57. Synthesis of *anti*-9-Bromo- and *anti*-9-Chlorobicyclo[4.2.1]nonatriene *via* Bicyclo[4.2.1]nonatriene→Bicyclo[4.2.1]nonatriene Rearrangement

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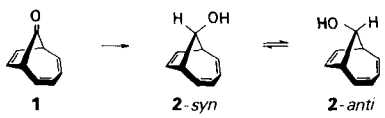
(11.X.85)

The first syntheses of 9-bromo- and 9-chlorobicyclo[4.2.1]nona-2,4,6-trienes were each achieved in three stereoselective steps from the 9,9-bis(selenophenyl) derivative **9** in 79% overall yield for the bromide and 64% for the chloride. A deuterium-labeling experiment reveals the first rearrangement of a bicyclo[4.2.1]nonatriene which leaves the ring system intact.

1. Introduction to the Synthetic Problem. – The *Shechter-Antkowiak* synthesis of bicyclo[4.2.1]nona-2,4,7-triene-9-one (**1**) [1] [2a] quickly led to the 9-*syn* alcohol (**2**-*syn*)[3]) [2a], later to its epimer (**2**-*anti*) *(Scheme 1)* [3], to a host of other 9-functionalized derivatives [4–8], even to bicyclo[4.3.2]undecatrienone [9], but not, however, to a 9-bicyclo[4.2.1]nonatrienyl bromide or chloride.

Scheme 1



1 **2**-*syn* **2**-*anti*

These halides would be useful, if only to understand the still obscure rearrangement mechanisms of their 9-bicyclo[6.1.0]nonatrienyl isomers [10]. Their synthesis would also make accessible the theoretically interesting 9-carbocation and 9-carbanion [11], as well as the wholly unexplored area of 9-bicyclo[4.2.1]nonatrienyl organometallic chemistry[4]).

Competitive rearrangements have hitherto frustrated their synthesis. The problem is an old one in the transformation of alcohols to halides, but numerous techniques that solve it elsewhere fail to do so at C(9) of the bicyclo[4.2.1]nonatrienols. The techniques have included: *a)* reagents such as Ph_3P/CCl_4, Ph_3P/CBr_4, Ph_3PBr_2, and hydrazine treatment of the ketone followed by iodine [13a], *b)* gas-phase chlorosulfite ester thermolysis [13], and *c)* the reactions of ionic bromides and iodides with 9-*syn*-*p*-toluenesulfonate, -*p*-nitrobenzoate, and -trifluoromethanesulfonate in acetone, MeCN, DMF, or dimethyl sulfoxide solutions [2a] [13a] [14]. In no case could an unrearranged halide be detected.

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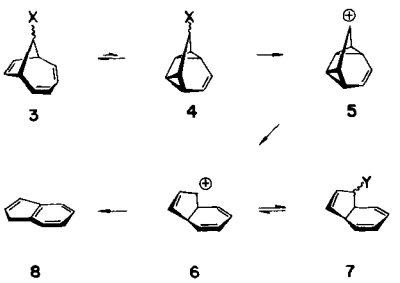
[3]) Following *Schechter* [2b], we denote C(9) configuration as being either *syn* or *anti* to the diene bridge.

[4]) We elsewhere describe the subsequent preparation of 9-lithio derivatives [12].

Such failures are easily understood by the mechanistic *Scheme 2*, the elaboration of a suggestion due to *Kirmse* and *Voigt* [3]. Rearrangement is driven by the release of angle strain (**3**→**6**) and by the stability of cationic intermediates; **5** is a 'phase-reversed' 7-nor-tricyclyl cation [15] and **6** a bishomoaromatic cation [16]. *Scheme 2* is also in accord with the insensitivity of *p*-toluenesulfonate acetolysis rate to precursor configuration [3] [17] and with the results of deuterium-labeling experiments [4] [18]. These are clearly not classical rearrangements of the *Wagner-Meerwein* type, but rather cation-accelerated thermal rearrangements [19]; the parent hydrocarbon suffers the same transposition of its C-atoms, when it thermally rearranges to *cis*-3a,7a-dihydroindene [20][5])[6]).

