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Studies on Organic Fluorine Compounds. XLIV.[1] The Diels–Alder Reaction of Trifluoromethylated Cyclopropenyl Ketone and Its Imine

YOSHIRO KOBAYASHI,*,[a] TSUTOMU YOSHIDA,[a] MASAHARU NAKAJIMA,[a] AKIRA ANDO,[a] YUJI HANZAWA,[a] and ITSUMARO KUMADAKI[b]

Tokyo College of Pharmacy,[a] Horinouchi, Hachioji, Tokyo 192–03, Japan and Faculty of Pharmaceutical Science, Setsunan University,[b] 45–1, Nagao-toge, Hirakata, Osaka 571–01, Japan

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The thermolysis of 1,5,6,7-tetrakis(trifluoromethyl)-2,3,4-triazabicyclo[3.2.0]hepta-2,6-diene (**3**) without a solvent gave 1-[1,2,3-tris(trifluoromethyl)cyclopropenyl]-2,2,2-trifluoroethylimine (**2**). The flash vacuum pyrolysis of **3** gave 1,2,3-tris(trifluoromethyl)cyclopropene (**6**). 1,2,3,4-Tetrakis-(trifluoromethyl)pyrrole (**5**) was produced in both reactions. 1,2,3-Tris(trifluoromethyl)cyclopropen-3-yl trifluoromethyl ketone (**1**) and **2** were found to react as good dienophiles and gave products obtained through the transition states where the electron-deficient part of the dienophiles attracted the electron-rich part of the diene components, a hetero atom or the diene moiety.

Keywords——trifluoromethyl; cyclopropenyl; ketone; imine; Diels–Alder reaction; butadiene; cyclopentadiene; furan; pyrrole; bromination

In the preliminary report,[2] the Diels–Alder reaction of 1,2,3-tris(trifluoromethyl)-cyclopropen-3-yl trifluoromethyl ketone (**1**) was briefly described. We have now obtained the imine (**2**) by the pyrolysis of 1,5,6,7-tetrakis(trifluoromethyl)-2,3,4-triazabicyclo[3.2.0]-hepta-2,6-diene (**3**). In this paper, the formation of **2** is discussed first, and then the Diels–Alder reactions of **1** and **2** are presented.

Previously, we obtained **3** by the 1,3-dipolar cycloaddition reaction of tetrakis(trifluoromethyl) Dewar thiophene with hydrogen azide followed by desulfurization of the adduct. The photolysis of **3** gave the Dewar pyrrole (**4**), while its thermolysis in the liquid phase afforded the pyrrole (**5**) through a diazo compound (see Chart 1).[3–5]

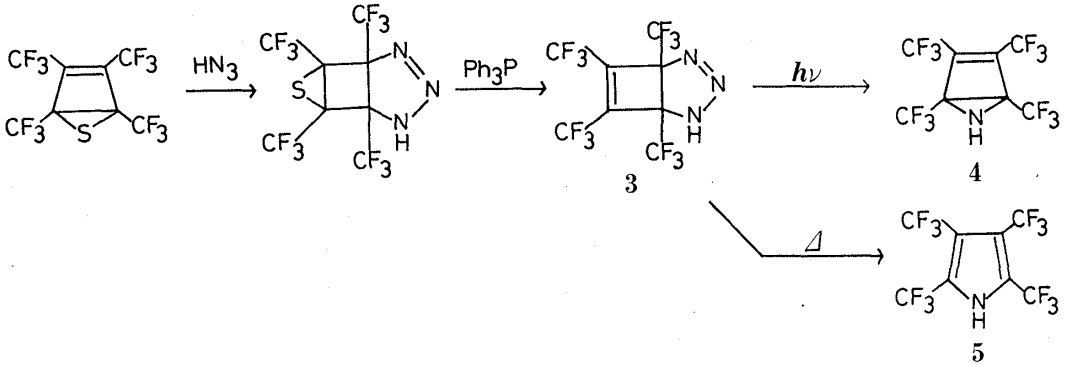

Chart 1

More detailed investigation of this thermolysis showed that **2** was formed with **5** by the thermolysis of **3** at 140—150 °C without a solvent. Separation of **2** and **5** was accomplished by a vaccum-line distillation and preparative gas-chromatography (GLC). The structure of **2** was

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determined by comparison of its fluorine-19 nuclear magnetic resonance (^{19}F-NMR) spectrum with those of N-substituted cyclopropenyl ketone imines.[4] The formation of **2** may be explained by the mechanism shown in Chart 2; the bicyclic compound is cleaved through a *retro*-1,3-dipolar reaction to the diazoimine, which affords a carbene intermediate by loss of a nitrogen molecule. The carbene attacks the double bond or the nitrogen atom to give **2** or **5**.

Since the above results suggested that rapid reaction without a solvent might be important for the formation of the imine (**2**), we examined flash vacuum pyrolysis. Interestingly, the flash vacuum pyrolysis of **3** at 650 °C (10 mmHg) gave tris(trifluoromethyl)cyclopropene (**6**, 12%), **5** (43%), and trifluoroacetonitrile. Therefore, the environment of the starting material seems to control the reaction. The structure of **6** was estimated from its infrared (IR) and ^{19}F-NMR spectra. Since the imine (**2**) was not converted to the cyclopropene (**6**) under these reaction conditions. **6** may be formed directly from the carbene intermediate (Chart 2).

