International Journal of ChemTech Research
CODEN(USA): IJCRGG ISSN : 0974-4290
Vol.1, No.3 , pp 483-493, July-Sept 2009

Reactions of Perfluoro(2,4-dimethyl-3-oxa-2,4-diazapentane) with alkylbenzenes (Part I)

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Abstract: Perfluoro(2,4-dimethyl-3-oxa-2,4-diazapentane) **(I)**, is a colourless liquid which freezes to a colourless solid and it has a b.p. of 48.5°C at atmospheric pressure. It is a very reactive compound and should be stored in sealed tubes, in vacuo. The primary objective of the present work was to study the reactions of diazapentane **(I)** with a series of alkylbenzenes. Three types of product were observed from the reactions of diazapentane **(I)** with the alkylbenzenes PhR (R=Me and Et), i.e. products resulting from side-chain substitution, ring substitution and addition to the aromatic ring. The side-chain substitution product is considered to arise via benzylic hydrogen abstraction by the **$(CF_3)_2N.$** radical. The ring-substituted products were **NN-bistrifluoromethylaminoarenes.** The major addition products from all the reactions were **2:1** adducts of the diazapentane **(I)** and the alkylbenzene.

Keywords: Perfluoro(2,4-dimethyl-3-oxa-2,4-diazapentane),diazapentane**(I)**,alkylbenzene,(NN-bistrifluoromethylamino) methylbenzene,(NN-bistrifluoromethylamino)ethylbenzene.

Introduction

Perfluoro(2,4-dimethyl-3-oxa-2,4-diazapentane)(for brevity it is called diazapentane) **(I)**, is a colourless liquid which freezes to a colourless solid and it has a b.p. of 48.5°C at atmospheric pressure.[1] It is a very reactive compound and should be stored in sealed tubes, in vacuo. Its reactivity is due to the weak N-O bond which cleaves homolytically under thermal or photochemical conditions to give **NN-bistrifluoromethylintroxide (II)** and **NN-bistrifluoromethylamino radicals (III)**, the latter radical dimerizes to the hydrazine derivative **(IV).**

The diazapentane **(I)** was first prepared by the photolysis of tristrifluoromethylhydroxylamine (figure 1)[1] and later on by photolysis of the oxyl **(II)** [bistrifluoromethylamino-oxyl or bistrifluoromethylnitroxide **$(CF_3)_2NO.$**]. However, a more convenient method of preparation involves the reaction of oxyl **(II)** with trifluoronitrosomethane which is an important reaction and has been used for the synthesis of diazapentane **(I)** in near quantitative yield (99%), as shown in figure 2.[2]

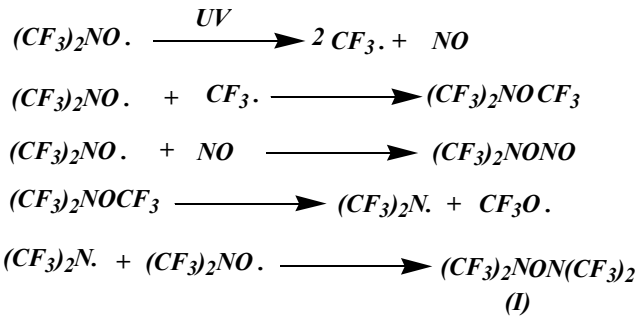


Figure 1. Synthesis of diazapentane (I) by photolysis of oxyl (II)

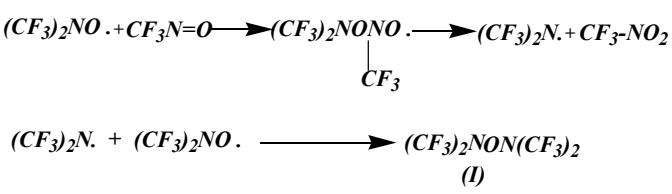


Figure 2. Synthesis of diazapentane (I) by using trifluoronitrosomethane

Chemically, [1]the structure of the diazapentane **(I)** was established by its thermal decomposition to give **NN-bistrifluoromethylintroxide** and the hydrazine derivative **(IV)** and by its reactions with:

(i) anhydrous hydrogen iodide HI which gives an equimol a rmixture ofNN-bistrifluoromethylhydroxylamine and NN-bistrifluoromethylamine

$$(CF_3)_2NON(CF_3)_2 + 2HI \rightarrow (CF_3)_2NOH + (CF_3)_2NH + I_2$$

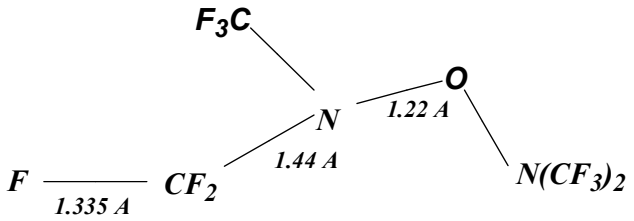
(ii) nitric oxide to give the following compounds:

$$(CF_3)_2NON(CF_3)_2 + 2NO \rightarrow (CF_3)_2NONO + (CF_3)_2NNO$$

(iii) with fluorinated olefins, e.g.

$$CF_3)_2NON(CF_3)_2 + CF_2 = CF_2 \rightarrow (CF_3)_2N\,CF_2\text{-}CF_2ON(CF_3)_2$$

Electron diffraction studies have given the following parameters.[3]



The primary objective of the present work was to study the reactions of Perfluoro(2,4-dimethyl-3-oxa-2,4-diazapentane)**(I)** with the alkylbenzenes. Since these reactions involve the intermediacy of the $(CF_3)_2N.$ and $(CF_3)_2NO.$ radicals, it is considered necessary to discuss the preparation, general properties and chemistry of these radicals briefly.

