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

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SUMMARY

Reaction of the amines $(CF_3)_2NX$ (X=Cl,Br) with norbornadiene either in solvent (CH_2Cl_2) at -78 °C in the dark or in the vapour phase at 20 °C in daylight gives a mixture of 3-halogeno-5-(NN-bistrifluoromethylamino)nortricyclene (exo,endo-and exo, exo-isomers) and exo-5-(NN-bistrifluoromethylamino)-anti-7-halogenonorbornene in quantitative yield formed via halonium ion addition to the diene. The reaction of the amine $(CF_3)_2NBr$ in solvent Me_2O or Et_2O at -78 °C in the dark gives the same products in low yield, together with 3-bromo-5-alkoxynortricyclene (exo, endo- and exo, exo-isomers) and the amine $(CF_3)_2NR$ (R=Me, Et) in high yield.

INTRODUCTION

The reactions of the N-halogenoamines$(CF_3)_2NX$ (X=Cl, Br or I) with various dienes under ionic conditions (low temperature in the dark) have been reported. Thus treatment of buta-1,3-diene, 2-methylbuta-1,3-diene and 2,3-dimethylbuta-1,3-diene with the N-bromoamine gave both 1,2- and 1,4- adducts [2], e.g.

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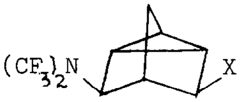
$$(CF_3)_2NBr + CH_2{=}CHCH{=}CH_2 \xrightarrow{-78\ ^{\circ}C} (CF_3)_2NCH(CH_2Br)CH{=}CH_2 + CH_2BrCH{=}CHCH_2N(CF_3)_2$$

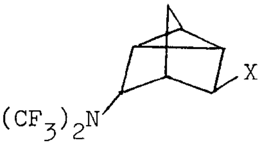
Cyclohexa-1,3-diene similarly afforded trans-1,2- and cis- and trans- 1,4-adducts with both the N-chloro- and N-bromo-amines, but reaction involving the N-iodoamine gave the trans-1,2-adduct exclusively [3]. All three amines gave only trans-1,2-adducts with cyclohexa-1,4-diene [3].

RESULTS AND DISCUSSION

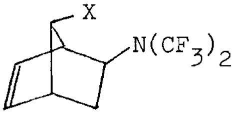
In the present work the reactions of the amines $(CF_3)_2NBr$ and $(CF_3)_2NCl$ with norbornadiene (1:1 molar ratio) under various conditions have been investigated and the results obtained are shown in Table 1.



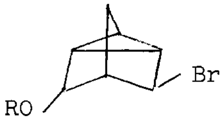
(Ia) X=Br
(Ib) X=Cl



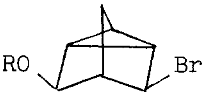
(IIa) X=Br
(IIb) X=Cl



(IIIa) X=Br
(IIIb) X=Cl



(IVa) R=Et
(IVb) R=Me



(Va) R=Et
(Vb) R=Me

$(CF_3)_2NR$

(VIa) R=Et
(VIb) R=Me

(all compounds shown here = (n.c.))

Each of the nortricyclenes (I), (II), (IV) and (V) showed characteristic bands in their i.r. spectra, i.e. at $\lambda_{max.}$ ca. 3·25 and 3·30 (cyclopropyl C-H str.), ca. 3·45 (alkane C-H str.) and ca. 12·2 µm (C-C str.), and an absence of low field

TABLE 1

Reactions of the amines $(CF_3)_2NX$ (X=Cl, Br) with norbornadiene

$(CF_3)_2NX$	Phase	Solvent	Conditions	Temp. (°C)	Products (%)					
					(I)	(II)	(III)	(IV)	(V)	(VI)
X=Br	liquid	CH_2Cl_2	dark	-78	53	33	14			
					56	31	13			
X=Br	gas		daylight	20	56	23	21			
					59·5	19·5	21			
X=Br	gas		tungsten lamp	20	60	21	19			
X=Br	gas		u.v.	20	59	23	18			
X=Br	liquid	Et_2O^a	dark	-78	19·5	12·5	10·5	19·5	38	58
X=Br	liquid	$Et_2O^{b,c}$	dark	-78	7·5	5·5	12·5	18	56·5	e
X=Br	liquid	$Et_2O^{b,d}$	dark	-78	9·5	7	9·5	21	53	e
X=Br	liquid	Me_2O^a	dark	-78	7·5	5	5	33·5	49	82
X=Cl	liquid	CH_2Cl_2	dark	-78	43	29	28			
X=Cl	gas		daylight	20	38	25	37			

Notes

[a] Excess (*ca*. 25 mmol) of ether used. [b] Large excess (540 mmol) of ether used.

