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Reaction of Trifluoromethanesulfonamide with Alkenes and Cycloocta-1,5-diene under Oxidative Conditions. Direct Assembly of 9-Heterobicyclo[4.2.1]nonanes

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Abstract—Reactions of trifluoromethanesulfonamide with α-methylstyrene, 2-methylpent-1-ene, and cycloocta-1,5-diene in the system *t*-BuOCl–NaI were studied. In the reaction with α-methylstyrene 1-iodo-2-phenylpropan-2-ol was the only isolated product. The reaction with 2-methylpent-1-ene gave a mixture of *N*,*N*′-(2-methylpentane-1,2-diyl)bis(trifluoromethanesulfonamide), trifluoro-*N*-(2-hydroxy-2-methylpentyl)methanesulfonamide, and *N*,*N*′-[oxybis(2-methylpentan-2,1-diyl)]bis(trifluoromethanesulfonamide). Trifluoromethanesulfonamide reacted with cycloocta-1,5-diene to produce a mixture of 2,5-diiodo-9-(trifluoromethylsulfonyl)-9-azabicyclo[4.2.1]nonane and 2,5-diiodo-9-oxabicyclo[4.2.1]nonane; this reaction may be regarded as the first example of direct assembly of bicyclononane skeleton.

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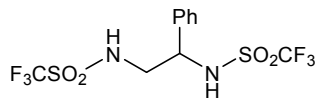
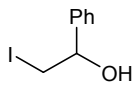
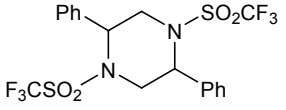
We recently showed that aziridination of styrene with trifluoromethanesulfonamide in the oxidative system *t*-BuOCl–NaI·2H_2O leads to formation of both linear structures **I** and **II** and heterocyclization product, 2,5-diphenyl-1,4-bis(trifluoromethylsulfonyl)piperazine (**III**) [1]. The structure of **III** was proved by X-ray analysis, and a mechanism involving intermediate formation of 2-phenyl-1-trifluoromethylaziridine was proposed [1]. However, the formation of substituted piperazine instead of expected aziridine contradicted the data reported by Minakata et al. [2], according to which aziridines were obtained in reactions of styrene and other alkenes with sulfonamides under analogous conditions due to strong electron-withdrawing effect of the CF_3 group [1]. We tried to reproduce the conditions described in [2] more accurately and carried out the reaction of styrene with trifluoromethanesulfonamide in the presence of anhydrous sodium iodide. In this case, we isolated compounds **I** and **II** and 2,6-diphenyl-1,4-bis(trifluoromethylsulfonyl)piperazine (**IV**) which is isomeric to **III** [3].



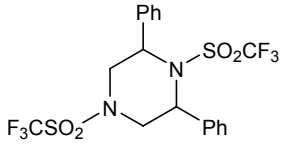
I



II



III



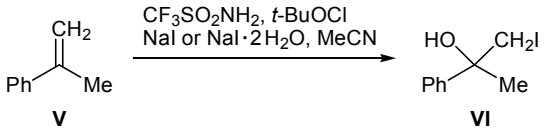
IV

In the present work we studied reactions of trifluoromethanesulfonamide with α-methylstyrene, 2-methylpent-1-ene, and cycloocta-1,5-diene under oxidative conditions (in the presence of *t*-BuOCl–NaI or *t*-BuOCl– NaI·2H_2O) and analyzed possible ways of formation of the corresponding products.

Taking into account that α-methylstyrene reacted with trifluoromethanesulfonamide in a way similar to styrene [2], i.e., with formation of the corresponding aziridine, and that the reaction direction strongly depends on the composition of the oxidative system, α-methylstyrene (**V**) was brought into reaction with trifluoromethanesulfonamide in two systems containing NaI·2H_2O or anhydrous NaI (as in [2]). In both cases, the only product was 1-iodo-2-phenylpropan-2-ol (**VI**) (Scheme 1). Compound **VI** is likely to be formed via iodination of α-methylstyrene with *t*-BuOI to

$[PhC(Me)CH_2I]^+$ and subsequent fast reaction of the latter with water. This was proved by the formation of the same product in the absence of trifluoromethanesulfonamide.

