Tetrahedron. Vol. 26, pp. 3435 to 3440. Pergamon Press 1970. Printed in Great Britain

THE FLUORINATION OF BENZOTRIFLUORIDE OVER CERIUM (IV) FLUORIDE

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(*Received in UK* 20 *February* 1970; *Accepted for publication* 31 *March* 1970)

Abstract—Benzotrifluoride has been fluorinated over cerium (IV) fluoride at 480–510° and some of the products identified. These include deca- and 1*H*-nona-fluorocyclohexene, 1*H*-hepta- and 1*H*, 4*H*-hexafluorocyclohexa-1,4-diene, 1-trifluoromethylnonafluorocyclohexene, 1*H*,2-trifluoromethyloctafluorocyclohexene, 1,4-bistrifluoromethylhexafluorocyclohexa-1,4-diene and benzotrifluoride, all known compounds which were identified by Ir spectra. In addition, 1*H*,4-trifluoromethylhexafluorocyclohexa-1,4-diene and 1-trifluoromethyl-2*H*, 4*H*,-pentafluorocyclohexa-1,4-diene were isolated and characterized by UV and NMR spectroscopy and by fluorination to *cis*- and *trans*-4*H*-tridecafluoromethylcyclohexane and 2*H*/4*H*-dodecafluoromethylcyclohexane respectively. The polyfluorocyclohexanes were identified by NMR spectroscopy and their fluorination and dehydrofluorination reactions.

IN A previous paper[1] we reported the products obtained by the fluorination of benzene over cerium tetrafluoride at 450–500°. In contrast with fluorination over cobalt (III) fluoride, cerium (IV) fluoride resulted in the formation of olefins and dienes together with polyfluorobenzenes. We now describe some of the products obtained from the fluorination of benzotrifluoride over cerium (IV) fluoride at 480–510°.

Benzotrifluoride was fluorinated over a heated, stirred bed of cerium (IV) fluoride, and the products collected at −80°. After washing with water, the products were dried and fractionally distilled, fractions being taken at suitable temperature intervals; no single component fractions could be obtained. The multi component fractions were then separated by preparative scale GLC using dinonylphthalate, Kel-F oil and tricresyl phosphate stationary phases.

The first three fractions of the distillation (fraction A, B, and C, Table 1) were broadly similar in composition, each containing 1*H*-nona and 1-trifluoromethylnonafluorocyclohexene and 1*H*-heptafluorocyclohexa-1,4-diene, all of which were known compounds, and which were identified by a comparison of IR spectra with those of authentic samples. They also contained mixture IV, consisting of two components, which could not be separated on any of the stationary phases available. 1*H*, 2-Trifluoromethylhexafluorocyclohexa-1,4-diene was also tentatively identified by proton and ^{19}F NMR spectroscopy as a common constituent of the three fractions. From fraction A was also isolated decafluorocyclohexene, from fractions B and C 1*H*,4*H*-hexafluorocyclohexa-1,4-diene, and from fraction C a three component mixture which was not separated into pure components.

From fraction D was isolated 1*H*-nonafluorocyclohexene, 1*H*-heptafluorocyclohexa-1,4-diene, and 1*H*,4*H*-hexafluorocyclohexa-1,4-diene, compounds also found in fractions B and C, together with 1*H*,2-trifluoromethyloctafluorocyclohexene. These were all known compounds and were identified by their IR spectra. Also isolated from the mixture was a trifluoromethylheptafluorocyclohexa-1,3-diene subsequently obtained by the dehydrofluorination of 2*H*/4*H*-dodecafluoromethylcyclohexane, and characterized as 1-trifluoromethylheptafluorocyclohexa-1,3-diene by elemental analysis and IR and UV spectroscopy.

Fraction G was also investigated and from this was separated benzotrifluoride and 1,4-bistrifluoromethylhexafluorocyclohexa-1,4-diene (identified by IR spectra), and two new compounds. The first of these was identified as 1*H*,4-trifluoromethylhexafluorocyclohexa-1,4-diene. Elemental analysis was correct for the named compound, and the UV spectrum showed a very weak absorption at 250 n.m, which indicated that the compound was not a 1,3-diene. Mild fluorination over CoF_3 gave a mixture of *cis*- and *trans*-4*H*-tridecafluoromethylcyclohexane, which were separated by preparative scale GLC into pure components and identified by a comparison of IR spectra with those of samples prepared by an alternative route.