Oxyl **(II)** or **[**bistrifluoromethylamino-oxyl or bistrifluoromethylnitroxide $(CF_3)_2NO.]$ is an extremely stable free radical (up to 200 °C).[4] However, pyrolysis at 350 °C in silica (contact time 2 minutes) yields nitric oxide,nitrogendioxide, tristrifluoromethylhydroxylamine, perfluoro-2-azapropene and silicon tetrafluoride (figure 3):

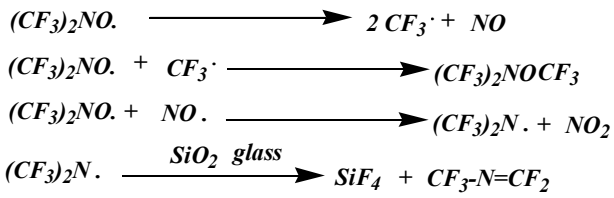


Figure 3. Pyrolysis of oxyl (II) radical

When heated with iron powder deoxyfluorination occurs:[2]

$$(CF_3)_2NO. \xrightarrow[200\ C]{Fe\ powder} CF_3\text{-}N{=}CF_2 \quad (88\%)$$

At room temperature the oxyl **(II)** is a purple monomeric gas which condenses, on cooling, to a brown liquid at -25 °C and it finally dimerises at -70 °C to a yellow diamagnetic solid.[5] It is not affected chemically by water, aqueous sodium hydroxide (10%), air, stainless steel, copper or glass, but it reacts readily with other free radicals, unsaturated linkages and C-H bonds.[5] Meanwhile the usual method of preparation of the oxyl **(II)** involves oxidation of NN-bistrifluoromethylhydroxylamine which is itself made by the gas phase reaction of trifluoronitrosomethane with ammonia ; the following reaction path has been postulated (figure 4):[6]

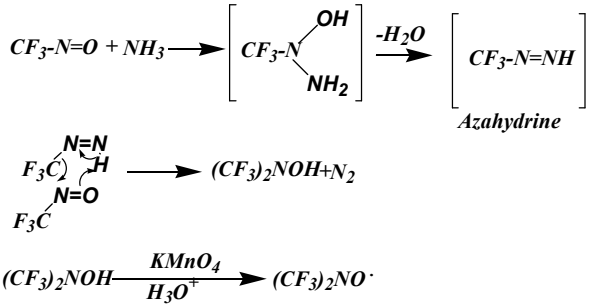


Figure 4. Preparation of oxyl (II)

For the latter step a number of oxidation systems have been shown to be effective,[7] e.g. silver (I) oxide, silver (II) oxide, fluorine. Other methods of preparation of the oxyl **(II)** is available.[5]

The oxyl **(II)** dimerised on photolysis,[8]

$$2\,(CF_3)_2NO. \longrightarrow (CF_3)_2NO\,ON(CF_3)_2 \quad 60\%$$

However, it has been shown that the major organic compound arising from photolysis of bistrifluoromethylnitroxide is the diazapentane **(I)** as was previously shown in figure 1 (73%).[1]

Bistrifluoromethylamino radical **(III)** is a very reactive radical which is the chain carrier in the reactions of diazapentane **(I)** with other compounds. Unlike the oxyl **(II)** radical, it is not isolable and has to be generated in situ.

One method of generation of the radical involves homolytic fission of the N-halogen bond in N-halogenobistrifluoromethylamines, $(CF_3)_2NX$; **(X= Cl, Br, or I)** (figure 5).

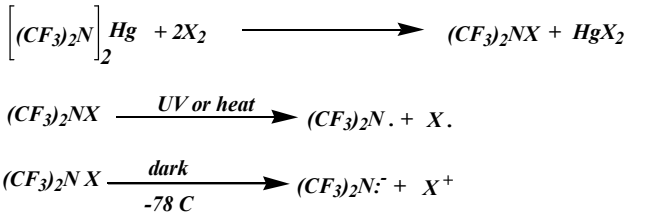
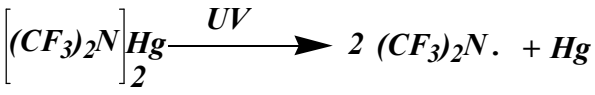


Figure 5. Preparation of Bistrifluoromethylamino radical (III)

As shown in figure 5, the **N-X** bond fission can be either homolytic or heterolytic depending upon the conditions employed.[9] Another method of generation of bistrifluoromethylamino radical is the photolysis of the mercury bistrifluoromethylamide.



