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SOME REACTIONS OF 1,2,3,4,7,7-HEXAFLUOROBICYCLO[2,2,1]HEPTA-2,5-DIENE: THERMOLYSIS AND ATTACK BY METHOXIDE ION AND BY BISTRIFLUOROMETHYL NITROXIDE

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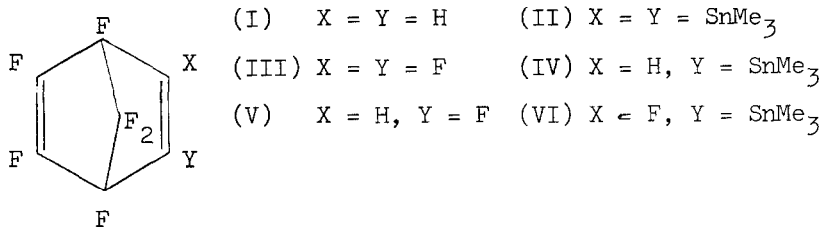
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SUMMARY

1,2,3,4,7,7-Hexafluorobicyclo[2,2,1]hepta-2,5-diene gave 1,2,3,4-tetrafluorobenzene in at least 73% yield when heated to 450 °C in a sealed tube; the CF₂ bridge appeared, in part, as octafluorocyclobutane. Nucleophilic attack by sodium methoxide-methanol on the diene occurred exclusively at the CF=CF bond, causing the formation of 1,2,4,7,7-pentafluoro-3-methoxybicyclo[2,2,1]hepta-2,5-diene and a 1,4,5,6,7,7-hexafluoro-5-methoxybicyclo[2,2,1]hept-2-ene thought, on the basis of ¹⁹F nmr data, to be the 6-endo-F,5-exo-MeO isomer. Radical attack on 1,2,3,4,7,7-hexafluorobicyclo[2,2,1]hepta-2,5-diene by bistrifluoromethyl nitroxide took place at both olefinic sites, with a ca. 10:1 preference for the CF=CF linkage; all three geometrical isomers of 5,6-bis(bistrifluoromethylamino-oxy)-1,4,5,6,7,7-hexafluorobicyclo[2,2,1]hept-2-ene were formed.

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INTRODUCTION

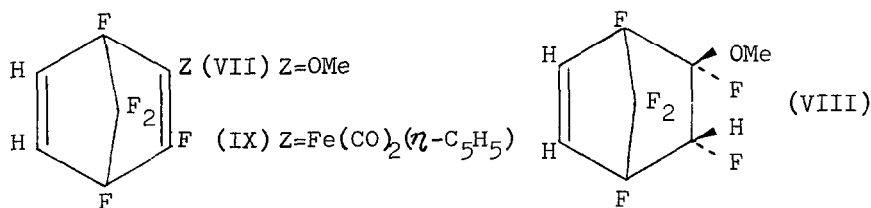


Except for a report [1] on reactions involving low-valency transition metal complexes carried out since the work described below was completed [2], published information concerning 1,2,3,4,7,7-hexafluorobicyclo[2,2,1]hepta-2,5-diene (F₆BCHD; I) relates to only its synthesis via a Diels-Alder reaction between perfluorocyclopentadiene and acetylene [3] or protonolysis (with HCl) of the corresponding {4 + 2} cycloadduct (II) derived from bis(trimethylstannyl)acetylene [4]. The latter route was used to procure F₆BCHD for a study of its thermolysis and of its behaviour towards methoxide ion and bistrifluoromethyl nitroxide because the C₅F₆-Me₃SnC≡CSnMe₃ adduct (II) was available here in quantity for work on the synthesis of perfluoronorbornadiene (III) [4]. Note that the 'direct' route [4] to perfluoronorbornadiene, ie (II) + 2F₂ → (III) + 2Me₃SnF, currently being examined by Lemal's group [5], proved inefficient in our hands when conducted at ca -72 °C in Freon 11 (CFCl₃) solution [2] owing to protonolysis of C-Sn bonds by hydrogen fluoride derived from attack on methyl groups in (II) and/or Me₃SnF [→ (IV) and (V)], coupled with incomplete fluorination [→ (VI)].

