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

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Abstract: Three types of products were observed from the reactions of Perfluoro(2,4-dimethyl-3-oxa-2,4-diazapentane); diazapentane **(I)**; with the alkylbenzenes PhR (R=i-Pr and tert-But), 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 (in case of i-Pr) 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.
Key words: Perfluoro(2,4-dimethyl-3-oxa-2,4-diazapentane), diazapentane **(I)**, alkylbenzene, (NN-bistrifluoromethylamino)isopropylbenzene, (NN-bistrifluoromethylamino)tert-butylbenzene.

Introduction

Perfluoro(2,4-dimethyl-3-oxa-2,4-diazapentane)(for brevity it is called diazapentane) **(I)** is a very reactive compound. Its reactivity is due to the weak N-O bond which cleaves homolytically under thermal or photochemical conditions to give **NN-bistrifluoromethylnitroxide (II)** and **NN-bistrifluoromethylamino radicals (III).** It reacts with alkenes via addition reaction and gives the corresponding 1 : 1 adducts in high yield.[1]

In part (I) of this work, the reaction of diazapentane **(I)** with methylbenzene (toluene) and ethylbenzene were described.[2] The reader should refer to this reference for a more elaborate introduction.

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. These reactions involve the intermediacy of the **$(CF_3)_2N.$**and **$(CF_3)_2NO.$**radicals. Oxyl**(II)**or **[**bistrifluoromethylamino-oxyl or bistrifluoromethylnitroxide **$(CF_3)_2NO.$**is an extremely stable free radical (up to 200 °C).[3]

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.[4]

$$2\,(CF_3)_2NO. \xrightarrow{\quad 60\% \quad} (CF_3)_2NO\,ON(CF_3)_2$$

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.

Materials and methods

1. The general procedure: was described in article Part (I)[2]of this series.

2. Analytical methods: were described in article Part (I)[2]of this series.

3. Reaction of the diazapentane (I) with isopropylbenzene (cumene)

A mixture of isopropylbenzene (1.20g, 10.0 mmol) and the diazapentane **(I)** (3.52 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 two months. After 5 days the original two phases had changed to a homogeneous brown-red liquid. After two months, 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 tert-butylbenzene

A mixture of tert-butylbenzene (1.82g, 13.6 mmol) and the diazapentane **(I)**(6.03 g, 18.8 mmol) was sealed in a Pyrex reaction tube (ca. 110 cm^3) in vacuo and kept at room temperature in the dark for 5 days after which the original two phases had changed to a homogeneous brown liquid. After 5 days, the volatile products were taken into the vacuum system and were separated by fractional distillation in vacuo into the following fractions (Table 2).

Results:

1- Reaction of the diazapentane (I) with isopropylbenzene (cumene)

The ^{1}HNMR and IR spectral data for some of products are given in tables 4 and 6, respectively.

(i) A -196 °C fraction (3.26 mmol) which was shown by IR to be mainly of NN-bistriflurormethylamine **(III)**.

(ii) A -78 °C fraction (0.62 g) which was shown by glc (2m TXP at 120 °C) to contain four major components (A, D, H, K) in the ratio of 3 : 21.5 : 2 : 71 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 (0.22 g) which was shown by glc (2m TXP at 120 °C) to contain seven major components (B, D, E, H, J, K, L) in the ratio of 9 : 5 : 2 : 6 : 3 : 14 : 61 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).**

(iv) A -23 °C fraction (0.05 g), which was shown by glc to consist of six major components (B, D, E, H, J, L**)** in the ratio of 4 : 2 : 1 : 13 : 7 : 72. The IR spectrum of the fraction showed a strong band at 3600 cm^{-1}, assigned to O-H stretching in NN-bistrifluoromethylhydroxylamine **(II).**

(v) A 0 °C fraction (0.54 g), which was shown by glc to contain five major components (E, H, J, L, M) in the ratio 2 : 22 : 19 : 52 : 4.

The non-volatile material (2.23 g) material which remained in the tube was shown by glc to contain eight major components (**C, E, F, G, H, I, L, M**) in the ratio 68 : 2 : 3 : 9 : 3 : 5 : 5 : 8.

Components **A, B,** and **D** could not be identified. Component **C** was present in the non-volatile fraction and was separated by preparative scale glc. From a consideration of its I.R. , ^{1}H and ^{19}FNMR and mass spectra it was identified as NN-bistriflurormethylamino)bis(NN-bistriflurormethylamino-oxy)isopropylcyclohexene (1.47 g, 1.93 mmol, 35% based on cumene, 35% based on diazapentane).

