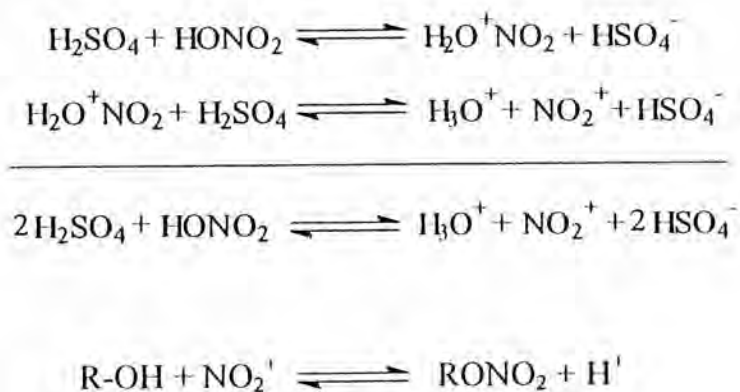


## CHAPTER IV

### RESULTS AND DISCUSSION

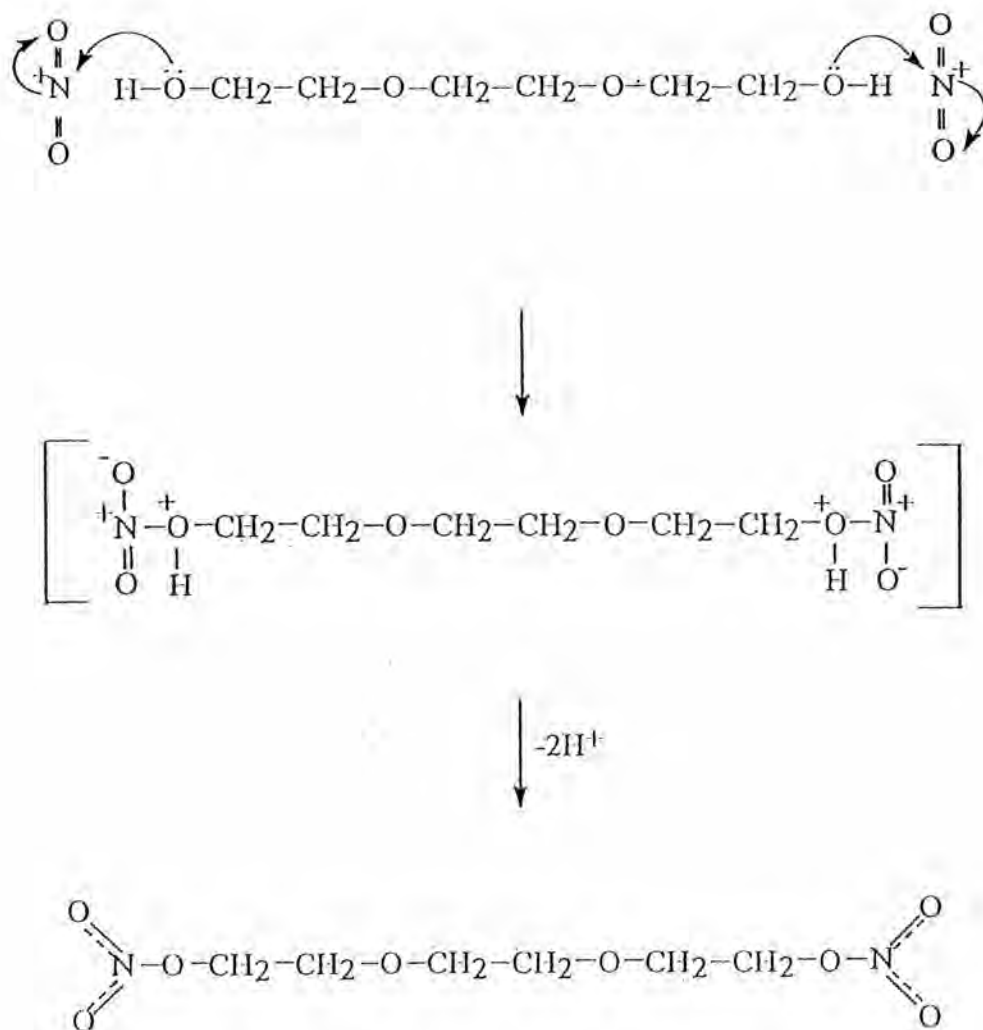
#### 4.1 Synthesis of dinitrate compounds

Dinitrate compounds could be prepared by reacting an organic hydroxy compound with nitric acid in the presence of sulphuric acid and solvent, while maintaining the temperature of the reaction at 10<sup>0</sup> C or lower. This synthesis of dinitrate compounds was indicated in the following reaction.