The mixed 4*H*-tridecafluoromethylcyclohexane isomers were prepared as previously described[2] by the fluorination of p-chlorobenzotrifluoride over CoF_3 to yield the mixed 4-chlorotridecafluoromethylcyclohexane isomers. There were reduced with LAH to give the mixed *cis*- and *trans*-4*H*-tridecafluoromethylcyclohexane isomers, which were separated by preparative scale GLC into pure components. Treatment of an equimolar mixture of the two isomers with aqueous potassium hydroxide solution showed that one of the isomers was dehydrofluorinated more quickly than the other. In hydrocarbon cyclohexane systems an equatorial trifluoromethyl group is preferred by 2·4 Kcal/mole[3], and since compounds in which a *trans*-coplanar elimination of HF can occur lose hydrogen fluoride most readily,[4] the most reactive isomer may be identified as *cis*-4*H*-tridecafluoromethylcyclohexane. This assignment of structure was confirmed by NMR spectroscopy.[12]

The second of the new compounds was shown to be 1-trifluoromethyl-2*H*,4*H*-pentafluorocyclohexa-1,4-diene. Characterization was by elemental analysis, which was in agreement with the molecular formula, the UV spectrum which showed that it was not a 1,3-diene, and ^1H and ^{19}F NMR spectroscopy. Fluorination over cobalt (III) fluoride gave 2*H*/4*H*-dodecafluoromethylcyclohexane, which was itself identified by NMR spectroscopy, chemical analysis and further fluorination over CoF_3 to *cis*-4*H*-tridecafluoromethylcyclohexane and a new compound 2*H*-tridecafluoromethylcyclohexane. This was characterized by dehydrofluorination over NaF at 360° to give a single product, 1-trifluoromethylnonafluorocyclohexene.

Confirmation of the structure of 2*H*/4*H*-dodecafluoromethylcyclohexane was provided by dehydrofluorination over NaF at 410° to yield 1-trifluoromethylheptafluorocyclohexa-1,4-diene (identified by a comparison of IR spectra), 1-trifluoromethylheptafluorocyclohexa-1,3-diene and 4*H*-undecafluoromethylcyclohex-1-ene, characterixed by elemental analysis and IR and UV spectra. 1-Trifluoromethyl-2*H*-4*H*-pentafluorocyclohexa-1,4-diene was also obtained by the reduction with LAH at 0° of 1*H*,4-trifluoromethylhexafluorocyclohexa-1,4-diene.

It is of interest that the fluorination of benzotrifluoride over cerium (IV) fluoride results not only in cyclic olefins and dienes derived from benzotrifluoride, but also in compounds arising from both from the loss and gain of a trifluoromethyl group. However, the lability of the trifluoromethyl group at high temperatures has been noted[5] during the pyrolysis of dodecafluoro-1,2-dimethylcyclohexane over nickel at 450–500°.

EXPERIMENTAL

Gas-liquid chromatography. Mixtures were separated by preparative scale GLC, components being collected in traps cooled in liquid air. Products were removed from the traps for further investigation by vacuum distillation. The column dimensions and operating conditions used were as follows; (i) Unit A, 13 mm diam × 2·00 m packed with dinonyl phthalate on celite (1:2), N_2 flow rate 5 *l*./hr, at 90° (ii) Unit B, 35 mm diam × 4·88 m packed with dinonyl phthalate on celite (1:2), N_2 flow rate 15 *l*./hr, at 100° (iii) Unit C, 35 mm diam × 4·88 m packed with Kel-F oil on celite (1:4), N_2 flow rate 10 *l*./hr at 70° and (iv) Unit D, 13 mm diam × 2·00 m packed with tricresyl phosphate on celite (1:2), N_2 flow rate 5 *l*./hr, at 70°.

A Perkin–Elmer Fractometer with a katharometer detector was used for analytical GLC. The following stationary phases, contained in tubes 4 mm diam × 1·83 m were used: (i) dinonyl phthalate on celite (1:2), (ii) Kel-F oil on celite (1:4), and (iii) tricresyl phosphate on celite (1:3).

Fluorination of benzotrifluoride. The apparatus and technique used for the fluorinations was similar to that previously used for the fluorination of organic compounds with metallic fluorides of variable valency.[6] The ceric fluoride (3 Kg, prepared as previously described[1]), was contained in a nickel tube (10 cm diam × 92 cm) fitted with a stirrer. Benzotrifluoride (70 ml) was added dropwise (45–50 ml/hr) to the reactor at 480–510°, and the product (84·2g) collected in a trap cooled in solid CO_2 washed free of HF with water and dried over P_2O_5.