[c] The reactants were allowed to warm up from -196 °C to -78 °C *in vacuo*

[d] The amine was condensed *in vacuo* into a solution of the diene in ether at -78 °C

[e] The volatile fraction containing unchanged ether and compound (VI) was not examined.

^1H n.m.r. absorptions due to vinylic protons. There are four possible 3,5-disubstituted nortricyclene isomers and the structural assignments for the amine adducts (I) and (II) were made by a comparison of the ^1H n.m.r. chemical shifts of the 3- and 5-protons with those for *exo*, *exo* - 3,5-dibromonortricyclene (δ_H 3·84 p.p.m.) [4], and of the 3-protons with that for *exo*-3-bromonortricyclene (δ_H 4·30 p.p.m.) and for *exo*-3-chloronortricylene (δ_H 4·20 p.p.m.) [4].

Data obtained from an n.m.r. study of alkene - $(CF_3)_2NBr$ adducts [5] showed that protons in CHBr or CHCl groups absorb at δ_H *ca*. 4 p.p.m. while protons in $CHN(CF_3)_2$ groups absorb at δ_H *ca*. 3·5 p.p.m. and the relevant chemical shifts for these protons in compounds (I) and (II) are shown in Table 2.

TABLE 2

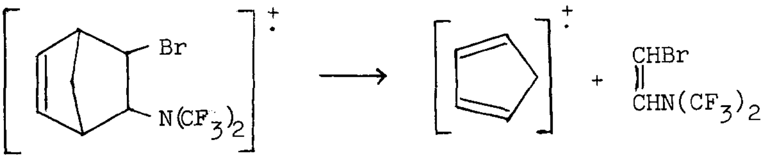
Chemical shifts of the 3- and 5- protons in adducts (I) and(II)

Adduct	δ_H CHBr(Cl) (p.p.m.)	δ_H CHN (p.p.m.)
(Ia)	4·29	3·49
(Ib)	4·32	3·44
(IIa)	3·94	3·41
(IIb)	3·92	3·42

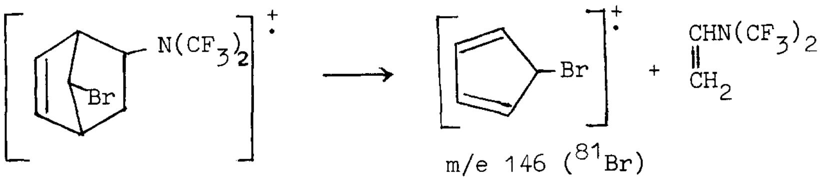
In an n.m.r. study of the 5-bromo-3-nortricyclyl phenyl sulphones [6] it was observed that an *endo*-bromine has a marked deshielding effect on an *endo*-proton on C-5 but that an *exo*-bromine had little effect on *endo*- or *exo*-protons on C-5. The chemical shifts for the $CHN(CF_3)_2$ protons in the adducts (I) and (II) were all very similar and so it is considered that all the adducts contain an *exo*-halogen atom as expected for ionic attack on norbornadiene involving initial halonium ion transfer [7]. A comparison of the chemical shifts for the CHX (X=Br, Cl) protons in adducts (I) and (II) with those for the CHBr protons in *exo*, *exo*-3,5-dibromonortricyclene would indicate that the minor adducts are the *exo*-*exo* isomers (comparable CHX chemical shifts). However, it is considered that a better comparison is that with the chemical shifts of the C-3 protons in 3-bromo- and 3-chloro-nortricyclene which indicates that the chemical shift of an endo - proton on C-3 in the presence of an endo-proton on C-5 is δ_H ca. 4·3 p.p.m., i.e. the major adducts are the exo, exo-isomers (I) and the minor adducts are the exo, endo-isomers (II) in which an endo-$(CF_3)_2N$-substituent has an upfield effect on an endo-C-5 proton.

