CHAPTER II
EXPERIMENTAL

2.1) Material

There are a number of chemicals used but the following listings are the major ones: 3-nitro-4-toluidine (>98%, Fluka), cuprous cyanide (>99%, Fluka), *N*-bromosuccinimide (>97%, Fluka), 4-ethylbenzaldehyde (>98%, Aldrich), triethylamine (>99.5%, Carlo elba), potassiumpersulfate (>98%, Carlo elba), potassium dichromate (99.5%, Carlo elba), tetrahydrofuran (99.5%, Carlo elba), sulfuric acid (96%, Carlo elba), and fuming nitric acid (90%, Carlo elba).

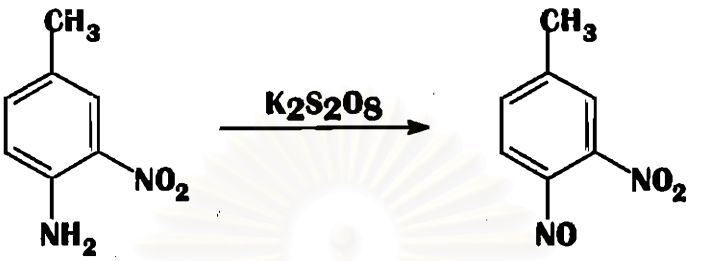
2.2) Instrument

Followings are the list of major instruments used in this study.

1) DSC4 Perkin-Elmer Differential Scanning Calorimeter.
2) 1760X Perkin-Elmer FT-IR spectrophotometer
3) FT-NMR spectrometer ACF. 200 MHz, Bruker.

2.3) Experimental

2.3.1 Synthesis of 3-Nitro-4-nitroso Toluene



Mw =152.15 Mw =166.14

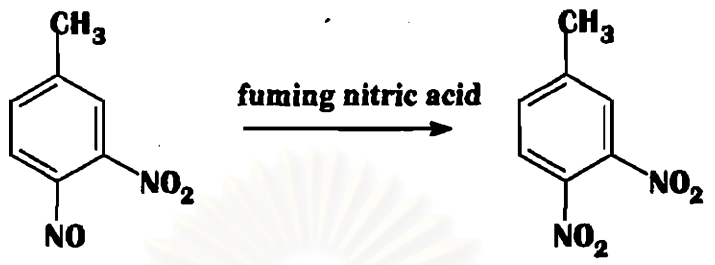
(1) (2)

Scheme 2.1

Solid potassium persulfate (320 g, 1.18 mol) was slowly added to 280 mL of concentrated sulfuric acid within an hour in an ice-cooled basin and then stirred in 3 L of ice water. A suspension containing 87 g (0.57 mol) of finely powdered 3-nitro-4-aminotoluene in 2 L of water was added to the above solution and stirred for 24 h. The resulting precipitate was filtered and again mixed with the same amount of concentrated sulfuric acid previously described for another 24 h. Yield 87 g (0.52 mol) of pale yellow 3-nitro-4-nitroso toluene (92%) m.p. 147 ^{0}C, lit[22]: 146^{O}C.

IR (cm^{-1}, KBr) : 3093 (w, aromatic C-H); 1542 and 1355 (s, NO_2); 1282 (s, C-N of NO); 851(m, C-N of NO_2). ^{1}H-NMR (δ in $CDCl_3$) : 2.5 (s, 3H, CH_3); 6.46-6.42 (d, 1H, aromatic, J_{HH} 8.09 Hz); 7.42-7.38 (d, 1H, aromatic, J_{HH}8.16 Hz); 7.81 (s,1H, aromatic).

2.3.2 Synthesis of 3,4-Dinitrotoluene



Mw =166.14 (2)

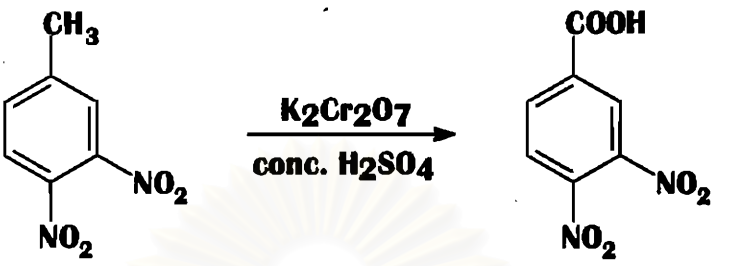
Mw =182.14 (3)

Scheme 2.2

10 g (0.06 mol) of 3-nitro-4-nitrosotoluene was dissolved slowly in 50 g of fuming nitric acid; the mixture temperature was kept at 25 ^{0}C. The yellow brown product of 3,4-dinitrotoluene was filtered off by suction and washed with water.Yield 10.6 g (0.06 mol, 96%). m.p. 60 ^{0}C, lit[22]: 54-57 ^{O}C.