Fractional distillation. The combined products (1,968 g) of a number of fluorinations were fractionally distilled using a vacuum-jacketted column (1·3 cm diam × 120 cm) packed with Dixon gauze rings (1/18″ × 1/18″). Table 1 gives details of the fractions taken.

TABLE 1

Fraction	Temp	Weight of fraction (g.)
A	42–60	32·6
B	60–63	36·4
C	63–66	23·3
D	66–76	74·2
E	76–81	41·2
F	81–87	95·2
G	87–90	76·9

Separation and identification of fraction components. Fractions from the distillation were separated into components by preparative scale GLC (Unit B): unless otherwise stated components which were shown by analytical GLC to be single compounds were identified wherever possible by a comparison of their IR spectra with those of authentic samples. Components which were shown to be mixtures were further separated by preparative scale GLC using other stationary phases.

Fraction A. A sample (21·2 g) of sample A was separated by preparative scale GLC (Unit B) into (i) Mixture I (15·5 g), (ii) mixture II (5·3 g), and 1-*H*-heptafluorocyclohexa-1,4-diene[7] (trace). Mixture I (15·5 g) was separated (Unit C) into (i) 2-trifluoromethylnonafluorocyclohexene[8] (7·8 g) and (ii) mixture III (4·8 g). A sample of mixture III (1·2 g) was separated using Unit A (38°, N_2 5 *l*./hr) into (i) mixture IV (0·4 g) and (ii) decafluorocyclohexene[9] (0·4 g). Mixture IV could not be further separated on any of the stationary phases available. Mixture II (3·3 g) was separated (Unit C) into (i) an unidentified component (0·5 g), (ii) suspected 1*H*,2-trifluoromethylhexafluorocyclohexa-1,4-diene (1·6 g) and (iii) 1*H*-nonafluorocyclohexene[7] (0·8 g).

Fraction B. A Sample of fraction B(18·6 g) was separated (Unit B) into (i) mixture V (8·1 g), (ii) mixture VI (4·7 g) and (iii) 1*H*,4*H*-hexafluorocyclohexa-1,4-diene[10] (0·8 g). Mixture V (8·1 g) was separated (Unit C) into (i) an inseparable mixture similar in composition to mixture IV (5·7 g) and (ii) 1-trifluoromethylnonafluorocyclohexene (1·0 g). Mixture VI (2·8 g) was separated by GLC (Unit C) into (i) suspected 1*H*,2-trifluoromethylhexafluorocyclohexa-1,4-diene (0·7 g), (ii) 1*H*-nonafluorocyclohexene (1·5 g) and (iii) 1*H*-heptafluorocyclohexa-1,4-diene (0·1 g).

Fraction C. A sample of fraction C (21·8 g) was separated (Unit B) into 5 components. These were (i) mixture VII (9·8 g), (ii) mixture VIII (3·8 g), (iii) *1H*-heptafluorocyclohexa-1,4-diene (0·9 g), (iv) mixture IX (0·2 g) and (v) *1H,4H*-hexafluorocyclohexa-1,4-diene (1·9 g). Mixture VII (3·2 g) was separated into (i) a mixture similar in composition to mixture IV (0·6 g) and (ii) 1-trifluoromethylnonafluorocyclohexene ((1·9 g). Mixture VIII (2·9 g) was separated (Unit C) into (i) suspected 1H-2-trifluoromethylhexafluorocyclohexa-1,4-diene (0·5 g) and (ii) *1H*-nonafluorocyclohexene (2·3 g). Insufficient sample was available for the separation of mixture IX, but analytical GLC (KelF oil/celite, 60°, N_2 flow rate 1·4 *l*./hr) showed the presence of 3 components.

Fraction D. A sample (38·4 g) was separated (Unit B) into 6 components, (i) mixture X (9·6 g), (ii) mixture XI (4·0 g) (iii) mixture XII (3·1 g), (iv) mixture XIII (0·6 g) (v) mixture XIV (1·1 g) and *1H,4H*-hexafluorocyclohexa-1,4-diene (6·3 g). Mixture X was a multicomponent mixture from which no pure components could be separated. Mixture XI (1·5 g) was separated (Unit C) into (i) an unidentified component (0·6 g) and (ii) 1-*trifluoromethylheptafluorocyclohexa*-1,3-*diene* (0·6 g). Mixture XII (1·4 g) was separated (Unit C) into (i) *1H*-nonafluorocyclohexene (0·7 g) and (ii) *1H*-2-trifluoromethyloctafluorocyclohexene[11] (0·7 g). Mixture XIII (0·4 g) was separated (Unit C) into (i) *1H*-heptafluorocyclohexa-1,4-diene (0·1 g) and (ii) a trace of an unidentified material. Mixture XIV was shown by GLC (Kel F oil/celite) to be a 3-component mixture.