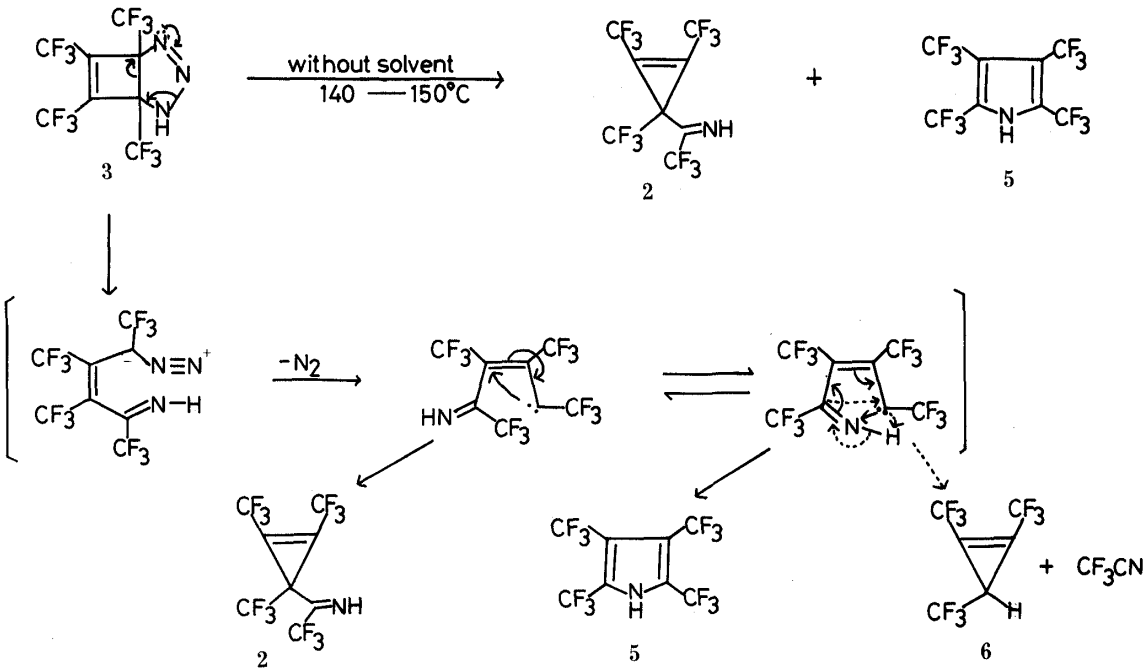

Chart 2

Since the cyclopropene part of **1** and **2** has an extremely hindered double bond substituted with highly electronegative trifluoromethyl groups, these compounds were expected to be good dienophiles and the products of the Diels–Alder reaction might be good precursors for strained compounds. Thus, the Diels–Alder reactions of **1** and **2** with some dienes were examined and the stereochemical features of these reactions were investigated.

The reaction of **1** with 1,3-butadiene gave two adducts (**7** and **8**) in the ratio of 6 : 1. The structures of **7** and **8** were estimated to be *syn* and *anti* adducts from the coupling patterns of the CF_3CO groups in the ^{19}F-NMR spectra; the signal of the CF_3CO group of **7** appears in a quartet coupled only with a vicinal CF_3 group, while that of **8** appears as a multiplet due to the through-space coupling with *cis* CF_3 groups. Further, the signal of the 7-CF_3 group of **8** appears in a quartet coupled only with CF_3CO-fluorines. These considerations were confirmed by bromination of both compounds. Compound **8** gave the dibromide (**9**),[7] while **7** gave cage compounds (**10**, **11** and **12**), possibly through the path shown in Chart 3. In this case, the usual *trans* addition of bromine is sterically hindered and a substitution reaction

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occurs, followed by a transannular attack of hydrogen bromide. The characteristic feature of the Diels–Alder reaction of **1** is that the *syn* adduct (**7**) was preferentially formed, though 3-acetylcyclopropene was reported to give *anti* adduct.[6]

The reaction of **1** with 2,3-dimethylbutadiene at 60 °C for 6 h gave two adducts in the ratio of 8 : 1. The minor one (**14**) is an *anti* adduct and the major one (**13**) is a cage compound, which was assumed to be formed through an intramolecular ene reaction of the *syn* adduct. Namely, the primary addition again occurred mainly in *syn* form. It was surprising that this reaction needed as strong conditions as that with butadiene, since 2,3-dimethylbutadiene is usually much more reactive than butadiene in Diels–Alder reactions.[8] We assumed that this was due to the stereochemistry of the transition state; the transition state has an *endo* conformation and repulsion between the methyl substituents on the diene and the trifluoroacetyl group may offset the higher reactivity of the dimethylbutadiene. To confirm the preference for the *endo* conformation, the reaction of cyclic dienes was examined.

Compound **1** reacted with cyclopentadiene smoothly and quantitatively to give an adduct (**15**), the structure of which was estimated to be *endo–syn* from the ^{19}F- and proton (^{1}H-NMR) spectra. Bromination of **15** gave cage compounds (**16** and **17**). This result supported the hypothesis that the transition state took *endo–syn* conformation; namely, the electron-rich diene part was located near the electron-deficient trifluoroacetyl group.

Furan reacted with **1** at room temperature to give an adduct (**18**), the structure of which was assumed to be *syn* from the coupling pattern in the ^{19}F-NMR spectrum. The ^{1}H-NMR showed one peak due to two olefinic protons, while two peaks were observed for two methine protons, probably because the latter became nonequivalent due to hindered rotation of the trifluoroacetyl group. Bromination of **18** gave the usual adduct (**19**),[7] but no cage compounds. These results showed that **18** was the *exo–syn* adduct. 2,5-Dimethylfuran and 2,3,4,5-tetramethylfuran showed similar reactivities to furan, giving **20** and **21**, respectively. The very small steric effect of the methyl groups on the 3- and 4-positions in the reaction of tetramethylfuran supported the *exo–syn* stereochemistry.

Pyrrole reacted with **1** at room temperature to give a cage compound (**22**). This suggested that pyrrole reacted in an *exo–syn* manner and that the intramolecular addition of the N-hydrogen to the C=O group of the primary adduct gave **22**. *N*-Methylpyrrole did not react with **1** even under drastic conditions. This result indicates that steric repulsion between the N-methyl group and the trifluoroacetyl group inhibited the reaction. All the reactions are summarized in Chart 3.

The above results show that **1** reacts with dienes in a *syn* form rather than in an *anti* form. This may be explained by the electronic interaction between the electron-deficient trifluoroacetyl group and the electron-rich part of the diene compounds. This explanation is supported by the fact that cyclopentadiene gave the *endo* adduct while furan or pyrrole gave the *exo* adduct; namely, the electron-rich part, the diene part or the hetero atom took a position near to the trifluoroacetyl group.

Next, the Diels–Alder reactions of **2** will be presented. The reaction of **2** with butadiene at 60 °C gave an adduct (**23**) in 41% yield. The ^{19}F-NMR signals of the $CF_3C=NH$ group of **23** appeared in two regions [1.3 (m) and 3.6 ppm (q, $J=5.2$ Hz)], though gas-liquid chromatography (GLC) or thin-layer chromatography (TLC) of **23** showed only one component. Since signals of other CF_3 groups appeared unresolved, the appearance of two peaks of the $CF_3C=NH$ group may be explained by the *syn–anti* isomerization of the imino N–H group. The fact that the major peak at 3.6 ppm is split into a quartet suggests that the CF_3 group is *anti* to the hydrogen, while the minor multiplet at 1.3 ppm corresponds to the CF_3 group *syn* to the hydrogen. Since the major $CF_3C=NH$ fluorine peak did not show any long-range coupling, the stereochemistry of **23** was determined to be *syn* form. This result is comparable to that for **1**.