Scheme 1.



With a view to elucidate the effect of the presence of two geminal substituents in the initial alkene on the reaction direction, analogous reaction was carried out with 2-methylpent-1-ene as substrate. Under the above conditions, we isolated three products **VII**–**IX** (Scheme 2), each containing trifluoromethanesulfonamide residues. Unlike the data reported for other sulfonamides [2], no aziridines were isolated or identified in the reaction mixture by spectral methods.

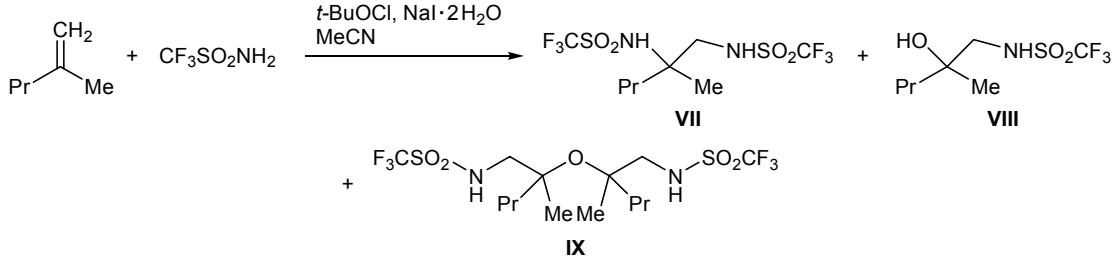
Aziridination of dienes with sulfonylnitrenes generated by oxidation of sulfonamides was not reported previously, though the behavior of a number of linear and cyclic 1,3-dienes in the reaction with *p*-methylphenylsulfonylnitrene generated from (4-methylphenylsulfonylimino)phenyl-λ^3-iodane (PhI=NTs) was studied. As a rule, *p*-methylphenylsulfonylnitrene adds at only one C=C bond of conjugated diene to give the corresponding aziridine [4]. The only exception was the reaction of *p*-methylphenylsulfonylnitrene with cycloocta-1,3-diene, which followed the 1,4-addition pattern and afforded 9-(4-methylphenylsulfonyl)-9-azabicyclo[4.2.1]non-7-ene [4]. Below are given the results of our study on the reaction of an isolated diene, cycloocta-1,5-diene (1,5-COD), with trifluoromethanesulfonamide in the oxidative system *t*-BuOCl–$NaI\cdot 2H_2O$.

Cycloocta-1,5-diene is known not only as ligand for complexation with transition metals but also as important synthon for design of various carbo- and heterocycles. Electrophilic transannular addition to 1,5-COD could give rise to bicyclic compounds of three types, bicyclo[3.3.0]octanes [5], 9-heterobicyclo[3.3.1]-nonanes [6–11], or mixtures of the latter with isomeric 2,5-disubstituted 9-heterobicyclo[4.2.1]nonanes [12–25] (Scheme 3). We have found no published data on the synthesis of fluorinated azabicyclononanes from 1,5-COD.