Since the corresponding ethers (IV) and (V) could not be separated from each other structural assignments could not be made, but it seems probable that the major products (V) are the exo, exo-isomers and the minor products (IV) are the exo, endo-isomers by analogy with adducts (I) and (II).

The adducts (III) were shown to be norbornenes by their i.r. and ^1H n.m.r. spectra, i.e. $\lambda_{max.}$ ca. 6·35 μm (cyclic C=C str.) and δ_H ca. 6·25 p.p.m. (2H, HC=CH) and, by analogy with other additions to norbornadiene, they could either be 5,6- (VII) or 5,7-isomers [6-9]. Cyclohexenes undergo retro-Diels-Alder reactions in the mass spectrometer with the resulting diene fragment appearing as the radical ion and the olefin as the neutral fragment [10]. Retro-Diels-Alder cleavage of the 5,6- and 5,7-bromonorbornene isomers would give the following fragments.



m/e 66



m/e 146 (^{81}Br)

and 144 (^{79}Br)

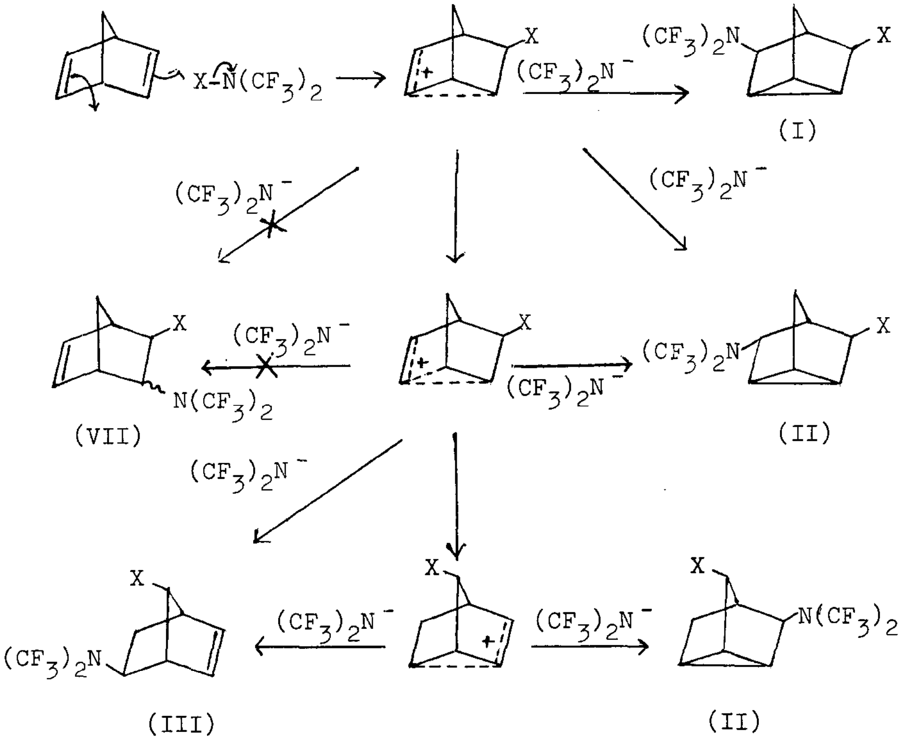
Strong peaks were observed in the mass spectrum of the adduct at m/e 146 and 144 (52 and 53%, respectively) and in that of the chlorine analogue at m/e 102 and 100 ($C_5H_5Cl^+$, 39 and 100%, respectively) and so they are considered to be the 5,7-adducts probably the exo, anti-isomer (III) (see later). Additional support for the structure was given by the failure of the bromo-compound (IIIa) to dehydrobrominate when heated under reflux with ethanolic potassium hydroxide; the 5,7-isomer would not be expected to react in contrast to the 5,6-isomer [11].

The amines (VI) were identified on the basis of their n.m.r. and mass spectra, i.e. absorptions for $(CF_3)_2N$ and CH_3 (or CH_3 and CH_2 in C_2H_5 group) only in the n.m.r. spectra and peaks at m/e 181 or 167 (M^+) and 166[100%, $(CF_3)_2NCH_2^+$] in the mass spectra.