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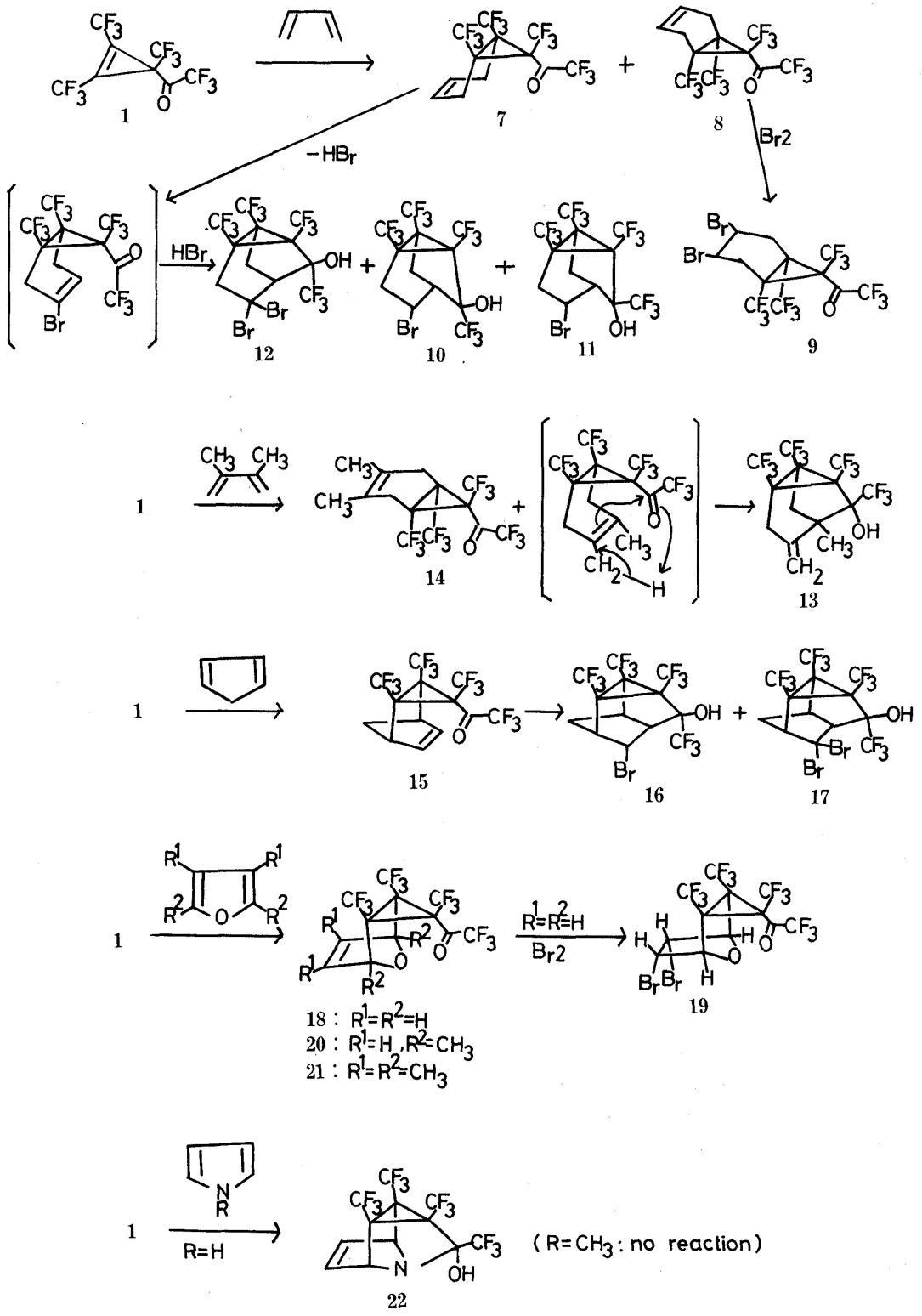

Chart 3

The reaction of **2** with 2,3-dimethylbutadiene gave a similar result. Thus, a *syn* adduct (**24**) was formed in 45% yield. The spectral data are comparable to those of **23**.

The reaction of **2** with cyclopentadiene gave an *endo–syn* adduct (**25**) in 53% yield. The ^{19}F-NMR spectrum of **25** showed a quartet signal due to the $CF_3C{=}NH$ group. This suggested the *syn* configuration between the cyclopentene and the $CF_3C{=}NH$ groups. The

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^{1}H-NMR signals of the olefinic protons appeared in two different places, while those of the methine protons appeared in the same region. These chemical shifts suggested that the olefinic protons were differently deshielded by the adjacent $CF_3C=NH$ group, the free rotation of which was sterically hindered.

Furan reacted with **2** to give an *exo–syn* adduct (**26**) in 84% yield. In the ^{1}H-NMR spectrum of **26**, the methine protons appeared at different positions, while the olefinic protons appeared at the same place.

Pyrrole reacted with **2** to give a cage compound, 8-amino-5,6,7,8-tetrakis(trifluoromethyl)-9-azatetracyclo[4.3.0.0^{4,9}.0^{5,7}]non-2-ene (**27**) in 80% yield. This product was formed by intramolecular reaction of the N–H group of the pyrrole ring with the imino group of the primary *exo–syn* adduct.

All the results of the reactions of **2** are shown in Chart 4, and are comparable to those of **1**. This may be due to the similar electronic and steric effects of the trifluoroacetyl group and the trifluoroiminoethyl group.

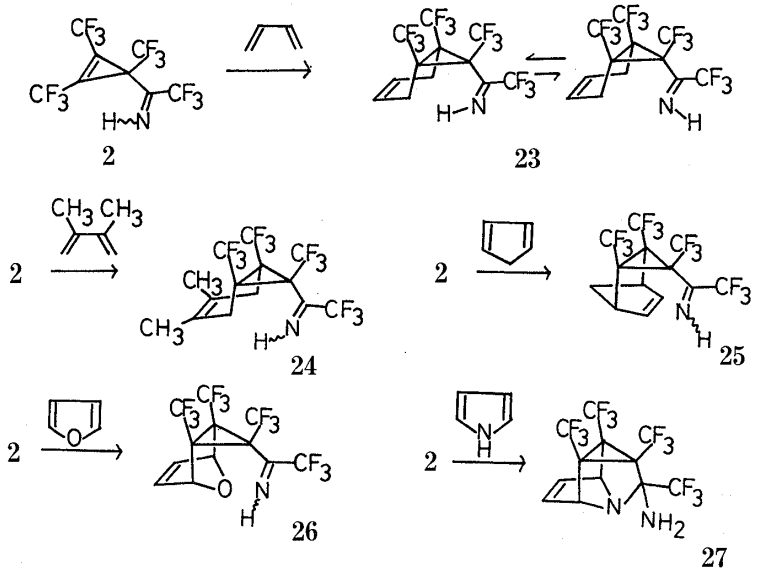

Chart 4

In conclusion, the Diels–Alder reactions of **1** and **2** proceed through a transition state where the electron-rich part of the diene comes close to the electron-deficient trifluoroacetyl or trifluoroiminoethyl group. The products of these reactions may be useful for the synthesis of highly strained cage compounds.