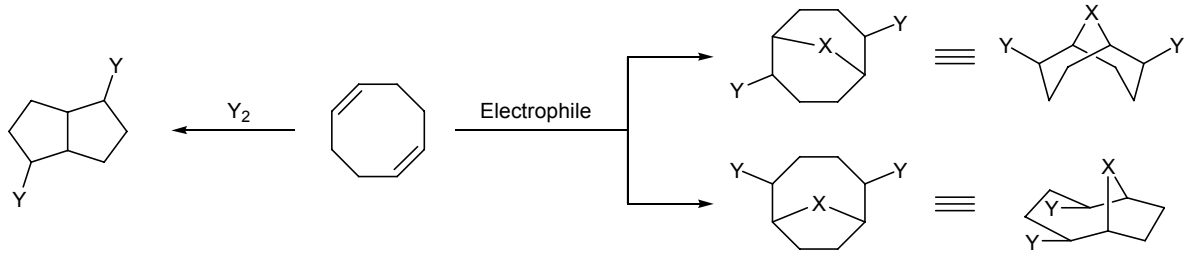
As a first attempt to assemble *N*-(trifluoromethylsulfonyl)-substituted azabicyclononane skeleton from 1,5-COD we examined its reaction with trifluoromethanesulfonamide in the presence of *t*-BuOCl–$NaI\cdot 2H_2O$. In the reaction with equimolar amounts of the reactants and 3 equiv of the oxidant we isolated two compounds which were identified by X-ray analysis as *endo*-2,*endo*-5-diiodo-9-trifluoromethylsulfonyl-9-azabicyclo[4.2.1]nonane (**X**) and *endo*-2,*endo*-5-diiodo-9-oxabicyclo[4.2.1]nonane (**XI**) (Scheme 4, see figure).

Compounds **X** and **XI** crystallized in centrosymmetric point symmetry group, and both enantiomers were present in crystal. Molecules **X** and **XI** have

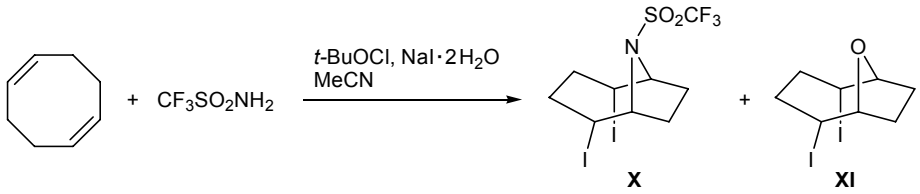
Scheme 2.



Scheme 3.



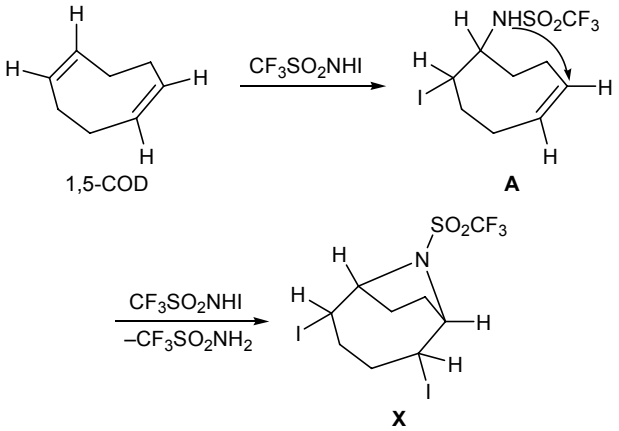
Scheme 4.



similar conformations. The pyrrolidine ring in **X** and tetrahydrofuran ring in **XI** adopt *envelope* conformation. The seven-membered azepane and oxepane rings, as well as cyclooctane fragments, have distorted *chair* conformation. The iodine atoms occupy quasiaxial and quasiequatorial positions with respect to the seven-membered rings. Compound **XI** resembles its bromo-substituted analog [26]. By contrast, isomeric 2,6-diiodo-9-oxabicyclo[3.3.1]nonane exists in a *boat* conformation [27]. The geometric parameters of molecules **X** and **XI** are listed in table.