The same products were obtained regardless of whether the reactions were carried out under conditions conducive to the formation of ionic (liquid phase at low temperature, dark in CH_2Cl_2) or radical (vapour phase in daylight or photochemical conditions) intermediates. It is considered that the reactions all involve ionic intermediates via electrophilic transfer of halonium ion to the diene and in the vapour phase reactions the exceptional reactivity of norbornadiene towards electrophilic attack precluded radical addition initiated by $(CF_3)_2N$ radical attack.

The rearranged products formed by ionic addition to norbornadiene have been rationalised [8,9,12] in terms of 'non-classical' carbocation intermediates, although an alternative explanation based on rapid interconversion between 'classical' carbocations has been proposed [13]. Most ionic additions result in mixtures composed largely of the tricyclene adducts probably because nortricyclene is thermodynamically more stable than norbornene [14].

Assuming that 'non-classical' carbocation intermediates are involved the products (I-III) could arise as shown in Scheme 1.



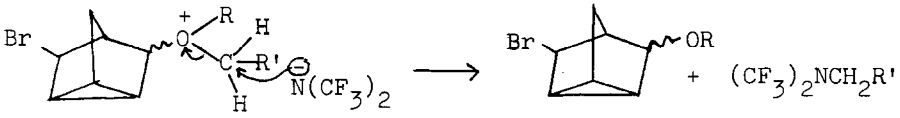
SCHEME 1

The higher yield of norbornene adducts (III) at the expense of nortricyclene adducts (I) and (II) in the vapour-phase reactions relative to the liquid-phase reactions in dichloromethane is possibly due to the anion $(CF_3)_2N^-$, liberated on the same side of the molecule as the halogen substituent, having unhindered approach by solvent molecules to C-1. This approach would also be more favoured (less hindered) the smaller the exo-halogen substituent and therefore higher yields of adduct (III b) (X=Cl) were obtained than adduct (III a) (X=Br).

It is difficult to rationalise, however, why the increased yield of adduct (III a) in the vapour-phase reactions should be at the expense of the nortricyclene adduct (II a), while the increased yield of adduct (III b) was at the expense of both nortricyclene adducts (I b) and (II b).

The additions in the ethereal solvents produced the ethers (IV) and (V) at the expense mainly of the adducts (I a) and (II a). This was surprising because reaction of the N-bromoamine with cyclohexa-1,3-diene in diethyl ether gave only $(CF_3)_2NBr$-diene adducts [3]. Attack at C-5 to give the nortricyclene adducts is relatively unhindered and competition could occur between ether molecules and the $(CF_3)_2N^-$ anion for attack at this position. The $(CF_3)_2N^-$ anion is well placed after initial bromination for attack at C-1 but, since the solvent is in excess, there is also a reasonable likelihood for an ether molecule to be in a favourable orientation for attack at this position (especially for Me_2O which is similar in size to the $(CF_3)_2N^-$ anion). Consequently, exclusive formation of the ethers (IV) and (V) indicates possibly that there is a difference in electron deficiency at the C-1 and C-5 atoms in the 'non-classical' carbocation intermediate, i.e. the C-1 position is less electrophilic than C-5 and attack here is only favourable with the nucleophile bearing a full negative charge ($(CF_3)_2N^-$), while the more electrophilic C-5 position is susceptible to nucleophilic attack by either the anion or the neutral ether via its lone pair electrons. Furthermore, as charge develops at C-5 the $(CF_3)_2N^-$ anion has to diffuse through the solvent from the other side of the molecule to a favourable position to attack C-5 while solvent molecules are already favourably placed.

The amines (VI) are considered to be formed by S_N2 attack by the $(CF_3)_2N^-$ anion on the intermediate oxonium ions (VIII) (R=Me or Et and R'=H or Me), i.e.



(VIII) (IV) and(V) (VI)

EXPERIMENTAL

Spectroscopy

N.m.r., i.r. and mass spectra were obtained using a Varian Associates HA 100 Spectrometer (operating at 100 MHz for ^{1}H and 94·1 MHz for ^{19}F with external TMS and trifluoroacetic acid as the respective references; shifts to low field of reference are designated positive), a Perkin-Elmer 257 spectrophotometer and a G.E.C.-A.E.I. MS 902 spectrometer with an electron beam energy of 70 eV, respectively.