Component **E** was present in the -48, -23, 0 °C and non-volatile fractions. It was separated by glc together with component F as a mixture from the non-volatile fraction. On the basis of its I.R., ^{1}H, ^{19}FNMR and mass spectra and a comparison of its mass spectrum with that obtained by a glc-mass spectrometric examination of the fraction, it was identified as a 2:1 adduct of diazapentane and cumene (0.10 g, 0.14 mmol, 2% based on cumene, 2% based on diazapentane).

Component **G** was separated by glc from the non-volatile fraction. On the basis of its I.R., ^{1}H, ^{19}FNMR and mass spectra it was identified as a further 2:1 adduct of diazapentane and cumene (0.20 g, 026 mmol, 5% based on cumene, 5% based on diazapentane).

Component **H** was present in the -78, -48, -23, 0 °C and non-volatile fractions. It was separated by glc from the 0 °C fraction. On the basis of its I.R., ^{1}H, ^{19}FNMR and mass spectra, it was identified as bis(NN-bistriflurormethylamino)isopropylcyclo-hexadiene (0.20 g, 0.52 mmol, 10% based on cumene, 10% based on diazapentane).

Component **I** was present in the non-volatile fraction. From a consideration of the mass spectrum of the component obtained by a glc-mass spectrometric examination of the whole fraction, it was tentatively identified as a 2:1 adduct of diazapentane and cumene (0.101g, 0.14 mmol, 3% based on cumene, 3% based on diazapentane).

2- Reaction of the diazapentane (I) with tert-butylbenzene

The ^{1}HNMR and IR spectral data for some of products are given in tables 5 and 6, respectively.

(i) A -196 °C fraction (1.82 mmol) which was shown by IR spectroscopy to consist mainly of NN-bistriflurormethylamine **(III)** together with a lesser amount of NN-bistrifluoromethylhydroxylamine **(II)**.

(ii) A -78 °C fraction (2.0 g) which was shown by glc (2 m TXP at 104 °C) to contain four major components (**A-D**) in the ratio of 2 : 1 : 20 : 75 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 (0.10 g), which was shown by glc (2 m TXP at 104 °C) to contain six major components (**F-H** and **J-L**) in the ratio of 9: 5 : 16 : 37 :20 : 6.
(v) A 0 °C fraction (2.0 g), which was shown by glc (2 m TXP at 104 °C) to contain five major components (**F, H** and **J-L**) in the ratio of 4: 29 : 16 : 5.
(vi) The non-volatile material (2.15 g) material which remained in the tube was shown by glc (2 m TXP at 104 °C) to contain major six major components (**F, J, K, I, M,** and **N**) in the ratio of 64: 2 : 13 : 12 : 5 : 3.
Components **A, B, E, G** and **N** were only minor and could not be identified. Component **C** was present in the -78 °C fraction. From the glc-mass spectrometric examination of the fraction, it was tentatively identified as an adduct formed between a (NN-bistriflurormethylamino)-t-butylebenzene and diazapentane (0.40 g, 0.66 mmol, 7% based on tert-butylebenzene, and 7% based on diazapentane).

Component **D** was present in the -78 °C and -48 °C fractions and by a consideration of its glc retention time and the IR spectra of both fractions it was identified as bistrifluoromethylhydroxylamine **(II)** (1.53 g, 9.1 mmol, 48%).

Component **F** was present in the -48, -23, 0 °C and non-volatile fractions. From a consideration of its mass spectrum obtained by a glc-mass spectrometric examination of the non-volatile and 0 °C fraction, it was tentatively identified as a 2 : 1 adduct of diazapentane and tert-butylebenzene (1.38 g, 1.78 mmol, 20% based on tert-butylebenzene, and 19% based on diazapentane).

Component **H** was present in the -48, -23 and 0 °C and fractions. It was separated by glc from the 0 °C fraction. On the basis of its I.R., ^{1}H, $^{19}FNMR$ and mass spectra, it was identified as 3-(NN-bistriflurormethylamino)-t-butylbenzene (0.58 g, 2.04 mmol, 23% based on tert-butylebenzene, 11% based on diazapentane).

Component **J** was present in the -48, -23 and 0 °C and non-volatile fractions. It was separated by preparative scale glc from the 0 °C fraction. On the basis of its I.R., ^{1}H, $^{19}FNMR$ and mass spectra, it was identified as 4-(NN-bistriflurormethylamino)-t-butylbenzene (0.88 g, 3.09 mmol, 35% based on tert-butylebenzene, 16% based on diazapentane).