Fraction G. A sample (22·2 g) of fraction G was separated (Unit B) into 6 components: (i) 1,4-bistrifluoromethylhexafluorocyclohexa-1,4-diene[8] (2·5 g), (ii) Mixture XV (0·3 g), (iii) *1H,4-trifluoromethylhexafluorocyclohexa*-1,4-*diene* (5·0 g), b.p. 84–85°, (iv) mixture XVI (5·5 g), (v) mixture XVII (1·2 g) and (vi) benzotrifluoride (1·2 g). Insufficient of mixture XV was available for separation into pure components. Mixture XVI (0·5 g) was separated (Unit D) into (i) 1-*trifluoromethyl-2H,4H-pentafluorocyclohexa*-1,4-*diene* (0·2 g), b.p. 87–88° and (ii) mixture XVIII (0·2 g), which could not be further resolved by GLC. The mixture XVII was shown to be a two component mixture by analytical GLC (Kel F oil/celite) which could not be resolved into pure components.

Characterization of 1*H,4-trifluoromethylhexafluorocyclohexa*-1,4-*diene*. Elemental analysis corresponded to the formula C_7HF_9 (Found: C, 32·6; H, 0·4. requires: C, 32·8; H, 0·4%). UV spectroscopy showed very weak absorption at approximately 250nm., indicating that the compound was not a 1,3-diene. The ^{1}H and ^{19}F NMR spectra have been described elsewhere,[11] and were consistent with the structure proposed. A sample (0·4 g) of *1H*,4-trifluoromethylhexafluorocyclohex-1,4-diene was passed over CoF_3 at 200°, and the product collected in a cold trap. A sample (0·2 g) of the product, a two component mexture, was separated by preparative scale GLC (Unit A) into *cis-4H-tridecalfluoromethylcyclohexane* and *trans-4H-tridecafluoromethylcyclohexane* identified by a comparison of the IR spectra with those of compounds synthesized by an alternative route.

Characterization of cis- and trans-4H-tridecafluoromethylcyclohexane (with D. J. Alsop and R. P. Smith). Samples of mixed *4H*-tridecafluoromethylcyclohexane isomers were obtained by the LAH reduction of 4-chlorotridecafluoromethylcyclohexane as previously described.[2] Separation of the isomers by preparative scale GLC (Unit A, 80°) gave *cis-4H-tridecafluoromethylcyclohexane*, b.p. 89°. (Found: C, 25·4; H, 0·4. C_7HF_{13} requires: C, 25·3; H, 0·3%) and *trans-4H-tridecafluoromethylcyclohexane*, b.p. 92–93°. (Found: C, 25·5; H, 0·5%). The conformation of the compounds was determined from their ^{19}F NMR spectra.[12]

A mixture of the *cis-4H*-cyclohexane (2·0 g) and the *trans-4H*-cyclohexane (2·0 g) was treated with KOH (3·3 g) and water (5 ml) at 100–105°. Analysis by GLC of the fluorocarbon mixture after 15 min showed that the ratio of *trans-4H-*:*cis-4H*-remaining unreacted was ca. 4:1, and that only one product was found.

Characterization of 1-*trifluoromethyl-2H,4H-pentafluorocyclohexa*-1,4-*diene*. Elemental analysis confirmed the empirical formula $C_7H_2F_8$. (Found: C, 35·0; H, 0·5: requires: C, 35·3; H, 0·8%). The UV spectrum (EtOH) showed no absorption at approx 250 nm. indicating that the compound was not a 1,3-diene. The ^{1}H and ^{19}F NMR spectra have been previously described,[11] and were in agreement with the assigned structure.

A sample (0·85 g) of the compound was fluorinated at 210° over CoF_3 and the product (0·9 g) collected in the usual way. A sample (0·8 g) of the fluorination mixture was separated by preparative scale GLC (Unit A) into (i) *2H/4H-dodecafluoromethylcyclohexane* (0·2 g), b.p. 95–96°, and (ii) an unidentified mixture (0·4 g).

Characterization of 2H/4H-dodecafluoromethylcyclohexane. (with P. A. Carter and C. R. Patrick). Elemental analysis was confirmed the empirical formula. (Found: C, 27·0; H, 0·6. $C_7H_2F_{12}$ requires: C, 26·7; H, 0·6%). The ^{19}F NMR spectrum had a total intensity ratio 12. The signal at δ 6·6 (relative to external T.F.A. (δ=0) of intensity ratio 3 was due to the —CF_3 group at C—1, and the signal at δ—108·6 of intensity ratio 1 to an axial F atom also at C—1. The signals at δ—129·5 and δ—158·8 each of intensity ratio 1 may be ascribed to an axial F atom at C—2 and an equatorial F atom at C—4 respectively, or to an equatorial F atom at C—2 and an axial F atom at C—4. In either case, the H atoms attached at C-2 and C-4 are *trans* to one another.