Other techniques

Liquid-phase reactions were carried out *in vacuo* in Pyrex tubes (*ca*. 300 cm^3) and gas-phase reactions were carried out in Pyrex bulbs (*ca*. 10 dm^3). G.l.c. employed columns packed with Apiezon L grease (APL), polyethylene glycol adipate (PEGA) or trixylyl phosphate (TXP) on Celite (*ca*. 15% w/w). Boiling points were determined by Siwoloboff's method. Volatile products were removed *in vacuo* and were separated into fractions by fractional condensation *in vacuo*.

Preparation of starting materials

The *N*-halogeno amines were prepared by reaction of the appropriate halogen with the mercurial $[(CF_3)_2N]_2Hg$ *in vacuo* [15].

Reactions of N-bromobistrifluoromethylamine with norbornadiene

(a) At -78 °C in dichloromethane

A mixture of the *N*-bromo-amine (2·28 g, 9·8 mmol), norbornadiene (0·90 g, 9·8 mmol), and dichloromethane (10 g), kept in the dark at -78 °C with intermittent shaking of the tube, gave (i) a volatile fraction consisting of dichloromethane (10 g, 100% recovered) and (ii) non-volatile material (3·18 g, 100%) which was separated by g.l.c. (6m PEGA at 140 °C) into its three components (ratio 53:33:14) identified as exo-3-bromo-exo-5-(NN-bistrifluoromethylamino)nortricyclene (I a) (1·68 g, 5·2 mmol, 53%) (Found:C, 33·6; H, 2·7; N, 4·2; F, 35·0; Br, 25·0%, $C_9H_9F_6NBr$ requires C, 33·3; H, 2·5; N, 4·3; F, 35·2; Br, 24·6%), b.p. 198 °C, $\lambda_{max.}$ 3·25 and 3·29 (cyclopropyl C-H str.), 3·46 (alkane C-H str.), 7·64 to 8·70 (broad, C-F str.), 10·21 [C-N str. in $(CF_3)_2N$] and 12·20 μm (characteristic C-C str. in nortricyclenes), δ_F (30% solution in CCl_4) +24·0 [$(CF_3)_2N$] p.p.m. and δ_H 1·60 (complex; 2CH + CH_2), 2·25 (complex; 2CH), 3·49 (complex; CHN) and 4·29 (complex; CHBr) p.p.m., m/e 244 [100%, $(M-Br)^+$], 166 [45, $(CF_3)_2NCH_2^+$], 91 (56, $C_7H_7^+$), 79(9, $C_6H_7^+$), and 69 (25, CF_3^+), exo-3-bromo-endo-5-(NN-bistrifluoromethylamino)nortricyclene (II a) (1·05 g, 3·2 mmol, 33%) (Found: C, 33·5; H, 2·5; N, 4·4; F, 34·8%), b.p. 200 °C, $\lambda_{max.}$ (assignments as above) 3·25 and 3·29, 3·46, 7·60 to 8·70, 10·26 and 12·20 μm, δ_F (30% solution in CCl_4) +24·1 [$(CF_3)_2N$]p.p.m., δ_H 1·75 (complex; 2CH and CH_2), 2·25 (complex; 2CH), 3·41 (complex; CHN) and 3·84 (complex; CHBr), m/e 244 (100%), 166 (55), 91 (65), 78(26, $C_6H_6^+$), and 69 (38), and exo-5-(NN-bistrifluoromethylamino)-anti-7-bromonorbornene (III a) (0·45 g, 1·4 mmol, 14%) (Found: C, 33·0; H, 2·5; N, 4·3; F, 34·8%), b.p. 207 °C, $_{max.}$3·26 (olefinic C-H str.), 3·33 and 3·38 (alkane C-H str.), 6·35 (cyclic C=C str.), 7·58 to 8·73 (C-F str.) and 10·15 [C-N str. in $(CF_3)_2N$] μm, δ_F (30% solution in CCl_4) +24·2 [$(CF_3)_2N$] p.p.m., δ_H 1·95 (complex; CH), 2·65 (complex; CH), 3·00 (complex; CH), 3·45 (complex; CH and CHN), 4·01 (complex; CHBr) and 3·74 (mult.; HC=CH) p.p.m., m/e 244 [100%, $(M-Br)^+$], 166 [81, $(CF_3)_2NCH_2^+$], 146 (52, $C_5H_5{}^{81}Br^+$), 144 (53, $C_5H_5{}^{79}Br^+$), 91 (92, $C_7H_7^+$), 69 (60, CF_3), and 65 (85, $C_5H_5^+$). A second reaction carried out under identical conditions gave the same products (100%) in the ratio 56:31:13.