DISCUSSION

Thermolysis Thermal extrusion of difluorocarbene from F_6BCHD (I) was effected by heating the diene in an evacuated silica ampoule at $450^\circ C$ for 30 minutes. Although a seemingly thick film of carbonaceous matter appeared on the inner surface of the reaction vessel, a good yield (73%) of 1,2,3,4-tetrafluorobenzene was achieved; the only other volatile product was perfluorocyclobutane ($CF_2 \rightarrow C_2F_4 \rightarrow \text{cyclo-}C_4F_8$). Other 1,2,3,4,7,7-hexafluorobicyclo[2,2,1]hepta-2,5-dienes undergo this type of cheletropic aromatization [2,3].

Attack by methoxide ion The structures of the two products [(VII) and (VIII)] isolated after treatment of F_6BCHD with sodium methoxide contaminated by methanol at ambient temperature are consistent with a well-established sequence of events where fluorocarbon olefins are concerned, viz formation of a carbanion [$-(MeO)CF-\bar{C}F-$] which ejects a β -fluorine (non-bridgehead in type for F_6BCHD , of course) and/or becomes quenched by a proton donor (the minor event here). The absence in the ^{19}F nmr spectrum of the methanol adduct (VIII) of fine structure assignable to coupling between the C_7 fluorine anti to the $CH=CH$ bond and fluorines of the $MeOCFCHF$ moiety (neither branch of the AB pattern caused by the bridging CF_2 group was appropriately split) implies that exo,cis-addition of methanol to F_6BCHD is the predominant or exclusive mode of saturation of the $CF=CF$ link. Neither this geometrical situation [6] nor the preference for attachment of methoxide at a $-CF=$ rather than a $-CH=$ site is unexpected.



Under the conditions used in the single experiment performed [room temperature; F_6BCHD 'extended' with Et_2O ; ca 3:2 (by wt) MeONa-MeOH mixture], the yields of the new ethers (VII) and (VIII) were 70 and 23%, respectively, after isolation by g.l.c. Their structures were established by elemental analysis and spectroscopic methods (^{19}F and ^1H nmr, ir, and mass). The base peak in the mass spectrum of the norbornadiene (VII) corresponded to loss of difluorocarbene from the molecular ion $\{[\text{C}_8\text{H}_5\text{F}_5\text{O}]^+\cdot$ (m/z 212, 91%) \longrightarrow $[\text{C}_7\text{H}_5\text{F}_3\text{O}]^+\cdot$ (162, 100%) + CF_2 (50)}\}, as does that in the spectrum of F_6BCHD [3], whereas the most abundant fragment in the case of the mono-ene (VIII) conformed with a retro Diels-Alder cleavage $\{[\text{C}_8\text{H}_6\text{F}_6\text{O}]^+\cdot$ (232, 3%) \longrightarrow $[\text{C}_3\text{H}_4\text{F}_2\text{O}]^+\cdot$ (94, 100%) + $\text{C}_5\text{H}_2\text{F}_4$ (138)}\}.

The metal-containing analogue (IX) of the F-by-OMe substitution product (VII) has been isolated chromatographically in 13% yield following treatment of F_6BCHD with $\text{Na}[\text{Fe}(\text{CO})_2(\eta\text{-C}_5\text{H}_5)]$ in THF at room temperature; under similar conditions, the more weakly nucleophilic carbonylmetal anion $(\text{CO})_5\text{Mn}^-$ apparently fails to attack the hexafluorodiene [1].

Reaction with Bistrifluoromethyl Nitroxide As expected [7], this proceeded with great ease, complete conversion of reactants to a ca 35:30:24:6:3:1 (by glc analysis) molar mixture of products (X)-(XV)* occurring when just in excess of a two-molar proportion of the nitroxide was condensed on to F₆BCHD at -196 °C and the reaction vessel was then stored at room temperature for two hours. The ir spectra of the three main products (X, XI and XII) were amazingly similar, showing weak CH=CH str absorption at 6.29, 6.30 and 6.28 μm, respectively, N-O str at 9.71, 9.65 and 9.78 μm, and C-N str at 10.42, 10.38 and 10.42 μm; none of the mass spectra given by the isomers exhibited a molecular ion, but weak [M - F]⁺ and prominent[†] [M - (CF₃)₂NO]⁺ peaks were displayed in each case [the base peak for every product (ie X-XV) corresponded to CF₃⁺].