Scheme 2



syn-9-Fluorobicyclo[4.2.1]nonatriene manages to escape the attraction of *Scheme 2*, when it is generated by thermal rearrangement of its 9-bicyclo[6.1.0]nonatrienyl isomer [22]. The 9-bicyclo[6.1.0]nonatrienyl chloride and bromide, however, provide only bicyclo[4.3.0] products, both thermally and *via* molybdenum tricarbonyl complexing [10] [23] [24].

We, therefore, returned to a direct synthesis from the bicyclononatrienone **1**. Rearrangements were to be avoided by selecting reagents that favor anionic or free radical mechanisms, and at the lowest feasible temperatures.

2. Solution of the Synthetic Problem. – *Scheme 3* begins with *Gelissen*'s selenophenyl derivative **9** [8], which we transformed to the intensely red carbanion **10** with *t*-BuLi at −78°. Addition of Me_3SnCl at this temperature provided the trimethyltin-selenophenyl compound **11** in 81% yield. Subsequent reduction to the *syn*-Me_3Sn compound **12** was achieved by Bu_3SnH, assisted at 0° by photochemical activation of azo-*bis*(isobutyronitrile) and in 100% yield.

The *anti*-9-bromide **13** was then obtained by treating **12** with *N*-bromosuccinimide (NBS) in acetone, at −78° and in 98% yield. Finally, treatment of **12** with Cl_2 at −96° provided the *anti*-9-chloride **14** in 78% yield (65% conversion)[7]).

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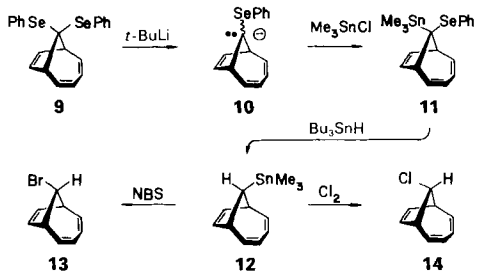
[5]) Others, however, prefer to have heterolysis precede, rather than follow intramolecular *Diels-Alder* cycloaddition [4] [17] [18]. We know of no compelling experimental evidence that distinguishes between these alternatives.

[6]) *Wagner-Meerwein* structurally related products are, however, obtained by: *1)* treating the ketone **1** with several strong acids [2a] [14a], *2)* treating the *anti*-9-phenyl-*syn*-9 alcohol with $SOCl_2$ [21], *3)* treating the *anti*-9-chloro-*syn*-9 methyl ether with fluorosulfonic acid [7], and *4)* photolyzing the 9-tosylhydrazone in MeONa/MeOH [3].

[7]) All yields are those of products isolated after column chromatographic purification.

Scheme 3



3. Stereochemical Assignments. – The exclusive stereoselectivities of *Scheme 3* faithfully reflect experimental information; the ^{1}H-NMR spectrum of none of the crude products revealed evidence for the alternative epimer. Like others before us [2a] [8] [22] [25–27], we use the *Karplus* relationship to assign configuration to 9-monosubstituted derivatives. The H(*syn*)–C(9) bonds of **13** and **14** each span a dihedral angle of *ca.* 95° with the bridgehead H–C(1) and H–C(6) bonds; their ^{1}H-NMR signals appear as unsplit singlets. The corresponding signal of the H(*anti*)–C(9) appears as a triplet in **12**, in the *syn*-9-(phenylseleno), and in the *syn*-9-(phenylselenoxy) derivatives *(cf. Exper. Part)*.

A necessary corollary criterion is now also apparent in 300-MHz ^{1}H-NMR spectra; this resolves the dienyl H–C(2,5) signal from the dienyl H–C(3,4) signal. Spin decoupling then shows the bridgehead H–C(1,6) signal to be split more by the adjacent H–C(2,5) dienyl protons than by the adjacent H–C(7,8). The bridgehead signal then appears as a doublet, whenever it is not further split by H–C(9) (*i.e.*, H(*syn*)–C(9)); it appears as a triplet, whenever it is (*i.e.*, H(*anti*)–C(9)).

To assign configuration to the C(9)-distributed **11**, we assume that the *Karplus* relationship applies also to the two Sn isotopes of spin 1/2: ^{117}Sn (7.7%) and ^{119}Sn (8.7%). The illustrated *anti*-Me_3Sn assignment then follows from the observed isotopic satellite doublet-splitting of the bridgehead H–C(1,6) signal: J(H, ^{117}Sn) = 41 Hz and J(H, ^{119}Sn) = 28 Hz[8]). Independent confirmation comes from the absence of Sn-isotopic splitting in the H–C(1,6) signal of the *syn*-Me_3Sn compound **12** of previously assigned configuration.