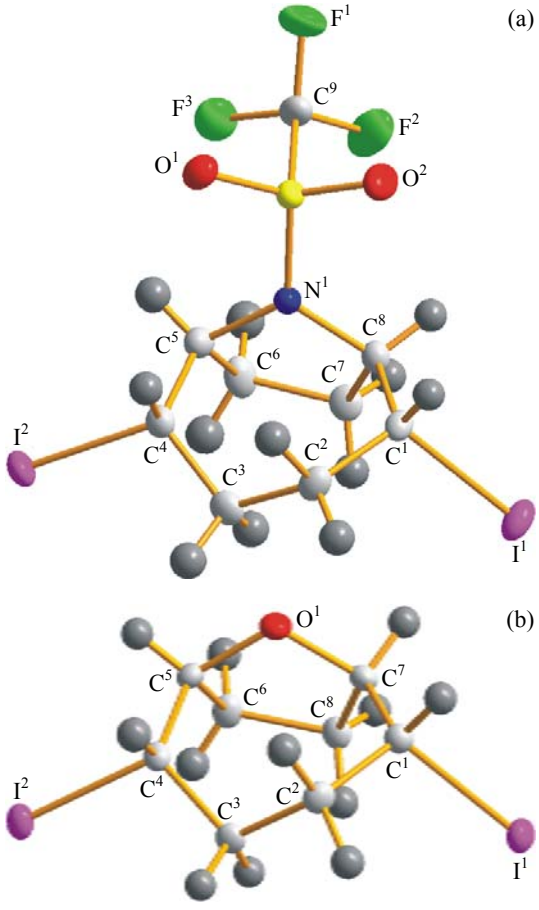
endo Orientation of both iodine atoms in molecules **X** and **XI** allowed us to draw some conclusions on the mechanism of their formation. Presumably, initial reaction of trifluoromethanesulfonamide with *t*-BuOCl–NaI·2H_2O gives intermadiate trifluoro-*N*-iodomethanesulfonamide CF_3SO_2NHI which reacts with 1,5-COD according to the *trans*-addition pattern. The formation of bicyclo[4.2.1]nonane rather than isomeric bicyclo[3.3.1]nonane skeleton is determined by more facile attack by the nitrogen atom in intermediate **A** on the nearest double-bonded carbon atom (Scheme 5).

Scheme 5.



Compound **XI** is formed via replacement of the trifluoromethylsulfonylamino group in intermediate **A** by hydroxy group, followed by closure of tetrahydrofuran ring. The formation of compounds **X** and **XI** is the first example of direct assembly of N-trifluoromethylsulfonyl-substituted azabicyclo[4.2.1]nonane-skeleton.

Selective formation of 9-heterobicyclo[4.2.1]-nonane skeleton is not consistent with the lower (according to the molecular mechanics data [28]) stability of bicyclo[4.2.1]nonane compared to bicyclo[3.3.1]-nonane. We performed MP2/6-311G** calculations of chloro-substituted analogs of compounds **X** and **XI** and their bicyclo[3.3.1]nonane isomers with complete optimization of geometric parameters [29]. The potential energy surface of the chloro analog of **X** contained



Structures of the molecules of (a) *endo*-2,*endo*-5-diiodo-9-trifluoromethylsulfonyl-9-azabicyclo[4.2.1]nonane (**X**) and (b) *endo*-2,*endo*-5-diiodo-9-oxabicyclo[4.2.1]nonane (**XI**) according to the X-ray diffraction data.

Selected bond lengths (*d*) and bond angles (ω) in the molecules of *endo*-2,*endo*-5-diiodo-9-trifluoromethylsulfonyl-9-azabicyclo[4.2.1]nonane (**X**) and *endo*-2,*endo*-5-diiodo-9-oxabicyclo[4.2.1]nonane (**XI**)