The fluorination of 2*H*/4*H*-dodecafluoromethylcyclohexane over CoF_3 at 155° gave a mixture of 4 components (i) perfluoromethylcyclohexane. (ii) *cis*-4*H*-tridecafluoromethylcyclohexane, (iii) starting material (all identified by IR spectroscopy) and (iv) *2H-tridecafluoromethylcyclohexane*, b.p. 88°. (Found: C, 25·5; H, 0·4. C_7HF_{13} requires: C, 25·3; H, 0·3%). This compound was characterized by dehydrofluorination over NaF at 360° to give 1-trifluoromethylnonafluorocyclohexane as the sole product.

A sample of 2*H*/4*H*-dodecafluoromethylcyclohexane (7·0 g) was passed over NaF at 410° and the product (4·9 g) separated by preparative scale GLC (Unit B, 85°) to give (i) 1-*trifluoromethylheptafluorocyclohexa*-1,3-*diene* (0·6 g), b.p. 84°. (Found: C, 30·5; H, 0·0. C_7F_{10} requires: C, 30·6; H, 0·0%). The IR spectrum showed absorption bands at 1708 cm^{-1} and 1780 cm^{-1} consistent with CF_3—C=CF and —CF=CF— groups respectively and the UV spectrum (in ethanol) gave λ_{max} = 257 nm., ε = 3040, indicating the presence of conjugated double bonds. Also isolated from the fluorination mixture were (ii) 1-trifluoromethylheptafluorocyclohexa-1,4-diene (0·4 g), b.p. 92° identified by a comparison of IR spectra[8] and (iii) *4H-undecafluoromethylcyclohex*-1-*ene* (0·9 g) b.p. 88°. (Found: C, 28·7; H, 0·2. C_7HF_{11} requires: C, 28·5; H, 0·3%). The IR spectrum showed an absorption band at 1702 cm^{-1} consistent with a CF_3—C=CF group and the UV spectrum (EtOH) a very weak absorption at 270 nm., ε = 300.

Reduction of 1*H*,4-*trifluoromethylhexafluorocyclohexa*-1,4-*diene*. A suspension of LAH (0·5 g) in dry ether (50 ml) was added dropwise over a period of 30 min, to a sample (1·2 g) of the diene in dry ether (50 ml) at 0°. The mixture was stirred for 100 min and the excess LAH destroyed with water (5 ml) and dil. H_2SO_4 added. The ether layer was separated, dried ($MgSO_4$) and the bulk of the ether removed by fractional distillation. The residue (2·2 g), containing residual ether, was separated by preparative scale GLC (Unit B) into (i) ether (1·0 g), (ii) starting material (0·3 g), (ii) an unidentified component (0·2 g) and (iv) 1-trifluoromethyl-2*H*,4*H*-pentafluorocyclohexa-1,4-diene (0·4 g).

Suspected 1*H*,2-*trifluoromethylhexafluorocyclohexa*-1,4-*diene*. The proton NMR spectrum showed one signal, which was a broad singlet, chemical shift δ 6·97, corresponding to a vinylic proton. The ^{19}F NMR spectrum showed 4 signals in the ratio 3:2:2:2[11]. The first of these, chemical shift δ −65·7, was assigned to the trifluoromethyl group, and was a doublet of septets, J = 1·22 Hz and 2·55 Hz arising from coupling of the —CF_3 group with the remaining F atoms in the molecule. The second signal, chemical shift δ −112·1 was a sextet and was assigned to a —CF_2— group adjacent to the —CF_3 group. The third signal, chemical shift δ −113·3 was a septet with J = 2·8 Hz, and was assigned to the second —CF_2— group. The fourth signal, chemical shift δ −132·3 was a sextet with J = 2·8 Hz, which was ascribed to the vinylic F atoms.

These results are consistent with 1*H*,2-trifluoromethylhexafluorocyclohexa-1,4-diene.

Acknowledgements—Thanks are due to Professor J. C. Tatlow for his interest, Dr. E. F. Mooney and Dr. L. F. Thomas for the measurement and interpretation of NMR spectra. One of us (A.G.H.) is grateful to Coates and Son Co. Ltd., for a maintainance award.

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