# Knoevenagel condensation catalyzed by $K_2NiP_2O_7$ . Synthesis of (E)-methyl- $\alpha$ -cyanocinnamates in high yields

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The Knoevenagel reaction of benzaldehyde and several chloroderivatives with methyl cyanoacetate catalyzed by  $K_2NiP_2O_7$  leads to methyl (E)- $\alpha$ -cyanocinnamate derivatives in 40 min with yields of 71.65–83.45%. Pure products are easily obtained in crystalline form, uncontaminated by side products or by stereoisomers. Methyl 2-chlorocyanocinnamate, methyl 2,4-dichlorocyanocinnamate, and a new polymorph of methyl cyanocinnamate have been characterized by single crystal X-ray diffraction.

**KEY WORDS:** heterogeneous catalysis; diphosphate catalysis; Knoevenagel condensation; methyl (E)- $\alpha$ -cyanocinnamate derivatives.

## Introduction

The Knoevenagel condensation of an aldehyde and an active methylene compound is normally carried out in the presence of a base to remove the somewhat acidic or "active" hydrogen atom (Scheme 1).

Often secondary amines or piperidine are used as the base. Of late there has been interest in carrying out synthetic organic reactions under conditions which do not require separation of the product from other organic materials (such as the base), which are fast, effective, and which do not require heating or the use of large quantities of solvent. In an attempt to meet these conditions for the Knoevenagel condensation, a number of efforts have been directed at the use of heterogeneous catalysts which can be removed from the reaction mixture by filtration. Weak basic ion exchange resins,<sup>1</sup> KF, CsF,<sup>2,3</sup> TiCl<sub>4</sub><sup>4</sup>, CdI<sub>2</sub>,<sup>5</sup> and ZnCl<sub>2</sub><sup>6</sup> have found use in this domain.

 $Al_2O_3$ , which has both basic and acidic sites, has been used to catalyze the condensation of active methylene compounds and aldehydes on the surface of solid  $Al_2O_3$ . The reaction is reported to be fast (2–3 min). The product is extracted from the surface of the solid  $Al_2O_3$  with dichloromethane.<sup>7</sup>

4-Chlorobenzaldehyde plus ethyl cyanoacetate gives high yields of the E product (84%) using Xonotlite doped with Me<sub>3</sub>COK at ambient temperatures.<sup>8</sup>

Alkali and alkaline earth containing phosphate materials (Na<sub>2</sub>CaP<sub>2</sub>O<sub>7</sub>, Na<sub>4</sub>P<sub>2</sub>O<sub>7</sub>, and Ca<sub>2</sub>P<sub>2</sub>O<sub>7</sub> have shown effectiveness in Knoevenagel catalysis.<sup>9</sup> Natural phosphate (similar to

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Scheme 1.

 $Ca_{10}(PO_4)_6F_2$ ) doped with KF and/or sodium nitrate has been reported to catalyze Knoevenagel reactions.<sup>10</sup> Magnesium phosphates, NaMg<sub>4</sub>(PO<sub>4</sub>)<sub>3</sub>, Mg<sub>3</sub>(PO<sub>4</sub>)<sub>2</sub>,  $\alpha$ -Mg<sub>2</sub>P<sub>2</sub>O<sub>7</sub>, and NaMgPO<sub>4</sub> have been studied as catalysts.<sup>11</sup>

However phosphates containing transition metals such as  $K_2NiP_2O_7$  etc. have also shown effectiveness.<sup>12,13</sup> In this effort, we have investigated the use of  $K_2NiP_2O_7$  as a heterogeneous catalyst in the reaction of methyl cyanoacetate with benzaldehyde, 2-chlorobenzaldehyde, and 2,4-dichlorobenzaldehyde, stirred in methanol for 40 min.