X		**XI**	
Bond	*d*, Å	Bond	*d*, Å
C^1–I^1	2.179(6)	C^1–I^1	2.194(5)
C^4–I^2	2.179(6)	C^4–I^2	2.182(4)
C^5–N^1	1.491(7)	C^5–O^1	1.444(5)
C^8–N^1	1.490(7)	C^8–O^1	1.434(6)
N^1–S^1	1.589(5)		
Angle	ω, deg	Angle	ω, deg
$C^5N^1C^8$	110.4(4)	$C^5O^1C^8$	108.8(3)
$C^1C^2C^3$	119.2(5)	$C^1C^2C^3$	118.2(4)
$C^2C^3C^4$	113.1(5)	$C^2C^3C^4$	111.2(4)
$C^3C^4C^5$	116.0(5)	$C^3C^4C^5$	117.0(4)
$C^4C^5C^6$	115.5(5)	$C^4C^5C^6$	116.6(4)
$C^5C^6C^7$	107.0(4)	$C^5C^6C^7$	104.5(3)
$C^6C^7C^8$	107.0(5)	$C^6C^7C^8$	104.7(4)
$C^7C^8C^1$	117.1(5)	$C^7C^8C^1$	118.2(4)
$C^1C^2C^3C^4$	–75.5(7)	$C^1C^2C^3C^4$	–76.7(6)
$C^2C^3C^4C^5$	71.1(6)	$C^2C^3C^4C^5$	67.6(5)
$C^3C^4C^5C^6$	49.5(7)	$C^3C^4C^5C^6$	55.3(5)
$C^4C^5C^6C^7$	–86.5(6)	$C^4C^5C^6C^7$	–86.6(5)
$C^5C^6C^7C^8$	–16.0(7)	$C^5C^6C^7C^8$	–18.0(6)
$C^6C^7C^8C^1$	113.3(6)	$C^6C^7C^8C^1$	118.0(5)
$C^7C^8C^1C^2$	–69.3(7)	$C^7C^8C^1C^2$	–75.0(6)
$C^8C^1C^2C^3$	27.8(8)	$C^8C^1C^2C^3$	32.6(7)

two minima corresponding to rotamers with respect to the N–S bond with different orientations of the trifluoromethyl group. The rotamer with the CF_3 group oriented toward the five-membered ring was more stable (by 0.7 kcal/mol) than the 180° rotamer but less stable (by 3.9 kcal/mol) than the [3.3.1] isomer. The energy difference between the chloro analog of **XI** and its [3.3.1] isomer is even smaller, 3.5 kcal/mol. These data confirm the previous conclusion [19] that more sterically strained bicyclo[4.2.1]nonanes are kinetically controlled products, for their formation is accompanied by smaller distortions of the substrate geometry.

Thus, unlike other sulfonamides, reactions of trifluoromethanesulfonamide with alkenes in the oxidative system *t*-BuOCl–NaI do not produce aziridines. The reaction of trifluoromethanesulfonamide with cycloocta-1,5-diene in the system *t*-BuOCl–NaI·$2H_2O$ demonstrated for the first time direct assembly of *N*-(trifluoromethylsulfonyl)-substituted bicyclononane skeleton and afforded 2,5-diiodo-9-trifluoromethylsulfonyl-9-azabicyclo[4.2.1]nonane and 2,5-diiodo-9-oxabicyclo[4.2.1]nonane.

EXPERIMENTAL

The IR spectra were recorded on a Bruker Vertex 70 spectrometer. The ^1H, ^{13}C, and ^{19}F NMR spectra were measured from solutions in CD_3CN on a Bruker DPX 400 spectrometer operating at 400, 100, and 376 MHz, respectively. The chemical shifts were determined relative to tetramethylsilane (^1H, ^{13}C) or trichlorofluoromethane (^{19}F). The high-resolution mass spectra (electrospray ionization, positive ion detection) of compounds **VII** and **XI** were obtained on a Micromass Q-TOF_{micro} instrument. X-Ray analysis of single crystals of compounds **X** and **XI** was performed at 210 K on an STOE Imaging Plate Diffraction System IPDS-2 (graphite monochromator, MoK_α irradiation, λ = 0.71073 nm) with account taken of Lorentz, polarization, and absorption effects. The structures were solved by the direct method [30] and were refined by the full-matrix least-squares procedure in anisotropic approximation for non-hydrogen atoms and isotropic approximation for hydrogen atoms [31].