IR (cm^{-1}, KBr) : 3100 (w, aromatic C-H); 1543 and 1350 (s, NO_2); 847 (m, C-N). ^{1}H-NMR (δ in $CDCl_3$) : 2.53 (s, 3H, CH_3); 7.50-7.54 (d, 1H, aromatic, J_{HH} 8.26 Hz); 7.64 (s, 1H, aromatic); 7.87-7.83 (d, 1H, aromatic, J_{HH} 8.26 Hz). ^{13}C-NMR (δ in $CDCl_3$) : 21.43 (CH_3); 125.27 (aromatic), 133.40 (aromatic); 145.79 (=C-NO_2).

2.3.3 Synthesis of 3,4-Dinitrobenzoic Acid



Mw =182.14 Mw =212.12

(3) (4)

Scheme 2.3

29 g (0.16 mol) of 3,4-dinitrotoluene was dissolved in 360 g of concentrated sulfuric acid at 30 ^{0}C. 60 g of potassium dichromate flake was added slowly under stirring. The mixture temperature was kept at 45-55 ^{0}C. After 4 h the mixture was poured on to ice, the greenish precipitate was recrystallized from dilute hydrochloride acid. Yield 30.21 g (0.14mol) 3,4-dinitrobenzoic acid (89%). m.p. 161^{0}C, lit[22]: 165^{0}C.

IR (cm^{-1}, KBr) : 3400 (broad, O-H); 3107 (m, aromatic C-H); 1713 (s, C=O of acid); 1599 (m, aromatic C=C); 1543 and 1369 (s, NO_2); 847 (m, C-N). ^{1}H-NMR (δ in DMSO) : 8.29-8.33 (d,1H, aromatic, J_{HH}8.28 Hz); 8.39-8.43 (d, 1H, aromatic, J_{HH}8.31 Hz); 8.57 (s, 1H, aromatic). ^{13}C-NMR (δ in DMSO) : 126.14 (aromatic); 135.11 (aromatic); 135.90 (aromatic); 141.64 and 144.19 (=C-NO_2); 164.10 (C=O of carboxylic acid).

2.3.4 Synthesis of 3,4-Dinitrobenzoyl Chloride

Mw =212.12 (4)

Mw =230.56 (5)

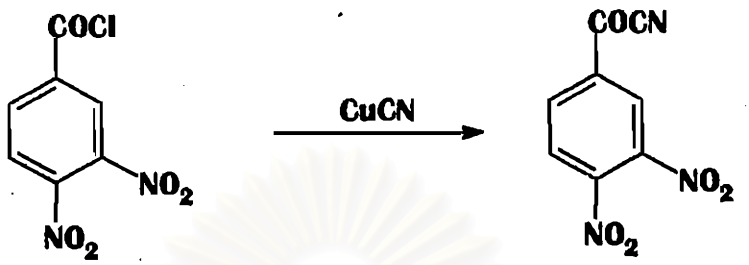
Scheme 2.4

A mixture of 3,4-dinitrobenzoic acid 21.6g (0.5 mol), thionyl chloride 47.7 g (0.75 mol) and 1 drop of DMF was refluxed while stirring until the initially vigorous gas evolution (hood ! SO_2 and HCl form) ends (ca. 2 h.).

Excess thionyl chloride was evaporated in vacuo (hood) and the residue istilled to give a yellow solid. Yield 23.24 g (0.10 mol, 99%). m.p. 50.6 ^{0}C, lit [23]: 50-51^{0}C.

IR (cm^{-1}, KBr) : 3087 (m, aromatic C-H); 1757 (s, C=O); 1594 (m, aromatic C=C); 1541 and 1354 (s, =C-NO_2); 847 (m, C-N); 746 (m, C-Cl).

2.3.5 Synthesis of 3,4-Dinitrobenzoyl Cyanide



Mw =230.56 (5)

Mw =221.13 (6)

Scheme 2.5

Method I : Using phase transfer catalysis [24]

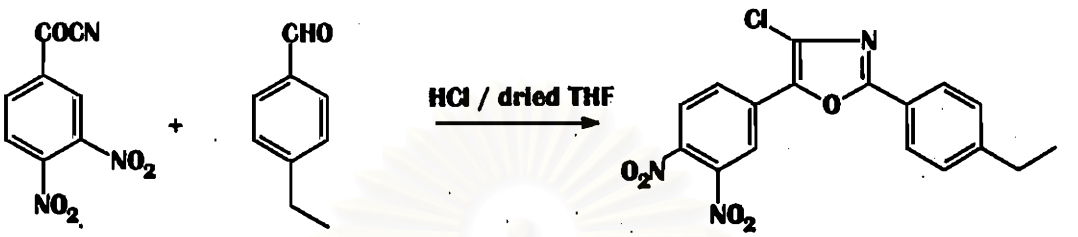
In a 500 mL round bottom flask equipped with a magnetic stirring bar and a nitrogen inlet tube was piaced 82.98 g (0.36 mol) 3,4-dinitrobenzoyl chloride, 100 mg (0.03 mol) of tetrabutylammonium bromide and 300 mL of methylene chloride. After the catalyst was totally dissolved, a solution of sodium cyanide 18 g (0.37 mol) in 20 mL of water were added while the reaction flask was cooled to 0^0C using an ice/salt mixture. The reaction took about an hour to complete. The solids were filtered, washed with methylene chloride, the organic layer separated, dried over anhydrous magnesium sulfate, and the solvent removed by evaporation under reduced pressure. The residue was dissolved in dried toluene, filtered and evaporated. The red brown viscous liquid product (78.5 g) could not be purified.