Besides the product yield and the identity of the product, of specific interest was the stereochemistry of the methyl- $\alpha$ -cyanocinnamates produced. Both (E)- and (Z)-methyl- $\alpha$ -cyanocinnamate are known.<sup>7,14</sup> Only the (E) form of methyl 2-chloro- $\alpha$ -cyanocinnamate is known<sup>15</sup> and there have been reports of methyl 2,4dichloro- $\alpha$ -cyanocinnamate of undetermined stereochemistry.<sup>16</sup> Thus we have identified the stereochemistry of the products of the phosphatecatalyzed Knoevenagel reaction by single crystal X-ray diffraction (Table 1).

#### **Experimental**

#### Synthesis

Benzaldehyde(I), 2-chlorobenzaldehyde(II) or 2,4-dichlorobenzaldehyde(III) (3 mmol), and methyl cyanoacetate (3 mmol) and four drops of water in methanol (1.6 mL (I), 7 mL (II), and 10 mL (III)) were mixed to give a solution.  $K_2NiP_2O_7(0.200 \text{ g})$  was added and the mixture stirred for 40 min at ambient temperature. The

 Table 1. Crystallographic Data for Methyl (E)- $\alpha$ -Cyanocinnamate

 (I), Methyl (E)-2-Chloro- $\alpha$ -Cyanocinnamate (II), and Methyl (E) 

 2,4-Dichloro- $\alpha$ -Cyanocinnamate (III)

Compound	Ι	II	III
CODC deposit no.	192568	192628	192629
Molecular formula	$C_{11}H_9NO_2$	C <sub>11</sub> H <sub>8</sub> NO <sub>2</sub> Cl	$C_{11}H_7NO_2Cl_2$
Mass	187.19	221.63	256.08
a. Å	5.531(1)	18.887(9)	3.919(2)
h Å	10.053(1)	7.505(4)	8.377(4)
c Å	17.374(4)	7 308(3)	17 539(8)
a deg	90.0	90.0	87 75(3)
B deg	90.0	101.07(1)	88 98(4)
p, deg	90.0	90.0	80.25(4)
$\gamma$ , ueg	90.0	10166(9)	567.0(5)
volume, A <sup>2</sup>	900.0(3)	1010.0(8)	307.0(3)
L L Ma (m 3	4	4	2 1.500
$a, Mg/m^3$	1.287	1.448	1.500
F(000)	392	456	260
$\mu$ , mm <sup>-1</sup>	0.090	0.352	0.554
Crystal system	Orthorhombic	Monoclinic	Triclinic
Space group	$P2_12_12_1$	$P2_{1}/c$	P-1
Diffractometer	Siemens P4	Siemens P4	Siemens P4
Radiation	Μο Κα	Μο Κα	Μο Κα
Monochromator	Highly oriented graphite	Highly oriented graphite	Highly oriented graphite
~	crystal	crystal	crystal
Crystal size	$0.1 \times 0.1 \times$	$0.05 \times 0.1 \times$	$0.1 \times 0.1 \times$
G 11	0.1	0.1	0.1
Crystal form	needle	prism	needle
Temperature, K	301	301	301
Data collecting mode	$\theta - 2\theta$	$\theta - 2\theta$	$\theta - 2\theta$
$\theta$ range, deg	2.34 to 28.70	2.20 to 29.99	2.32 to 25.02
Reciprocal lattice	-1 < h <	-26 < h < 1;	-4 < h < 1;
segment	7; -1 < k <	-10 < k <	-9 < k < 9
	13;	1; -10 <	-20 < 1 < 20
	-1 < 1 < 13	1 < 10	
Reflections measured	2026	2119	2911
Number of symmetry independent	1852	1843	1997
Mathad of	Direct	Diment	Dimont
Method of	Direct	Direct	Direct
solution	<b>F H</b>	<b>F</b> 11	<b>F</b> 11
Method of	Full-matrix	Full-matrix	Full-matrix
refinement	least-	least-	least-
D (D	squares	squares	squares
Parameter/Fo	128/1852	137/1843	145/2911
R <sub>equiv</sub>	0.0233	0.0878	0.0733
$R[I > 2\sigma(I)]$	0.0521	0.0597	0.0697
Rw	0.0822	0.0865	0.0954

catalyst was removed by filtration and washed with methanol. The filtrate and the MeOH used for washing were combined and used for GC-MS analysis. After standing for 3–5 h, crystallization took place. Percent yields: 71.65% (I). 77.10% (II), 83.45% (III). Melting points, (I) 87; (II) 104; (III) 104°C.