Reaction of trifluoromethanesulfonamide with α-methylstyrene. *tert*-Butyl hypochlorite, 6.5 g (0.06 mol), was added dropwise to a mixture of 3 g (0.02 mol) of trifluoromethanesulfonamide, 2.36 g (0.02 mol) of α-methylstyrene, and 0.06 mol of NaI or NaI·$2H_2O$ in 100 ml of acetonitrile. The mixture was stirred for 10 h at –6°C, the solvent was removed under reduced pressure at room temperature, the residue was dissolved in chloroform, and the solution was treated with 120 ml of a 0.3 M solution of $Na_2S_2O_3$, dried over $MgSO_4$, and evaporated. The liquid residue (4.8 g) was subjected to column chromatography on silica gel (0.063–0.200 μm) using hexane as eluent to remove tarry products, and the residue (3.0 g) was separated by column chromatography on silica gel (0.015–0.040 μm) using diethyl ether–hexane (1:2) as eluent to isolate 1.0 g of unreacted trifluoromethanesulfonamide, 0.5 g of alcohol **VI**, and 0.5 g of tarry substances which were not analyzed.

1-Iodo-2-phenylpropan-2-ol (VI) [32]**.** Oily substance. ^1H NMR spectrum, δ, ppm: 1.38 s (3H, CH_3),

3.49 s (1H, OH), 3.59 d and 3.64 d (1H each, CH_2I, J = 10.4 Hz), 7.27 t (1H, *p*-H, J = 7.3 Hz), 7.36 t (2H, *m*-H, J = 7.7 Hz), 7.47 d (2H, *o*-H, J = 8.1 Hz). ^{13}C NMR spectrum, δ, ppm: 23.7 (CH_2I), 29.4 (CH_3), 73.1 (Ph**C**H), 125.8 (C^o), 127.9 (C^p), 128.9 (C^m), 146.5 (C^i).

Reaction of trifluoromethanesulfonamide with 2-methylpent-1-ene. *tert*-Butyl hypochlorite, 4.4 g (0.04 mol), was added dropwise to a mixture of 2 g (13.4 mmol) of trifluoromethanesulfonamide, 1.12 g (13.4 mmol) of 2-methylpent-1-ene, and 7.4 g (0.04 mol) of $NaI \cdot 2H_2O$ in 80 ml of acetonitrile. The mixture was stirred for 5 h at –6°C, the solvent was removed under reduced pressure at room temperature, the residue was dissolved in chloroform, and the solution was washed with a 0.3 M solution of $Na_2S_2O_3$, dried over $MgSO_4$, and evaporated. The liquid residue (3.8 g) was passed through a column charged with silica gel (0.063–0.200 μm) using diethyl ether–hexane (1:2) as eluent to remove tarry products. The colorless residue (3.0 g) was separated by column chromatography on silica gel (0.015–0.040 μm) using diethyl ether–hexane (1:2) as eluent to isolate 1.8 g (71%) of compound **VII** as solid substance and 0.8 g of a liquid mixture of compounds **VIII** and **IX**, which was separated by preparative thin-layer chromatography on silica gel using the same eluent. We thus isolated 0.3 g (9%) of compound **VIII** and 0.2 g (6%) of **IX**.

***N*,*N*′-(2-Methylpentane-1,2-diyl)bis(trifluoromethanesulfonamide) (VII).** mp 103–105°C. IR spectrum (CCl_4), ν, cm^{-1}: 3374, 3290 (NH). ^1H NMR spectrum, δ, ppm: 0.94 t (3H, CH_2CH_3, J = 7.2 Hz), 1.36 s (3H, CCH_3), 1.38 m (2H, CH_2CH_3), 1.57 m (2H, CCH_2), 3.33 d and 3.41 d (1H each, NCH_2, J = 14.1 Hz), 6.66 br.s (2H, NH). ^{13}C NMR spectrum, δ_C, ppm: 14.2 (CH_3CH_2), 17.1 (CH_3CH_2), 21.1 ($NCCH_3$), 41.0 ($C_2H_5CH_2$), 53.4 (NCH_2), 63.0 (NCMe), 120.3 q (2-CF_3, J = 320.3 Hz), 120.9 q (1-CF_3, J = 321.0 Hz). ^{19}F NMR spectrum, δ_F, ppm: –77.23, –77.76. Found: m/z 380.0299 $[M]^+$. $C_8H_{14}F_6N_2O_4S_2$. Calculated: M 380.0294.