4. The Origins of Stereospecificity. – A single stereogenic rule accommodates the various assignments of *Scheme 3:* each reagent introduces its new substituent *anti* to the diene bridge. This is identical to the general rule for kinetically controlled nucleophilic attack at an electron-deficient C(9) [2a] [7] [28] and it can be rationalized in the same way. Reagents attack a trigonal C(9) center from the sterically more accessible *anti* side, whether the trigonal center be that of a ketone (**1**), a methoxyl-stabilized carbocation, a carbanion (**10**→**11**), or a free radical intermediate (**11**→**12**, **12**→**13**, **12**→**14**[9]). The assumed free radical halogenation is the least certain of these mechanistic judgements [29].

For this and other reasons [12], we treated the compound **11** with Bu_3SnD – rather than hydride – and the resulting deuterated product D-**12** with NBS *(Scheme 4)*.

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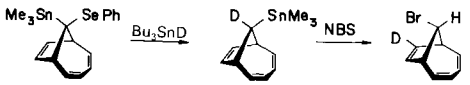
[8]) A similar hypothesis was used to assign *anti*-configuration to a 9-phosphonium salt [7].

[9]) 9-Tosylhydrazone photolysis in MeONa/MeOH [3] reveals an apparent exception to this rule.

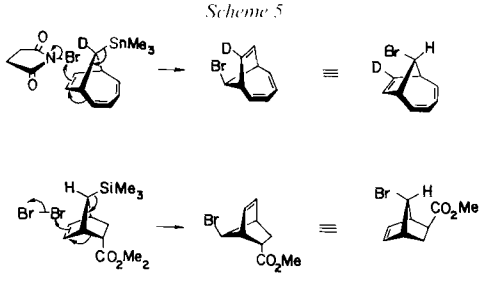
Scheme 4



11 D-**12** D-**13**

It is apparent that the first reaction proceeds as expected for a radical-chain substitution process, but the second does not. The proposed mechanism *(Scheme 5)* defines ultimate stereospecificity by the stereospecificity of *exo* attack on a bridged alkene. The reaction might be facilitated by the concerted departure of cationic Me_3Sn^+ as indicated, or by the intervention of a stabilized homopentadienyl/allylcyclopropylcarbinyl cation. *Scheme 5* also illustrates a similar Br-induced rearrangement of a (trimethylsilyl)-norbornene [30]. However closely Sn might resemble Si, bicyclo[4.2.1]nonatrienes do not usually resemble norbornenes; the norbornyl C skeleton is normally conserved in a rearrangement. To the best of our knowledge, this represents the first rearrangement of a bicyclo[4.2.1]nonatriene that conserves the C skeleton.

Scheme 5



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Experimental Part

1. *General.* In prep. procedures: solvent 'purging' refers to performing at least three evacuation/inert-gas-replenishment operations, 'evaporation' refers to rotary evaporation at water-aspirator pressure and ambient temp. M.p. were obtained in open capillaries, using a *Thomas-Hoover Unimelt* apparatus, and are uncorrected. TLC used *Machery-Nagel* pre-coated *SIL G/UV$_{254}$* 0.25 mm plates with visualization either by UV, I_2 vapor, or 3% phosphomolybdic acid in i-PrOH. Preparative HPLC used a *Waters' Associates Prep LC/System 500A*, operated at 300–500 ml/min and equipped with two *PrePAK-500* silica-packed cartridges. Flash chromatography was done on *Riedel-DeHaen Kieselgel S* (0.032–0.063 mm), following the procedures recommended by *Still et al.* [31]. A *Bruker WM-300* was used for ^{1}H(300.14 MHz)-, ^{13}C(75.47 Mz)-, and ^{2}H(46.07 Mz)-NMR spectra, supplemented by a *Varian CFT-20* for ^{1}H and *Jeol FX-90Q* for ^{13}C. Chemical shifts are reported as δ values relative to internal Me_4Si in $CDCl_3$ soln.; ^{2}H-NMR spectra used δ ($CDCl_3$) at 7.24 ppm as standard. Broad-band decoupling was used for ^{2}H and ^{13}C spectra, modified in a gated decoupling sequence when ^1J(C,H) were determined. Unless explicitly specified otherwise, J refers to J(H,H). All of them, measured in Hz, are apparent splittings, not true coupling constants. In reporting multiplicities, satellite splittings due to minor isotopes are ignored, but the corresponding J are listed separately. All ^{13}C-NMR assignments were correlated with ^{1}H-NMR assignments by single-frequency off-resonance decoupling, Microanalyses were by *Galbraith Laboratories, Inc.*, Knoxville, TE.