Photolysis of the mercurical gave the following compounds (figure 6):[10]

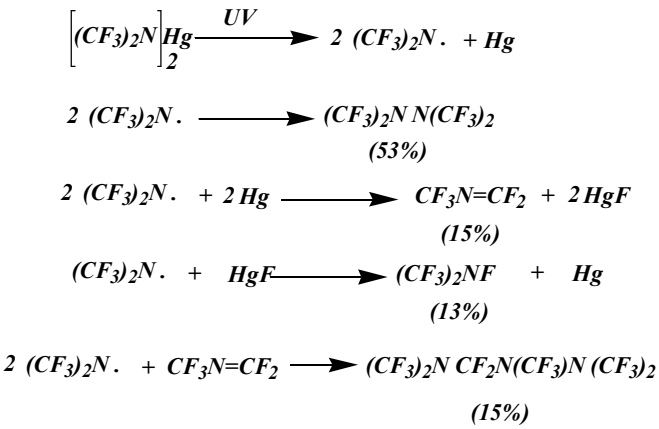


Figure6.Photolysis of mercury bistrifluoromethylamide and its by products.

Materials and methods

1. The general procedure:

The reactant diazapentane **(I)** and a number of the products were either gases or volatile liquids at room temperature. They were manipulated in a conventional Pyrex vacuum system consisting of storage and distillation sections of known volume. The separate units of each section were connected by high vacuum glass stopcocks and pressures were monitored by individual mercury manometers. The vacuum obtained by the use of an Edward two stage Speedivac pump which gave pressures down to 10^{-3}mmHg.

The reactions between the diazapentane **(I)** and the alkylbenzenes were carried out in thick walled (3-4 mm) Pyrex tubes fitted with P.T.F.E. Rotaflo taps. First the alkylbenzene was introduced into the tube at atmospheric pressure and then carefully degassed by cooling to – 196 °C (liquid nitrogen) followed by evacuating. Then the diazapentane **(I)** was condensed in vacuo from the vacuum system into the tube at -196 °C. The reaction tube was then sealed, allowed to warm to room temperature and then stored for the appropriate length of time before it was opened. Volatile reaction products were condensed into the vacuum system at -196°C and separated by trap-to-trap fractional condensation in vacuo.

This technique involves passing the gaseous mixture at low pressure (1-2 mmHg) through a series of traps, each cooled to a successively lower temperature by means of slush baths. These were slushes of melting organic solvents maintained at their melting points by the addition of liquid nitrogen [(melting CCl_4 , -23 °C) , melting Genklene (CCl_3-CH_3 , -48 °C)], a slush of solid carbon dioxide in methylated spirits (-78 °C) , or liquid nitrogen (-196 °C) with which the last trap was cooled. Meanwhile melting ice bath slush (0 °C) was also used.

2. Analytical methods:

Analytical GLC separations were carried out on a Pye Unicam Model 104 chromatograph fitted with a flame ionization detector using nitrogen as the carrier gas. Samples were injected into the glass or stainless steel columns (2 m, 3-4 mm i.d.) packed with acid washed Celite coated with trixylyl phosphate (TXP) or Apiezon L grease (APL) (ca. 15% v/v) with the columns heated to 50 – 150 °C. Preparative scale GLC separations were carried out using TXP columns (2 m and 4 m) and the individual products were collected in traps cooled to -78 °C which were connected to the gas exit of the gas chromatograph.

Infrared (IR) spectra were recorded with a Pekin Elmer model 197 double beam infrared spectrophotometer equipped with sodium chloride optics. Volatile substances were examined in a gas cell (10 cm path length) and liquids were examined as capillary films. ^{1}H and $^{19}FNMR$ were recroded on a Varian Associate HA 100 or a Perkin Elmer R32 spectrometer operating at 100 and 90 MHz for ^{1}H and at 94.12 and 84.6 MHz for ^{19}F spectra, respectively. Mass spectra were recorded on an A.E.I. MS45 double focusing spectrometer operating with an ionization electron beam energy of 70 eV. GLC-Mass spectrometric analysis utilized helium as the carrier gas with a Pye model 104 chromatograph connected to the above mentioned mass spectrometer.

3. Reaction of the diazapentane (I) with ethylbenzene

A mixture of ethylbenzene (1.14g, 10.6 mmol) and the diazapentane **(I)**(3.54 g, 11.0 mmol) was sealed in a Pyrex reaction tube (ca. 110 cm^3) in vacuo and kept at room temperature in the dark for 27 days. After 5 days the original two phases had changed to a homogeneous yellow liquid. After 27 days, the volatile products were taken into the vacuum system and were separated by

fractional distillation in vacuo into the following fractions (Table 1).

4. Reaction of the diazapentane (I) with toluene

A mixture of toluene (1.10g, 11.96 mmol) and the diazapentane **(I)**(4.65 g, 14.53 mmol) was sealed in a Pyrex reaction tube (ca. 110 cm^3) in vacuo and kept at room temperature in the dark for 7 days. After 5 days the original two phases had changed to a homogeneous yellow liquid. After 7 days, the volatile products were taken into the vacuum system and were separated by fractional distillation in vacuo into the following fractions which were then examined by glc (2m, TXP column at 100 °C (Table 2).

Results and discussion:

1- Reaction of the diazapentane (I) with ethylbenzene

(i) A -196 °C fraction (0.68 g) which was shown by IR spectroscopy and by comparison of the glc retention time of the components with those of authentic samples to consist mainly of NN-bistriflurormethylamine **(III)** and NN-bistrifluoromethylhydroxylamine **(II)** and unchanged ethylbenzene.