Trifluoro-*N*-(2-hydroxy-2-methylpentyl)methanesulfonamide (VIII). IR spectrum (CCl_4), ν, cm^{-1}: 3622 (OH), 3390 (NH). ^1H NMR spectrum, δ, ppm: 0.92 t (3H, CH_2CH_3, J = 7.0 Hz), 1.14 s (3H, CCH_3), 1.36 m (2H, CH_2CH_3), 1.44 m (2H, CCH_2), 2.80 br.s (1H, OH), 3.15 m (2H, NCH_2), 6.60 br.s (1H, NH). ^{13}C NMR spectrum, δ_C, ppm: 14.9 (CH_2CH_3), 17.5 (CH_2CH_3), 24.5 (CCH_3), 42.5 (CCH_2), 54.1 (NCH_2), 72.1 (COH), 121.0 q (CF_3, J = 320.1 Hz). ^{19}F NMR spectrum: δ_F –77.65 ppm. Found, %: C 34.18; H 5.69; F 22.29; N 6.05. $C_7H_{14}F_3NO_3S$. Calculated, %: C 33.73; H 5.66; F 22.87; N 5.62.

***N*,*N*′-[Oxybis(2-methylpentane-2,1-diyl)]bis(trifluoromethanesulfonamide) (IX).** IR spectrum (CCl_4): ν 3383 cm^{-1} (NH). ^1H NMR spectrum, δ, ppm: 0.95 t (3H, CH_2CH_3, J = 7.3 Hz), 1.49 m (2H, CH_2CH_3), 1.54 s (3H, CCH_3), 1.75 m (2H, CCH_2), 3.47 m (2H, NCH_2), 6.85 br.s (1H, NH). ^{13}C NMR spectrum, δ_C, ppm: 14.3 (CH_2CH_3), 18.3 (CH_2CH_3), 27.5 (CCH_3), 44.0 (CCH_2), 55.3 (NCH_2), 72.9 (COC), 120.9 q (CF_3, J = 320.7 Hz). ^{19}F NMR spectrum: δ_F –77.43 ppm.

Reaction of trifluoromethanesulfonamide with cycloocta-1,5-diene. *tert*-Butyl hypochlorite, 7 g (65 mmol), was added dropwise to a mixture of 3.3 g (22 mmol) of trifluoromethanesulfonamide, 2.38 g (22 mmol) of cycloocta-1,5-diene, and 12 g (65 mmol) of $NaI \cdot 2H_2O$ in 100 ml of acetonitrile. The mixture was stirred for 1.5 h at –10°C, the solvent was removed under reduced pressure, the residue was dissolved in chloroform, and the solution was treated with a 0.3 M solution of $Na_2S_2O_3$, dried over $CaCl_2$, and evaporated. The residue was 6.4 g of a tarry material which was subjected to column chromatography on silica gel (63–200 μm) using hexane as eluent to isolate 3 g of a colorless liquid which was subjected to repeated chromatography on a column charged with silica gel (15–40 μm) using hexane as eluent to isolate 1.5 g (14%) of compound **X** and 0.6 g (7%) of **XI** as colorless finely crystalline substances. Single crystals of **X** and **XI** suitable for X-ray analysis were obtained by crystallization from hexane.