In the first step, a mixture of nitric and sulfuric acids, in equilibrium was established in which many species were present. One of these species was nitronium ion (  $\text{NO}_2^+$  ) which was a linear molecule and powerful electrophilic reagent. The structure of its was illustrated as  $\text{O}=\text{N}^+=\text{O}$ . Electrophilic attack of the nitronium ion on an organic hydroxy compound, followed by removal of a proton by hydrogen sulfate ion, generated organic nitrate compounds.

The mechanism of nitration was illustrated below using the case of triethylene glycol to triethylene glycol dinitrate as an example.



In this study, all products were obtained in high yield. Moreover, the products were substantially pure which was the benefit of this process.

## 4.2 Characteristics of dinitrate compounds

### 4.2.1 Triethylene glycol dinitrate ( I )

This compound ( I ) was a colorless liquid ( 70.4 % yield ).

The IR spectrum of ( I ) ( Figure A1 ) indicated an important absorption bands of  $\text{NO}_2$  ( asymmetric stretching and symmetric stretching ) at 1632 and 1280  $\text{cm}^{-1}$ , C-O stretching vibration at 1126  $\text{cm}^{-1}$ , and O-N stretching vibration at 878  $\text{cm}^{-1}$ . There was no absorption band of OH stretching group of triethylene glycol starting material at 3400  $\text{cm}^{-1}$  ( compared to Figure A2 ) The assignments of IR spectrum were shown in Table 4.1

**Table 4.1** The IR absorption bands assignments of ( I )

Wave number ( $\text{cm}^{-1}$ )	Bond type
2899	C-H stretching, aliphatic
1632	$\text{NO}_2$ asymmetric stretching
1280	$\text{NO}_2$ symmetric stretching
1445, 1368	C-H bending, aliphatic
1126	C-O stretching
878	O-N stretching vibration

The  $^1\text{H-NMR}$  spectrums of ( I ) ( Figure A3, and Table 4.2 ) indicated 3 signals at 3.55, 3.63 and 4.48 ppm corresponded to  $^{13}\text{C-NMR}$  spectrum ( Figure A4, and Table 4.3 ) which indicated 3 signals at 66.99, 70.49 and 72.27 ppm.

**Table 4.2** The assignment of  $^1\text{H}$ -NMR spectrum of (1)

Chemical shift ( $\delta$ , ppm)	Multiplicity	Position of proton	Number of proton
4.48	triplet	1,6	4
3.63	triplet	2,5	4
3.55	triplet	3,4	4

**Table 4.3** The assignment of  $^{13}\text{C}$ -NMR spectrum of (1)  
( in deuterated chloroform )

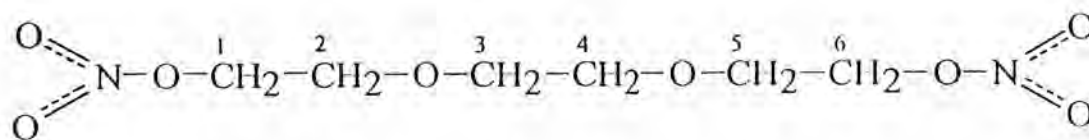
Chemical shift ( $\delta$ , ppm )	Carbon type	Position of carbon
72.27	$\text{CH}_2$	1,6
70.49	$\text{CH}_2$	2,5
66.99	$\text{CH}_2$	3,4

CHNO analysis of (1) ( Table 4.4 ) gave the % of C, H, N and O which were corresponded to the values calculated from the molecular formula.

**Table 4.4** CHNO analysis of (1)

Source	%C	%H	%N	%O <sup>c</sup>
1) Elemental analyzer	30.05	5.02	13.85	51.08
2) Calculation from formula (1)	30.93	5.15	14.43	49.48

All of these results suggested that I was triethylene glycol dinitrate which has the structure shown below :



#### 4.2.2 1,5-pentane dinitrate ( II )

This compound ( II ) was a colorless liquid ( 69.8 % yield ).

