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## Titanium Tetrachloride-Mediated Carbon-Carbon Chlorocyanoethylation of Anisole: Synthesis of Tyrosine Derivatives

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### TITANIUM TETRACHLORIDE-MEDIATED CARBON-CARBON CHLOROCYANOETHYLATION OF ANISOLE: SYNTHESIS OF TYROSINE DERIVATIVES<sup>1</sup>

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**Abstract:** Chlorocyanoethylation of anisole with 2-chloroacrylonitrile in presence of titanium tetrachloride furnished  $\alpha$ -chloro- $\beta$ -(4-methoxyphenyl)propionitrile. This on simple reaction sequence was converted to (<u>+</u>) methyl- $\alpha$ -amino- $\beta$ -(4-methoxyphenyl)propionate, a tyrosine derivative.

Carbon-carbon cyanoethylation of more active phenols, such as resorcinol to give  $\beta$ -substituted propionic acid and the corresponding lactone in the presence of anhydrous zinc chloride and anhydrous hydrogen chloride is well known.<sup>2</sup> Phenol, anisole and its derivatives do not react under these conditions, but in the presence of more active catalyst such as anhydrous aluminium chloride and hydrogen chloride afford in good yields  $\beta$ -(4-hydroxyphenyl)propionitrile<sup>3</sup> or  $\beta$ -(4-methoxy phenyl)propionitrile<sup>4</sup> respectively. Aluminium chloride catalyzed reactions of vinylidine cyanide and anisole to form  $\alpha$ -cyano- $\beta$ -(4-methoxyphenyl)propionitrile is also documented.<sup>5</sup> In connection with the synthesis of tyrosine derivative we required an efficient direct method of introducing  $\alpha$ -chloropropionitrile side chain para to a methoxy group in an aromatic ring. From the above

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literature precedence it is likely that reaction of 2-chloroacrylonitrile with anisole in the presence of a suitable Lewis acid will produce  $\alpha$ -chloro- $\beta$ -(4-methoxyphenyl)propionitrile which can be elaborated further. Preparation of  $\alpha$ -chloro- $\beta$ -(4-methoxyphenyl) propionitrile by arylation of acrylonitrile in the deamination of *p*-anisidine by alkyl nitriles and copper (II) chloride is reported.<sup>6</sup> This method suffers from the use of relatively large excess of acrylonitrile (30fold) and low yield (32%). The reported conversion of  $\alpha$ -chloro- $\beta$ -(4-methoxyphenyl)propionitrile to tyrosine derivative was carried out in two steps with low overall yield (28%)<sup>7</sup>. Here, we wish to report a hitherto unknown titanium tetrachloride mediated chlorocyanoethylation of anisole with 2-chloroacrylonitrile to afford  $\alpha$ -chloro- $\beta$ -(4-methoxyphenyl)propionitrile 3 (Scheme 1) and its simple transformation in three steps to (±) methyl- $\alpha$ - amino- $\beta$ -(4-methoxyphenyl)propionate 10, a tyrosine derivative in 78% overall yield, (Scheme 2).

#### **Results and Discussion**

Chlorocyanoethylation of anisole 1 with 2-chloroacrylonitrile 2 in the presence of anhydrous AlCl<sub>3</sub> and dry HCl gas in sym-tetrachloroethane afforded a mixture of two products. From the reaction mixture  $\alpha$ -chloro- $\beta$ -(4-methoxyphenyl) propionitrile 3 (19%) and the dimer 5 (2%) were isolated along with unreacted anisole. Using SnCl<sub>4</sub> as a Lewis acid for this reaction, a mixture of three products, *para*-isomer 3 (14%), *ortho isomer* 4 (5.5%) and the dimer 5 (0.3%) were isolated. The best results were obtained using TiCl<sub>4</sub> as a Lewis acid catalyst for this reaction. The reaction mixture on column chromatographic purification over silica gel furnished compound 3 (62%), 4 (18%) and 5 (1%) and no starting anisole was recovered. The results are summarized in Table 1.

