Regio- and stereochemical aspects of bromochlorination of norbornene

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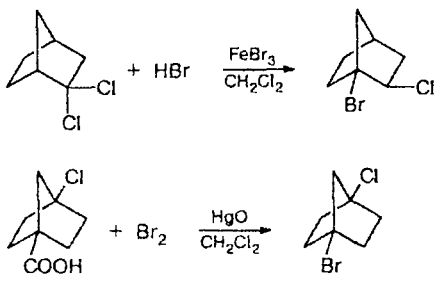
Bromochlorination of norbornene whose chemo- and regio-selectivity is determined by the type of the halogenating reagent used was studied. Three isomeric bromochloronorbornanes (2-*endo*-bromo-3-*exo*-chloro-, 2-*exo*-bromo-3-*endo*-chloro-, and 2-*exo*-bromo-7-*syn*-chlorobicyclo[2.2.1.]heptanes), 2-*exo*-7-*syn*- and 2-*exo*-7-*anti*-dibromo- and -dichloronorbornanes, and 2-bromonortricyclane were isolated and characterized by ^1H and ^{13}C NMR spectra. The spectral and structural characteristics of the resulting compounds are discussed.

Key words: bromochlorination, norbornene, bromochloronorbornane, dibromonorbornane, dichloronorbornane.

Norbornene (bicyclo[2.2.1]hept-2-ene) is a convenient substrate for investigating the mechanism of addition to C=C bonds.[1,2] The ratio of the addition products obtained from norbornene under various conditions allows drawing conclusions concerning the fundamental features of these reactions such as their electrophilic or radical character, the effective electrophilicity of the reagents in the case of electrophilic reactions, the intermediate formation of onium ions, and participation of contact or solvent-separated ion pairs.[1] Therefore, it is quite natural that it is the reaction with this substrate whose outcome is used to compare various bromochlorinating reagents.

The mechanism and conditions of norbornene halogenation have been studied fairly comprehensively; however, whereas the addition of fluorine,[3] chlorine,[4,5] bromine,[6,7] and iodine[8] has been studied in detail, the problem of mixed halogenation of norbornene has not received much attention. By now, iodochlorination,[9] chlorofluorination,[10] and bromofluorination[11] of norbornene have been reported, but its bromochlorination has not been studied at all. The two 1-bromochloronorbornanes known to date have been prepared by replacement of a chlorine atom in 2,2-dichloronorbornane[12] or the carboxyl group in the corresponding 4-chloronorbornane-1-carboxylic acid.[13]



Previously we proposed using phosphorus halides and oxohalides to activate electrophilic sulfenylation processes and showed that at the second step of electrophilic addition, a halogen atom of the phosphorus-containing Lewis acid acts as a nucleophile; as a rule, this results in the formation of β-halo sulfides.[14–16] In our opinion, the use of this approach to promote electrophilic reactions of *N*-chloramines should result in the generation of a new bromochlorinating reagent.

If the mechanism of bromochlorination with the *N*-chloramine—phosphorus bromide system proves to be identical to the known mechanism of bromosulfenylation with arylsufenamide—phosphorus bromide, formation of products resulting from the addition of the $[Cl^+Br^-]$ species, which is a synthetic equivalent of mixed halogen, should be expected. No synthons of this type with abnormal polarization of halogen atoms have been described so far.

Therefore, we studied electrophilic bromochlorination of norbornene by known reagents and by the *N*-chloramine—phosphorus bromide system and compared the regio- and stereoselectivities of these reactions.

The structures of the products obtained in these reactions were determined by ^1H and ^{13}C NMR spectroscopy. The spectra were analyzed and the signals were assigned based on the data on the influence of substituents on the chemical shifts and the ^1H-^1H and ^1H-^{13}C spin-spin coupling constants and using homo- and heteronuclear selective decoupling experiments, nuclear Overhauser effect (NOE) difference spectroscopy,[17] and ^1H-^1H and ^1H-^{13}C 2D correlation spectroscopy (COSY).[18]

We studied the reaction of *N*-chlorodiethylamine with norbornene in the presence of PBr_3, $POBr_3$, and PBr_5 and found that it affords chloro bromide **1**, dibromide **2**, and a minor amount of 2-bromonortricyclane (**3**).

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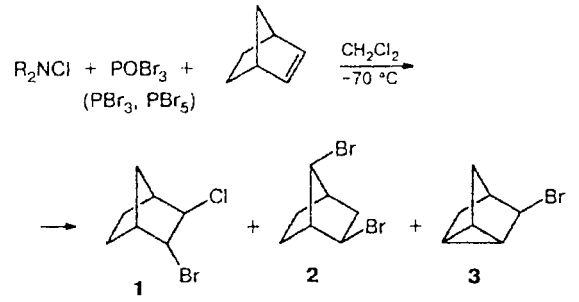
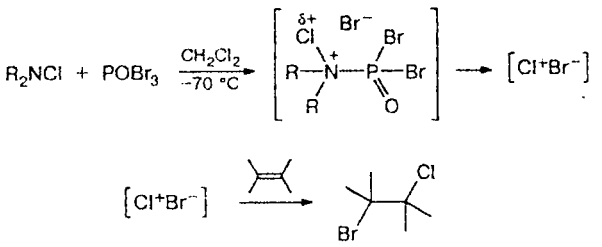