The IR spectrum of ( II ) ( Figure A5 ) indicated an important absorption bands of  $\text{NO}_2$  ( asymmetric stretching and symmetric stretching ) at 1629 and 1280  $\text{cm}^{-1}$ , C-O stretching vibration at 974  $\text{cm}^{-1}$ , and O-N stretching vibration at 866  $\text{cm}^{-1}$ . There was no absorption band of OH stretching group of 1,5-pentanediol starting material at 3400  $\text{cm}^{-1}$  ( compared to Figure A6 ) The assignments of IR spectrum were shown in Table 4.5

**Table 4.5** The IR absorption bands assignments of ( II )

Wave number ( $\text{cm}^{-1}$ )	Bond type
2955,2883	C-H stretching, aliphatic
1629	$\text{NO}_2$ asymmetric stretching
1280	$\text{NO}_2$ symmetric stretching
1440, 1378	C-H bending, aliphatic
974	C-O stretching
866	O-N stretching

The  $^1\text{H}$ -NMR spectrums of ( II ) ( Figure A7, and Table 4.6 ) indicated 3 signals at 1.43, 1.67 and 4.37 ppm corresponded to  $^{13}\text{C}$ -NMR spectrum ( Figure A8, and Table 4.7 ) which indicated 3 signals at 21.93, 26.21 and 72.93 ppm.

**Table 4.6** The assignment of  $^1\text{H}$ -NMR spectrum of ( II )  
( in deuterated chloroform )

Chemical shift ( $\delta$ , ppm)	Multiplicity	Position of proton	Number of proton
4.37	triplet	1,5	4
1.67	multiplet	2,4	4
1.43	multiplet	3	2

**Table 4.7** The assignment of  $^{13}\text{C}$ -NMR spectrum of ( II )  
( in deuterated chloroform )

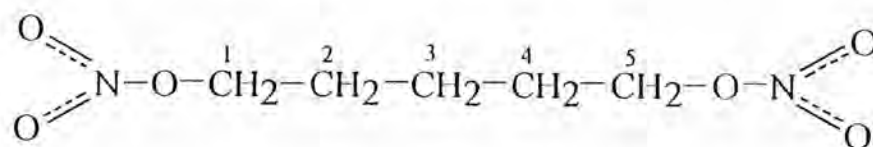
Chemical shift ( $\delta$ , ppm)	Carbon type	Position of carbon
72.93	$\text{CH}_2$	1,5
26.21	$\text{CH}_2$	2,4
21.93	$\text{CH}_2$	3

CHNO analysis of ( II ) ( Table 4.8 ) gave the % of C, H, N and O which were corresponded to the values calculated form the molecular formula.

**Table 4.8** CHNO analyzer of ( II )

Source	%C	%H	%N	%O <sup>c</sup>
1) Elemental analyzer	39.94	7.04	8.86	44.16
2) Calculation from formula (2)	40.27	7.38	9.40	42.95

All of these results suggested that I was 1,5-pentane dinitrate which has the structure shown below :



#### 4.2.2 1,4-butane dinitrate ( III )

This compound ( III ) was a colorless liquid ( 71.3 % yield ).

The IR spectrum of (III) ( Figure A9 ) indicated an important absorption bands of  $\text{NO}_2$  ( asymmetric stretching and symmetric stretching ) at  $1629$  and  $1286 \text{ cm}^{-1}$ , C-O stretching vibration at  $1204 \text{ cm}^{-1}$ , and O-N stretching vibration at  $871 \text{ cm}^{-1}$ . There was no absorption band of OH stretching group of 1,4-butanediol starting material at  $3400 \text{ cm}^{-1}$  ( compared to Figure A10 ). The assignments of IR spectrum were shown in Table 4.9

**Table 4.9** The IR absorption bands assignments of ( III )

Wave number ( $\text{cm}^{-1}$ )	Bond type
2966,2889	C-H stretching , aliphatic
1629	$\text{NO}_2$ asymmetric stretching
1286	$\text{NO}_2$ symmetric stretching
1470, 1445	C-H bending, aliphatic
1204	C-O stretching
871	O-N stretching

The  $^1\text{H}$ -NMR spectrums of (III) ( Figure A11, and Table 4.10 ) indicated 2 signals at 1.75 and 4.39 ppm corresponded to  $^{13}\text{C}$ -NMR spectrum ( Figure A12, and Table 4.11 ) which indicated 2 signals at 21.93 and 72.93 ppm.