Method II : Using acetonitrile as solvent [25]

In a 250 mL two necked round bottom flask equipped with a reflux condenser and a magnetic stirrer was placed 70 mL of dried acetonitrile and 18 g (0.2 mol) of cuprous cyanide. The reaction flask was fitted with a nitrogen inlet tube. The suspended mixture was stirred for about 5 min, and then 25 g (0.1 mol) of 3,4-dinitrobenzoyl chloride was added slowly to the reaction flask. Gentle reflux for 6 h, the mixture became dark brown. The crude product was evaporated to remove the residue solvent. The solvent free product was dissolved in dry toluene, filtered and the dried evaporated. The red brown viscous liquid (20.18 g, 84%yield) could not be purified, but was used for the preparation of 4-chloro -5-(3′,4′-dinitrophenyl)-2-(4-ethylphenyl)oxazole.

IR(cm^{-1}, KBr) : 3100 (m, aromatic C-H); 2226 (s, C≡N); 1804 (s, C=O); 1602 (m, aromatic C=C); 1543 and 1350 (s, =C-NO_2); 846 (m, C-N).

2.3.6 Synthesis of 4-Chloro-5-(3′,4′-dinitrophenyl)-2-(4-ethylphenyl) Oxazole [26]



221.13 135.10 373.50

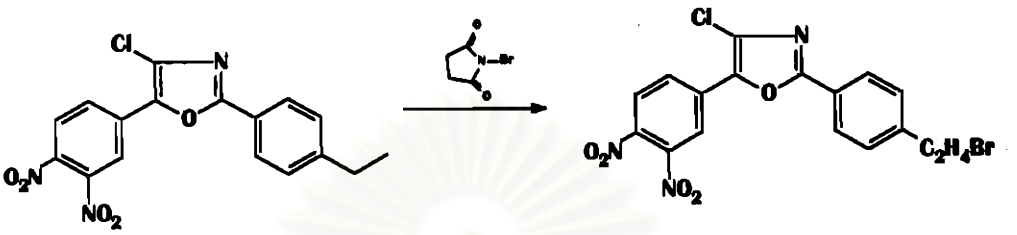
(6) (7) (8)

Scheme 2.6

Hydrogen chloride was passed into an ice-cooled solution of of *p*-ethylbenzaldehyde (13.4 g, 0.1 mol) and 3,4-dinitrobenzoyl cyanide (24.32 g, 0.11 mol) in 100 mL of dry tetrahydrofuran for 3.5 h. The reaction mixture was kept at 0^0C for 90 h. The orange mixture was then poured on to crushed ice (300 g) and extracted with THF (200 mL). The THF extract was washed with water, saturated sodium bisulphite solution, and water again, then dried and evaporated. The residue was purified using chromatography on a 12 in column of alumina (200 g) in three different batches using a mixture of light petroleum (b.p. 40-60 ^{0}C) and chloroform mixture in the ratio of 3:1 as the eluent. The yellow solid was twice recrystallised from methanol and methanol /acetone (1:1) mixture. Yield (8.23 g , 22 mmol) of 4-chloro-5-(3′,4′-dinitrophenyl) -2-(4-ethylphenyl)oxazole, m.p.133.8^{0}C (by DSC)