(ii) A -78 °C fraction (1.18 g) which was shown by glc (2m TXP at 120 °C) to contain five major components (A-E) in the ratio of 8.5 : 11.5 : 51 : 21.5 : 2 in order of increasing retention time. The IR spectrum of the fraction showed a strong band at 3571 cm^{-1}, assigned to O-H stretching in NN-bistrifluoromethylhydroxylamine **(II).**

(iii) A -48 °C fraction (0.01 g) which, because of small amount available, was not examined further.

(iv) A -23 °C fraction (0.06 g), which was shown by glc to consist of two components (**B** and **F)** in the ratio of 46:52.

(v) A 0 °C fraction (0.67 g), which was shown by glc to contain two components (**G** and **H**) in the ratio 33:63.

The non-volatile material (1.95 g) material which remained in the tube was heated in vacuo to give a high-boiling volatile fraction (0.25 g) and a non-volatile residue (1.70 g). Examination of the high-boiling fraction by glc showed the presence of 8 main components (**I – P)** in the ratio of 4 : 1 : 20 : 6 : 4 : 24.5 : 11 : 29. The non-volatile residue was also examined by glc and 10 components (**I, Q, L – P** and **R – T**) were shown to be present in the ratio of 32.5 : 26 : 5 : 9 : 5 : 2 : 5.5 : 7 : 7.5 : 1.5.

On the basis of a comparison of the retention times of components **A** and **F** with those of authentic samples and by consideration of the ^1H and ^{19}FNMR spectra of the -78 and -23 °C fractions the components were identified as NN-bistriflurormethylamine **(III)** (0.1 g, 0.65 mmol, 6%) and unchanged ethylbenzene (0.03 g, 0.30 mmol, 3% recovered). Component **B** was identified as NN-bistrifluoromethylamino)ethylbenzene (0.16 g, 0.64 mmol, 6% based on PhEt, 6% based on diazapentane **(I)**) by a consideration of the NMR spectra of the -23°C fraction; the assigned NMR bands are tabulated in table (4).

Components **G** and **H** were separated by glc from the 0 °C fraction. Component **G** was identified as an (NN-bistrifluoromethylamino)ethylbenzene) (probably the 3-isomer) (0.22 g, 0.86 mmol, 8%) by a consideration of its IR (Table 3), NMR (Table 4) and mass. Component **H** was shown by NMR spectroscopy and GC-Mass to be a mixture of 1-(NN-bistrifluoromethylamino-oxyethyl)benzene (0.25 g, 0.92 mmol, 9% based on PhEt, 8% base on diazapentan) and 4-(NN-bistrifluoromethylamino)ethylbenzene (0.20 g, 0.78 mmol, 8% based on PhEt, 7% based on diazapentane **(I)**)(Found: M^+ = 257, calc. for $C_{10}H_9F_6N$, M = 257); the NMR bands assigned to the (amino-oxyethyl)benzene are tabulated in table 4.

An attempted separation of the major components of the higher-boiling volatile fraction and the non-volatile residue was carried out. However, a GC-Mass examination of the mixture showed that it consisted of three components and a number of minor components and it was not examined further.

The attempted separation of components (**I, Q, L+M+N,** and **R+S**) was carried out by glc from the non-volatile residue. Component **I** was identified as a bis(NN-trifluoromethylamino)bis(NN-bistrifluoromethylamino-oxy)ethylcyclohexene (0.57 g, 0.75 mmol, 8% based on PhEt, 14% based on diazapentane **(I)**) (Found: M^+ = 746, calc. for $C_{16}H_{10}F_{24}N_4O_2$, M = 746), by consideration of its IR (table 3), NMR (table 4) and the mass spectra.

Component **Q** was non-aromatic (IR) and the mass spectrum showed bands at m/z 408 (1.0%, $C_{12}H_{18}F_{12}N_2^+$), 393(1.0%, $C_{11}H_5F_{12}N_2^+$), 285(6.1%), 270 (39.2%), 257(19.2%, $C_{10}H_9F_6N^+$), 242 (54.2%, $C_9H_6F_6N^+$), 154 (13.2%, $C_5H_4F_4N^+$), 114 (11.6%, $C_2F_4N^+$), 105 (30.2%, $C_8H_9^+$), 103 (13%, $C_8H_7^+$), 92 (26.2%, $C_7H_8^+$), 91 (71.4%, $C_7H_7^+$), 77 (24.3%, $C_6H_5^+$), 69 (100%, CF_3^+), 65 (14.5%, $C_5H_5^+$), and 51 (13.0%, CHF_2^+ and $C_4H_3^+$) but the compound was not identified.

The ^{1}HNMR spectrum of the mixture of components **L**, **M** and **N** was complex and these components could not be identified.

The ^{19}FNMR spectrum of the mixture of components **R** and **S** showed bands at -9.75 $[(CF_3)_2NO]$ and -21.8 $[(CF_3)_2N]$ ppm in the ratio of ca. 4:1 and the rest of the spectrum was so complex, therefore, these components could not be identified.

A GLC-mass spectrometric examination on the higher boiling volatile fraction was undertaken. Component **J** was tentatively identified as a bis(NN-trifluoromethylamino)-(NN-bistrifluoromethylamino-oxy)ethylcyclohexene (0.02 g, 0.04 mmol, <1% based on PhEt) (Found: M^+ = 579).