The regioisomeric products 3 and 4 were identified by their <sup>1</sup>H NMR spectrum. The major *para* alkylated product 3 showed a simple AB-pattern in the aromatic region at  $\delta$  6.8 and 7.15 and the *ortho* alkylated product 4 as expected showed a complex set of signals at  $\delta$  6.9 and 7.15. The <sup>1</sup>H NMR of the dialkylated product 5 showed interesting features. Since, the molecule has now two chiral centers, two diastereoisomers should exist. It showed two doublets at  $\delta$  3.26 and 3.35 for *para* (C-2, H) and *ortho* (C-4, H)  $\alpha$  methylene protons respectively. Two separate signals each consisting of two closely spaced triplets at  $\delta$  4.45 and 4.76 for *para* (C-1, H) and *ortho* (C-3, H)  $\alpha$  methine protons. In the aromatic region a doublet at  $\delta$  6.9, J=12Hz for the proton *ortho* (C-3', H) to -OCH<sub>3</sub>, a multiplet at  $\delta$  7.15,





Scheme 1 Reagents and conditions: i, TiCl<sub>4</sub>, sym-tetra--chloroethone, 70 °C, 6h



#### Table 1

Reaction of anisole <sup>a</sup> 1	with 2-chloroacr	ylonitrile <sup>b</sup> 2 in a	sym-tetrachloroethane <sup>c</sup> .
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Entry	Lewis Acid <sup>4</sup>	Temp (0°C)	Time (hours)	Product Distribution (% Yield <sup>e</sup> )		
				3	4	5
$1^{\rm f}$	AlCl <sub>3</sub>	55-60	15	12	0	0
2 <sup>f</sup>	AlCl <sub>3</sub>	60-70	12	19	0	2
3 <sup>f</sup>	AlCl <sub>3</sub>	70-75	14	15	0	3
4 <sup>f</sup>	TiCl₄	50-55	16	27	7	0.8
5 <sup>f</sup>	TiCl <sub>4</sub>	70-75	3	26	8	0.4
6	TiCl₄	70-75	6	62	18	1
7	TiCl₄	70-75	12	58	15	2
8	SnCl₄	55-65	12	14	5.5	0.3

<sup>a</sup>Anisole (1mmol), <sup>b</sup>CH2=CHClCN (2.5mmol), <sup>c</sup>Sym-tetrachloroethane (3ml), <sup>d</sup>Lewis acid (1.2mmol), <sup>e</sup>isolated yield, <sup>f</sup>some starting anisole recovered.

J=<2Hz for the proton *meta* (C-6', H) to -OCH<sub>3</sub>, and flanked by two alkyl chains and a doublet of a doublet at  $\delta$  7.28, J=2.5 and 12 Hz for the proton *meta* (C-2', H) to -OCH<sub>3</sub> clearly indicates the structure 5 assigned to the dichlorocyanoethylated product. In compound 5 decoupling of the  $\beta$ -methylene protons of the *para* (C-2, H) alkylated side chain at  $\delta$  3.26 leads to a collapse of six lines at  $\delta$  4.45 into two lines. In a similar manner decoupling of the  $\beta$ -methylene protons of the *ortho* (C-4, H) alkylated side chain at  $\delta$  3.35 leads to the collapse of six lines at  $\delta$  4.76 into two lines of equal intensity. This decoupling experiments conclusively proves the presence of two diastereoisomers in almost 1:1 ratio in compound 5.

A solution of compound 3 in dry methanol and anhydrous ether was treated with anhydrous HCl gas<sup>7</sup> to afford the methylester 6 in 86% yield (Scheme 2). The chloro ester 6 on reaction with NaN<sub>3</sub> in DMF furnished the azido methylester 8 (92%). Catalytic

#### **TYROSINE DERIVATIVES**

hydrogenation of 8 with 10% Pd-C in ethanol gave amino ester 10 in 99% yield (overall yield in three steps is 78%). In a similar way compound 4 was transformed to its amino ester 11 in three steps with an overall yield of 68%.