#### Gas chromatography/mass spectral analysis

Methanol filtrates were examined by GC/MS analysis using a Hewlett Packard G1800A GCD System [column: crosslinked 5% Ph Me Silicone coating in 30 m × 0.25 mm × 0.25  $\mu$ m film thickness; helium flow 1.0 mL/min, inlet 150°C, detector 280°C, oven 70–290°C, ramp rate 4°/min] retention times 35.89 (I), 39.62 (II), 44.4 min (III).

## Single crystal X-ray diffraction

Crystals of (I), (II), and (III) were mounted on glass fibers for single crystal X-ray diffraction analysis. Diffraction data were collected using an automated four-circle Siemens P4 diffractometer equipped with graphite monochromated Mo K $\alpha$ radiation ( $\lambda = 0.71073$  Å). Data was collected at ambient temperature with a  $\theta$ -2 $\theta$  data collection mode (XSCANS).<sup>17</sup> Three standard reflections were remeasured after each 97 data points and these showed no decline in intensity during data collection. Data were corrected for Lorentz, polarization, and background effects. Atomic positional parameters were determined using direct methods (SHELXS)<sup>18</sup> and refinement was carried out using full-matrix least-squares techniques (SHELXL).<sup>19</sup> Semiempirical absorption corrections were applied using XEMP.<sup>20</sup> Hydrogen atoms were placed in theoretical positions 0.97 Å from the bonded carbon atom. Details of data collection and crystal structure are presented in Table 1.

#### Discussion

Catalysis of the Knoevenagel reaction of benzaldehyde, 2-chlorobenzaldehyde and 2,4dichlorobenzaldehyde with methyl cyanoacetate using  $K_2NiP_2O_7$  led to a yield of 71.65% of the condensation product. Higher yields (77.10% (II) and 83.45% (III)) were observed when the benzaldehyde was substituted with electron withdrawing groups. The purity of the product was established by GC-MS. A single product was present in each case. Because of the low solubility of the products in methanol, crystalline condensation products, (I), (II), and (III), were easily isolated. Single crystal X-ray diffraction allowed identification of the stereochemistry of the product.

The single product produced in each case was an (E)-methyl- $\alpha$ -cyanocinnamate; methyl cyanocinnamate (I), methyl 2-chlorocyanocinnamate (II), and methyl 2,4-dichlorocyanocinnamate (III). Figures 1(a-c) are based on the positional parameters of Tables 2, 3, and 4. One might predict the stability of the E isomer on the basis of relief of steric crowding about the double bond, i.e. the bulky phenyl and methylacetate groups would prefer to be trans to each other about the double bond; however both (E) and (Z) methyl cyanocinnamate isomers are known. Only the (E) isomer of methyl 2-chlorocyanocinnamate is known and the conformation of the methyl 2,4-dichlorocinnamate previously isolated has not been reported.

