Journal of Fluorine Chemistry, 22 (1983) 145–153

Received: July 1, 1982

PERFLUOROALKYL DERIVATIVES OF NITROGEN. PART LII [1]. REACTION OF THE N-HALOGENOBISTRIFLUOROMETHYLAMINES $(CF_3)_2NX$ (X=Cl,Br) WITH NORBORNENE

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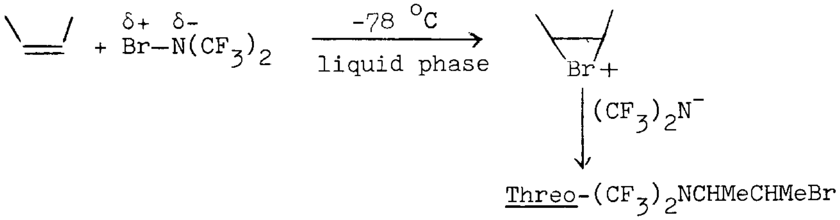
SUMMARY

Reaction of the amines $(CF_3)_2NX$ (X=Cl and Br) with norbornene gives the corresponding <u>exo</u>-3-halogenonortricyclene and <u>syn</u>-7-halogeno-<u>exo</u>-2-(<u>NN</u>-bistrifluoromethylamino)norbornane together with <u>NN</u>-bistrifluoromethylamine in the ratio 85:15:85 (X=Cl) and 91:9:91 (X=Br) at -78 °C in the dark (solvent CH_2Cl_2) and in the ratio 40:60:40 (X=Cl) and 60:40:59 (X=Br) in the vapour phase in daylight.

INTRODUCTION

It has been found previously that reaction of the amines $(CF_3)_2NX$ (X=Cl,Br or I) with alkenes can occur by two distinct mechanisms. With olefins susceptible to electrophilic attack, <u>e.g</u>. hydrocarbon olefins, reaction in the liquid phase at low temperature gives 1:1 adducts formed <u>via</u> cyclic halonium ion intermediates [2,3] <u>e.g</u>.[3]



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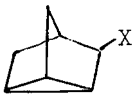
In contrast reaction with hydrocarbon olefins or fluoro-olefins in the vapour phase under photochemical conditions affords 1:1 adducts *via* a radical-chain mechanism with the $(CF_3)_2N\cdot$ radical as the chain carrier [4,5], *e.g.* [4]

$$\begin{tikzcd}
(CF_3)_2N\cdot \ + \ CF_2{=}CFCl \arrow[r, "\text{gas phase}", "\text{daylight}"'] & (CF_3)_2NCF_2\dot{C}FCl \arrow[d, "(CF_3)_2NBr"] \\
 & (CF_3)_2NCF_2CFClBr
\end{tikzcd}$$

In the present work the reactions of the amines $(CF_3)_2NX$ (X=Cl and Br) with norbornene in the liquid phase at -78 °C and in the gas phase at room temperature in daylight were investigated. A preliminary study of the reaction of the *N*-bromo-amine with 5-bromonorbornene was also carried out.

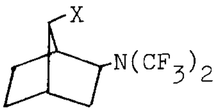
RESULTS and DISCUSSION

The results obtained using a 1:1 molar ratio of reactants are shown in Table 1.



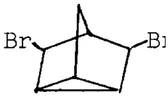
(Ia) X=Cl

(Ib) X=Br

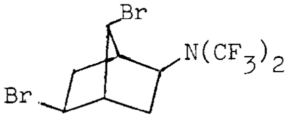


(IIa) X=Cl

(IIb) X=Br



(III)



(IV)

$(CF_3)_2NH$

(V)

TABLE 1

Reaction of the amines $(CF_3)_2NX$ with norbornene and 5-bromonorbornene

$(CF_3)_2NX$	Solvent	Phase	Temp (°C)	Products (%)				
				(I)	(II)	(III)	(IV)	(V)
X=Cl	CH_2Cl_2	liquid	-78	85	15			85
X=Cl		gas	20	40	60			40
X=Br	CH_2Cl_2	liquid	-78	91	9			91
X=Br		gas	20	60	40			59
*X=Br	CH_2Cl_2	liquid	-78			81	19	81

* Reaction with 5-bromonorbornene; all other reactions involved norbornene.