Component **K** (0.64 g) was present in the -48, -23 and 0 °C and non-volatile fractions. It was separated by preparative scale glc from the 0 °C fraction, but it could not be obtained pure (admixed with component **J**). From a consideration of its I.R., ^{1}H, $^{19}FNMR$ and mass spectra, it was shown that component K was at lest mainly tert-butylbenzene. However, the mass spectrum of component **K,** obtained by a glc-mass spectrometric examination of both the 0 °C and non-volatile fractions, indicated that it was a mixture of unchanged tert-butylbenzene and an NN-bistriflurormethylamino-tert-butylbenzene presumably the ortho-isomer.

Component **L** was present in the -23 and 0 °C fractions. On the basis of its mass spectrum obtained by a glc-mass spectrometric examination of the 0 °C fraction, it was tentatively identified as bis(NN-bistriflurormethylamino)-tert-butylcyclohexadiene (0.10 g, 0.23 mmol, 3% based on tert-butylebenzene, 2% based on diazapentane).

Components **I** and **M** were present in the non-volatile fraction and from a glc-mass spectrometric examination of the fraction, they were identified as 2 : 1 adducts of the diazapentane and tert-butylebenzene (0.26 g, 0.3 mmol, 4% based on tert-butylebenzene, and 3% based on diazapentane) and (0.11 g, 0.14 mmol, 2% based on tert-butylebenzene, and 2% based on diazapentane), respectively.

Discussion:

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 products were observed from the reactions of diazapentane **(I)** with the alkylbenzenes PhR (R=Me, Et; Part I of the work[2]; i-Pr and tert-Butyl, Part II , the present work), i.e. products resulting from side-chain substitution, ring substitution and addition to the aromatic ring as discussed below:

(I) Side-chain substitution

This type of product was observed in the reactions involving toluene and ethylbenzene. The side-chain substitution product is considered to arise via benzylic hydrogen abstraction by the **$(CF_3)_2N.$**radical **(Scheme 1).**

(II) Ring-substitution

The ring-substituted products were NN-bistrifluoromethylaminoarenes; the NN-bistrifluoromethylamino-oxyarenes were not detected. There are two mechanisms by which such products could arise and both involve initial attack by the **$(CF_3)_2N.$**radical as shown in **Scheme 2** for attack at the 4-position. The intermediate radical (VI) can either undergo a chain-transfer reaction with diazapentane (I) to give the aromatic compound (VII), **NN**-bistrifluoromethylhydroxylamine (VIII), and another **$(CF_3)_2N.$**radical to carry on the chain, or it can undergo hydrogen abstraction by an oxyl radical. A higher concentration of diazapentane (I) would be expected to favour the chain-transfer reaction.
It was previously reported[5] that the reaction of diazapentane (I) with tert-butylbenzene gave among the products two NN-bistrifluoromethylamino-tert-butylbenzenes in the ratio of 40:31.5. The major product

was identified as the para-isomer but the other isomer was not identified, although it was considered that it was probably the meta-isomer. One object of the present work was to repeat the reaction and separate and identify the second isomer. This was carried our successfully and the isomer was shown by its ^{1}HNMR spectrum run at 300 MHz to be meta-isomer.

In the previously reported reaction no evidence was obtained for the formation of the ortho-isomer. However, in the present work mass spectral evidence was obtained for the presence of this isomer, but, unfortunately it had the same glc retention time on the column used as unchanged tert-butylbenzene and so it could not be separated and its structure proved.

The observed order of retention times on a TXP column for the tert-butylbenzene isomers is the same s that found for the chlorobenzene isomers on the same column, i.e. meta< para< ortho. The yields of the **$(CF_3)_2N$**-substituted alkylbenzene isomers are given in Table 3.

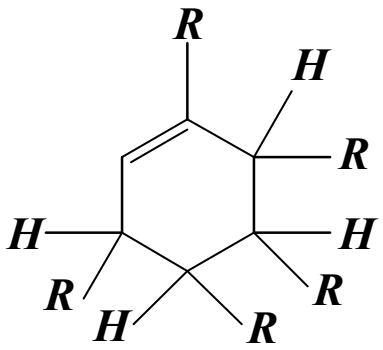
The yield of para-isomer from the toluene reaction could not be calculated since it had the same retention time as unchanged toluene. From Table 5 it is apparent that the ease of **$(CF_3)_2N$.** radical attack at the various ring positions of the alkylbenzenes is in the order para > meta > ortho. Attack at the para-position is even more favoured than the figures indicate because there are two ortho- and two meta- positions available for attack but only one para-position. The factors which will determine the relative proportions of attack at the three positions in the alkylbenzenes are:

(i) electron-density at these positions
(ii) stabilization of the intermediate readicals, and
(iii) steric effects.