Experimental

Melting points were determined in sealed tubes on a Yanaco MP apparatus and are uncorrected. ^{1}H-NMR spectra were obtained on Varian T-60, Varian EM-360L, and JEOL JNM-PS-100 NMR spectrometers. ^{19}F-NMR spectra were determined with the T-60 and EM-360L spectrometers using benzotrifluoride as an internal standard (upper field taken as plus). Spectral patterns are designated as follows: br, broad; s, singlet; d, doublet; t, triplet; q, quartet; sept, septet; m, multiplet. Mass spectra (MS) were determined with a Hitachi M-80 double-focusing mass spectrometer. Analytical GLC was performed on a Shimadzu GC-3AF gas chromatograph and Hitachi 163 gas chromatography.

Preparative GLC was performed on an Ohkura gas chromatograph (model 701) and the Hitachi 163 instrument. Columns of SE-30 and diethylene glycol succinate (DEGS) were used on both GLC, instruments.

1-[1,2,3-Tris(trifluoromethyl)cyclopropenyl]-2,2,2-trifluoroethylimine (2)——1,5,6,7-Tetrakis(trifluoromethyl)-2,3,4-triazabicyclo[3.2.0]hepta-2,6-diene (**3**, 1.29 g) was sealed in Pyrex tube under a vacuum and heated at 140—150 °C until the brown color disappeared. After cooling, the tube was opened and the mixture was distilled by using a

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vacuum line at −20 °C. The distillate was further purified by prep. GLC (SE-30, at 30 °C) to give a colorless volatile oil (**2**, 520 mg, 44%). The residue from the vacuum-line distillation was distilled under a vacuum to give a colorless oil, 2,3,4-tetrakis(trifluoromethyl)pyrrole (**5**, 432 mg, 41%).[3] **2**: MS *m/e*: 339 (M^+). High-resolution MS (HRMS) Calcd for $C_8HF_{12}N$: 338.992. Found: 338.992. IR (CCl_4) 3280 (N–H), 1910 (C=C), and 1670 (C=N), 1320 and 1020 cm^{-1} (C–F). ^{1}H-NMR ($CDCl_3$) δ: 11.4 (1H, br, =NH). ^{19}F-NMR ($CDCl_3$) ppm: −4.0 (6F, s, 1-, 2-CF_3), 2.3 (3F, s, 3-CF_3), and 8.3 (3F, s, 1-CF_3).

1,2,3-Tris(trifluoromethyl)cyclopropene (6)——Compound **3** (779 mg) was passed through a quarts tube (i.d. 8 mm, L 600 mm heated at 650 °C) in a stream of nitrogen at 10 mmHg. The product was collected in a trap cooled in liquid nitrogen and distilled by using a vacuum line at −20 °C. The distillate was further purified by prep. GLC (SE-30, at 30 °C) to give a highly volatile oil (**6**, 63 mg, 12%). The residue from the vaccum-line distillation was distilled under a vacuum to give **5** (311 mg, 43%). **6**: MS *m/e*: 225 (M−F). HRMS Calcd for C_6HF_8 (M−F): 224.995. Found: 224.992. IR (CCl_4) 1900 cm^{-1} (C=C). ^{1}H-NMR ($CDCl_3$) δ: 3.1 (1H, br, 3-H). ^{19}F-NMR ($CDCl_3$) ppm: −2.6 (6F, s, 1-, 2-CF_3), 4.6 (3F, s, 3-CF_3).

1,6,7-Tris(trifluoromethyl)-7-*endo*-(trifluoroacetyl)bicyclo[4.1.0]hept-3-ene (7) and 1,6,7-Tris(trifluoromethyl)-7-*exo*-(trifluoroacetyl)bicyclo[4.1.0]hept-3-ene (8)——1,2,3-Tris(trifluoromethyl)cyclopropen-3-yl trifluoromethyl ketone (**1**, 3.1 g) and methylene chloride (10 ml) were sealed in a stainless steel tube (50 ml), and butadiene (5 ml) was added through a vacuum line. The sealed tube was kept at 60 °C for 6 h. After cooling, the content of the tube was concentrated by using a vacuum line and the residue was subjected to bulb-to-bulb distillation at 85—95 °C (50 mmHg) to give a colorless oil, a mixture of **7** and **8** (6 : 1, 2.90 g, 81%). This oil (300 mg) was separated by prep. GLC to give **7** (181 mg) and **8** (39 mg). **7**: Colorless amorphous solid; mp 53—54 °C. MS *m/e*: 394 (M^+). HRMS Calcd for $C_{11}H_6F_9O$ (M−CF_3): 325.028. Found: 325.027. IR (CCl_4) 1755 (C=O), 1280, and 1220—1160 cm^{-1} (C–F). ^{1}H-NMR ($CDCl_3$) δ: 5.52 (2H, br s, 3-, 4-H), 2.84 (4H, br s, 2-, 5-H). ^{19}F-NMR ($CDCl_3$) ppm: −12.7 (3F, m, 7-CF_3), −2.8 (6F, q, J=13.7 Hz, 1-, 6-CF_3), 7.8 (3F, q, J=5.4 Hz, $COCF_3$). **8**: Colorless oil; bp 89—90 °C (50 mmHg) (bulb-to-bulb distillation). MS *m/e*: 394 (M^+). HRMS Calcd for $C_{12}H_6F_{12}O$: 394.023. Found: 394.026. IR (CCl_4) 1770 cm^{-1} (C=O). ^{1}H-NMR ($CDCl_3$) δ: 5.70 (2H, br s, 3-, 4-H), 2.82 (4H, br s, 2-, 5-H). ^{19}F-NMR ($CDCl_3$) ppm: −9.1 (3F, q, J=5.9 Hz, 7-CF_3), −1.9 (6F, m, 1-, 6-CF_3), 10.3 (3F, m, $COCF_3$).