#### Experimental

All the b.p.s are uncorrected. IR spectra were recorded on a Perkin Elmer 599B spectrophotometer using NaCl optics. <sup>1</sup>H NMR spectra were recorded either at 80MHz on a Varian FT-80A or at 200MHz on a Bruker ACF-200 NMR spectrophotometer. Chemical shifts were recorded in ppm( $\delta$ ) using Me<sub>4</sub>Si as an internal standard an coupling constants were expressed in Hz. Mass spectra were recorded on a Finnigan 1020C mass spectro-photometer at 70ev. Column chromatography was carried out over SiO<sub>2</sub> (silica gel, 60-120 mesh, SD Fine Chemicals, Bombay). For dry reactions glass wares were thoroughly dried in oven and were cooled under nitrogen. The reactions were monitored by TLC using TLC aluminium sheets, Silica gel 60 F<sub>254</sub> precoated, Merck, Germany and locating the spots by spraying with ethanolic solution of phosphomolybdic acid and heating and also by UV light. TiCl<sub>4</sub> and 2-chloroacrylonitrile were purchased from Aldrich, USA and were used without further purification.

#### Chlorocyanoethylation of anisole 1 using AlCl3 and dry HCl gas

Mixture of anisole 1 (4.32g, 40mmol) and 2-chloroacrylonitrile 2 (8.8g, 100mmol) in *sym*-tetrachloroethane (20 cm<sup>3</sup>)was cooled to 5°C and AlCl<sub>3</sub> (6.39g, 48mmol) was added in 3 lots keeping the temperature below 10°C. The reaction mixture was stirred at 10°C for 1.5h and then heated at 60-70°C for 12h with continuous passage of dry hydrogen chloride. The reaction mixture was brought to 20°C and was poured on crushed ice. It was then extracted with methylene dichloride (3x75cm<sup>3</sup>). The organic layer was washed with water (2x100cm<sup>3</sup>), 5% sodium hydroxide solution (2x50cm<sup>3</sup>), water (2x50cm<sup>3</sup>) and finally with brine (2x50cm<sup>3</sup>). The organic extract was dried over anhydrous sodium sulphate. Methylene dichloride and *sym*-tetrachloroethane was removed under vacuum. The crude gummy oil on distillation under vacuum afforded compound 3 (1.52g, 19%) as a pale yellow liquid b.p. 140-150°C / 0.7 torr (Found: C, 61.23; H, 5.30. C<sub>10</sub>H<sub>10</sub>ClNO requires C, 61.38; H, 5.11%);  $v_{max}$  (neat)/ Cm-1 2960, 2836, 2240, 1615, 1520, 1310, 990;  $\delta_{\rm H}$  (80 MHz) 3.2 (d, 2H, J=8, C<sub>2</sub>H), 3.75 (s, 3H, -OCH<sub>3</sub>), 4.45 (t, 1H, J=8, H<sub>1</sub>), 6.81 (d, 2H, J=10, H<sub>3</sub>, s), 7.15 (d, 2H, J=10, H<sub>2</sub>, s).

H<sub>2',6</sub>); m/z 121 (100%), 160, 195, 197 (M<sup>+</sup>). The gummy residue after distillation solidified which was crystallized from hexane-ethylacetate to afford compound 5 (0.230g, 2%) m.p. 72-73°C;  $v_{max}$  (nujol)/ Cm<sup>-1</sup> 3030, 2252, 1620, 1610;  $\delta_{H}$  3.26 (d, 2H, J=7, H<sub>2</sub>), 3.35 (d, 2H, J=7, H<sub>4</sub>), 3.89 (s, 3H, -OCH<sub>3</sub>), 4.55 (two closely overlapping triplets, 1H, J=7, H<sub>1</sub>, two diastereoisomers), 4.76 (two closely overlapping triplets, 1H, J=7, H<sub>3</sub>, two diastereoisomers), 6.9 (d, 1H, J=12, H<sub>3</sub>·), 7.15 (m, 1H, J<2, H<sub>6</sub>·), 7.28 (dd, 1H, J=2, H<sub>2</sub>·); m/z 104, 172, 208 (100%), 282, 284 (M<sup>+</sup>).