Substitution products were not detected which contained more than one **$(CF_3)_2N$** group, which perhaps indicated that the presence of a ring **$(CF_3)_2N$** group somewhat deactivates the ring towards further **$(CF_3)_2N$** radical attack.

(III) **Addition products**

The major addition products from all the reactions were 2:1 adducts of the diazapentane (I) and the alkylbenzene. The ^{1}HNMR spectra of a number of these adducts showed only on vinylic hydrogen atom which indicates that they have the structure (IX) where **R=$(CF_3)_2N$** or **$(CF_3)_2NO$** groups.



(IX)

Steric hindrance to addition of a **$(CF_3)_2N$** or **$(CF_3)_2NO$** group to the carbon atom bearing the alkyl group would be expected. Also if addition did occur then the resulting product would contain either two cis **$CF_3)_2N$** or **$(CF_3)_2NO$** groups or a **$(CF_3)_2N$** or **$(CF_3)_2NO$** groups cis to the alkyl group which would be sterically unfavourable.

It is considered that the 2 : 1 adducts are formed via the same intermediate radicals from which the ring-substituted products are derived as shown in **Scheme 3** for initial attack at the 4-position.

This preliminary investigation of the reactions of diazapentane (I) with the alkylbenzenes has given interesting results. The reactions need to be repeated using varying ratios of diazapentane (I) : alkylbenzene to find out whether a high ratio favours susbstitution. The effect of changes in reaction temperature could also give useful information. Careful separation and absolute identification of the products is essential and the effect of increasing the bulk of the alkyl group could then be clearly seen.