Based on the ^{19}FNMR and the mass spectra, component **K** was tentatively identified as a bis(NN-trifluoromethylamino)bis(NN-bistrifluoromethylamino-

oxy)ethylcyclohexene (0.05 g, 0.06 mmol, 1% based on PhEt).
Based on the ^{19}FNMR and the mass spectra, component **P** was tentatively identified as a bis(NN-trifluoromethylamino-NN-bistrifluoromethylamino-oxy)ethylcyclohexadiene (0.17 g, 0.4 mmol, 4% based on PhEt) with peaks in its spectrum at m/z 274 ((1.5%, $C_{10}H_{10}F_6NO^+$) and 258 (10%, $C_{10}H_{10}F_6N^+$).

2- Reaction of the diazapentane (I) with methylbenzene

(i) A -196 °C fraction (2.93 g) which was shown by IR spectroscopy and by comparison of the glc retention time of the components with those of authentic samples to consist mainly of NN-bistriflurormethylamine **(III)** together with some NN-bistrifluoromethylhydroxylamine **(II)**.

(ii) A -78 °C fraction (0.70 g) which contained eight major components (A-H) in the ratio of 11 : 1 : 3 : 6.5 : 9 : 39.5 : 1.5 : 26.5 in order of increasing retention time. The IR spectrum of the fraction showed a strong band at 3600 cm^{-1}, assigned to O-H stretching in NN-bistrifluoromethylhydroxylamine **(II).**
(iii) A -48 °C fraction (0.60 g) which contained four major components (**A, E,F, H**) in the ratio of 20 : 13 : 63.5 : 1.5.
(iv) A -23 °C fraction (0.70 g), which contained three major components (**E, F, G**) in the ratio of 36: 41:16.
(v) A 0 °C fraction (1.10 g), which contained eight components (**I – L, F, M** and **G**) in the ratio 2 : 5.5 : 4 : 9 : 27 : 15 : 6 : 29.

The non-volatile material (1.85 g) material which remained in the tube consisted of five major components (**I , N, O, G, P)** in the ratio of 36.5 : 26 : 28.5 : 5.5 : 5. Separation of the peaks was not satisfactory to allow preparative scale glc to be attempted. The material was then heated (180 °C) in vacuo overnight and the product obtained (1.80 g) consisted of seven major components (**A, Q, I, K, E, R, G,** and **S**) in the ratio of 20 : 20 : 16.5 : 33 : 2 : 5: 1.5 , but although peak separation of this mixture was improved it was not good enough to allow individual component separation to be attempted.

On the basis of a comparison of the retention times of component **A** in the -78 and -48 °C fractions and a consideration of the mass spectrum of the component from each fraction, it was identified as a 2 : 1 adduct of the diazapentane **(I)** and toluene (0.20 g, 0.27 mmol, 3% based on PhMe and diazapentane).
Components **B, C,** and **D** were only minor and could not be identified. Component **E** was present in the -78, -48, -23 and 0 °C fractions. The component was separated from the -23 °C fraction by glc and from a consideration of its IR , ^{1}HNMR, ^{19}FNMR (table 5) and mass spectra, it was identified as a mixture of 3-(NN-bistrifluoromethylamino)toluene (o.20 g, 0.82 mmol, 7% based on PhMe, 6% based on diazapentane) and an unknown impurity (0.05 g) in the ratio of 35 : 8.
Component **E** was also separated from 0 °C fraction by glc and from a consideration of its IR , ^{1}HNMR, ^{19}FNMR (table 5) and mass spectra, it was shown to be a mixture of 3-(NN-bistrifluoromethylamino)toluene (o.21 g, 0.86 mmol, 7% based on PhMe, 6% based on diazapentane) and an unknown impurity (0.09 g) in the ratio of 26 : 11.
The mass spectra of component **E** from the -78, -48 °C fractions were almost identical to those obtained for the same component from the -23 and 0 °C fractions and on this basis it was identified in the -78 °C and -48 °C fractions as a mixture of 3-(NN-bistrifluoromethylamino)methylbenzene (o.09 g, 0.37 mmol, 3% based on PhMe, 2% based on diazapentane) and an unknown impurity (0.05 g), respectively.
Component **F** was present in the -78, -48, -23 and 0 °C fractions. The component was separated from the -23 °C fraction by glc and on the basis of its IR , ^{1}HNMR, ^{19}FNMR (table 5) and mass spectra, it was identified as a mixture of unchanged toluene (0.06 g, 0.65 mmol, 5% recovered) and 4-(NN-bistrifluoromethylamino)toluene (o.23 g, 0.94 mmol, 8% based on PhMe, 4% based on diazapentane) in the ratio of 42 :58.
Component **F** on separation by glc from -48 °C fractions was shown by a consideration of its IR, ^{1}HNMR, ^{19}FNMR (table 5) and mass spectra to be a mixture of almost entirely unchanged toluene (0.38 g, ca. 4.1 mmol, ca. 34% recovered) and 4-(NN-bistrifluoromethylamino)toluene.
A glc-mass spectrometric examination of the 0 °C fraction showed that component **F** in this fraction was a mixture (0.16 g) of a 1 : 1 adduct of the diazapentane and toluene and 2-(NN-bistrifluoromethylamino)toluene with possibly toluene also present.
Component **G** was present in the -23 and 0 °C, and non-volatile fractions. The component was separated from the -23 °C fraction by glc and on the basis of its IR , ^{1}HNMR, ^{19}FNMR (table 5) and mass spectra, it was identified as (NN-bistrifluoromethylamino-oxymethyl)benzene (o.11 g, 0.42 mmol, 4% based on PhMe, 3% based on diazapentane).
The same component was separated from the 0 °C fraction by glc and on the basis of its IR, ^{1}HNMR, ^{19}FNMR (table 5) and mass spectra, it was shown to be a mixture of 2-(NN-bistrifluoromethylamino)toluene and (NN-bistrifluoromethylamino-oxymethyl)benzene (0.28 g, 1.15 mmol, 10% based on PhMe, 8% on diazapentane) and (0.04 g, 0.15 mmol, 1% based on PhMe, 1% based on diazapentane) in the ratio of 15 : 2 , resepectively.
Component **H** was present in the -78 °C fraction. The component was separated from the -78 °C fraction by glc and on the basis of its IR , ^{1}HNMR, ^{19}FNMR and mass spectra, it was identified as NN-bistrifluoromethylhydroxylamine (0.20 g, 1.18 mmol, 8%).

