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Synthesis of Ethyl α-Cyanocinnamates Catalyzed by Al₂O₃-OK Solid Base

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ABSTRACT

Condensation of ethyl cyanoacetate with aromatic aldehydes catalyzed by Al_2O_3 -OK solid base in ethanol results ethyl α -cyano-cinnamates in 80–99% yields.

Ethyl α -cyanocinnamates are a class of important organic compounds. For instance, ethyl α -cyano-*m*-nitrocinnamate is used as the photosensitive composition^[1] and intermediate of plant growth regulator,^[2] ethyl α -cyanocinnamate with a alkoxy or hydroxy group in the

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benzene ring is used as part of ultraviolet filter composition for protecting light-sensitive foods, wood-product, paper, dyes, fibers, plastics, etc.^[3] The usual catalyst for the preparation of ethyl α -cyanocinnamates are ammonia and ammonium salts, primary and secondary amines and their salts.^[4] Subsequently the use of pyridine.^[4,5] TiCl₄ and base,^[6] Al₂O₃–AlPO₄,^[7] CdI₂,^[8] ZnCl₂,^[9] ZnO, and MgO^[10] have been reported. However, each of the methods has its merit and some shortcomings. Some of these methods are not entirely satisfactory due to drawbacks such as long reaction time, low yields of the product, tedious workup, harshness of the reaction conditions (Sch. 1).

Al₂O₃–OK, a new type of solid base has been studied recently.^[11] It has been widely used in the fields of alkylation, condensation and isomerization under mild conditions.^[11] Herein we demonstrated a facile method for preparation of ethyl α -cyanocinnamates catalyzed by Al₂O₃–OK solid base (Table 1).

From Table 1 we found that electron donating groups such as –OH, –OCH₃, –OCH₂O–, –CH₃, and –N(CH₃)₂ in the aromatic ring can undergo the desired transformation without much difficulty. (Entries 6, 7, 8, 10 and 11). Electron withdrowing groups such as –Cl, –NO₂ in the aromatic ring increased the activity of aldehydes, so the condensation reaction can be carried out in relatively shorter time. For instance, preparation of the phenyl derivates (Entry 1) was reported 62–86% yield in the presence of Al₂O₃–AlPO₄^[7] or ZnCl₂^[9] in 1–2 h. However, it obtained 98% yield catalyzed by Al₂O₃–OK solid base for 30 min in our experiment. In the spectrum analysis of compound **3f**, a weak NOE relationship was observed between the benzylic methyl (δ 2.50) and the vinyl (δ 8.61) protons, but no NOE was seen between ethyl and the aromatic protons. These data suggest a configuration where the aryl and the cyano groups are in the cis relationship.

In summary, we have shown that Al_2O_3 -OK solid base is the efficient catalyst for the condensation of aromatic aldehydes and ethyl cyanoacetate in the refluxing temperature of ethanol, because of its operational simplicity, short reaction time and high yields.

ArCHO + NCCH₂CO₂Et $\frac{Al_2O_3 - OK}{ethanol/reflux}$ ArCH=C(CN)CO₂Et 1 2 80-99 % 3

Scheme 1.

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Ethyl α-Cyanocinnamates

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Table 1. Synthesis of ethyl α -cyanocinnamates catalyzed by Al₂O₃–OK solid base.

Entry	Aldehydes	Reaction time (min)	Yields ^a (%)	M.p. (°C)	
				Found	Reported
1	О- СНО 1а	30	98	48-50	49–51 ^[12]
2	О ₂ № (О)- СНО 1b	30	99	171-172	172-173 ^[12]
3	O-CHO 1c	35	95	133–135	134–136 ^[13]
4	с⊢⊘≻сно 1d	40	98	89–91	90 ^[8]
5	CH ^{CHO} 1e	35	97	101-103	101-102 ^[14]
6	\bigcirc -CHO CH ₃ If	30	96	52–54	
7	но- () -сно 1g	50	95	169–170	
8	сн ₃ 0-@-сно 1h	55	97	79–81	
9		45	97	106–108	106-108 ^[15]
10	но- (О)- Сно 1 ј Сн _з о	100	95	110-111	111-112 ^[12]
11	н₃С-(О)-СНО 1к	35	98	94–95	
12	(СН ₃₎₂ N-О-СНО 11	35	96	124–125	124-126 ^[12]
13		40	80	115-116	116 ^[8]
14	G _{CHO} 1n	25	90	90–91	91-92 ^[16]

^aYields refer to isolated products.