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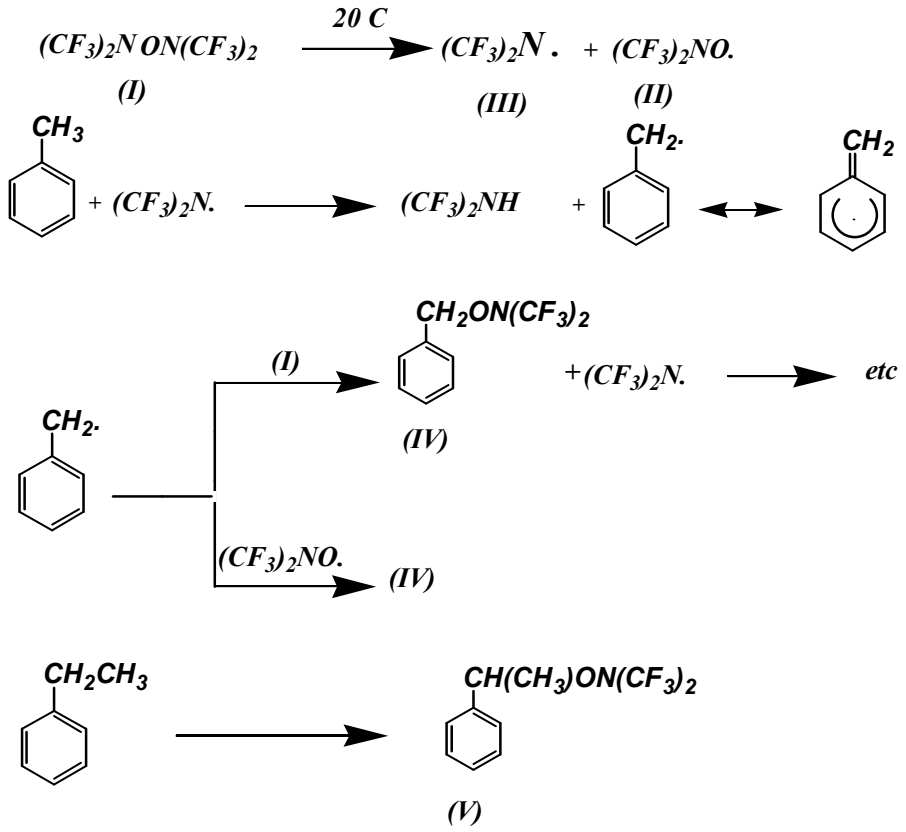
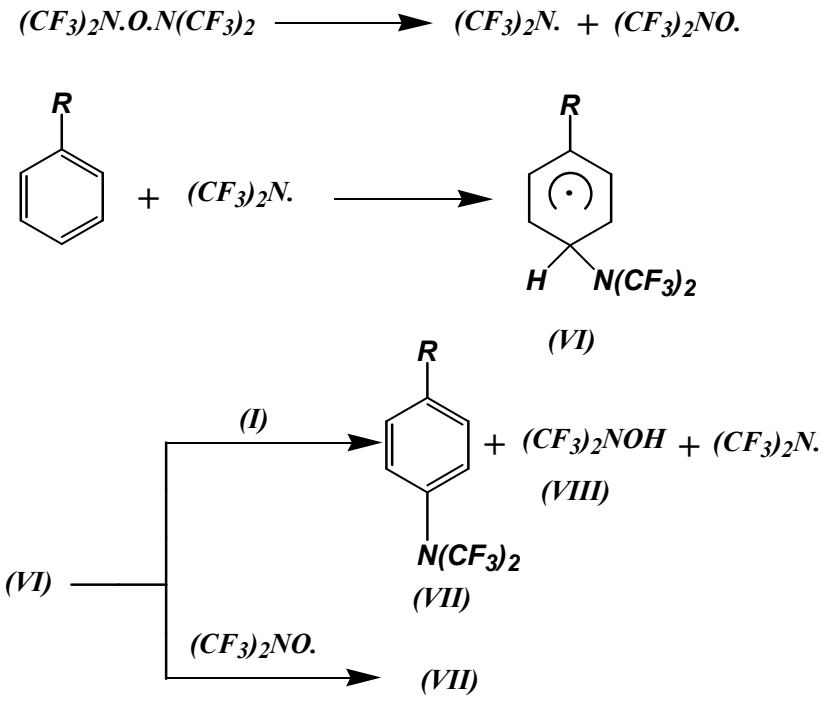
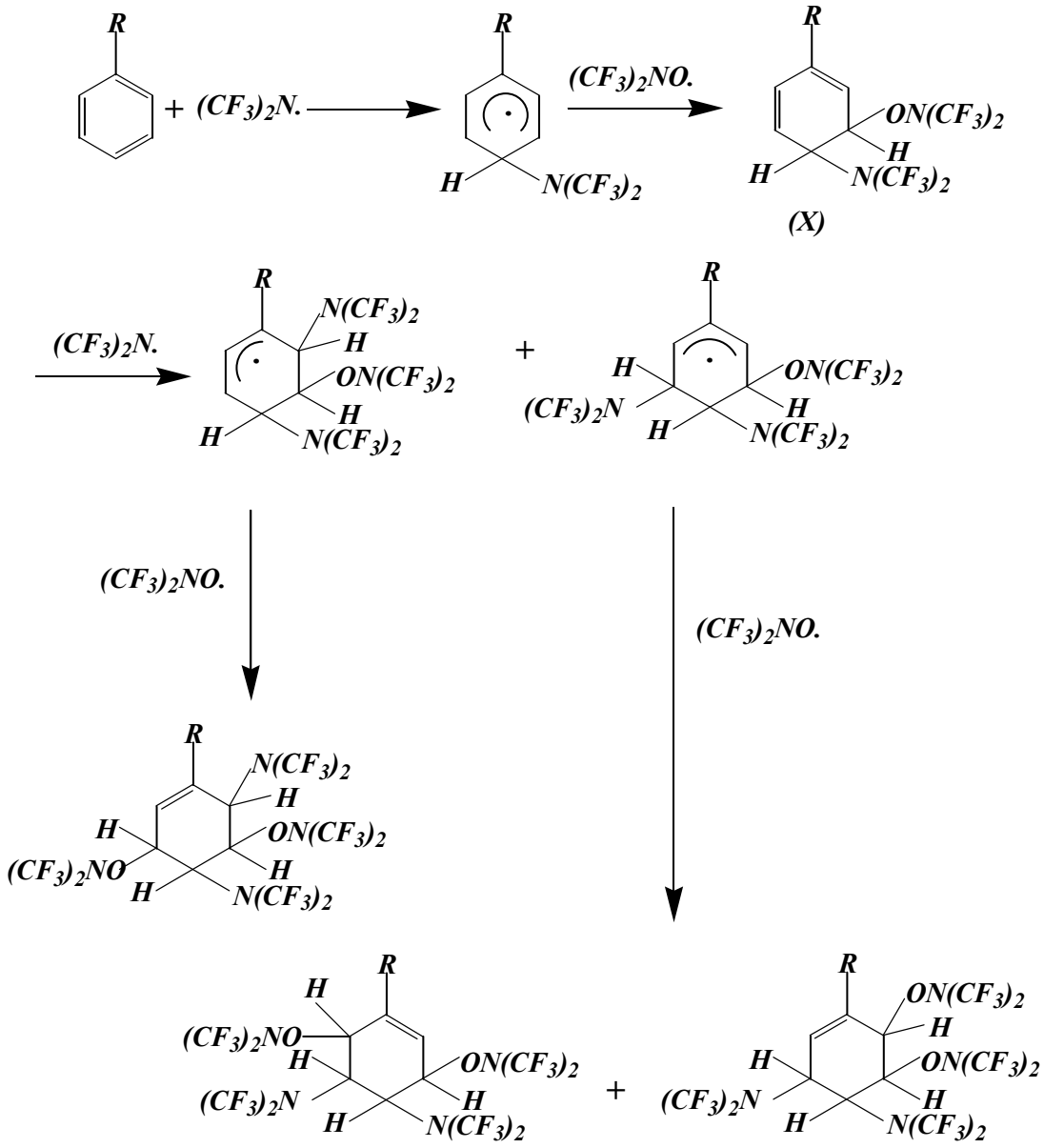