Component **I** was separated from the 0 °C fraction by glc. The glc-mass indicated that the component **I** was a 2 : 1 adduct of the diazapentane and toluene (0.65 g, 0.89 mmol, 7% based on PhMe, 12% based on diazapentane). The following components were tentatively identified by a glc-mass spectrometric examination of the 0 °C and non-volatile fractions:

Components **K** and **L**: as bis(NN-bistrifluoromethylamino)methylcyclohexadienes (0.05 g, 0.13 mmol, 1% based on PhMe, 2% based on diazapentane) and (0.1 g, 0.25 mmol, 2% based on PhMe,4% based on diazapentane) , resepectively.

Component **M**: (NN-bistrifluoromethylamino)((NN-bistrifluoromethylamino-oxy)methylcyclohexadiene (and (0.07 g, 0.17 mmol, 1% based on PhMe,1% based on diazapentane).

Component **N**: a mixture of (NN-bistrifluoromethylamino)tris((NN-bistrifluoromethylamino)bis((NN-bistrifluoromethylamino-oxy)methylcyclohexene and (NN-bistrifluoromethylamino)bis((NN-bistrifluoromethylamino)bis((NN-bistrifluoromethylamino-oxy)methylcyclohexene (0.09 g, 0.12 mmol, 1% based on PhMe, 2% based on diazapentane). Component **O**:bis(NN-bistrifluoromethylamino)bis((NN-bistrifluoromethylamino-oxy)methylcyclohexene (0.36 g, 0.49 mmol, 4% based on PhMe, 7% based on diazapentane). Components **J, P, Q, R** and **S** could not be identified.

As it was mentioned earlier in this paper, the primary objective of the present work was to study the reactions of diazapentane **(I)** with a series of alkylbenzenes. In general three types of product were observed from the reactions of diazapentane **(I)** with the alkylbenzenes PhR (R=Me and Et), i.e. products resulting from side-chain substitution, ring substitution and addition to the aromatic ring. The side-chain substitution product is considered to arise via benzylic hydrogen abstraction by the **$(CF_3)_2N.$** radical. The ring-substituted products were NN-bistrifluoromethylaminoarenes. The major addition products from all the reactions were **2:1** adducts of the diazapentane **(I)** and the alkylbenzene. A well detailed mechanism of the reactions will be presented in the incoming paper (PART II) after studying the reactions of diazapentane **(I)** with more alkylbenzenes.

Table 1. Products from the reaction of the diazapentane (I) with ethylbenzene

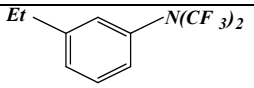
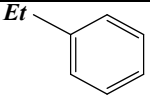
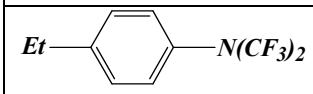
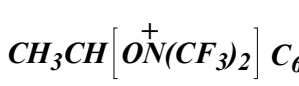
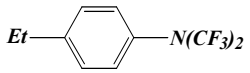
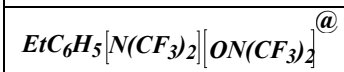
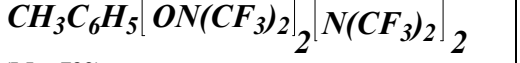
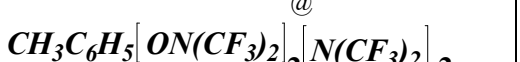
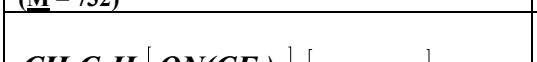
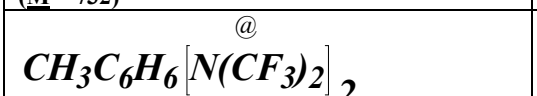
Compound	Peak	Weight (g)	Mmol	RT (min)	Yield[1] %	Yield[2] %	Present in fractions
$EtC_6H_5[(CF_3)_2N]_2[(CF_3)_2NO]_2$ (M = 746)	I	0.57	0.75	1.36	8	14	Non-volatile, Higher boiling volatile
$(CF_3)_2NH$ (M = 153)	A	0.10	0.65	1.67	-	6	-196, -78°C
$EtC_6H_6[N(CF_3)_2]_2[ON(CF_3)_2]$ (M = 579)	J	0.02	0.04	1.82	<1	-	Higher boiling volatile
Unidentified	Q	0.44	-	1.93	-	-	Non-volatile
$EtC_6H_6[N(CF_3)_2]_2[ON(CF_3)_2]_2$ (M = 746)	K	0.05	0.06	2.24	1	1	Higher boiling volatile
 (M = 257)	G	0.22	0.86	2.53	8	8	0 °C
 (M = 106)	F	0.03	0.30	2.58	3 Reco-vered	-	-23 °C
$EtC_6H_5[N(CF_3)_2]_3[ON(CF_3)_2]$ (M = 730)	L	0.10	0.14	2.65	1	3	Non-volatile, Higher boiling volatile
Unidentified	M	0.163	-	3.04	-	-	Non-volatile, Higher boiling volatile