3,4-Dibromo-1,6,7-tris(trifluoromethyl)-7-*exo*-(trifluoroacetyl)bicyclo[4.1.0]heptane (9), 4-*exo*-Bromo-6-*endo*-hydroxy-1,2,6,7-tetrakis(trifluoromethyl)tricyclo[3.2.1.0^{2,7}]octane (10), 4-*exo*-Bromo-6-*exo*-hydroxy-1,2,6,7-tetrakis(trifluoromethyl)tricyclo[3.2.1.0^{2,7}]octane (11), and 4,4-Dibromo-6-hydroxy-1,2,6,7-tetrakis(trifluoromethyl)tricyclo[3.2.1.0^{2,7}]octane (12)——The mixture of **7** and **8** obtained above (1.55 g) was dissolved in methylene chloride and bromine (excess) was added. The mixture was allowed to stand in the dark at room temperature for 2 d, then the solvent and bromine were removed by using a vacuum line. The residue was subjected to bulb-to-bulb distillation at 90—130 °C (5 mmHg) to give a mixture of **9**—**12** (1.98 g). A part of this oil (659 mg) was separated by prep. GLC (SE-30, 100 °C). The first fraction, **10** (40 mg, 5.2%); the second fraction, **11** (34 mg, 4.4%); the third fraction, **9** (91 mg, 10%); the last fraction, **12** (281 mg, 31%). **9**: Colorless prisms; mp 65—67 °C. MS *m/e*: 483 (M−CF_3). *Anal.* Calcd for $C_{12}H_6Br_2F_{12}O$: C, 26.02; H, 1.09; Br, 28.85. Found: C, 26.09; H, 1.28; Br, 28.68. IR (CCl_4) 1770 cm^{-1} (C=O). ^{1}H-NMR ($CDCl_3$) δ: 4.14—3.80 (2H, m, 3-, 4-H), 3.38—2.80 (4H, m, 2-, 5-H). ^{19}F-NMR ($CDCl_3$) ppm: −8.9 (3H, q, J=7.9 Hz, 7-CF_3), −0.5 (6F, br, 1-, 6-CF_3), 10.2 (3F, m, $COCF_3$). **10**: Colorless oil; bp 114 °C (15 mmHg) (bulb-to-bulb distillation). MS *m/e*: 437 (M−H). *Anal.* Calcd for $C_{12}H_7BrF_{12}O$: C, 30.33; H, 1.49; Br, 16.82: Found: C, 30.30; H, 1.49; Br, 16.80. IR (CCl_4) 3600 cm^{-1} (O–H). ^{1}H-NMR ($CDCl_3$) δ: 4.38 (1H, br, 4-H), 3.61 (1H, q, J_{H-F}=5.6 Hz, disappeared on addition of D_2O, 6-OH), 3.09 (1H, dd, J=10.4, 16.4 Hz, 3-H), 2.84—2.64—2.48 (4H, m). ^{19}F-NMR ($CDCl_3$) ppm: −10.8 (3F, br, 7-CF_3), −2.4 (6F, m, 1-, 2-CF_3), 8.4 (3F, q, J=7.5 Hz, 6-CF_3). **11**: Colorless oil; bp 112 °C (15 mmHg) (bulb-to-bulb distillation). MS *m/e*: 473 (M^+). *Anal.* Calcd for $C_{12}H_7BrF_{12}O$: C, 30.33; H, 1.49; Br, 16.82. Found: C, 30.35; H, 1.451; Br, 16.57. IR (CCl_4) 3590 cm^{-1} (O–H). ^{1}H-NMR ($CDCl_3$) δ: 4.80 (1H, br, 4-H), 3.30 (1H, br, disappeared on addition of D_2O, 6-OH), 3.11 (1H, dd, J=9.6, 16.0 Hz, 3-H), 2.96—2.76, and 2.68—2.56 (4H, m). ^{19}F-NMR ($CDCl_3$) ppm: −7.9 (3F, br, 7-CF_3), −3.2 (6F, m, 1-, 2-CF_3), 11.2 (3F, q, J=11.7 Hz, 6-CF_3). **12**: Colorless oil; bp 110—112 °C (5 mmHg) (bulb-to-bulb distillation). MS *m/e*: 515 (M−HF−OH), 473 (M−Br). *Anal.* Calcd for $C_{12}H_6Br_2F_{12}O$: C, 26.02; H, 1.09; Br, 28.85. Found: C, 26.20; H, 1.03; Br, 28.58. IR (CCl_4) 3580 cm^{-1} (O–H). ^{1}H-NMR ($CDCl_3$) δ: 4.06 (1H, d, J=18.4 Hz, 3-H), 3.77 (1H, d, J=18.4 Hz, 3-H), 3.36 (1H, br, disappeared on addition of D_2O, 6-OH), 3.25 (1H, d, J=1.0 Hz, 5-H), 3.21 (1H, d, J=14.4 Hz, 8-H), 2.77 (1H, dd, J=6.0, 14.4 Hz, 8-H). ^{19}F-NMR ($CDCl_3$) ppm: −8.3 (3F, m, 7-CF_3), −3.5 (6F, m, 1-, 2-CF_3), 10.0 (3F, q, J=12.1 Hz, 6-CF_3).

6-*endo*-Hydroxy-5-methyl-4-methylene-1,2,6,7-tetrakis(trifluoromethyl)tricyclo[3.2.1.0^{2,7}]octane (13) and 3,4-Dimethyl-1,6,7-tris(trifluoromethyl)-7-*exo*-(trifluoroacetyl)bicyclo[4.1.0]hept-3-ene (14)——Compound **1** (174 mg) and 2,3-dimethylbutadiene (excess) were sealed with pentane as a solvent in a Pyrex tube and heated at 60 °C for 6 h. After the completion of the reaction had been confirmed by ^{19}F-NMR, the tube was opened and the content was separated by prep. GLC (SE-30, at 90 °C). The first fraction was subjected to bulb-to-bulb distillation to give **14** (19 mg, 9%). The second fraction gave **13** (139 mg, 64%) in a similar manner. **13**: Colorless oil; bp 127 °C (16 mmHg) (bulb-to-bulb distillation). MS *m/e*: 422 (M^+). HRMS Calcd for $C_{14}H_8F_{12}$: (M−H_2O) 404.043. Found: 404.045. IR (film) 3500 cm^{-1} (O–H). ^{1}H-NMR ($CDCl_3$) δ: 5.05 (2H, br, =CH_2), 3.26 (1H, d, J=20.0 Hz, 3-H), 3.05 (1H, d, J=

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20.0 Hz, 3-H), 2.72 (1H, br, disappeared on addition of D_2O, 6-OH), 2.59 (1H, d, J=12.8 Hz, 8-H), 1.29 (2H, q, J_{H-F}=3.1 Hz, CH_3). ^{19}F-NMR ($CDCl_3$) ppm: −6.6 (3F, m), −3.4 (3F, m), −2.1 (3F, m), 7.8 (3F, q, J=15.4 Hz, 6-CF_3). **14**: Colorless oil; bp 114 °C (29 mmHg) (bulb-to-bulb distillation). MS *m/e*: 422 (M^+). HRMS Calcd for $C_{14}H_{10}F_{12}O$: 422.054. Found: 422.056. IR (film) 1780 cm^{-1} (C=O). ^{1}H-NMR ($CDCl_3$) δ: 2.70 (4H, br, CH_2), 1.65 (6H, s, CH_3). ^{19}F-NMR ($CDCl_3$) ppm: −7.3 (3F, q, J=7.7 Hz, 7-CF_3), −0.5 (6F, m, 1-, 6-CF_3), 11.4 (3F, m, $COCF_3$).