**Table 4.10** The assignment of  $^1\text{H}$ -NMR spectrum of (III)  
( in deuterated chloroform )

Chemical shift ( $\delta$ , ppm)	Multiplicity	Position of proton	Number of proton
4.39	triplet	1,4	4
1.75	multiplet	2,3	4

**Table 4.11** The assignment of  $^{13}\text{C}$ -NMR spectrum of (III)  
( in deuterated chloroform )

Chemical shift ( $\delta$ , ppm)	Carbon type	Position of carbon
72.93	$\text{CH}_2$	1,4
21.93	$\text{CH}_2$	2,3

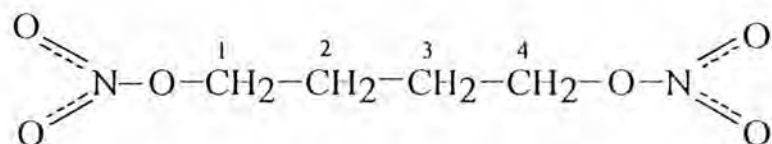


CHNO analysis of ( III ) ( Table 4.12 ) gave the % of C, H, N and O which were corresponded to the values calculated from the molecular formula.

**Table 4.12** CHNO analysis of ( III )

Source	%C	%H	%N	%O <sup>c</sup>
1) Elemental analyzer	43.90	7.85	8.49	39.76
2) Calculation from formula (3)	44.17	7.98	8.59	39.26

All of these results suggested that I was 1,4-butane dinitrate which has the structure shown below :



#### 4.2.4 1,2-ethane dinitrate ( IV )

This compound ( IV ) was a colorless liquid ( 65.4 % yield ).

The IR spectrum of (IV) ( Figure A13 ) indicated an important absorption bands of NO<sub>2</sub> ( asymmetric stretching and symmetric stretching ) at 1644 and 1281 cm<sup>-1</sup>, C-O stretching vibration at 1035 cm<sup>-1</sup>, and O-N stretching vibration at 872 cm<sup>-1</sup>. There was no absorption band of OH stretching group of 1,2-ethanediol starting material at 3400 cm<sup>-1</sup> ( compared to Figure A14 ). The assignments of IR spectrum were shown in Table 4.13

**Table 4.13** The IR absorption bands assignments of ( IV )

Wave number ( $\text{cm}^{-1}$ )	Bond type
3027,2976,2964	C-H stretching , aliphatic
1644	$\text{NO}_2$ asymmetric stretching
1281	$\text{NO}_2$ symmetric stretching
1429, 1363	C-H bending, aliphatic
1035	C-O stretching
872	O-N stretching

The  $^1\text{H-NMR}$  spectrums of (IV) ( Figure A15, and Table 4.14 ) indicated 1 signal at 4.71 ppm corresponded to  $^{13}\text{C-NMR}$  spectrum ( Figure A16, and Table 4.15 ) which indicated 1 signal at 68.48 ppm.

**Table 4.14** The assignment  $^1\text{H-NMR}$  spectrum of (IV)

( in deuterated chloroform

Chemical shift ( $\delta$ , ppm)	Multiplicity	Position of proton	Number of proton
4.71	triplet	1,2	4

**Table 4.15** The assignment of  $^{13}\text{C-NMR}$  spectrum.of (IV)

( in deuterated chloroform )

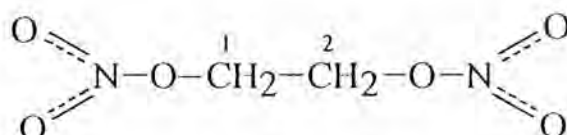
Chemical shift ( $\delta$ , ppm)	Carbon type	Position of carbon
68.48	$\text{CH}_2$	1,2

CHNO analysis of ( IV ) ( Table 4.16 ) gave the % of C, H, N and O which were corresponded to the values calculated form the molecular formula.

**Table 4.16** CHNO analysis of ( IV )

Source	%C	%H	%N	%O <sup>c</sup>
1) Elemental analyzer	39.83	6.98	6.37	46.82
2) Calculation from formula (3)	40.19	7.18	6.70	45.93

All of these results suggested that I was 1,2-ethane dinitrate which has the structure shown below :



### 4.3 Determination of cetane index of dinitrate compounds in base diesel fuel.

Each of 0.05 and 0.1 % by weight of triethylene glycol dinitrate, 1,5-pentane dinitrate, 1,4-butane dinitrate and 1,2-ethane dinitrate were blended in base diesel fuel. The cetane index of all blended base diesel fuels were determined and shown in Table 4.17