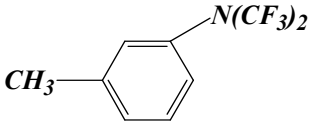
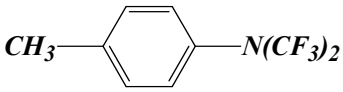
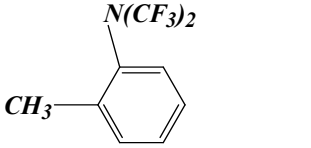
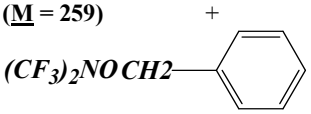
Table 1. Continued

Compound	Peak	Weight (g)	Mmol	RT (min)	Yield[1] %	Yield[2] %	Present in fractions
 **(M = 257)**  **(M = 273)**	H_A H_B	0.2 0.25	0.78 0.92	3.13	8 9	7 8	0 °C
 **(M = 257)**	B	0.16	0.64	3.24	6	6	-23, -78°C
Unidentified	N	0.15	-	3.51	-	-	Nonvolatile, Higher boiling volatile
Unidentified	O	0.06	-	3.90	-	-	Nonvolatile, Higher boiling volatile
Unidentified	C	0.63	-	4.33	-	-	-23, -78°C
 **(M = 426)**	P	0.17	0.40	4.37	4	4	Higher boiling volatile
Unidentified	R	0.12	-	5.05	-	-	nonvolatile
Unidentified	D	0.25	-	6.0	-	-	-78 °C
Unidentified	E	0.02	-	8.35	-	-	-78 °C
Unidentified	S	0.13	-	9.59	-	-	nonvolatile
Unidentified	T	0.02	-	14.8	-	-	nonvolatile

Yield[1]= Yield based on ethylbenzene Yield[2]= Yield based on diazapentane (I)
@ = tentatively identified

Table 2. Products from the reaction of the diazapentane (I) with toluene

Compounds	Peak	Weight (g)	Mmol	RT (min)	Yield[1] %	Yield[2] %	Present in fractions
 **(M = 732)**	A	0.20	0.27	0.54	2	3	-48, -78°C
 **(M = 732)**	O	0.36	0.49	0.90	4	7	nonvolatile
 **(M = 732)**	I	0.65	0.89	1.36	7	12	0 °C, Nonvolatile
 **(M = 396)**	K	0.05	0.13	1.73	1	2	0 °C, Nonvolatile

@ $CH_3C_6H_5[N(CF_3)_2]_2$ **(M = 396)**	**L**	0.10	0.25	1.87	2	4	0 °C
 **(M = 243)** + Unknown impurity	**E**	0.50 0.19	2.05 ?	2.27	17 ?	14 ?	-78, -48, -23, 0 °C
 **(M = 243)**+ Unchanged toluene	**F**	1.11	?	2.77	?	?	-78, -48, -23, 0 °C
@ $CH_3C_6H_5[ON(CF_3)_2][N(CF_3)_2]$ **(M = 412)**	**M**	0.07	0.17	3.30	1	1	0 °C
 **(M = 259)** +  **(M = 243)**	**G**	0.24 0.28	0.92 1.15	3.70	8 10	6 8	-23, 0 °C, nonvolatile
$(CF_3)_2NOH$ **(M = 169)**	**H**	0.20	1.18	6.72	-	8	-78 °C
@ $CH_3C_6H_5[ON(CF_3)_2]_3[N(CF_3)_2]$ **(M = 748)** + $CH_3C_6H_5[ON(CF_3)_2]_2[N(CF_3)_2]_2$ **(M = 732)**	**N**	0.09	0.12	6.80	1	2	nonvolatile
Unidentified	**B**	0.01	-	0.78	-	-	-78°C Nonvolatile
Unidentified	**C**	0.02	-	1.23	-	-	-78°C
Unidentified	**D**	0.05	-	1.27	-	-	-78°C
Unidentified	**J**	0.06	-	1.50	-	-	0 °C,

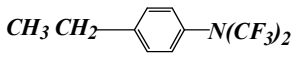
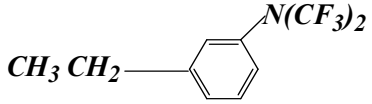
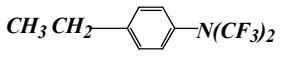
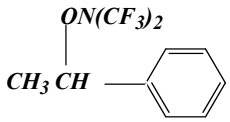
Yield[1]= Yield based on ethylbenzene **Yield[2]= Yield based on diazapentane (I)**
@ = tentatively identified