2,3,4-Tris(trifluoromethyl)-3-*endo*-(trifluoroacetyl)-*syn*-tricyclo[3.2.1.0^{2,4}]oct-6-ene (15)——Compound **1** (110 mg) and cyclopentadiene (excess) were sealed with pentane in a Pyrex tube (i.d. 4 mm) under a vacuum. After a few minutes at room temperature, the completion of the reaction was confirmed by ^{19}F-NMR. The residue obtained by evaporation of the solvent and cyclopentadiene was recrystallized from methanol to give **15** (97 mg, 74%). **15**: Colorless prisms; mp 79—83 °C. MS *m/e*: 406 (M^+). HRMS Calcd for $C_{12}H_6F_9O$: (M−CF_3) 337.028. Found: 337.027. IR (CCl_4) 1750 cm^{-1} (C=O). ^{1}H-NMR ($CDCl_3$) δ: 6.30 (1H, br, 6- or 7-H), 6.05 (1H, m, 7- or 6-H), 3.65 (2H, br, 1-, 5-H), 2.27 (1H, d, J=9.0 Hz, 8-H), 1.94 (1H, d, J=9.0 Hz, 8-H). ^{19}F-NMR ($CDCl_3$) ppm: −9.8 (3F, tridecet, J=7.0 Hz, 2- or 4-CF_3), −5.8 (3F, m, 3-CF_3), −6.0 (3F, tridecet, J=7.0 Hz, 4- or 2-CF_3), 10.0 (3F, q, J=6.2 Hz, $COCF_3$).

7-Bromo-5-hydroxy-2,3,4,5-tetrakis(trifluoromethyl)tetracyclo[4.3.0.0^{2,4}.0^{3,8}]nonane (16) and 7,7-Dibromo-5-hydroxy-2,3,4,5-tetrakis(trifluoromethyl)tetracyclo[4.3.0.0^{2,4}.0^{3,8}]nonane (17)——Compound **15** was dissolved in methylene chloride and bromine (excess) was added to this solution. The mixture was allowed to stand at room temperature for 3 d. After the solvent and bromine had been removed by using the vacuum line, the residue was separated by prep. GLC (SE-30, 120 °C). The first fraction gave a few miligrams of **16**. The second fraction was recrystallized from hexane to give **17** (70 mg, 53%). **16**: Colorless oil; bp 100 °C (5 mmHg) (bulb-to-bulb distillation). MS *m/e*: 468 (M−H_2O). *Anal.* Calcd for $C_{13}H_7BrF_{12}O$: C, 32.06; H, 1.45; Br, 16.40. Found: C, 31.60; H, 1.46; Br, 16.26. IR (CCl_4) 3600 cm^{-1} (O–H). ^{1}H-NMR ($CDCl_3$) δ: 4.12 (1H, br s, 7-H), 3.57 (1H, br, disappeared on addition of D_2O, 5-OH), 3.38 (1H, br), 3.14 (1H, br), 2.76 (1H, br), 2.61 (1H, d, J=11.6 Hz, 9-H), 2.31 (1H, d, J=11.6 Hz, 9-H). ^{19}F-NMR ($CDCl_3$) ppm: −9.2 (3F, m, 4-CF_3), −4.2 (3F, qq, J=7.2, 8.3 Hz, 2- or 3-CF_3), −4.1 (3F, decet, J=7.2 Hz, 3- or 2-CF_3), 2.6 (3F, q, J=9.5 Hz, 5-CF_3). **17**: Colorless prisms; mp 158 °C. MS *m/e*: 468 (M−Br−OH). *Anal.* Calcd for $C_{13}H_6Br_2F_{12}O$: C, 27.59; H, 1.07; Br, 28.24. Found: C, 27.63; H, 1.23; Br, 28.08. IR (CCl_4) 3460 cm^{-1} (O–H). ^{1}H-NMR ($CDCl_3$) δ: 4.82 (1H, br, disappeared on addition of D_2O, OH), 3.65 (1H, br s, 6-H), 3.24 (2H, br s, 6-, 8-H), 2.70 (1H, d, J=12.0 Hz, 9-H), 2.28 (1H, d, J=12.0 Hz, 9-H). ^{19}F-NMR ($CDCl_3$) ppm: −8.7 (3F, m, 4-CF_3), −5.9 (3F, sept, J=8.1 Hz, 2- or 3-CF_3), −4.7 (3F, decet, J=8.1 Hz, 3- or 2-CF_3), 7.3 (3H, qq, J=8.1, 11.1 Hz, 5-CF_3).

2,3,4-Tris(trifluoromethyl)-3-*endo*-trifluoroacetyl-8-oxa-*anti*-tricyclo[3.2.1.0^{2,4}]oct-6-ene (18)——A solution of **1** (236 mg) and furan (151 mg) in pentane was sealed in a Pyrex tube (i.d. 4 mm). After the signals of the starting material in ^{19}F-NMR had disappeared (within a few minutes), the solvent and furan were evaporated off and the residue was purified by sublimation to give **18** (272 mg, 96%). **18**: Colorless amorphous solid; mp 62 °C. MS *m/e*: 389 (M−F). HRMS Calcd for $C_{11}H_4F_9O$: (M−CF_3) 339.007. Found: 339.007. IR (CCl_4) 1760 cm^{-1} (C=O). ^{1}H-NMR ($CDCl_3$) δ: 6.72 (2H, br s, 6-, 7-H), 5.35 (1H, br s, 1- or 5-H), 5.08 (1H, br s, 5- or 1-H). ^{19}F-NMR ($CDCl_3$) ppm: −6.3 (3-F, m, 3-CF_3), −5.8 (6-F, m, 2-, 4-CF_3), 11.6 (3F, q, J=3.4 Hz, $COCF_3$).