The products (Ia), (Ib), (III) and (V) are known compounds and the structures were confirmed by a comparison of spectral data with that reported.

The other non-volatile products from the norbornene reactions were assigned the structures (IIa) and (IIb) on the basis of the following evidence.

The N-chloro-amine product was shown to be a 1:1 adduct by elemental analysis and the i.r. spectrum showed an absence of absorptions expected for a nortricyclene. By analogy with other additions to norbornene [6,7], 2,3-, 2,7- and 2,5-disubstituted norbornanes are possible products with the former two most commonly found.

The mass spectrum showed a base peak at m/e 67 ($C_5H_7^+$) and a less intense peak at m/e 179 [$(CF_3)_2NCHCH_2^+$] which indicated either a 2,7- or 2,5-adduct; the 2,3-adduct would be expected to show a strong peak at m/e 68 ($C_5H_8^+$) together with peaks at m/e 215 and 213 [$(CF_3)_2NCHCHCl^+$] in its spectrum. Furthermore, treatment of the adduct with potassium hydroxide and with potassium t-butoxide at elevated temperature did not result in dehydrochlorination; comparable 2,3- and 2,5- adducts have been reported to dehydrohalogenate under such conditions [8]. It is therefore considered that the compound is a 2,7-adduct.

In the n.m.r. spectra of the 2,7-dibromonorbornanes the two CHBr protons in the exo, syn-isomer absorb at δ_H 3.93 p.p. while in the exo, anti-isomer the C-2 proton absorbs at δ_H 4.43 p.p.m. and the C-7 proton at 3.93 p.p.m., i.e. the exo-bromine atom on C-2 deshields the syn-proton on C-7 [6]. The ^1H n.m.r. chemical shifts for the C-2 (CHN) proton (δ_H 3.5 p.p.m.) and C-7 (CHCl) proton (δ_H 3 95 p.p.m.) indicated no deshielding and on this basis the adduct is assigned the 7-syn-2-exo structure (IIa). The alternative 7-anti-2-endo conformer would be expected to show similar n.m.r. chemical shifts for the protons on C-2 and C-7, but this structure is unlikely since it requires initial endo attack which is generally not observed.

Although the corresponding N-bromo-amine adduct was not isolated pure its mass spectrum was similar to that of adduct (IIa) and it is assigned structure (IIb).

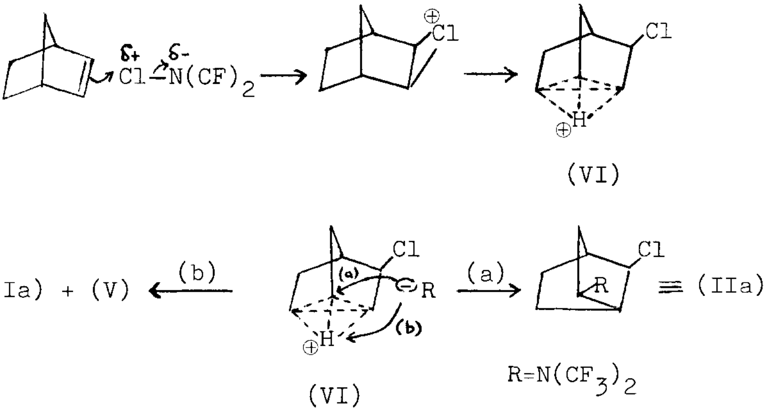
Radical additions to norbornene [9,10] produce mixtures of cis- and trans- 2,3- adducts, 5-substituted norbornenes and 3-substituted nortricyclenes and proceed via 'classical' radical intermediates. In contrast ionic additions gave cis- and/or trans-2,3-adducts and/or the rearranged 2,7-adducts and 3-substituted nortricyclenes and both 'classical' and 'non-classical' carbocation intermediates have been proposed [11-14]; chlorination [15] and bromination [6,16] under ionic conditions gave mixtures of all three types of product.

The ^1H n.m.r. spectra of the adducts were complex and it was possible that the adducts were the alternative 2-halogeno-7-(NN-bistrifluoromethylamino)norbornanes. However, their formation would require initial $(CF_3)_2N\cdot$ radical attack to give a non-classical radical intermediate; radical additions to norbornene do not afford 2,7-adducts and reaction of the amines $(CF_3)_2NX$ (X = Cl, Br) with other alkenes at - 78 °C proceed exclusively via ionic intermediates.