#### Chlorocyanoethylation of anisole 1 using SnCl4 as Lewis acid

To a magnetically stirred mixture of anisole 1 (0.542g, 5mmol) and 2-chloroacrylonitrile 2 (1.09g, 2.5mmol) in sym-tetrachloroethane (10cm<sup>3</sup>), stannic chloride (1.57g, 6mmol) was added at 5°C and the mixture was stirred for 10 minutes. The reaction mixture was then heated at 55-65°C for 12h, was brought to 20°C and poured on crushed ice. It was extracted with methylene dichloride (3x50cm<sup>3</sup>), washed with water (2x50cm<sup>3</sup>), saturated sodium bicarbonate solution (2x25cm<sup>3</sup>), water (2x50cm<sup>3</sup>) and finally with brine (2x25cm<sup>3</sup>). The methylene dichloride extract was dried over anhydrous sodium sulphate. Solvents were removed under vacuum to obtain a brown gum. This on column chromatographic purification over silica gel using hexane and ethyl acetate (20:1) afforded compound 4 (0.055g, 5.5%) as a pale yellow liquid b.p. 95°C/0.240 torr (Found: C, 61.54; H, 5.22. C<sub>10</sub>H<sub>10</sub>ClNO requires C, 61.38; H, 5.11%);  $v_{max}$  (neat)/cm<sup>-1</sup>2940, 2840, 2250, 1610, 1448, 1260, 1040;  $\delta_{\rm H}$  (80MHz) 3.29 (d, 2H, J=8, H<sub>2</sub>), 3.80 (s, 3H, -OCH<sub>3</sub>), 4.72 (t, 1H, H<sub>1</sub>), 6.70-7.00 (m, 1H, H<sub>3'</sub>), 7.01-7.35 (m, 3H, H<sub>2'</sub>, H<sub>4</sub> and H<sub>5'</sub>); m/z 121 (100%), 160, 195, 197 (M<sup>+</sup>). Further elution of the column with hexane ethyl acetate furnished compound 3 (0.135g, 14%) and finally compound 5 (0.005g, 0.3%).

#### Chlorocyanoethylation of anisole 1 using TiCl4 as Lewis acid

To a magnetically stirred solution of 2-chloroacrylonitrile 2 (2.18g, 25mmol) in *sym*-tetrachloroethane (12cm<sup>3</sup>), titanium tetrachloride (2.276g, 12mmol) was added at 0-5 °C during a period of 5 min. The resulting dark red reaction mixture was stirred for 10 min and then anisole 1 (1.084g, 10mmol) was added at 0-5 °C. The reaction mixture was then heated at 70-75 °C under nitrogen for 6h. After the completion of the reaction it was quenched with ice cold water (5cm<sup>3</sup>) and the resulting dark brown solution was extracted with methylene

dichloride  $(3x50cm^3)$ , washed with water  $(3x25cm^3)$  and finally with brine  $(2x25cm^3)$ . The organic extract was dried over anhydrous sodium sulphate and evaporation of the solvent under reduced pressure afforded 1.76g of dark yellow liquid. Column chromatography of the reaction mixture using hexane-ethyl acetate (20:1) furnished compound 4 (0.351g, 18.0%). Further elution with hexane ethyl acetate afforded compound 3 (1.21g, 62%) and finally compound 5 (0.056g, 2%).