2. *9,9-Bis(phenylseleno)bicyclo[4.2.1]nona-2,4,7-triene* (**9**). A thoroughly dried N_2-filled flask was charged with *bicyclo[4.2.1]nona-2,4,7-triene-9-one* [1] [2a] (**1**, 10,0 g, 0.076 mol), phenylselenol [32] (40.2 ml, 59.7 g, 0.380 mol), and dry Et_2O (10 ml), which were cooled to −12° with stirring. Gaseous HCl was then introduced sufficiently slowly that the temp. never exceeded −8°. After 45 min, the contents were poured into sat. aq. $NaHCO_3$ (400 ml), further neutralized with solid $NaHCO_3$, and the org. layer extracted with 7% aq. KOH (200, 100, 100 ml) and H_2O (100 ml). After drying ($MgSO_4$), filtering, and evaporating, the residual oil (30.3 g) was subjected to prep. HPLC (hexane/CH_2Cl_2 85:15) to provide **9** as an oil (26.7 g, 82.0%; [8]: 53%). ^{1}H-NMR: 7.8–7.2 (*m*, 10.4 H, Ph); 6.18 (*m*, 1.91 H, H–C(3,4)); 6.08 (*m*, 1.89 H, H–C(2,5)); 5.17 (*d*, *J* = 1.5, 1.89 H, H–C(7,8)); 3.20 (*d*, *J* = 7.5, 1.95 H, H–C(1,6)). ^{13}C-NMR: 137.24, 136.43, 133.25, 128.65, 128,42, 128.38, 126.80, 121.12, 56.22, 54.70 (*J*(C(9), Se) = 5.9).

3. syn-*9-(Phenylseleno)bicyclo[4.2.1]nona-2,4,7-triene and* syn-*9-(Phenylselenoxy)bicyclo[4.2.1]nona-2,4,7-triene*. An Ar-purged flask was charged with **9** (2.56 g, 5.99 mmol), azo-bis(isobutyronitrile) (1.15 ml of a 0.052M benzene soln., 0.060 mmol), Bu_3SnH (2.61 g, 8.98 mmol), and benzene (50 ml), and the contents heated 2 h at 80°. After cooling, H_2O was added, the suspension stirred 3 h, the benzene layer was removed, and the aq. layer extracted with CH_2Cl_2. The combined org. layers were dried (Na_2SO_4), filtered, and evaporated. Flash chromatography (hexane/CH_2Cl_2 70:30) of the residue (4.87 g) through 5.0 × 15.0 cm silica gel provided white crystalline 9-phenylseleno compound (1.42 g, 86.8%). IR (CCl_4): 3050, 2950, 1580, 1475, 1435, 1390, 1310, 1010, 880. ^{1}H-NMR: 7.33 (*m*, 5.28 H, Ph); 6.13 (*m*, 3.89 H, H–C(2,5)); 5.35 (*d*, *J* = 1.4, 1.85 H, H–C(7,8)); 3.77 (*t*, *J* = 6.0, 1.06 H, H–C(9)); 3.31 (*t*, *J* = 6.0, 1.32 H, H–C(1,6)); reported [8]: 7.53–6.87 (*m*, 5 H); 6.03 (*m*, 4 H); 5.27 (*d*, 2 H); 3.77 (*t*, 1 H); 3.27 (*t*, 2 H).

The 9-(phenylselenoxy) compound was obtained by conventional [33] *m*-chlorobenzoic-acid treatment, and isolated in 96.8% yield after flash chromatography (CH_2Cl_2/MeOH 90:10), m.p. 129°. IR (KBr): 963, 936, 880, 817, 760, 745, 718, 686[10]). ^{1}H-NMR: 7.50 (*m*, 5.28 H, Ph); 6.10 (*m*, 4.04 H, H–C(2,4)); 5.14 (*dq*, 1.83 H, H–C(7,8)); 3.57 (*m*, 0.91 H, H–C(1)); 3.21 (*t*, *J* = 6.2, 1.04 H, H–C(9)); 2.59 (*m*, 0.90 H, H–C(6)).