(b) Vapour-phase reactions

(i) At room temperature in daylight

Norbornadiene (0·78 g, 8·45 mmol) and then the N-bromoamine (1·96 g, 8·44 mmol) were expanded into a bulb which was then exposed to daylight. An immediate reaction occurred and the bulb was opened (after 10 min) to afford a mixture (100%) of compounds (I a), (IIa) and (III a) in the ratio 56:23:21 (g.l.c.; 2m PEGA and APL at 120 °C).

A second reaction carried out under identical conditions gave the same products (100%) in the ratio 59:19·5:21·5.

(ii) Under illumination with a tungsten bulb

The vapour-phase reaction was repeated using norbornadiene (0·40g, 4·32 mmol) and the N-bromo-amine (1·0 g, 4·32 mmol) with the bulb irradiated with a tungsten bulb (150W) to give a mixture (100%) of compounds (I a), (II a) and (III a) in the ratio 59:23:18 (g.l.c.; 2m PEGA and APL at 120 °C).

(iii) Under photochemical conditions

Norbornadiene (0·21 g, 2·28 mmol) was expanded into the bulb and the N-bromo-amine (0·53 g, 2·28 mmol) was passed into the bulb *via* a silica tube (length 1m) which was irradiated by a Hanovia medium-pressure u.v. lamp at a distance of 2cm to give a mixture (100%) of compounds (I a), (II a) and (III a) in the ratio 58:23:19 (g.l.c.; 2m PEGA and APL at 120 °C).

(c) At -78 °C in diethyl ether

A mixture of the diene (0·58 g, 6·4 mmol), the amine (1·50 g, 6·4 mmol) and anhydrous diethyl ether (1·92 g, 26·0 mmol), kept in the dark at -78 °C (30 min) gave a volatile fraction (2·32 g) and a non-volatile residue (1·68g). The volatile fraction was shown by g.l.c. (2m TXP at 20 °C) to consist of two components in the ratio 15:85 and these were separated by g.l.c. (6m TXP at 20 °C) and identified as (NN-bistrifluoromethyl)ethylamine (0·68 g, 3·7 mmol, 58% on amine) (Found: C, 26·8; H, 3·0; F, 63·0%. $C_4H_5F_6N$ requires C, 26·5; H, 2·7; F, 63·0%), δ_F (neat solution) +18·5[s; $(CF_3)_2N$], p.p.m., δ_H 0·83 (t; CH_3; J=4Hz) and 2·88 (q; CH_2; J=4 Hz) p.p.m., *m/e* 181 (4%, M^+), 166 [100, $(M\text{-}Me)^+$], 78 (67, $C_2H_2F_2N^+$), and 69 (68, CF_3^+) and diethyl ether (1·64 g, 22·2 mmol, 85% recovered). The non-volatile fraction was analysed by g.l.c. (2m PEGA and TXP at 140 °C) and shown to contain (I a) (0·40 g, 1·25 mmol, 19·5%), (II a) (0·26 g, 0·80 mmol, 12·5%), (III a) (0·22 g, 0·67 mmol, 10·5%) and two other components of much longer retention time (ratio 19·5 : 38). These latter products could not be separated by g.l.c. (decomposition on the columns), but they were separated from the other products by fractional distillation at reduced pressure to give a mixture of the two isomers of exo-3-bromo-5-ethoxynortricyclene (IV a) and (V a) (0·60 g, 3·68 mmol, 57·5%) (Found: C, 49·8, H, 5·7%. $C_9H_{12}BrO$ requires C, 50·0; H, 5·6 %), b.p. 50-58 °C at 1 mm Hg, δ_H (neat solution) 1·7 (t mult; CH_3, *J* 6Hz), 2·1 (complex; 3H), 2·5 (complex; 2H), 2·8 (complex; CH), 4·0 (q mult; OCH_2, *J* 6Hz), and 4·51 (complex; CHBr) p.p.m., *m/e* 137 [100%, $(M\text{-}Br)^+$], 109 (32, $C_7H_9O^+$), 91 (42, $C_7H_7^+$) and 78 (19, $C_6H_6^+$), $\lambda_{max.}$ 12·20 μm (characteristic C-C str. in nortricyclenes). The reaction was repeated twice (5·2 and 6·0 mmol scale) using a large excess of diethyl ether (540 mmol). In the first experiment the reactants were condensed into the tube at -196 °C *in vacuo* and allowed to warm up to -78 °C, while in the second experiment the *N*-bromo-amine was condensed into the solution of the diene in the ether at -78 °C. Only the non-volatile product mixtures(100%) were analysed (g.l.c., 2m PEGA and TXP at 140 °C) and shown to consist of the same products in the ratios 7·5:5·5:12·5:18:56·5 and 9·5:7:9·5:21:53, respectively.