Thus all the amine reactions are considered to be ionic and in the vapour-phase reactions which gave higher yields of 2,7-adducts it is probable that ionic reaction occurred on the walls of the reaction vessel.

Hydride shifts occur in ionic additions to norbornene and in norbornane solvolyses [6] and one description of the intermediate involved is the nortricyclonium ion (VI) [12].

If ion (VI) is the intermediate then attack on it by the $(CF_3)_2N^-$ anion involved both abstraction of the weakly held proton to give 3-chloronortricyclene (Ia) and nucleophilic attack at C-1 to give the 2,7-adduct (IIa) (Scheme 1).



SCHEME 1

A comparison of the product ratios (I):(II) obtained from the liquid-phase and gas-phase reactions (Table 1) indicates that attack at C-1 to give the adducts (II) is more subject to steric hindrance by solvent molecules than is proton abstraction to give (I). Furthermore, lower yields of adduct (IIb) than (IIa) were obtained in both the liquid and gas phases and this is possibly due to attack at C-1 being sterically hindered to some extent by the exo-halogen substituent.

The reaction of the amine $(CF_3)_2NBr$ with 5-bromonorbornene gave exo, exo-3,5-dibromonortricyclene and a compound tentatively identified as a 1:1 adduct on mass spectral evidence. On the basis of the products formed in the norbornene reactions the expected adduct would be the 5,7-dibromo-2-(NN-bistrifluoromethylamino)norbornane (IV).

Only in two previous instances have appreciable amounts of the amine (V) been reported as formed in reactions involving the N-halogeno-amines and alkenes or dienes, i.e. with isobutene [2] and cyclohexa-1,3- and -1,4-dienes [17].

EXPERIMENTAL

Techniques used are as described in the previous paper in this series [1]; n.m.r. chemical shifts to low field of the external references TMS (^1H) and trifluoroacetic acid (^{19}F) are positive.

Preparation of starting materials

The N-halogeno-amines were made by the reaction of the appropriate halogen with the mercurial $[(CF_3)_2N]_2Hg$ [18].

Reaction of N-chlorobistrifluoromethylamine with norbornene

(a) In the liquid phase

A mixture of the N-chloroamine (2 30 g, 12·2 mmol) and norbornene (1·15 g, 12·2 mmol) in dichloromethane (11·95 g) as solvent was sealed in vacuo in a Pyrex tube (ca. 300 cm^3) and kept at -78 °C (18h). The volatile products (13·55 g) were separated by fractional condensation in vacuo to give recovered dichloromethane (11·95 g, 100%) and NN-bistrifluoromethylamine (V) (1·60 g, 10·4 mmol, 85% on amine). The two components in the non-volatile fraction (ratio 85:15) were separated by g.l.c. (3m SE 30 at 160 °C) and identified as exo-3-chloronortricyclene (Ia) (1·34 g, 10·4 mmol, 85% on alkene) (Found: M^+ 128 and 130. Calc. for C_7H_9Cl: M, 128·5) by a comparison of its i.r. spectrum with that reported [19] and syn-7-chloro-exo-2-(NN- bistrifluoromethylamino)-norbornane (IIa) (0·51 g, 1·8 mmol, 15% on alkene and amine)

(Found: C, 38·6, H; 3·3; N, 5·0; F, 40·5%. $C_9H_{10}ClF_6N$ requires C, 38·3; H, 3·5; N, 4·9; F, 40·5%), b.p. 206 °C, δ_F (neat solution) +22·3 p.p.m. [$(CF_3)_2N$], δ_H 1·35 (2H), 1·80 (3H), 2·35 (1H), 2·55 (1H), 3·50 (CHN), and 3·95 p.p.m. (CHCl), m/e 245 [11%, $(M\text{-}HCl)^+$], 179 (8%, $C_4H_3F_6N^+$), 93 (17%, $C_7H_9^+$), 79 (10%, $C_6H_7^+$), 69 (14%, CF_3^+), 67 (100%, $C_5H_7^+$) and 66 (11%, $C_5H_6^+$).