Scheme 1

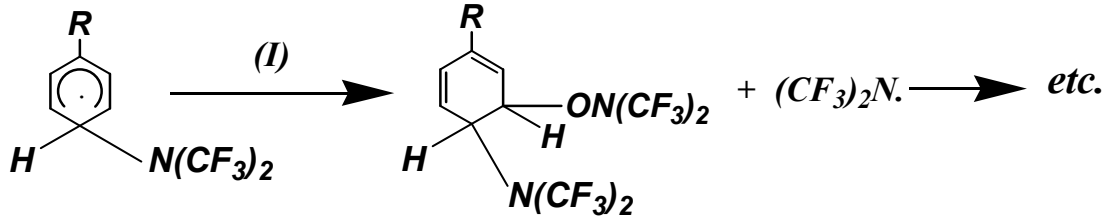


Scheme 2

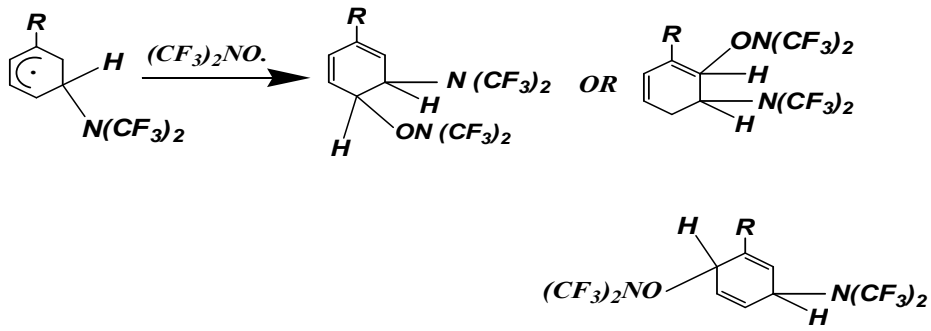


Scheme 3

However, it is possible that a proportion of the 2 : 1 adducts are formed via interaction of the diazapentane (I) with the intermdidate radicals.



In **Scheme 3** the 2:1 adducts are shown as derived via oxyl coupling with the intermediate radicals to give a cyclohexa-1,3-diene followed by further **$(CF_3)_2N.$**radical attack on the diene. Oxyl coupling with the intermediate radicals derived from initial attack at the 2- or 3-positions give cyclohexa-1,3- or 1,4- dienes, e.g.**(Scheme 4).**



Scheme 4

This preliminary investigation of the reactions of diazapentane (I) with the alkylbenzenes has given interesting results. The reactions need to be repeated using varying ratios of diazapentane (I) : alkylbenzene to find out whether a high ratio favours susbstitution. The effect of changes in reaction temperature could also give useful information. Careful separation and absolute identification of the products is essential and the effect of increasing the bulk of the alkyl group could then be clearly seen.