EXPERIMENTAL

The catalyst was prepared as follows: 26 g KNO_3 and $74 \text{ g Al}_2\text{O}_3$ were crushed in a mortar, then added appropriate deionized water which can be absorbed by Al₂O₃. After ground, the mixture was dried at 110°C for 1 h, and then activated at 600°C for 3 h. When the loading of KNO₃ is above the threshold, only about 7% of KNO₃ can be dispersed through the interaction with Al₂O₃ support and decomposed in a mild pretreatment such as evacuation at room temperature, while a lot of undispersed KNO₃ located in the pores of Al₂O₃ forms a new phase such as K₂[Al(NO₃)]₅. Both the residual KNO₃ and K₂[Al(NO₃)]₅ decomYYY

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pose during evacuation at 600° C, and potassium ions migrate from the inner to the external surface of Al₂O₃ during the evacuation process. Consequently, several layers of basic materials such as K₂O overlap on the Al₂O₃ result in some superbasic sites with a basic strength (H-) of 27.0. The catalyst could be reused by dealt out simply.

Liquid aldehyde was purified by distillation prior to use. Melting point was uncorrected. Infrared spectra was recorded on a Bio-Rad FTS-40 spectrometer (KBr). Proton NMR spectra was determined in D-chloroform solution on a FT-NMR Bruker 300 (300 MHz), and reported in δ ppm using tetramethylsilane as the standard. Mass spectra was measured on a VG-7070E spectrometer (EI, 70 eV).

General Procedure for the Condensation of Ethyl Cyanoacetate and Aldehydes

A mixture of aldehyde 1 (10 mmol), ethyl cyanoacetate 2 (1.36 g 12 mmol), 10 mL absolute ethanol (dried with Mg), Al_2O_3 -OK solid base (150 mg), was added to a 50 mL flask. It was stirred with a magnetic stirrer and refluxed for appropriate time as indicated in Table 1. The reaction was monitored by TLC. The crude product was washed with 5% aqueous alcohol, which give a good purity. The catalyst could be reused five times for the synthesis of compound **3d** without significant decrease in reactivity.

Spectral data of some compounds are as follows.

3f: IR (neat) 3100–2850, 2210, 1710, 1650, 1600, 1450, 1260, 1200, 1100 cm⁻¹; ¹H NMR (CDCl₃) δ 8.61 (1H, s, CH=), 8.17 (1H, d, Ph-H, J=7.7), 7.47–7.29 (3H, m, Ph-H), 4.40 (2H, q, J=7.1, OCH₂CH₃), 2.5 (3H, s, CH₃-Ph), 1.41 (3H, t, J=7.1, OCH₂CH₃); EIMS m/z 215 (M⁺, 100), 200 (28), 187 (42), 170 (78), 142 (32), 115 (63), 89 (20), 65 (25).

3g: IR (KBr) 3450–3180, 3070–2900, 2230, 1710, 1590, 1510, 1440, 1370, 1260, 1200, 1185, 1100 cm⁻¹; ¹H NMR (CDCl₃) δ 10.50 (1H, s, OH), 8.19 (1H, s, CH=), 7.92 (2H, d, J=8.13, Ph-H), 6.99 (2H, d, J=8.13, Ph-H), 4.39 (2H, q, J=7.31, OCH₂CH₃), 1.40 (3H, t, J=7.31, OCH₂CH₃); EIMS m/z 217 (M⁺, 100), 189 (50), 172 (98), 144 (45), 117 (25), 89 (45), 63 (8).

3h: IR (neat) 3100–2800, 2210, 1705, 1600, 1505, 1260, 1170 cm⁻¹; ¹H NMR (CDCl₃) δ 8.21 (1H, s, CH=), 7.95 (2H, d, *J*=8.4, Ph-H), 6.96 (2H, d, *J*=8.4, Ph-H), 4.40 (2H, q, *J*=7.4, OCH₂CH₃), 3.91 (3H, s, OCH₃), 1.40 (3H, t, *J*=7.4, OCH₂CH₃); EIMS *m*/*z* 231 (M⁺, 45), 200 (3), 170 (89), 143 (90), 115 (100), 89 (10), 70 (7), 65 (9).

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3k: IR (neat) 3100–2850, 2220, 1710, 1600, 1460, 1370, 1270, 1200, 1100 cm⁻¹; ¹H NMR (CDCl₃) δ 8.21 (1H, s, CH=), 7.91 (2H, d, J=8.14, Ph-H), 7.31 (2H, d, J=8.14, Ph-H), 4.38 (2H, q, J=7.06, OCH₂CH₃), 2.43 (3H, s, CH₃-Ar), 1.40 (3H, t, J=7.06, OCH₂CH₃); EIMS m/z 215 (M⁺, 100), 200 (28), 187 (42), 170 (78), 142 (32), 115 (63), 89 (20), 65 (25).

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