# Methyl- $\alpha$ -Chloro- $\beta$ -(4-methoxyphenyl)propionate 6 and Methyl- $\alpha$ -Chloro- $\beta$ -(2-methoxyphenyl)propionate 7

To a stirred solution of  $\alpha$ -chloro- $\beta$ -(4-methoxyphenyl)propionitrile (0.508g, 2.6mmol) in anhydrous ether (15cm<sup>3</sup>) and methanol (10cm<sup>3</sup>) dry hydrogen chloride gas was passed for 1h at 0°C. Then the reaction mixture was stirred at room temperature for a period of 1h. The reaction mixture was then poured on crushed ice and extracted with ether (3x50cm<sup>3</sup>). The ether layer was thoroughly washed with water (5x30cm<sup>3</sup>) till the washings are neutral and then with brine  $(2x25cm^3)$ . The ether extract was dried over anhydrous sodium sulphate and the solvent was removed to furnish the crude methyl ester, 0.610g, as an oil. This was distilled to afford pure methyl- $\alpha$ -chloro- $\beta$ -(4-methoxyphenyl)propionate **6** as a pale yellow liquid (0.510g, 86%) b.p. 105-110°C/ 0.025torr (Found C, 56.20; H, 5.30. C11H13ClO3 requires C, 57.76; H, 5.68%); v<sub>max</sub> (neat)/ cm-1 2962, 1755, 1620, 1595, 1622, 1260, 1044; δ<sub>H</sub> (80MHz) 3.15 (m, 2H, H<sub>2</sub>), 3.65 (s, 3H, -OCOCH<sub>3</sub>), 3.71 (s, 3H, -OCH<sub>3</sub>), 4.82 (t, 1H,  $J=8, H_2$ , 6.78 (d, 2H,  $J=10, H_3$  and  $H_5$ ), 7.18 (d, 2H,  $J=10, H_2$ , and  $H_6$ ); m/z 121 (100%), 161, 228, 230 (M<sup>+</sup>). In a similar way α-chloro-β-(2-me thoxyphenyl)propionitrile 4 (0.511g, 2.62mmol) gave pure methyl- $\alpha$ -chloro- $\beta$ -(2-methoxy phenyl)propionate (0.504g, 84.4%) b.p. 100°C/ 0.075 torr (Found C, 58.21; H, 5.81. C<sub>11</sub>H<sub>13</sub>ClO<sub>3</sub> requires C, 55.98; H, 5.68%);  $v_{max}$  (neat)/ cm<sup>-1</sup> 2980, 1765, 1620, 1264, 1045;  $\delta_{H}$  (80MHz) 3.21 (m, 1H, H<sub>2</sub>), 3.65 (s, 3H, -OCOCH<sub>3</sub>), 3.75 (s, 3H, -OCH<sub>3</sub>), 4.6 (t, 1H, J=8, H<sub>2</sub>), 6.7-7.0 (m, 2H, H<sub>3</sub> and H<sub>3</sub>), 7.00-7.35 (m, 2H, H2 and H4);

## Methyl- $\alpha$ -azido- $\beta$ -(4-methoxyphenyl)propioniate 8 and Methyl- $\alpha$ -azido- $\beta$ -(2-methoxy phenyl)propionate 9

To a solution of Methyl- $\alpha$ -chloro- $\beta$ -(4-methoxyphenyl)propionate (0.228g, 1mmol) in DMF (10cm<sup>3</sup>), NaN<sub>3</sub> (0.195g, 3mmol) was added and it was stirred at 50-60°C for 20h.