Table 2. Positional Parameters for (I)

Atom	$x(\sigma(x))$	$y(\sigma(y))$	$z(\sigma(z))$	$U_{(eq)} \times 10^{3^a}$
N1	0.5756(5)	0.5005(3)	0.23095(11)	0.0672(7)
01	0.7753(3)	0.25627(15)	0.34343(8)	0.0484(4)
O2	0.5271(3)	0.2147(2)	0.44228(8)	0.0580(5)
C1	0.5831(4)	0.2794(2)	0.38666(11)	0.0386(4)
C2	0.4453(4)	0.3977(2)	0.36021(10)	0.0371(4)
C3	0.5179(4)	0.4571(2)	0.28850(11)	0.0455(5)
C4	0.2622(4)	0.4421(2)	0.40401(10)	0.0388(4)
C5	0.1017(4)	0.5557(2)	0.39700(10)	0.0385(4)
C6	0.1261(5)	0.6572(2)	0.34227(13)	0.0504(5)
C7	-0.0404(5)	0.7592(2)	0.33975(14)	0.0575(6)
C8	-0.2289(5)	0.7636(2)	0.39101(15)	0.0551(6)
C9	-0.2528(4)	0.6660(2)	0.44633(14)	0.0515(6)
C10	-0.0883(4)	0.5638(2)	0.44946(11)	0.0447(5)
C11	0.9249(5)	0.1450(2)	0.36645(15)	0.0570(6)

 ${}^{a}U_{(eq)}$  is defined as one third of the trace of the orthogonalized  $U_{ij}$  tensor.



**Fig. 1.** (a) Projection view of methyl (E)- $\alpha$ -cyanocinnamate (I); (b) Projection view of methyl (E)-2-chloro- $\alpha$ -cyanocinnamate (II); (c) Projection view of methyl (E)-2,4-dichloro- $\alpha$ -cyanocinnamate(III). Thermal ellipsoids for (I), (II), and (III) are shown at the 50% probability level.

#### Methyl (E)- $\alpha$ -cyanocinnamate derivatives

**Table 3.** Positional Parameters for Methyl (E)-2-Chloro-α-Cyanocinnamate (II)

Atom	$x(\sigma(x))$	$y(\sigma(y))$	$z(\sigma(z))$	$U_{(eq)} \times 10^{3^a}$
Cl1	0 41072(5)	0.92590(11)	0.3462(2)	0.0615(5)
01	0.08479(12)	0.8280(3)	0.2373(5)	0.0467(9)
02	0.18291(15)	0.7079(4)	0.4115(6)	0.0626(11)
N1	0.1172(2)	1.2333(5)	0.0791(7)	0.0561(13)
C1	0.1530(2)	0.8282(4)	0.3226(6)	0.0418(11)
C2	0.1892(2)	0.9997(4)	0.2921(6)	0.0371(10)
C3	0.1488(2)	1.1294(5)	0.1750(6)	0.0405(10)
C4	0.2587(2)	1.0159(4)	0.3677(6)	0.0391(10)
C5	0.3056(2)	1.1671(4)	0.3552(6)	0.0366(10)
C6	0.2822(2)	1.3429(4)	0.3555(6)	0.0419(11)
C7	0.3286(2)	1.4817(4)	0.3480(7)	0.0506(14)
C8	0.3999(2)	1.4485(5)	0.3404(7)	0.0540(14)
C9	0.4242(2)	1.2770(5)	0.3391(7)	0.0503(13)
C10	0.3779(2)	1.1399(4)	0.3481(6)	0.0419(11)
C11	0.0463(2)	0.6627(5)	0.2446(7)	0.0622(15)

 $^{a}U_{(eq)}$  is defined as one third of the trace of the orthogonalized  $U_{ij}$  tensor.

The structure of the (E)-isomer, (E)-methyl-  $\alpha$ -cyanocinnamate(I) has already been reported in monoclinic space group C2/c with parameters a = 12.386(2) Å, b = 8.237(1) Å, c = 19.320(2) Å,  $\beta = 98.49(5)^{\circ}$ , and Z = 8. Those crystals were reported to be prisms.<sup>17</sup>

 
 Table 4. Positional Parameters for Methyl 2,4-Dichloro-α-Cyanocinnamate (III)