The ¹H nmr spectra of (X), (XI) and (XII) each comprised only a single absorption system (at τ 3.65, 3.07 and 3.17 respectively), and the geometrical assignments shown were made by analysis of ¹⁹F spectra. The trans-isomer (X) was easy to pick out owing to its asymmetry, and a doublet splitting of 26 Hz exhibited by the low-field pair of lines of the AB pattern associated with the CF₂ bridge supported the presence of only one exo-fluorine of the type CFON(CF₃)₂. The occurrence of such pseudo first-order coupling of, presumably [cf 8], F₇anti

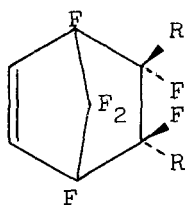
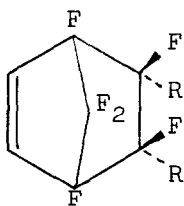
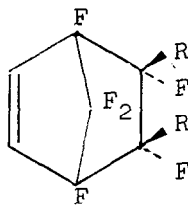
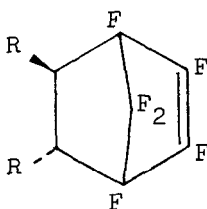
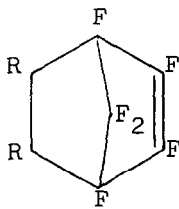
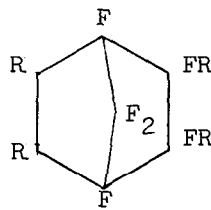
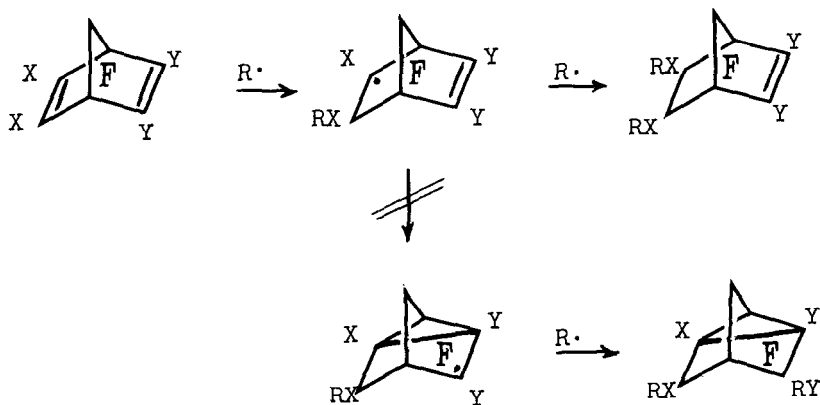
* Percentages quoted by the structures refer to yields of glc-isolated material, and R = ON(CF₃)₂.

† This is often the case with bistrifluoromethylamino-oxy compounds.

with $F_{5,6\text{exo}}$ in these polyfluorobicyclo[2,2,1]heptenes was also used to distinguish between the cis-isomers; thus, the product showing no observable coupling of this type was assigned structure (XII), while that with a spectrum displaying $F_{7\text{anti}}$ and $F_{5,6\text{exo}}$ absorptions split (28 Hz) respectively into a triplet and a doublet was allocated structure (XI).

The most abundant of the other three products (XIII-XV) was found by elemental analysis to be a 2:1 $(CF_3)_2NO \cdot / F_6BCHD$ adduct; it displayed $CF=CF$ str absorption at $5.69 \mu m$ in its ir spectrum, gave a mass spectrum containing a molecular ion [cf (X)-(XII)], possessed ^{19}F nmr characteristics expected of a 1,2,3,4,7,7-hexafluorobicyclo[2,2,1]hept-2-ene, and showed two absorptions of equal intensity in its 1H nmr spectrum. Therefore structure (XIII) was assigned.

The last two products were formed in such small amounts that the only coupled gc-ms analysis could be used to obtain structural information; the results are consistent with structures (XIV) and (XV). Briefly, a cis-adduct formulation (XIV) is supported by the close similarity between the mass spectrum of the material and that of the product assigned the corresponding trans structure (XIII); the mass spectrum of the material thought to comprise one or more 4:1 $(CF_3)_2NO \cdot / F_6BCHD$ adducts (XV) showed no molecular ion but displayed a prominent [M - $(CF_3)_2NO$] $^+$ peak, and also peaks corresponding to loss of three and four bistrifluoromethyl nitroxide molecules from the molecular ion.