(d) At -78 °C in dimethyl ether

The previous reaction was repeated using the diene (0·53g, 5·6 mmol), the *N*-bromo-amine (1·30 g, 5·6 mmol) and dimethyl ether (1·10 g, 24·0 mmol) in place of diethyl ether at -78 °C (12h). This gave a volatile fraction (1·65 g), consisting of unchanged dimethyl ether (0·89 g, 19·4 mmol, 81% recovered) and (*NN*-bistrifluoromethyl)methylamine (0·76 g, 4·6 mmol, 82%), δ_F (*ca*. 25% solution in Me_2O) +14·7 [$(CF_3)_2N$] p.p.m., δ_H 2·35 (s; CH_3) p.p.m., *m/e* 167 (19%, M^+), 166 [100, $(M\text{-}H)^+$], 78 (35, $C_2H_2F_2N^+$)and 69 (100, CF_3^+), and a non-volatile residue (1·28 g), shown by g.l.c. (2m TXP at 140 °C) to consist of (I a) (0·096 g, 0·29 mmol, 7%), (II a) (0·064 g, 0·196 mmol, 5%), (III a) (0·064 g, 0·196 mmol, 5%), and two compounds of longer retention time (ratio 33·5:49). The latter two products were separated as a mixture by g.l.c. (6m PEGA at 185 °C) and identified as the two isomers of exo-3-bromo-5-methoxynortricyclene (IV b) and (V b) (1·05 g, 5·1 mmol, 82·5%)(Found: C, 47·3; H, 5·1% $C_8H_{10}BrO$ requires C, 47·5; H, 4·95%), δ_H(neat solution) 1·8 (complex; 4H), 2·1 (complex; CH), 2·5 (complex; 1H), 3·5 (s; CH_3O), 3·7 (complex; CH) and 4·7 (complex; CHBr) p.p.m., m/e 123 [100%, $(M-Br)^+$], 109 (24, $C_7H_9O^+$), 91 (53, $C_7H_7^+$), 78 (22, $C_6H_6^+$), and 45 (54, $C_2H_5O^+$), $\lambda_{max.}$ 12·30 µm (C-C str. in nortricyclenes).

Reaction of N-chlorobistrifluoromethylamine with norbornadiene

(a) At -78 °C in dichloromethane.