4. syn-*9-(Phenylseleno)*-anti-*9-(trimethylstannyl)bicyclo[4.2.1]nona-2,4,7-triene* (**11**). Compound **9** (297 mg, 0.694 mmol) was dried by successive dissolution in, and then evaporation of, three 5.0 ml portions of benzene. It was then dissolved in dry THF (7.0 ml) and syringe-transferred into a N_2-purged flask, which was then cooled to −78°. An intense red color formed upon addition of *t*-BuLi (0.34 ml 2.02M in pentane, 0.694 mmol) with stirring. Two minutes later, addition of Me_3SnCl (753 mg, 0.694 mmol) in dry THF (1.0 ml) transformed the color to pale orange, and the resulting soln. was partitioned between CH_2Cl_2 (15 ml) and H_2O (20 ml). The org. layer was dried ($MgSO_4$), filtered, and evaporated. Flash chromatography (hexane/CH_2Cl_2 70:30) through 4.0 × 15.0 cm silica gel provided white crystalline **11** (242 mg, 81%, m.p. 78.5° from MeOH). Larger scale prep. HPLC used hexane CH_2Cl_2 92:8. IR (KBr): 1300, 765, 740, 730, 685, 670. ^{1}H-NMR: 7.40 (*m*, 2.01 H, Ph); 7.17 (*m*, 2.97 H, Ph); 6.24 (*dd*, *J* = 3.5, 8.8, 1.99 H, H–C(3,4)); 6.15 (*ddd*, *J* = 3.5, 6.8, 8.8, 2.04 H, H–C(2,5)); 5.31 (*d*, *J* = 1.0, 1.98 H, H–C(7,8)); 3.39 (*dd*, *J* = 6.8, 1.0, *J*(H, Sn) = 44.9, 36.9, 2.04 H, H–C(1,4)); −0.15 (*s*, *J*(H, Sn) = 51.6, 49.8, 8.98 H). ^{13}C-NMR: 135.58 (*d*, *J*(C,H) = 159.2, *J*(C, Sn) = 56.6, C(3,4)); 133.91 (*d*, *J*(C,H) = 162.5, Ph); 131.18 (*s*, Ph); 128.61 (*d*, *J*(C,H) = 161.0, Ph); 127.14 (*d*, *J*(C,H) = 160.6, Ph); 126.83 (*d*, *J*(C,H) = 145.2, C(2,5)); 122.75 (*d*, *J*(C,H) = 169.8, C(7,8)); 51.81 (*d*, *J*(C,H) = 136.2, C(1,6)); 34.90 (*s*, C(9)); −6.39 (*q*, *J*(C,H) = 128.9, Me). EI-MS: 165 (82), 163 (61), 161 (42), 116 (100), 115 (87). CI-MS: 439 (17), 438 (M^+, 6), 437 (17), 436 (M^+, 7), 435 (10), 423 (23), 421 (21), 419 (20), 169 (24), 167 (17), 165 (100), 164 (28), 163 (83), 162 (25), 161 (44), 117 (64), 116 (40), 115 (27). Anal. calc. for $C_{18}H_{22}SnSe$: C 49.58, H 5.09, Sn 27.22, Se 18.11; found: C 49.64, H 5.13, Sn 27.12, Se 18.32.