(X)
33%(XI)
28%(XII)
19%(XIII)
6%(XIV)
3%(XV)
1%

If X = F, Y = H and vice versa; R = (CF₃)₂NO

Scheme

Consideration of the combined yields of adducts (X), (XI) and (XII) with those of (XIII) and (XIV) reveals a nearly 10:1 preference for attack at the CF=CF olefinic site of F₆BCHD by bistrifluoromethyl nitroxide, a situation which finds a precedent in the comparative rates of reaction of the nitroxide with tetrafluoroethylene and ethylene [9]. Tetrafluoroethylene, of course, has been used in experiments designed to demonstrate the excellent radical-scavenging power of the nitroxide [9,10], a feature of its chemistry that can be invoked to explain our failure to detect the occurrence of homoallylic rearrangement (see the Scheme) - a well-known feature of radical addition to norbornadienes [11]. Clearly, the nature of the reaction under discussion here precludes estimation of the ratio of endo- to exo- attack of bistrifluoromethyl nitroxide on F₆BCHD; this aspect of radical addition to the diene must await the results of reactions involving unsymmetrical addenda.

EXPERIMENTAL

Preparation of Starting Materials

1,2,3,4,7,7-Hexafluorobicyclo[2,2,1]hepta-2,5-diene was prepared via treatment of 1,2,3,4,7,7-hexafluoro-5,6-bis(trimethylstannyl)bicyclo[2,2,1]hepta-2,5-diene with hydrogen chloride [4], and bistrifluoromethyl nitroxide via oxidation of NN-bistrifluoromethylhydroxylamine [12].

Identification of Products

New compounds were identified by elemental analysis (where possible) and spectroscopic methods (ir, nmr, and mass). Full details of the instruments used in the latter case have already been given [4]; note, however, that ^{19}F chemical shifts to high field of the reference (ext $\text{CF}_3\text{CO}_2\text{H}$) are designated negative in this paper. Boiling points were determined by Siwoloboff's method.

Reactions of 1,2,3,4,7,7-hexafluorobicyclo[2,2,1]hepta-2,5-diene

(a) Thermolysis

The diene (0.49 g, 2.45 mmol), contained in an evacuated silica ampoule (300 cm^3), was heated at $450\text{ }^\circ\text{C}$ for 30 minutes. Trap-to-trap fractional condensation of the volatile product at 2 mmHg gave perfluorocyclobutane ($-131\text{ }^\circ\text{C}$ trap; 0.07 g, 0.35 mmol, 56%) [Found: $\underline{\text{M}}$ (Regnault), 197. Calc for C_4F_8 : $\underline{\text{M}}$, 200], with correct ir properties, and 1,2,3,4-tetrafluorobenzene ($-76\text{ }^\circ\text{C}$ trap; 0.27 g, 1.8 mmol, 73%), with correct ir and nmr (^1H and ^{19}F) spectra. A black solid residue adhering to the wall of the reaction vessel was not examined.

(b) With sodium methoxide

A mixture of the diene (1.07 g, 5.35 mmol), sodium methoxide containing ca 40% w/w of methanol (1.05 g) and dry diethyl ether (ca 0.7 g) was shaken at $20\text{ }^\circ\text{C}$ for 48 h under anaerobic conditions in a Pyrex ampoule (60 cm^3). Volatile product was transferred, in vacuo, to a Pyrex vacuum system and separated by trap-to-trap fractional condensation at

2 mmHg pressure into diethyl ether (-196 °C trap) and a colourless liquid (-45 °C); glc techniques (6 m PEGA-Celite, 150 °C) were used to separate the latter into 1,2,4,7,7-pentafluoro-3-methoxybicyclo [2,2,1]hepta-2,5-diene (VII; nc) (0.79 g, 3.73 mmol, 70%) [Found: C, 45.5; H, 2.6; F, 44.8%; \underline{M} (mass spec), 212. $C_8H_5F_5O$ requires C, 45.3; H, 2.4; F, 44.8%; \underline{M} , 212], bp 143-144 °C at 758 mmHg, n_D^{20} 1.387, λ_{max} (film) 5.80s and 6.39w (CF=COME and CH=CH str, resp) μm , δ_F (neat) -58.6 (CF₂, AB pattern, $|\underline{J}_{gem}|$ 151 Hz, $\nu_o \delta$ 2.8 ppm), -92.8 (=CF, m), -129.7 (1- or 4-F, d, $|\underline{J}_{1,4}|$ 13 Hz), -131.8 (4- or 1-F, d) ppm (rel int 2:1:1:1), τ 3.29 (CH=CH, br m), 6.06 (OCH₃, 3 Hz doublet) (rel int 2:3) and 1,4,5,6-endo,7,7-hexafluoro-5-exo-methoxybicyclo[2,2,1]hept-2-ene (VIII; nc) (0.29 g, 1.25 mmol, 23%) [Found: C, 41.6; H, 2.7%; \underline{M} (mass spec), 232. $C_8H_6F_6O$ requires C, 41.3; H, 2.6; \underline{M} , 232], bp 146-147 °C at 758 mmHg, n_D^{20} 1.377, λ_{max} (film) 6.31w (CH=CH str) μm , δ_F (neat) -59.02 (CFOME, narrow m), -60.1 (CF₂, AB pattern, $|\underline{J}_{gem}|$ 195 Hz, $\nu_o \delta$ 21.7 ppm), -124.3 (1- or 4-F, s), -128.1 (CHF, d, $|\underline{J}_{gem}^{HF}|$ 55 Hz), -132.0 (4- or 1-F, s) ppm (rel int 1:2:1:1:1), τ 3.64 [CH=CH, m ('q')], 4.93 (CHF, d, $|\underline{J}_{HF}|$ 55 Hz), 6.39 (CH₃O, s) (rel int 2:1:3).