6,7-Dibromo-2,3,4-tris(trifluoromethyl)-3-*endo*-trifluoroacetyl-8-oxa-*anti*-tricyclo[3.2.1.0^{2,4}]octane (19)——Bromine (excess) was added to a solution of **18** (270 mg) in methylene chloride and the solution was kept at room temperature for 2 d. The solvent and bromine were removed by using the vacuum line, and the residue was recrystallized from pentane to give **19** (275 mg, 73%). **19**: Colorless prisms; mp 69 °C. MS *m/e*: 497 (M−CF_3). *Anal.* Calcd for $C_8H_4Br_2F_{12}O_2$: C, 25.38; H, 0.71; Br, 28.14. Found: C, 25.20; H, 0.79; Br, 27.96. IR (KBr) 1760 cm^{-1} (C=O). ^{1}H-NMR ($CDCl_3$) δ: 5.07 (1H, s, 2- or 5-H), 4.88 (1H, d, J=7.2 Hz, 6- or 7-H), 4.85 (1H, s, 5- or 2-H), 4.78 (1H, d, J=7.2 Hz, 7- or 6-H). ^{19}F-NMR ($CDCl_3$) ppm: −9.4 (3H, decet, J=5.9 Hz, 2- or 4-CF_3), −7.9 (3H, decet, J=5.9 Hz, 4- or 2-CF_3), −6.6 (3F, m, 3-CF_3), 11.4 (3F, q, J=4.3 Hz, $COCF_3$).

1,5-Dimethyl-2,3,4-tris(trifluoromethyl)-3-*endo*-trifluoroacetyl-8-oxa-*anti*-tricyclo[3.2.1.0^{2,4}]oct-6-ene (20)——A solution of **1** (221 mg) and 2,5-dimethylfuran (150 mg) in pentane was sealed in a Pyrex tube (i.d. 4 mm). After the completion of the reaction had been confirmed by ^{19}F-NMR (within a few minutes), the tube was opened and the content was concentrated under a vacuum. The residue was recrystallized from methanol to give **20** (190 mg, 69%). **20**: Colorless prisms; mp 94—97 °C. MS *m/e*: 417 (M−F). IR (Nujol) 1760 cm^{-1} (C=O). ^{1}H-NMR ($CDCl_3$) δ: 6.42 (2H, br s, 6-, 7-H), 1.82 (3H, s, CH_3), 1.72 (3H, s, CH_3). ^{19}F-NMR ($CDCl_3$) ppm: −8.0——5.4 (9F, m, CF_3 × 3), 8.4 (3F, q, J=6.0 Hz, $COCF_3$).

1,5,6,7-Tetramethyl-2,3,4-tris(trifluoromethyl)-3-*endo*-trifluoroacetyl-8-oxa-*anti*-tricyclo[3.2.1.0^{2,4}]oct-6-ene (21)——A solution of **1** (136 mg) and tetramethylfuran (excess) in pentane was sealed in a Pyrex tube. The completion of the reaction was confirmed by ^{19}F-NMR (within a few minutes). After evaporation of the solvent, the residue was recrystallized from pentane to give **21** (136 mg, 73%). **21**: Colorless prisms; mp 62—63 °C. MS *m/e*: 464 (M^+). *Anal.* Calcd for $C_{16}H_{12}F_{12}O$: C, 41.29; H, 2.61. Found: C, 41.05; H, 2.62. IR (KBr) 1750 cm^{-1} (C=O). ^{1}H-NMR ($CDCl_3$) δ: 1.75 (9H, s, CH_3 × 3), 1.64 (3H, s, CH_3). ^{19}F-NMR ($CDCl_3$) ppm: −8.2 (3F, q, J=9.5 Hz, 2- or 4-CF_3), −7.1 (3F, br, 3-CF_3), −6.2 (3F, q, J=9.5 Hz, 4- or 2-CF_3), 7.6 (3F, q, J=5.9 Hz, $COCF_3$).

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8-Hydroxy-5,6,7,8-tetrakis(trifluoromethyl)-9-azatetracyclo[4.3.0.0^{4,9}.0^{5,7}]non-2-ene (22)——A solution of **1** (119 mg) and pyrrole (excess) in pentane was sealed in a Pyrex tube. After 1 h at room temperature, the completion of the reaction was confirmed by ^{19}F-NMR. The content of the tube was concentrated under a vacuum and the residue was recrystallized from pentane to give **22** (84 mg, 56%). **22**: Colorless prisms; mp 78—79 °C. MS *m/e*: 407 (M^+). HRMS Calcd for $C_{12}H_5F_{12}NO$: 407.018. Found: 407.019. IR (KBr) 3200 cm^{-1} (O–H). ^{1}H-NMR ($CDCl_3$) δ: 6.70 (1H, br s, 3- or 4-H), 6.50 (1H, br s, 3- or 2-H), 3.76 (1H, br, disappeared on addition of D_2O, 8-OH), 3.62 (1H, br s, 1- or 4-H), 3.17 (1H, br s, 4- or 1-H). ^{19}F-NMR ($CDCl_3$) ppm: −4.0 (3F, m), −3.5 (3F, m), −1.3 (3F, m), 11.2 (3F, q, J=13.1 Hz, 8-CF_3).

1,6,7-Tris(trifluoromethyl)-7-*endo*-(2,2,2-trifluoro-1-iminoethyl)bicyclo[4.1.0]hept-3-ene (23)——A solution of **2** (321 mg) and 1,3-butadiene (2 ml) in ether (5 ml) was heated at 60 °C for 12 h in a sealed stainless steel tube. The content of the tube was concentrated by using the vacuum line and the residue was separated by prep. GLC (SE-30, at 80 °C). The main fraction was further purified by sublimation to give **23** (152 mg, 41%). **23**: Colorless crystals; mp 52—53 °C. MS *m/e*: 393 (M^+). HRMS Calcd for $C_{12}H_7F_{12}N$: 393.039. Found: 393.037. IR (CCl_4) 3230 (N–H) and 1640 cm^{-1} (C=N). ^{1}H-NMR ($CDCl_3$) δ: 10.8 (1H, br s, N–H), 5.4 (2H, br s, 3-, 4-H), 2.83 (4H, br s, 2-, 5-H). ^{19}F-NMR ($CDCl_3$) ppm: −10.0 (3F, m, 7-CF_3), −3.3 (3F, sept, J=15 Hz, 1- or 6-CF_3), −2.6 (3F, sept, J=15 Hz, 1- or 6-CF_3), [1.3 (minor, m) and 3.6 (major, q, J=5.2 Hz) (3F in total, N=C–CF_3)].