Atom	$x(\sigma(x))$	$y(\sigma(y))$	$z(\sigma(z))$	$U_{(eq)} \times 10^{3^a}$
Cl1	0.1631(4)	0.23745(15)	0.91978(9)	0.0694(5)
Cl2	0.4525(4)	-0.40406(14)	0.90434(8)	0.0647(5)
01	1.2315(10)	-0.5485(5)	0.5928(2)	0.0789(12)
O2	0.9702(11)	-0.6567(5)	0.6913(2)	0.0821(12)
N1	1.1635(15)	-0.1468(7)	0.5991(3)	0.0918(16)
C1	1.0515(13)	-0.5410(7)	0.6579(3)	0.0617(14)
C2	0.9623(11)	-0.3708(6)	0.6843(3)	0.0526(12)
C3	1.0715(13)	-0.2467(8)	0.6372(3)	0.0645(14)
C4	0.7897(11)	-0.3493(6)	0.7508(3)	0.0504(11)
C5	0.6556(11)	-0.2041(5)	0.7915(3)	0.0457(11)
C6	0.6667(12)	-0.0451(6)	0.7635(3)	0.0554(12)
C7	0.5252(12)	0.0899(6)	0.8021(3)	0.0552(12)
C8	0.3581(11)	0.0695(5)	0.8715(3)	0.0497(11)
C9	0.3461(11)	-0.0820(5)	0.9024(3)	0.0501(11)
C10	0.4932(10)	-0.2158(5)	0.8627(3)	0.0430(10)
C11	1.335(2)	-0.7074(8)	0.5622(4)	0.097(2)

 ${}^{a}U_{(eq)}$  is defined as one third of the trace of the orthogonalized  $U_{ij}$  tensor.



**Fig. 2.** (a) Packing of (E)-methyl- $\alpha$ -cyanocinnamate (monoclinic cell based on parameters of Ref. 21). Projection down the *b*-axis. (b) Packing of (I) (orthorhombic cell). Projection down the a axis. Thermal ellipsoids are shown at the 50% probability level.

The crystals isolated in this work were needlelike. The single crystal X-ray diffraction data showed the material isolated to be a polymorph of the reported (E)-methyl- $\alpha$ cyanocinnamate and to crystallize in orthorhombic space group  $P2_12_12_1$  with cell parameters a =5.531(1) Å, b = 10.053(1) Å, c = 17.374(4) Å. While both structures have E conformation, the packing of molecules in the unit cell differs in the two polymorphs. Both show stacking of aromatic rings. The monoclinic crystal shows stacks of molecules with their long axes parallel and with alternating placement of the aromatic ring (Fig. 2a). The orthorhombic crystal isolated in this work shows that the regular overall parallel packing has been disrupted to yield two different