5. syn-*9-(Trimethylstannyl)bicyclo[4.2.1]nona-2,4,7-triene* (**12**) *and* syn-*9-(Trimethylstannyl)[9-$^2H_1$]-bicyclo[4.2.1]nona-2,4,7-triene* (**D-12**). A soln. of **11** (2.30 g, 5.28 mmol) and azo-bis(isobutyronitrile) (0.16 g, 0.97 mmol) in dry benzene (40 ml) in a N_2-purged flask was cooled to 0° with stirring. Upon addition of Bu_3SnH (7.03 g, 24.1 mmol), the flask was irradiated with a commercial 'sunlamp' until disappearance of the reactant TLC spot (R_f 0.28 (**11**), 0.53 (**12**); hexane). Evaporation and flash chromatography of the residue (1.48 g, hexane) through 5.0 × 18.5 cm silica gel provided **12** as an oil (1.48 g, 100%). IR (CCl_4): 3000, 2915, 1380, 1295, 1185, 963, 910, 864. ^{1}H-NMR: 6.15 (*m*, 2.06 H, H–C(2,5)); 5.88 (*m*, 2.05 H, H–C(3,4)); 5.37 (*d*, *J* = 1.1, *J*(H, Sn) = 4.5, 1.92 H, H–C(7,8)); 3.28 (*ddd*, *J* = 7.1, 6.0, 1.1, 1.96 H, H–C(1,6)); 1.68 (*t*, *J* = 6.0, *J*(H, Sn) = 43.9, 0.98 H, H–C(9)); −0.02 (*s*, *J*(H, Sn) = 53.0, 50.6, 9.02 H). ^{13}C-NMR: 137.75 (*d*, *J*(C,H) = 155.7, *J*(C, Sn) = 19.3, C(2,5)); 124.72 (*d*, *J*(C,H) = 153.4, C(3,4)); 122.96 (*d*, *J*(C,H) = 163.5, *J*(C, Sn) = 59.0, C(7,8)); 46.78 (*d*, *J*(C,H) = 135.9, C(1,6)); 28.21 (*d*, *J*(C,H) = 125.8, *J*(C, Sn) = 420.4, 400.2, C(9)); −8.95 (*q*, *J*(C,H) = 128.0, *J*(C, Sn) = 325.1, Me). EI-MS

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[10]) Intense absorption between 840 and 800 cm^{-1} is ascribed to selenoxides [34].

282 (M^+, 0.50), 280 (M^+, 0.50), 267 (41), 266 (14), 265 (30), 264 (11), 263 (18), 165 (42), 164 (12), 163 (32), 162 (11), 161 (19), 117 (100), 116 (32), 115 (31). CI-MS: 282 (M^+, 1.5), 280 (M^+, 1.0), 267 (100), 266 (35), 265 (76), 264 (29), 263 (44), 165 (40), 164 (12), 163 (31), 162 (10), 161 (18), 117 (21). GLC through a 180 × 0.64 cm glass column, containing *Carbowax 20M on AW/DMCS Chromosorb G*, 60/80 mesh at 150°, provided a sample for elemental analysis: calc. for $C_{12}H_{18}Sn$: C 51.30, H 6.46, Sn 42.24; found: C 51.27, 51.23, H 6.44, 6.52, Sn 42.18, 42.08.

Compound **D-12** was similarly prepared, using Bu_3SnD in place of Bu_3SnH. IR (neat): 3045, 3015, 2975, 2915, 1385, 957, 890, 850, 760, 735, 710, 675. ^{1}H-NMR: 6.14 (*m*, 2.01 H); 5.88 (*m*, 1.98 H); 5.36 (*d*, J = 1.3, J(H, Sn) = 4.5, 1.97 H); 3.26 (*dd*, J = 7.3, 1.3, 2.07 H); −0.02 (*s*, J(H, Sn) = 53.0, 50.7, 8.94 H). ^{13}C-NMR: 137.84 (*s*, J(C, Sn) = 18.8); 124.73; 123.00 (*s*, J(C, Sn) = 59.1); 46.73; −8.93 (*s*, J(C, Sn) = 325.0, 310.2).