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

Compound	Peak	Weight (g)	Mmol	RT (min)	Yield[1] %	Yield[2] %	Present in fractions
Unidentified	**A**	0.02	-	0.41	-	-	-78°C
Unidentified	**B**	0.02	-	0.67	-	-	-48, -23°C
$Me_2CHC_6H_5[N(CF_3)_2]_2$ $[ON(CF_3)_2]_2$ (M = 760)	**C**	1.47	1.93	0.79	35	35	Non- volatile
Unidentified	**D**	0.15	-	0.84	-	-	-78, -48, -23°C
$Me_2CHC_6H_5[N(CF_3)_2]_2$ $[ON(CF_3)_2]_2$ (M = 760)	**E**	0.05	0.07	1.14	1	1	Non- volatile
$Me_2CHC_6H_5[N(CF_3)_2]_2$ $[ON(CF_3)_2]_2$ (M = 760)	**F**	0.05	0.07	1.33	1	1	Non-volatile
$Me_2CHC_6H_5[N(CF_3)_2]_2$ $[ON(CF_3)_2]_2$	**G**	0.20	0.26	1.69	5	5	Non-volatile

(M = 760)							
$Me_2CHC_6H_5[N(CF_3)_2]_2$ (M = 424)	**H**	0.22	0.52	1.90	10	9	-78, -48, -23, 0°C, Non-volatile
$Me_2CHC_6H_5[N(CF_3)_2]_2$ $[ON(CF_3)_2]_2$ (M = 760)@	**I**	0.11	0.14	2.19	3	3	Non-volatile
$Me_2CHC_6H_4$ - $N(CF_3)_2$ (M = 271)@ (1 : 1 mixture) probably ortho and para isomers	**J**	0.10	0.37	2.50	7	3	-48, -23, 0 °C
$(CF_3)_2$ NOH (M = 169)	**K**	0.47	2.78	2.75	-	25	-78, -48°C
Unchanged Cumene + a small amount of substituted $Me_2CHC_6H_4$ - $N(CF_3)_2$	**L**	0.55	4.58	2.98	46% reco-vered	-	-48, -23, 0 °C
$Me_2CHC_6H_5[N(CF_3)_2]_2$ $[ON(CF_3)_2]_2$ (M = 760)@	**M**	0.17	0.22	3.57	4	4	-78, -48°C

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

Table 2. Products from the reaction of the diazapentane (I) with tert-butylbenzene

Compounds	Peak	Weight (g)	Mmol	RT (min)	Yield[1] %	Yield[2] %	Present in fractions
Unidentified	**A**	0.04	-	0.31	-	-	-78, -48°C
Unidentified	**B**	0.02	-	0.37	-	-	-78, -48°C
\ **Unidentified**	**E**	0.005	-	0.61	-	-	-48°C
$Me_3CC_6H_4N(CF_3)_2$ + (I) adduct@ (M = 605)	**C**	0.40	0.66	0.07	7	7	-78°C
$Me_3CC_6H_5[N(CF_3)_2]_2$ $[ON(CF_3)_2]_2$ (M = 774)	**I**	0.26	0.34	1.68	4	4	Non-volatile

$Me_3CC_6H_5[N(CF_3)_2]_2$ $[ON(CF_3)_2]_2$ (M = 774)	**M**	0.11	0.14	1.83	2	2	Non-volatile
$Me_3CC_6H_5[N(CF_3)_2]_2$ $[ON(CF_3)_2]_2$ (M = 774)[@]	**F**	1.38	1.78	1.99	20	19	-48, 23, 0 °C, Non-volatile
Unidentified	**G**	0.003	-	2.31	-	-	-48, -23°C
$Me_3CC_6H_5[N(CF_3)_2]_2$ (M = 438)	**L**	0.10	0.23	2.45	3	2	-23, 0 °C
$Me_3CC_6H_4N(CF_3)_2$ meta-isomer (M = 285)	**H**	0.58	2.04	3.45	23	11	-48, -23, 0 °C
$(CF_3)_2NOH$ (M = 169)	**D**	1.53	9.10	5.04	-	48	-78, -48°C
$Me_3CC_6H_4N(CF_3)_2$ para-isomer (M = 285)	**J**	0.88	3.09	5.59	35	16	-48, -23, 0°C, Non-volatile
Unchanged $Me_3CC_6H_5$ (M = 134) + $Me_3CC_6H_4N(CF_3)_2$ Ortho-isomer	**K**	0.64	4.78	6.57	33 recov-red	-	-48, -23, 0°C, Non-volatile
Unidentified	**N**	0.07	-	6.00	-	-	Non-volatile

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

Table 3. Isomer yields from reaction of diazapentane (I) with alkylbenzene

Isomer	PhMe*	PhEt	PhPr [i]	PhBu [tert]
meta	17%	8%	+	23%
para	@	14%	3.5%	35%
ortho	10%	+	3.5%	@

@ Present but could not be determined. + not detected. * based on input toluene.