IR (cm^{-1}, KBr) : 3098 (w, aromatic C-H); 2964 (w, aliphatic C-H); 1612 (m, aromatic C=C); 1580 (m, -N=C-O-); 1531 and 1341 (s, $=C-NO_2$); 842 (m, C-N); 765 (m, C-Cl). ^{1}H-NMR (δ in $CDCl_3$) : 1.22-1.31 (t, 3H, CH_3, J_{HH} 7.6 Hz); 2.66-2.77 (q, 2H, CH_2, J_{HH} 7.6 Hz); 7.30-7.34 (d, 2H, aromatic, J_{HH} 8.23 Hz); 7.96-8.00 (d, 2H, aromatic, J_{HH} 8.26 Hz); 8.03-8.09 (d, 1H, aromatic, J_{HH} 8.56 Hz); 7.61-7.65 (d, 1H, aromatic, J_{HH} 8.62 Hz); 8.37 (d, 1H, aromatic, J_{HH} 2.10 Hz). ^{13}C-NMR (δ in $CDCl_3$) : 15.17 (CH_3); 28.94 (CH_2); 121.37 (CH); 123.18 (4C, aromatic); 126.78 (CH, aromatic); 128.63 (4CH, aromatic); 132.48 (CH, aromatic); 148.63 (0-C=C) and 160.50 (O-C=N). DEPT 90 (δ in $CDCl_3$) 121.37; 126.77; 128.63; 132.48. DEPT 135 (δ in $CDCl_3$) 15.17; 28.94; 121.37; 126.78; 128.63; 132.48. Elemental analysis (%) cal. : C 54.63; H 3.24; N 11.24 , found : C 57.14; H 3.15; N 11.17.

2.3.7 Synthesis of 4-Chloro-5-(3',4'-dinitrophenyl)-2-(4-bromoethyl phenyl)oxazole



Mw =373.50 Mw =451.61

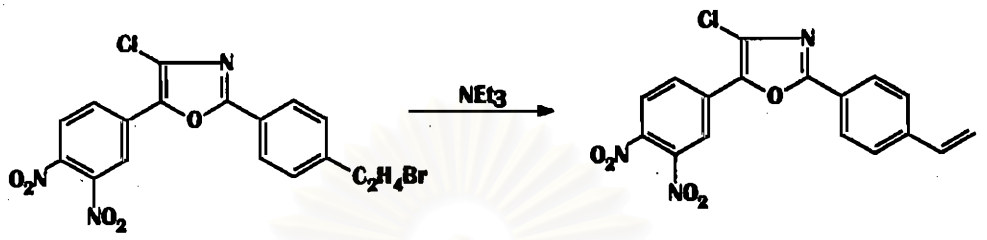
(8) (9)

Scheme 2.7

9.33 g (25 mmol) of 4-chloro-5- (3',4'-dinitrophenyl)-2-(4-ethyl phenyl)oxazole, 4.45 g (25 mmol) of powdered *N*-bromosuccinimide, 0.1 g (0.41 mmol) of dibenzoyl peroxide and 60 ml of dry, redistilled carbon tetrachloride were heated under reflux on a water-bath for an hour with occasional shaking. After cooling, the succinimide was filtered off at the pump, and washed with a dry carbontetrachloride. The solvent was removed to give a yellow oil which solidified on cooling in an ice-bath. Purification by column chromatography on alumina followed by crystallization from acetone-petroleum ether (40-60^{O}C) mixture (1:1) yielded 6.40 g (14 mmol, 70%), m.p.180.6^{O}C (DSC).

IR (cm^{-1}, KBr) : 3098 (w, aromatic C-H); 2964 (w, aliphatic C-H); 1612 (m, aromatic C=C); 1580 (m, -N=C-O-); 1531 and 1341 (s, $=C-NO_2$); 847 (m, C-N); 766 (m, C-Cl); 592 (m, C-Br). ^{1}H-NMR (δ in $CDCl_3$) : 2.02-2.08 (d, 3H, $CBr-CH_3$, J_{HH} 6.94 Hz); 2.99 (s, CBr_2-CH_3); 5.16-5.26 (q, 1H, -CHBr-, J_{HH} 6.94 Hz); 7.27-8.40 (m, aryloxazole).

2.3.8 Synthesis of 4-Chloro-5-(3′,4′-dinitrophenyl)-2-(4-vinylphenyl) Oxazole



(9) (10)

Scheme 2.8

A mixture of 4-chloro -5-(3′,4′-dinitrophenyl) -2-(4-bromoethyl phenyl)oxazole (0.68 g, 1.5 mmol) and triethylamine (10 mL, b.p.89 ^{0}C) was heated under reflux on a water bath for 3 h. Within the first 15 min the oxazole dissolved, and soon afterwards triethylammonium bromide started to precipitate. At the end of 3 h, the reaction product was cooled and unreacted triethylamine was distilled off under vacuum at 50 ^{0}C leaving a semi-solid residue. This was treated with 25 mL of ether, the mixture was filtered to remove the triethylammonium bromide, and the filtrate was evaporated to give 0.7 g of a yellow viscous oil. This was purified on chromatography over a column of alumina, using light petroleum (30-60 ^{0}C) and chloroform mixture (2:1) as the eluent, to gave a major fraction (fluorescent in UV light). The NMR spectrum (in $CDCl_3/CCl_4$) of which showed the presence of vinyl protons at chemical shift of 5.25-5.97 ppm (multiplet, 2H) and 6.52-6.86 ppm (multiplet, 1H). A crystalline sample of the pure compound could not be obtained.