6. anti-*9-Bromobicyclo[4.2.1]nona-2,4,7-triene* (**13**) *and* anti-*9-Bromo[7-$^2H_1$]bicyclo[4.2.1]nona-2,4,7-triene* (**D-13**). A N_2-purged flask was charged with a soln. of **12** (60.0 mg, 0.214 mmol), in dry acetone (1.0 ml) and cooled to −78° with stirring. A soln. of NBS (38.0 mg, 0.214 mmol) in acetone (2.3 ml) was added and the contents were degassed between −196° and −78°. After 10 min at 78°, the volatiles were vacuum-transferred (2 h, 10^{-6} Torr) and then evaporated. Flash chromatography of the residue (42.0 mg) through 2.0 × 15.0 cm silica gel (hexane) provided **13** as a clear oil (41.2 mg, 98.1%). IR (neat): 3060, 1312, 1232, 1180, 980, 852, 748, 703. ^{1}H-NMR: 5.97 (*m*, 1.96 H, H–C(2,5)); 5.85 (*m*, 2.08 H, H–C(3,4)); 5.32 (*ddd*, J = 1.1, 1.0, 0.9, 1.95 H, H–C(7,8)); 4.15 (*d*, J = 0.9, 0.95 H, H–C(9)); 3.41 (*dd*, J = 7.5, 1.1, 2.08 H, H–C(1,6)). ^{13}C-NMR: 132.60 (*d*, J(C,H) = 163.0, C(2,5)); 124.23 (*d*, J(C,H) = 156.6, C(3,4)); 120.58 (*d*, J(C,H) = 169.5, C(7,8)); 54.83 (*d*, J(C,H) = 162.9, C(9)); 54.11 (*d*, J(C,H) = 138.7, C(1,6)). EI-MS: 117 (12), 116 (99), 115 (100). CI-MS: 199 (M^+ + 1, 0.7), 197 (M^+ + 1, 0.7), 118 (11), 117 (100). Anal. calc. for C_9H_9Br: C 54.85, H 4.60, Br 40.55; found: C 54.99, 55.03, H 4.85, 4.79, Br 40.31.

Compound **D-13** was similarly prepared from **D-12**. IR (neat): 3020, 2945, 1330, 1275, 1231, 1175, 967, 870, 820, 720, 680, 620. ^{1}H-NMR: 5.97 (*m*, 1.97 H); 5.84 (*m*, 2.03 H); 5.31 (*d*, J = 0.6, 0.98 H); 4.15 (*d*, J = 0.6, 0.99 H); 3.41 (*d*, J = 7.73, 2.02 H). ^{2}H-NMR: 5.35 (*s*). ^{13}C-NMR: 132.58, 124.15, 120.39, 54.86, 53.94.

7. anti-*9-Chlorobicyclo[4.2.1]nona-2,4,7-triene* (**14**). A soln. of **12** (303 mg, 1.08 mmol) in dry trichlorofluoromethane in a septum-stoppered test tube was cannula-transferred under N_2 into a flask equipped with stirring bar and septum. Upon cooling to −96° with stirring, Cl_2 (2.82 ml of 0.383M soln. in CCl_4, 1.07 mmol) was added to the flask at 3.9 ml/min using a syringe pump. The precipitated solids failed to dissolve after 10 min, whereupon the bath temp. was raised to −78°. After 1 h stirring of the resulting soln., it was warmed to ambient temp., and the solvent was evaporated. Flash chromatography of the residual oil through 3.0 × 15.0 cm silica gel (hexane) provided a recovered reactant fraction (evaporated to 52.0 mg (17%)) and a product fraction which provided **14** as a clear oil (107 mg, 65% conversion, 78% yield). IR (neat): 3030, 1350, 1330, 1240, 978, 850, 836, 765, 715. ^{1}H-NMR: 5.99 (*m*, 2.04 H, H–C(2,5)); 5.85 (*m*, 2.08 H, H–C(3,4)); 5.31 (*dd*, J = 1.1, 1.4, 1.99 H, H–C(7,8)); 4.08 (*s*, 0.93 H, H–C(9)); 3.30 (*dd*, J = 7.5, 1.1, 1.96 H, H–C(1,6)). ^{13}C-NMR: 132.07 (*d*, J(C,H) = 161.8, C(2,5)); 124.38 (*d*, J(C,H) = 156.9, C(3,4)); 120.43 (*d*, J(C,H) = 172.2, C(7,8)); 63.41 (*d*, J(C,H) = 167.1, C(9)); 53.55 (*d*, J(C,H) = 139.7, C(1,6)). EI-MS: 154 (M^+, 6), 152 (M^+, 19), 118 (10), 117 (100), 116 (27), 115 (88), 91 (32), 89 (12), 63 (10), 40 (43), 39 (10). CI-MS: 155 (M^+ + 1,3), 154 (M^+, 1), 153 (M^+ + 1,8), 152 (M^+, 2), 118 (10), 117 (100). GLC through a 183 × 0.64 cm glass column, containing 16% *OV-1* on *AW/DMCS Chromosorb W*, 80/100 mesh at 110°, provided a sample for elemental analysis: calc. for C_9H_9Cl: C 70.83, H 5.94, Cl 23.23; found: C 70.68, 70.52, H 5.79, 6.05, Cl 23.09.

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