***endo*-2,*endo*-5-Diiodo-9-trifluoromethylsulfonyl-9-azabicyclo[4.2.1]nonane (X).** mp 84–86°C. IR spectrum (KBr), ν, cm^{-1}: 2966, 2890, 1640, 1435, 1394, 1363, 1231, 1189, 1159, 1073, 1038, 972, 894, 659, 605. ^1H NMR spectrum, δ, ppm: 2.29 d.d (2H, $NCHCH_2$, ^2J = 14.5 Hz), 2.30 d.d (2H, $ICHCH_2$, ^2J = 8.1 Hz), 2.38 d.d (2H, $NCHCH_2$), 2.56 d.d (2H, $ICHCH_2$), 4.60 m (4H, NCH, CHI). ^{13}C NMR spectrum, δ_C, ppm: 31.2 ($NCHCH_2$, $^1J_{CH}$ = 134 Hz), 32.8 (CHI, $^1J_{CH}$ = 144.5 Hz), 36.4 ($ICHCH_2$, $^1J_{CH}$ = 134 Hz), 66.9 (CHN, $^1J_{CH}$ = 153.7 Hz), 120.5 q (CF_3, J_{CF} = 323.1 Hz). ^{19}F NMR spectrum: δ_F –76.63 ppm. Found, %: C 21.99; H 2.36; N 2.79; S 6.21. $C_9H_{12}F_3I_2NO_2S$. Calculated, %: C 21.23; H 2.38; N 2.75; S 6.30. X-Ray diffraction data: M_R = 509.06; 1.00×0.75×0.65-mm single crystal, orthorhombic

crystal system, space group *Pbca*; a = 9.3600(4), b = 15.1754(5), c = 20.0671(7) Å; V = 2850.37(18) Å^3; Z = 8; d_{calc} = 2.372 g/cm^3; μ(MoK_α) = 4.59 mm^{-1}; $2\Theta_{max}$ = 49.99°; 16951 reflections, 2496 independent reflections (R_{int} = 0.099); R = 0.0384, wR = 0.0859 [$I > 2\sigma(I)$].

***endo*-2,*endo*-5-Diiodo-9-oxabicyclo[4.2.1]nonane (XI).** mp 76–78°C; published data [6]: mp 81–82°C. IR spectrum (KBr), ν, cm^{-1}: 2923, 1629, 1472, 1393, 1352, 1284, 1233, 1165, 1125, 1036, 896, 784, 682, 609, 567. ^{1}H NMR spectrum, δ, ppm: 2.11 d.d (2H, NCHC**H**$_2$, ^2J = 5.7 Hz), 2.21 d.d (2H, ICHC**H**$_2$, ^2J = 7.4 Hz), 2.28 d.d (2H, NCHC**H**$_2$), 2.41 d.d (2H, ICHC**H**$_2$), 4.64 m (2H, OCH), 4.52 m (4H, ICH). ^{13}C NMR spectrum, δ_C, ppm: 31.5 (NCH**C**H$_2$, $^1J_{CH}$ = 131.6 Hz), 36.1 (CHI, $^1J_{CH}$ = 151.9 Hz), 36.5 (ICH**C**H$_2$, $^1J_{CH}$ = 132.1 Hz), 84.0 (CHO, $^1J_{CH}$ = 154.4 Hz). Found: m/z 377.8972 $[M]^+$. $C_8H_{12}I_2O$. Calculated: M 377.8967. X-Ray diffraction data: M_R = 377.98; 0.45×0.40×0.35-mm single crystal, triclinic crystal system, space group $P\bar{1}$; a = 5.1059(8), b = 9.9078(15), c = 10.4345(16) Å; α = 86.063(13), β = 83.479(13), γ = 78.883(12)°; V = 514.01(14) Å^3; Z = 2; $d_{calc.}$ = 2.442 g/cm^3; μ(MoK_α) = 6.07 mm^{-1}; $2\Theta_{max}$ = 50.00°; 3261 reflections, 1696 independent reflections (R_{int} = 0.055); R = 0.0244, wR = 0.0577 [$I > 2\sigma(I)$].

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