The reaction mixture was then quenched with water and was extracted with ether (3x25 cm<sup>3</sup>). The ether layer was thoroughly washed with water (5x25cm<sup>3</sup>) and brine (2x10 cm<sup>3</sup>) and it was dried over anhydrous sodium sulphate. Removal of solvent followed by column chromatography furnished methyl- $\alpha$ -azido- $\beta$ -(4-methoxyphenyl)propionate **8** as an oil (0.216g, 92%);  $\nu_{max}$  (neat)/cm<sup>-1</sup> 2980, 2140, 1765, 1620, 1262, 1048;  $\delta_{H}$  (200 MHz) 3.1 (m, 2H, H<sub>2</sub>), 3.82 (s, 3H, -OCOCH<sub>3</sub>), 3.89 (s, 3H, -OCH<sub>3</sub>), 4.06 (m. 1H, H<sub>2</sub>), 6.87 (d, 2H, J=10, H<sub>3</sub>· and H<sub>5</sub>·), 7.17 (d, 2H, J=10, H<sub>2</sub>· and H<sub>6</sub>·); m/z 121(100%), 161, 192, 235 (M<sup>+</sup>). Similarly compound 7 (0.246g, 1.07mmol) furnished methyl- $\alpha$ -azido- $\beta$ -(2-methoxyphenyl) propionate (0.226g, 89%);  $\nu_{max}$  (neat) / cm<sup>-1</sup> 2980, 2120, 1760, 1610, 1600, 1038;  $\delta_{H}$  (80MHz) 3.1 (m, 2H, H<sub>2</sub>), 3.7 (s, 3H, -OCH<sub>3</sub>), 3.8 (s, 3H, -OCOCH<sub>3</sub>), 4.15 (m, 1H, H<sub>1</sub>), 6.75-7.05 (m, 2H, H<sub>3</sub>· and H<sub>5</sub>·), 7.05-7.4 (m, 2H, H<sub>2</sub>· and H<sub>4</sub>·); m/z 121 (100%), 192, 235 (M<sup>+</sup>)

# Methyl- $\alpha$ -amino- $\beta$ -(4-methoxyphenyl)propionate and methyl- $\alpha$ -amino- $\beta$ -(2-methoxy phenyl)propionate 10 and 11

Methyl-α-azido-β-(4-methoxyphenyl)propionate (0.117g, 0.5mmol) was dissolved in ethanol (10cm<sup>3</sup>) and was hydrogenated at 35 psi using 10% Pd/C (0.012g) for 5h. Filtration followed by removal of solvent under reduced pressure afforded pure (homogeneous on TLC) methyl-α-amino-β-(4-methoxyphenyl)propionate 10 as a gum (0.103g, 99%);  $v_{max}$ (neat) / cm<sup>-1</sup> 3330 (broad), 2930, 1735, 1616, 1590, 1455, 1255, 1040;  $\delta_{H}$  (80MHz) 2.88 (m, 2H, H<sub>2</sub>), 3.7 (s, 3H, -OCOCH<sub>3</sub>), 3.78 (s, 3H, -OCH<sub>3</sub> and m, 2H, H<sub>1</sub>), 6.75 (d, 2H, J=10, H<sub>3</sub>· and H<sub>5</sub>·), 7.03 (d, 2H, J=10, H<sub>2</sub>· and H<sub>6</sub>·); m/z 116, 121, (100%), 147, 178, 209 (M<sup>+</sup>). In a similar manner from compound 9 (0.122g, 0.52mmol) methyl-α-amino-β-(2- methoxyphenyl)propionate 11 was obtained (0.098g, 90%); vmax CHCl<sub>3</sub> / cm<sup>-1</sup> 3040, 1738, 1610, 1595, 1445, 1250, 1038;  $\delta_{H}$  (200 MHz) 2.82 (m, 2H, H<sub>2</sub>), 3.7 (s, 3H, -OCOCH<sub>3</sub>), 3.82 (s, 3H, -OCH<sub>3</sub>), 3.9 (t, 1H, H<sub>1</sub>), 6.82-7.00 (m, 2H, H<sub>3</sub>· and H<sub>5</sub>·), 7.05-7.35 (m, 2H, H<sub>2</sub>· and H<sub>4</sub>·)

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