(b) In the vapour phase

Norbornene (0·85 g, 9·0 mmol) was expanded into a Pyrex bulb (ca. 10 dm^3) in vacuo followed by the N-chloroamine (1·70 g, 9·0 mmol) and the bulb was exposed to daylight (30 min). The products were amine (V) (0·56 g, 3·6 mmol, 40% on amine) and a mixture of (Ia) (0·47 g, 3·6 mmol, 40% on alkene) and (IIa) (1·52 g, 5·4 mmol, 60% on alkene and amine) in the ratio 40:60 as shown by g.l.c. (2m TXP at 125 °C).

Reaction of N-bromobistrifluoromethylamine with norbornene

(a) In the liquid phase

A mixture of the amine (1·80 g, 7·7 mmol), norbornene (0·73 g, 7·7 mmol) and dichloromethane (15·0 g), sealed in vacuo in a Pyrex tube (ca. 300 cm^3) and kept at -78 °C (18h), gave (i) dichloromethane (15·0 g, 100% recovered), (ii) amine (V) (1·07 g, 7·0 mmol, 91% on amine) and (iii) non-volatile products (1·46 g) which were analysed by g.l.c. (2m TXP at 130 °C) and shown to contain two components in the ratio 91:9; the major component was separated by g.l.c. (6m TXP at 120 °C) and identified as exo-3-bromonortricyclene (Ib) (1·21 g, 7·0 mmol, 91% on alkene) by a comparison of its i.r. [20] and n.m.r. [21] spectra with those reported. The minor component was not separated but its mass spectrum obtained by coupled g.l.c. (2m TXP at 130 °C) - mass spectrometry was similar to that obtained for the N-chloroamine-norbornene 1:1 adduct and it was tentatively identified as syn-7-bromo-exo-2-(NN-bistrifluoromethylamino)norbornane (IIb) (0·25 g, 0·7 mmol, 9% on alkene and amine), m/e 245 [14%, $(M\text{-}HBr)^+$], 179 (10%, $C_4H_3F_6N^+$), and 67 (100%, $C_5H_7^+$).

(b) In the vapour phase

A mixture of the alkene (0·56 g, 5·8 mmol) and the amine (1·35 g, 5·8 mmol), sealed *in vacuo* in a Pyrex bulb (*ca*.10 dm^3) and exposed to daylight (30 min), gave amine (V) (0·51 g, 3·4 mmol), 59% on amine) and a mixture (1·40 g) of (Ib) (0·60 g, 3.5 mmol, 60%) and (IIb) (0·80 g, 2·4 mmol, 40%) in the ratio 60:40 as shown by g.l.c. (2m TXP at 130 °C).

Reaction of N-bromobistrifluoromethylamine with 5-bromonorbornene

A mixture of the amine (1·1 g, 4·7 mmol), the alkene (0·79 g, 4·7 mmol) and dichloromethane (17·95 g), sealed *in vacuo* in a Pyrex tube (*ca*. 300 cm^3) and kept at -78 °C in the dark (18h), gave (i) dichloromethane (17·95 g, 100% recovered), (ii) amine (V) (0·57 g, 3·8 mmol, 81% on amine) and (iii) non-volatile material (1·32 g) shown by g.l.c. (2m PEGA at 170 °C) to contain two components in the ratio (19:81). They could not be separated by g.l.c. (due to decomposition) or by distillation, but the major component was obtained pure by recrystallisation (1:1 EtOH/H_2O) and was identified as *exo*, *exo*-3,5-dibromonortricyclene (0·96 g, 3·8 mmol, 81% on alkene), m.p. 41-43 °C {lit. [22] m.p. 41-43 °C } , δ_H (30% solution in CCl_4) 1·62 (3H), 2·20 (3H) and 3·84 p.p.m. (2 CHBr). The minor component was not isolated but the ^{19}F n.m.r. spectrum of the mixture showed an absorption at +23·3 p.p.m. [$(CF_3)_2N$] and the mass spectrum showed peaks at *m/e* 326 and 324 (5%, $C_9H_8F_6NBr^+$) and 69 (10%, CF_3^+) indicating that the minor component was a 1:1 adduct (0·36 g, 0·9 mmol, 19%).

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