(c) With bistrifluoromethyl nitroxide

Samples of the nitroxide (1.81 g, 10.8 mmol) and the diene (10.5 g, 5.25 mmol) were condensed separately into a cold (-196 °C) evacuated Pyrex tube (60 cm³) fitted with a PTFE needle valve. After the valve had been closed, the tube was stored at room temperature for 2 hours. The colourless

liquid produced was separated by glc (10 m TXP-Celite, 110 °C) into: (i) trans-5,6-bis(bistrifluoromethylamino-oxy)-1,2,3,4,7,7-hexafluorobicyclo[2,2,1]hept-2-ene (XIII; nc) (0.18 g, 0.34 mmol, 6%) [Found: C, 24.9; H, 0.5; F, 63.4%; \underline{M} , (mass spec), 536. $C_{11}H_2F_{18}N_2O_2$ requires C, 24.6; H, 0.4; F, 63.8%; \underline{M} , 536], bp 158.5-159.5 °C at 758 mmHg, $\underline{m/z}$ 536 ($\underline{M}^{+\cdot}$, 51%), 517 [$\underline{M}^{+\cdot}$ -F \cdot , 15%], 368 [$\underline{M}^{+\cdot}$ -(CF₃)₂NO \cdot , 72%], 362 (C₆H₂F₁₂N₂O₂⁺, 60%), 210 (C₄H₂F₆NO₂⁺, 39%), 200 [$\underline{M}^{+\cdot}$ -2(CF₃)₂NO \cdot , 90%], 174 (C₅F₆⁺, 42%), 168 (C₂F₆NO⁺, 91%), 69 (CF₃⁺, 100%), λ_{\max} (film) 5.69m (CF=CF str) μm , δ_{F} (neat) +8.4 [ON(CF₃)₂, narrow m], -60.3 (CF₂, AB pattern, $|\underline{J}_{\text{gem}}|$ 192 Hz, ν_{O} 17.3 ppm), -71.5 (2- or 3-F,s), -82.2 (3- or 2-F, s), and -139.5 (\geq CF, br s) ppm, τ 4.15(br s), 5.15 (br d)(rel int 1:1); (ii) cis-endo-5,6-bis(bistrifluoromethylamino-oxy)-1,4,5,6,7,7-hexafluorobicyclo[2,2,1]hept-2-ene (XI; nc) (0.80 g, 1.49 mmol, 28%) (Found: C, 24.6; H, 0.7; F, 63.0; N, 5.0. $C_{11}H_2F_{18}N_2O_2$ requires C, 24.6; H, 0.4; F, 63.8; N, 5.2%), mp 56-56.5 °C, λ_{\max} (melt) 6.30vw (CH=CH str) μm , δ_{F} (30% soln w/w in Me₂CO) +10.0 [ON(CF₃)₂, s], -50.8 [CFON(CF₃)₂, br m], -58.3 [CF₂, AB pattern, $|\underline{J}_{\text{gem}}|$ 190.6 Hz (ν_{O} 20.5 ppm), $^4\underline{J}_{\text{FF}}$ (low-field component) 28 Hz], -133.3 (\geq CF, s) ppm (rel int 12:2:2:2), τ 3.07 (m), and $\underline{m/z}$ 517 ($\underline{M}^{+\cdot}$ -F \cdot , 2.5%), 368 [$\underline{M}^{+\cdot}$ -(CF₃)₂NO \cdot , 15%], 69 (CF₃⁺, 100%); (iii) trans-5,6-bis(bistrifluoromethylamino-oxy)-1,4,5-6,7,7-hexafluorobicyclo[2,2,1]hept-2-ene (X; nc) (0.94 g, 1.75 mmol, 33%) (Found: C, 24.4; H, 0.5; F, 63.5. $C_{11}H_2F_{18}N_2O_2$ requires C, 24.6; H, 0.4; F, 63.8%), bp 178-179 °C at 758 mmHg, $\underline{n}_{\text{D}}^{20}$ 1.416, λ_{\max} (film) 6.29 vw (CH=CH str) μm , δ_{F} (neat) +10.3 [ON(CF₃)₂, narrow m], +9.9 [ON(CF₃)₂, narrow m], -47.5 [CFON(CF₃)₂, br m], -53.8 [CFON(CF₃)₂, br s], -59.3 (CF₂, AB