Table 3. Infrared (IR) spectroscopy data

Assignment	Absorption range (cm^{-1})	
	Component (G)	Component (I)
C = C – H str.	3075 – 3050 (m)	3100 – 3010 (v. w.)
C – H str.	3000 – 2850 (s)	3000 – 2850 (s)
C = C - str.	1600 – 1500 (m)	1600 – 1500 (v.w.)
CH_2 bending	1465 (m)	1465 – 1440 (m)
C – F str.	1390 – 1090 (br, s)	1390 – 1070 (br, s)
N – O str.	1075 – 1010 (m)	1075 – 1010 (m)
C – N str.	1000 – 940 (s)	1000 – 940 (s)
C – N – C str.	930 – 840 (m)	930 – 840 (w)
CF_3 str.	745 – 670 (s)	745 – 670 (s)

m= medium ; s= strong ; br= broad ; v.w.= very weak ; w= weak

Table 4. NMR spectral data of the products from the reaction of diazapentane with ethylbenzene

Compound	^{1}HNMR spectrum		^{19}FNMR spectrum	
	Chemical Shift (δ)	Assignment & ratio	Chemical Shift (ppm)	Assignment
 **A B C D** **Component B**	A 1.10 B 2.60 C 7.06	3, CH_3 (t) 2 CH_2 (q) 4 aromatic (AA'BB')	D -22.1	$(CF_3)_2N$ (s)
 **A B C D** **Component G**	A 1.07 B 2.54 C 7.12	3, CH_3 (t) 2 CH_2 (q) 4 aromatic	D -22.04	$(CF_3)_2N$ (s)
 **A C E G**  **B D** **Component H**	A 0.90 B 1.30 C 2.33 D 4.90 E 7.00	2, CH_3 (t) 3, CH_3 (t) 1.3 CH_2 (q) 1, CHO(sept) 7.7 aromatic	F -9.01 G -20.87	$(CF_3)_2NO$ (s) $(CF_3)_2N$ (s)

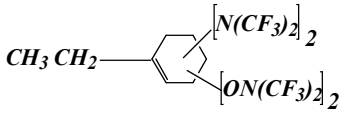
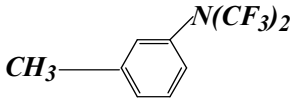
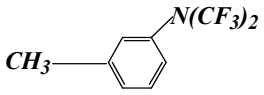
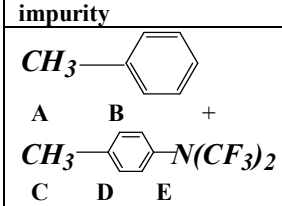
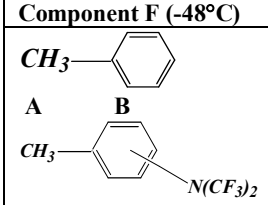
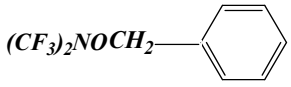
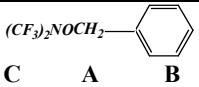
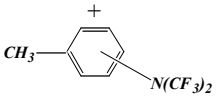
 **A B (C-F) H** **Component I**	A 0.90 B 2.00 C 3.60 D 4.30 E 4.65 F 5.90	3, CH_3 2 CH_2 1 CHN } 3 CHO 1 Vinylic	G -8.55 H -25.44	$(CF_3)_2NO$ **(broad)** $(CF_3)_2N$ **(broad)**

Table 5. NMR spectral data of the products from the reaction of diazapentane with toluene

Compound	^{1}HNMR spectrum		^{19}FNMR spectrum	
	Chemical Shift (δ)	Assignment	Chemical Shift (ppm)	Assignment
 **A B C** **Component E (0 °C) + unknown impurity**	A 2.10 D 1.97 B+E 6.9-7.2	CH_3 (s) CH_3 (s) aromatic (m)	C -22.70 F -21.90	$(CF_3)_2N$ **(s)** $(CF_3)_2N$ **(s)**
 **A B C** **Component E (-23°C) + unknown impurity**	A 2.00 D 1.88 B+E 6.9-7.2	CH_3 (t) CH_2 (s) Aromatic (m)	C -21.50 F -21.80	$(CF_3)_2N$ **(s)** $(CF_3)_2N$ **(s)**
 **A B + C D E** **Component F (-48°C)**	A+C 2.00 B+D 6.80	CH_3 (s) Aromatic (broad)	E -23.00	$(CF_3)_2N$ **(s)**
 **A B C D E** **Component F (-23°C)**	A 1.95 C 1.87 B+D 6.7-7.0	CH_3 (s) CH_3 (s) Aromatic (m)	E -22.00	$(CF_3)_2N$ **(s)**
 **C A B** **Component G (-23°C)**	A 5.00 B 7.30	CH_2O (s) Aromatic (broad)	C -10.30	$(CF_3)_2N$ **(s)**
 **C A B** +  **(ortho ?)** **D E F+G**	A 5.10 D 2.50 B+E 7.3-7.45	CH_2O (s) CH_3 (s) Aromatic (broad)	C -10.50 F -23.20 G -23.00	$(CF_3)_2NO$ **(s)** $(CF_3)_2N$ **(s)**

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