to α-keto esters is readily achieved using 1,4-diazabicyclo[2.2.2]-octane(DABCO) as a catalyst to produce 2-[1-carboalkoxy-1-hydroxyalkyl]acrylonitriles in good yields. Similar reaction with methyl acrylate produces the corresponding 2-substituted acrylates.

Multifunctional molecules play an important role in bringing latitude to organic synthesis. In recent years there has been much emphasis on 1,4-diazabicyclo[2.2.2]octane(DABCO) catalyzed reactions for synthesis of multifunctional molecules.[1,8] In continuation of our research programme[5-8] on synthesis of multifunctional molecules we now report a simple synthesis of 2-[1-carboalkoxy-1-hydroxyalkyl]acrylonitriles and 2-[1-carboalkoxy-1-hydroxyalkyl]acrylates via DABCO catalyzed coupling of α-keto esters with acrylonitrile and methyl acrylate respectively.

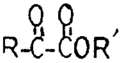
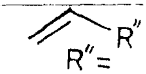
It has been documented[1-7] that aldehydes react with α, β-unsaturated ketones, esters and nitriles to produce corresponding multifunctional molecules. It occured to us that α-keto esters might also couple with these α, β-unsaturated molecules to provide the multifunctional molecules. The reaction of acrylonitrile with the readily available ethyl phenylglyoxylate was carried out in the presence of 30 mol % of DABCO at room temperature to produce the expected 2-[carboethoxyhydroxyphenyl]methylacrylonitrile. A representative group of multifunctional molecules (1-6) was prepared via the coupling of α-keto esters with acrylonitrile and with methyl acrylate [Table 1]



$R = -CH_3$, -phenyl, -p-tolyl
$R' = -CH_3$, $-C_2H_5$
$R'' = -CN$, $-COOCH_3$

The following procedure for the synthesis of 2-[carboethoxyhydroxyphenyl]methylacrylonitrile(1) is representative. A mixture of ethyl phenylglyoxylate(1.78g, 10 mM), acrylonitrile(1.3 mL, 20 mM) and DABCO(336mg, 3 mM) was allowed to stand at room temperature for 5 days. The reaction mixture taken up in dichloromethane (25 mL) and washed with 2N hydrochloric acid, aqueous sodium bicarbonate solution and dried over anhydrous sodium sulphate. After the removal of the solvent, the product was purified by column chromatography (10% ethyl acetate, 90% hexane) followed by distillation to give 1.50g (65%) of 2-[carboethoxyhydroxyphenyl]methylacrylonitrile (1) bp : 164° - 166°/4 mm. IR (neat): 3450, 2250, 1725, 1610 cm^{-1}; ^1H NMR ($CDCl_3/SiMe_4$): 1.32 (t, 3H), 4.32 (m, 3H, 1H D_2O washable) 6.15 (d, 2H), 7.40 (m, 5H); ^{13}C NMR ($CDCl_3/SiMe_4$): 13.76, 63.76, 78.59, 116.88, 125.30, 126.36, 128.65, 129.06, 132.95, 137.65, 171.65.

Table 1 : Preparation of 2-[1-carboalkoxy-1-hydroxyalkyl]acrylonitriles (from α-keto esters and acrylonitrile) and 2-[1-carboalkoxy-1-hydroxyalkyl]acrylates (from α-keto esters and methyl acrylate).[a,b]

 $R-\overset{O}{\overset{\|}{C}}-\overset{O}{\overset{\|}{C}}OR'$		Product	Reaction Time	bp/mm or mp	Yield (%)[c]
R' = $-C_2H_5$					
R = -phenyl	CN	1	5 days	164-166/4	65
R = -p-tolyl	CN	2	7 days	162-164/1	74
R = -phenyl	$COOCH_3$	3	7 days	154-155/1.5(mp 54-56)	49
R = -p-tolyl	$COOCH_3$	4	9 days	87-89	41
R = CH_3					
R' = $-CH_3$	CN	5[d]	24h	98-100/5	38[e]
R' = C_2H_5	CN	6[d]	24h	84-86/2	41[e]

a) All reactions (1-4) were carried out on 10 mM scale (α-keto esters) using 30 mol % DABCO at room temperature. b) All products were identified spectroscopically by IR, ^1H NMR and ^{13}C NMR . c) Yields of the compounds purified by column chromatography followed by distillation or crystallization. d) The reaction of acrylonitrile (20 mM) with these pyruvates (10 mM) is not clean. Therefore, pyruvates (10 mM) were added slowly to acrylonitrile (100 mM) containing DABCO (1.5 mM). e) Yields of pure distilled products.

This procedure represents a simple synthesis of 2-[1-carboalkoxy-1-hydroxyalkyl]acrylonitriles and acrylates. The use of chiral pyruvates to achieve the optical induction will be the subject of our future reports.

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