pattern, $|\underline{J}_{\text{gem}}|$ 199.6 Hz $\nu_{\text{O}}\delta$ 21.3 ppm), -132.0 (\geq CF, br s), -132.4 (\geq CF, br s) ppm, τ 3.65, and $\underline{m}/\underline{z}$ 517 ($\underline{M}^{+\cdot}$ -F \cdot , 2%), 368 [$\underline{M}^{+\cdot}$ -(CF $_3$) $_2$ NO \cdot , 45%], 69 (CF $_3^+$, 100%); and (iv) cis-exo-5,6-bis(bistrifluoromethylamino-oxy)-1,4,5,6,7,7-hexafluorobicyclo[2,2,1]hept-2-ene (XII; nc) (0.53 g, 0.99 mmol, 19%) (Found: C, 24.4; H, 0.6; F, 62.1; N, 5.5. C $_{11}$ H $_2$ F $_{18}$ N $_2$ O $_2$ requires C, 24.6; H, 0.4; F, 63.8; N, 5.2%), mp 30-31 $^{\circ}$ C, λ_{max} 6.28vw (CH=CH str) μm , δ_{F} [neat (probe temp 35 $^{\circ}$ C)] +10.8 [ON(CF $_3$) $_2$, narrow m], -45.5 [CFON(CF $_3$) $_2$, br m], -59.5 (CF $_2$, AB pattern, $|\underline{J}_{\text{gem}}|$ 197.4 Hz, $\nu_{\text{O}}\delta$ 19.7 ppm), -130.7 (\geq CF, br s) ppm, τ 3.17 (m), and $\underline{m}/\underline{z}$ 517 ($\underline{M}^{+\cdot}$ -F \cdot , 1%), 368 [$\underline{M}^{+\cdot}$ -(CF $_3$) $_2$ NO \cdot , 62%], 69 (CF $_3^+$, 100%). Two other (minor) components were examined by coupled gc-ms techniques and thereby identified as cis-5,6-bis(bistrifluoromethylamino-oxy)-1,2,3,4,7,7-hexafluorobicyclo[2,2,1]hept-2-ene (XIV; nc) (ca 3% yield), $\underline{m}/\underline{z}$ 536 ($\underline{M}^{+\cdot}$, 19%), 517 ($\underline{M}^{+\cdot}$ -F \cdot , 7%), 368 [$\underline{M}^{+\cdot}$ -(CF $_3$) $_2$ NO \cdot , 25%], 362 (C $_6$ H $_2$ F $_{12}$ N $_2$ O $_2^{+\cdot}$, 23%), 210 (C $_4$ H $_2$ F $_6$ NO $_2^+$, 18%), 200 [$\underline{M}^{+\cdot}$ - 2(CF $_3$) $_2$ NO \cdot , 37.5%], 174 (C $_5$ F $_6^+$, 29%), 168 (C $_2$ F $_6$ NO $^+$, 58%), 69 (CF $_3^+$, 100%), and 2,3,5,6-tetrakis(bistrifluoromethylamino-oxy)-1,2,3,4,7,7-hexafluorobicyclo[2,2,1]heptane (XV; nc) (ca 1% yield), $\underline{m}/\underline{z}$ 704 [$\underline{M}^{+\cdot}$ - (CF $_3$) $_2$ NO \cdot , 40%], 368 [$\underline{M}^{+\cdot}$ - 3(CF $_3$) $_2$ NO \cdot , 13%], 200 [$\underline{M}^{+\cdot}$ - 4(CF $_3$) $_2$ NO \cdot , 47%], 69(CF $_3^+$, 100%).

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