A mixture of the N-chloro-amine (1·70 g, 9·0 mmol), the diene (0·83 g, 9·0 mmol) and dichloromethane (10·0 g), kept in the dark (30 min), gave dichloromethane (10·0 g, 100% recovered) and a non-volatile residue (2·53 g, 100%) which was shown by g.l.c. (2m PEGA and TXP at 120 °C) to contain three components in the ratio 43:29:28. The components were separated by g.l.c. (6m TXP at 120 °C) and identified as (i) exo-3-chloro-exo-5-(NN-bistrifluoromethylamino)nortricyclene (I b) (1·09 g, 3·87 mmol, 43%) (Found: C, 39·0; H, 2·7; N, 4·8; F, 40·6%. $C_9H_9F_6NCl$ requires C, 38·7; H, 2·9; N, 5·0; F, 40·7%), b.p. 190 °C, $\lambda_{max.}$ 3·25 and 3·29 (cyclopropyl C-H str.), 3·46 (alkane C-H str.) 7·64 to 8·7 (C-F str.), 10·21 [C-N str. in $(CF_3)_2N$], and 12·2 µm (C-C str. in nortricyclenes), δ_F (30% solution in CCl_4) +23·9 [$(CF_3)_2N$] p.p.m., δ_H 1·65 (complex; 4H), 2·20 (complex; 2H), 3·44 (complex; CHN) and 4·32 (complex; CHCl) p.p.m., m/e 244 [92%, $(M-Cl)^+$], 166 [68, $(CF_3)_2NCH_2^+$], 129 and 127 (31, $C_7H_8Cl^+$), 91 (100, $C_7H_7^+$), 79 (68, $C_6H_7^+$), 78 (54, $C_6H_6^+$), 77 (36, $C_6H_5^+$), 69 (88, CF_3^+), 66(89, $C_5H_6^+$), 65 (48, $C_5H_5^+$) and 39 (61, $C_3H_3^+$), (ii) exo-3-chloro-endo-5-(NN-bistrifluoromethylamino)nortricyclene (II b) (0·73 g, 2·61 mmol, 29%) (Found: C, 38·9; H, 3·0; N, 4·6%), b.p. 192 °C, $\lambda_{max.}$ 3·25 and 3·29, 3·38, 7·64 to 8·7, 10·26, and 12·20 cm^{-1} (assignments as for previous isomer), δ_F (30% solution in CCl_4) +24·25 [$(CF_3)_2N$] p.p.m., δ_H 1·70 (complex; 3H), 2·05 (complex; 2H), 7·62 (complex; CH), 3·42 (complex; CHN) and 3·92 (complex; CHCl) p.p.m., m/e 244 (84%), 166 (55), 129 and 127 (23) 91 (100), 79 (58), 78 (45), 77 (31), 69 (88), 66 (93), 65 (43) and 39 (55) (assignments as for previous isomer) and (iii) exo-5-(NN-bistrifluoromethylamino)-anti-7-chloronorbornene (IIIb) (0·71 g, 2 52 mmol, 28%) (Found: C, 39·0; H, 2·9; N, 4·7%), b.p. 197 °C, $\lambda_{max.}$ 3·25 (olefinic C-H str.), 3·33 (alkane C-H str.), 6·34 (cyclic C=C str.), 7·64 to 8·7 (C-F str.) and 10·10 [C-N str. in $(CF_3)_2N$)], δ_F (30% solution in CCl_4) +24·5 [$(CF_3)_2N$] p.p.m., δ_H 1·8 (complex; CH), 2·45 (complex; 2H), 2·92 (complex; CH), 3·40 (complex; CH and CHN), 3·94 (complex; CHCl) and 6·25 (mult; CH=CH) p.p.m., m/e 244 [12%, $(M\text{-}Cl)^+$], 166 [19, $(CF_3)_2NCH_2^+$], 102 (59, $C_5H_5{}^{37}Cl^+$), 100(100, $C_5H_5{}^{35}Cl^+$), 91 (77, $C_7H_7^+$), 79 (88, $C_6H_7^+$), 78 (32, $C_6H_6^+$), 77 (46, $C_6H_5^+$), 69(81, CF_3^+), 66(28, $C_5H_6^+$), 65(75, $C_5H_5^+$) and 39 (65, $C_3H_3^+$).

(b) In the vapour phase

A mixture of the diene (0·49 g, 5·3 mmol) and the N-chloro-amine (1·0g, 5·3 mmol), exposed to daylight (10 min), gave a mixture of non-volatile products (1·49 g, 100%), shown by g.l.c. (2m PEGA and TXP at 120 °C) to consist of compounds (I b) (0·56 g, 2·01 mmol, 38%), (II b) (0·37 g, 1·32 mmol, 25%) and (III b) (0·56 g, 1·97 mmol, 37%).

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