3,4-Dimethyl-1,6,7-tris(trifluoromethyl)-7-*endo*-(2,2,2-trifluoro-1-iminoethyl)bicyclo[4.1.0]hept-3-ene (24)——A solution of **2** (232 mg) and 2,3-dimethyl-1,3-butadiene (excess) in ether was heated in a sealed Pyrex tube at 60 °C for 6 h. The reaction mixture was concentrated under a vacuum and the residue was subjected to prep. GLC (SE-30, at 80 °C) to give **24** (131 mg, 45%). **24**: Colorless oil. MS *m/e*: 421 (M^+). HRMS Calcd for $C_{14}H_{11}F_{12}N$: 421.070. Found: 421.068. IR (CCl_4) 3260 (N–H) and 1640 cm^{-1} (C=N). ^{1}H-NMR ($CDCl_3$) δ: 10.56 (1H, br s, N–H), 2.66 (4H, br s, 2-, 5-H), 1.61 (3H, d, J=6.0 Hz, 3- or 4-CH_3), 1.30 (3H, d, J=7.5 Hz, 4- or 3-CH_3). ^{19}F-NMR ($CDCl_3$) ppm: −9.6 (3F, m, 7-CF_3), −3.83 (3F, sept, J=14 Hz, 1- or 6-CF_3), −2.50 (3F, sept, J=14 Hz, 6- or 1-CF_3), [3.16 (minor, br q, J=5.3 Hz) and 5.16 (major, q, J=5.3 Hz) (3F, in total, N–CCF_3)].

2,3,4-Tris(trifluoromethyl)-3-*endo*-(2,2,2-trifluoro-1-iminoethyl)-*syn*-tricyclo[3.2.1.0^{2,4}]oct-6-ene (25)——A solution of **2** (168 mg) and cyclopentadiene (excess) in ether was sealed in a Pyrex tube under a vacuum and allowed to stand at room temperature for 6 h. The solvent and the excess cyclopentadiene were evaporated off under a vacuum, and the residue was separated by prep. GLC (SE-30, 90 °C). The product was recrystallized from methanol to give **25** (106 mg, 53%). **25**: Colorless crystals; mp 60.5—62.0 °C. MS *m/e*: 405 (M^+). HRMS Calcd for $C_{13}H_7F_{12}N$: 405.039. Found: 405.038. IR (CCl_4) 3250 (N–H) and 1640 cm^{-1} (C=N). ^{1}H-NMR ($CDCl_3$) δ: [10.9 (minor, br) and 10.8 (major, br) (1H, in total, N–H)], 6.7 (1H, br s, 6- or 7-H), 5.9 (1H, br s, 6- or 7-H), 3.7 (2H, br s, 1-, 5-H), 2.3 (1H, d, J=8 Hz, 8-H), 1.9 (1H, d, J=8 Hz, 8-H). ^{19}F-NMR ($CDCl_3$) ppm: −7.0 (6F, m), −5.6 (3F, sept, J=5.3 Hz, 2- or 4-CF_3), [3.8 (major, q, J=5.3) and 6.0 (minor, m) (3F in total, N–CCF_3)].

2,3,4-Tris(trifluoromethyl)-3-*endo*-(2,2,2-trifluoro-1-iminoethyl)-8-oxa-*anti*-tricyclo[3.2.1.0^{2,4}]oct-6-ene (26)——A solution of **1** (131 mg) and furan (excess) in ether sealed in a Pyrex tube under a vacuum was kept at room temperature for a few minutes. After the completion of the reaction had been confirmed by ^{19}F-NMR, the reaction mixture was concentrated under a vacuum and the residue was separated by prep. GLC (SE-30, at 50 °C) and further purified by sublimation to give **26** (132 mg, 84%). **26**: Colorless needles; mp 79—80 °C. MS *m/e*: 407 (M^+). HRMS Calcd for $C_{12}H_5F_{12}NO$: 407.020. Found: 407.019. IR (CCl_4) 3250 (N–H) and 1650 cm^{-1} (C=N). ^{1}H-NMR ($CDCl_3$) δ: 10.4 (1H, br, N–H), 6.8 (2H, br s, 6-, 7-H), 5.25 (1H, br s, 1- or 5-H), 5.06 (1H, br s, 5- or 1-H). ^{19}F-NMR ($CDCl_3$) ppm: −9.0 (qq, J=12.7, 6.4 Hz, 2- or 4-CF_3), −8.0 (3F, qq, J=12.7, 6.4 Hz, 4- or 2- CF_3), −4.6 (3F, sept-q, J=12.7, 3.7 Hz), [4.3 (minor, m) and 6.3 (major, q, J=3.7 Hz) (3F, in total, N=CCF_3)].

8-Amino-5,6,7,8-tetrakis(trifluoromethyl)-azatetracyclo[4.3.0.0^{4,9}.0^{5,7}]non-3-ene (27)——A solution of **2** (209 mg) and pyrrole (excess) in ether sealed in a Pyrex tube was kept at room temperature for 5 h. After the completion of the reaction had been confirmed by ^{19}F-NMR, the mixture was concentrated under a vacuum. The residue was purified by sublimation to give **27** (109 mg, 80%). **27**: Colorless prisms; mp 123—124 °C. MS *m/e*: 406 (M^+). HRMS Calcd for $C_{12}H_{16}F_{12}N_2$: 406.034. Found: 406.036. IR (CCl_4) 3420 and 3340 cm^{-1} (NH_2). ^{1}H-NMR ($CDCl_3$) δ: 6.4 (2H, br s, 2-, 3-H), 5.0 (1H, br s, 1- or 4-H), 4.5 (1H, m, 4- or 1-H), 2.6 (2H, br s, disappeared on addition of D_2O, NH_2). ^{19}F-NMR ($CDCl_3$) ppm: −6.6 (6F, m, 5-, 6-CF_3), −5.6 (3F, m, 7-CF_3),10.6 (3F, q, J=5.3 Hz, 8-CF_3).

References and Notes

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7) The structures of the bromine adducts are tentatively assigned as *cis*, since the Diels–Alder adducts of tetrakis(trifluoromethyl) Dewar thiophene[a] or hexakis(trifluoromethyl)benzvalene[b] were found to give *cis*-dibromo compounds. *a*) Y. Kobayashi, unpublished data. *b*) Y. Kobayashi, I. Kumadaki, A. Ohsawa, Y. Hanzawa, M. Honda, and Y. Iitaka, *Tetrahedron Lett.*, **1976**, 2545.
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