(I)		(II)		(III)	
N1-C3	1.137(3)	N1-C3	1.137(5)	N1-C3	1.152(7)
O1-C1	1.322(3)	O1-C1	1.319(5)	O1-C1	1.329(6)
O1-C11	1.448(3)	O1-C11	1.444(4)	O1-C11	1.445(7)
O2-C1	1.205(2)	O2-C1	1.190(5)	O2-C1	1.200(6)
C1-C2	1.485(3)	C1-C2	1.494(4)	C1-C2	1.498(7)
C2-C4	1.343(3)	C2-C4	1.329(6)	C2-C4	1.342(6)
C2-C3	1.439(3)	C2-C3	1.419(6)	C2-C3	1.420(8)
C4-C5	1.451(3)	C4-C5	1.453(4)	C4-C5	1.450(7)
C5-C10	1.393(3)	C5-C10	1.392(4)	C5-C10	1.399(6)
C5-C6	1.402(3)	C5-C6	1.392(4)	C5-C6	1.409(6)
C6-C7	1.379(3)	C6-C7	1.369(5)	C6-C7	1.371(7)
C7-C8	1.372(4)	C7-C8	1.381(5)	C7-C8	1.390(7)
C8-C9	1.380(3)	C8-C9	1.367(5)	C8-C9	1.369(6)
C9-C10	1.374(3)	C9-C10	1.360(5)	C9-C10	1.379(6)
		Cl1-C10	1.723(3)	Cl1-C8	1.728(5)
				Cl2-C10	1.742(4)
C1-01-C11	116.00(17)	C1-01-C11	115.8(3)	C1-01-C11	116.7(5)
O2-C1-O1	124.57(19)	O2-C1-O1	125.2(3)	O2-C1-O1	123.9(5)
O2-C1-C2	123.24(19)	O2-C1-C2	123.5(4)	O2-C1-C2	124.2(5)
01-C1-C2	112.17(16)	01-C1-C2	111.3(3)	01-C1-C2	111.9(5)
C4-C2-C3	124.23(19)	C4-C2-C3	124.2(3)	C4-C2-C3	125.7(5)
C4-C2-C1	118.55(17)	C4-C2-C1	117.5(3)	C4-C2-C1	117.1(5)
C3-C2-C1	117.21(19)	C3-C2-C1	118.2(3)	C3-C2-C1	117.3(4)
N1-C3-C2	178.0(2)	N1-C3-C2	178.8(3)	N1-C3-C2	179.3(6)
C2-C4-C5	132.48(18)	C2-C4-C5	127.7(4)	C2-C4-C5	131.7(5)
C10-C5-C6	118.30(19)	C10-C5-C6	116.9(3)	C10-C5-C6	115.3(4)
C10-C5-C4	116.88(17)	C10-C5-C4	120.2(3)	C10-C5-C4	120.2(4)
C6-C5-C4	124.82(19)	C6-C5-C4	122.9(3)	C6-C5-C4	124.5(4)
C7-C6-C5	119.9(2)	C7-C6-C5	121.0(3)	C7-C6-C5	123.0(4)
C8-C7-C6	120.7(2)	C6-C7-C8	120.0(3)	C6-C7-C8	118.7(4)
С7-С8-С9	120.1(2)	C9-C8-C7	120.1(3)	C9-C8-C7	120.9(4)
С10-С9-С8	119.8(2)	C10-C9-C8	119.5(3)	C9-C8-Cl1	119.3(4)
C9-C10-C5	121.14(19)	C9-C10-C5	122.4(3)	C7-C8-C11	119.8(4)
		C9-C10-Cl1	118.0(2)	C8-C9-C10	119.2(4)
		C5-C10-Cl1	119.6(2)	C9-C10-C5	122.9(4)
				C9-C10-Cl2	116.3(3)
				C5-C10-Cl2	120.8(3)

Table 5. Bond Angles and Distances for (I), (II), and (III)

directions of placement of the long molecular axis (Fig. 2b).

The catalyst has been consistent in producing only the E isomer. Further experimental work will be needed to establish if the stereochemical preference is a due to thermodynamic considerations or to the noncentric space  $\text{group}^{22}$  of the solid  $K_2 \text{NiP}_2 \text{O}_7$  used as catalyst.

Products (I), (II), and (III) show relative coplanarity of the cyanoacetate moiety of the molecule. However, the angles subtended by the phenyl ring and this moiety differ greatly: (5.1, (I); 37.6, (II); 6.8° (III)). Since both (II) and (III) involve ortho substitution of chloride groups on the phenyl ring, the larger deviation from coplanarity observed for (II) must be due to packing influences. Bond angles and distances are similar for the three compounds (Table 5).

## **Supplementry material**

Crystallographic Data for (I), (II), and (III) have been deposited with the Cambridge Crystallographic Data Center as supplementary

#### Methyl (E)- $\alpha$ -cyanocinnamate derivatives

publication numbers CCDC 192568, 192628, 192629. Copies of the data can be obtained, free of charge, on application to CCDC, 12 Union Road, Cambridge, CB2, 1EZ, UK [FAX: +44(0)-1223-336033 or e-mail: deposit@ccdc.cam.ac.uk].

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