**Table 4.17** Cetane Index of the blended base diesel fuels

Add . Level (.% by weight)	Blended composi- tion	Mid- boiling point (°F)	API gravity @ 60 °F	CCI	Improved value	CCI improver
NONE	base	527.00	37.2	52.64	-	-
0.05	base + A	528.80	37.2	52.83	3.90	56.73
	base + B	529.16	37.2	52.88	3.90	56.78
	base + C	526.64	37.2	52.60	3.89	56.49
	base + D	529.16	37.2	52.58	3.90	56.78
	base + E	526.64	37.3	52.78	3.90	56.68
0.10	base + A	526.56	37.3	52.65	6.27	58.92
	base + B	526.10	37.2	52.54	6.25	58.79
	base + C	524.48	37.2	52.36	6.23	58.59
	base + D	525.20	37.2	52.44	6.24	58.68
	base + E	525.02	37.2	52.42	6.24	58.66

Note : A = Triethylene glycol dinitrate

B = 1,5 - pentane dinitrate

C = 1,4 - butane dinitrate

D = 1,2-ethane dinitrate

E = Isooctylnitrate

CCI= Calculated Cetane Index

CCI improver = CCI + Improver value

From Table 4.17, it could be seen that API gravity of concentration at 0.05 and 1.0 % by weight of all blended base diesel fuels gave the same values of 37.2. It was found that Calculated Cetane Index of these synthesized compounds did not give the different values compared to the values of no improver added, on account of using only an equation according to the method of ASTM D976. In fact, this equation was not applicable to the fuels containing additives for raising cetane number. Therefore, another equation having additional value was considered.

It was found that the improved equation for considering the improver value could be calculated by the following equation [15]:

$$\text{Improver value} = 0.1742 (0.1G)^{1.4444} (0.01M)^{1.0052} [\ln (1+17.5534D)]$$

where

G = API gravity, determined by test method D287 or D1298.

M = mid-boiling temperature, °F, determined by Test Method D86

D = percent weight of cetane improver, % wt.

By adding this equation to an equation in ASTM D976, the right Calculated Cetane Index of fuel containing cetane improver would be appeared as shown in Table 4.17. It could be seen that the Calculated Cetane Index for all samples were increased by 4 units at the concentrations 0.05 % by weight, and 6 units at the concentrations 0.10 % by weight, compared with base diesel fuels.

#### **4.4. Determination of cetane number of dinitrate compounds comparison with Isooctylnitrate in base diesel fuels**

The cetane number of blended base diesel fuels were determined at the concentrations of 0.05 % and 0.10 % by weight. The standard method for

determining the cetane number of a diesel fuel was the ASTM D613 CFR engine technique and was shown in Table 4.18

**Table 4.18** Composition and properties of blended base diesel fuels

No.	Add.Level (% by weight)	Base + A		Base + B		Base + C	
		CN	Increase	CN	Increase	CN	Increase
1.	none	52.7	-	52.7	-	52.7	-
2.	0.05	53.4	0.7	53.2	0.5	53.7	1.0
3.	0.05	54.0	1.3	52.8	0.1	53.3	0.6
-	<b>Average</b>	<b>53.7</b>	<b>1.0</b>	<b>53.0</b>	<b>0.3</b>	<b>53.5</b>	<b>0.8</b>
4.	0.10	58.6	5.9	53.9	1.2	56.4	3.7
5.	0.10	58.0	5.3	54.5	1.8	57.0	4.3
-	<b>Average</b>	<b>58.3</b>	<b>5.6</b>	<b>54.2</b>	<b>1.5</b>	<b>56.7</b>	<b>4.0</b>

Note: A = Triethylene glycol dinitrate.

B = 1,5-pentane dinitrate.

C = Isooctyl nitrate

CN = Cetane Number

From table 4.18, it could be seen that at 0.05 % by weight of triethylene glycol dinitrate and isooctyl nitrate gave similar cetane number. However, at 0.10 % by weight, triethylene glycol dinitrate, gave 1.6 unit of cetane number higher than that of isooctyl nitrate. On the other hand 1,5-

pentane dinitrate, it gave less cetane number than the others. This finding was very interesting because the dinitrate of simple straight chain hydrocarbon could not improve the cetane number better than that of isooctyl nitrate. By incorporating oxygen atom in hydrocarbon chain, significant improve of cetane number was observed. The effect was clearly seen at 0.10% by weight of addition. This point out that oxygen atom in the hydrocarbon chain may enhance the autoxidation which resulted in increasing of cetane number.