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

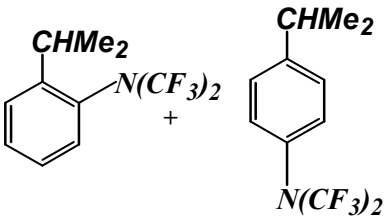
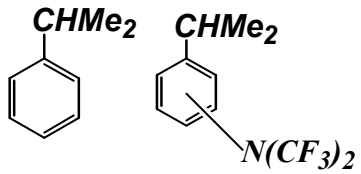
Compound	^{1}HNMR spectrum		^{19}FNMR spectrum	
	Chemical Shift (δ)	Assignment & ratio	Chemical Shift (ppm)	Assignment
$Me_2CHC_6H_5$ $[N(CF_3)_2]_2$ $[ON(CF_3)_2]_2$ A B (C- E) (G-J) F Component C	A 0.85 B 2.20 C 4.70 D 5.30 E 5.75	Me_2 CH (o.d) $CHMe_2$ (o. sept) CHN (c) CHN/CHO (c) CHO (c)	F 8.76 G 19.24 H 19.81 I 20.44 J 25.55	$(CF_3)_2NO$ (br,s) $(CF_3)_2N$ (c, br)
$Me_2CHC_6H_5$ $[N(CF_3)_2]_2$ $[ON(CF_3)_2]_2$ A B-D Component (E+F)	-	--	A 8.78 B 19.39 C 20.51 D 21.55	$(CF_3)_2NO$ (br,s) $(CF_3)_2N$ (c)
$Me_2CHC_6H_5$ $[N(CF_3)_2]_2$ $[ON(CF_3)_2]_2$ A B (C- F) (L-O) (G-K) Component (G)	A 0.90 B 2.20 C 3.70 D 4.30 E 4.80 F 6.1-5.50	Me_2 CH (c) $CHMe_2$ (c) CHN/CHO (c) C=C-H (c)	***G 8.90*** ***H 8.80*** ***I 9.15*** ***J 9.55*** ***K 10.00*** ***L 19.45*** ***M 20.45*** ***N 21.00*** ***O 25.87***	$(CF_3)_2NO$ (c) $(CF_3)_2N$ (c)
$Me_2CHC_6H_5$ $[N(CF_3)_2]_2$ A B (C-D) E, F Component (H)	A 1.15 B 2.20 C 3.40 D 7.30	Me_2 CH (c) $CHMe_2$ (c) CHN? (c) C=C-H (br,c)	E 23.36 F 22.19	$(CF_3)_2N$ (s)
D B G C A  F Component (J)	A 0.70 B 0.72 C 2.36 D 2.98 E 6.80	Me_2 CH (d) Me_2 CH (d) $CHMe_2$ (sept) $CHMe_2$ (sept) aromatic (c)	F 20.62 G 20.70	$(CF_3)_2N$ (s)
B A B A  C C D Cumene component (L)	A 0.60 B 2.25 C 6.60	Me_2 CH (d) $CHMe_2$ (sept) aromatic (c)	D 21.59	$(CF_3)_2N$ (s)

Table 5. NMR spectral data of the products from the reaction of diazapentane with tert-butylbenzene

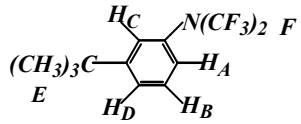
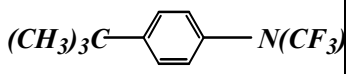
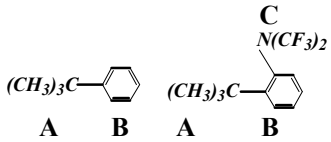
Compound	^{1}HNMR spectrum		^{19}FNMR spectrum	
	Chemical Shift (δ)	Assignment	Chemical Shift (ppm)	Assignment
 **Component (H)**	E 1.23 D 7.22 B 7.39 C 7.41 A 7.58	$(CH_3)_3C$ (s) Aromatic	F -22.00	$(CF_3)_2N$ (s)
 **A B C** **Component (J)**	A 1.10 B 7.00	$(CH_3)_3C$ (s) Aromatic (AA'BB')	C -22.00	$(CF_3)_2N$ (s)
 **A B A B** **Component (K)**	A 1.10 B 7.00	$CH_3)_3C$ (s) Aromatic (c)	C -23.50	$(CF_3)_2N$ (s)

Table 6. 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

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