The ratio of the reaction products (a substantial amount of Wagner—Meerwein rearrangement products and the presence of nortricyclane, Table 1) points to the formation of a highly electrophilic reagent and to low probability of radical transformations. The rate of addition (1 h, −70 °C, whereas BrCl reacts with olefins at a temperature of 0 to +25 °C [19]) also suggests a high electrophilicity of the reagent, exceeding that of BrCl by a large factor. This is apparently due to the polarization of the N—Cl bond caused by the formation of an *N*-chloramine—phosphorus bromide donor-acceptor complex, which results in the chlorine atom becoming cationic. The Cl^+ ion rapidly adds to the double bond to give a carbocation, which is subsequently stabilized upon reaction with a nucleophile, *viz.*, bromide anion detached from phosphorus bromide or oxobromide:

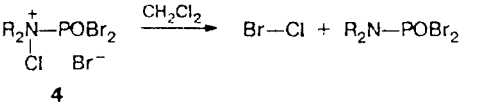


From our viewpoint, the formation of dibromide **2** in a fairly high yield (see Table 1) can be explained as follows:

Table 1. Products of norbornene halogenation by various bromochlorinating reagents

Halogenating reagent	Yield (%)							
	Bromo chlorides			Dibromides		Dichlorides		
	1	**8**	**9**	**2**	**5**	**10**	**11**	**3**
$Et_2NCl + PBr_3$	57	—	—	10	—	—	—	8
$Et_2NCl + POBr_3$	53	—	—	25	—	—	—	5
$Et_2NCl + PBr_5$	13	—	—	72	—	—	—	12
$Et_2NCl + AlBr_3$	—	—	—	80	9	—	—	7
1) $Et_2NCl + SO_3$, 2) HBr	—	24	—	—	8	—	—	—
NBS + PCl_3	—	—	20	—	—	42	—	15
$SbCl_5$ + KBr	—	—	—	—	—	35	30	—
$SbCl_5 + Br_2$	—	—	—	—	—	—	38	—
$Bu_4N^+BrCl_2^-$	—	—	53	—	—	—	—	—

if reagent **4** corresponding to the synthon $[Cl^+Br^-]$ does not enter into electrophilic addition immediately after it appear, it undergoes transpolarization to yield amidobromide of phosphoric acid and the mixed halogen ClBr characterized by energetically more favorable "normal" charge distribution, $[Cl^-Br^+]$.

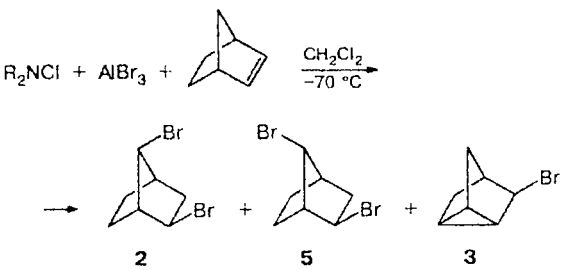


Therefore, the subsequent reaction steps give the products of addition of the synthon $[Br^+Cl^-]$ (according to GLC, they are formed in relatively small amounts, 1—3%) as well as the $[Br^+Br^-]$ species, since the role of nucleophile can be played by either the bromide anions of complex **4** or the bromide anions detached from aminobromide:

It should be noted that the ratio of dihalides **2** : **1** increases in the series of reagents PBr_3, $POBr_3$, PBr_5 (see Table 1). This is in good agreement with the fact that PBr_5 is a brominating reagent, whereas PBr_3 and $POBr_3$ are not. Thus, the use of the *N*-chloramine—PBr_3 system seems to be the optimum reagent for the bromochlorination of norbornene by the $[Cl^+Br^-]$ synthon.

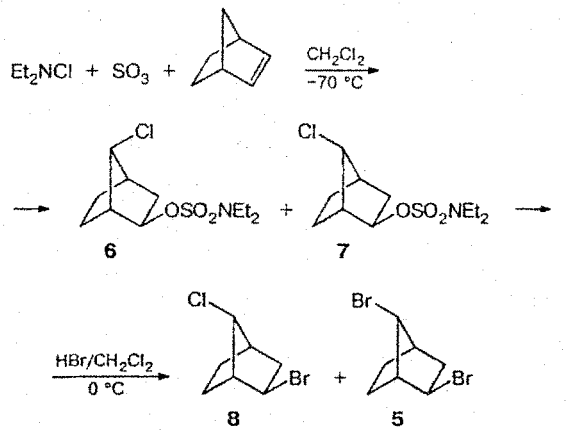
The formation of the nonrearranged bromo chloride **1** apparently shows that the nucleophile (bromide anion) is formed from a contact ion pair. Conversely, dibromide **2** is a product of the Wagner—Meerwein rearrangement, which is formed obviously from a solvent-separated ion pair, because in this case, the lifetime of the cation proves to be long enough for the rearrangement to occur.

For comparison, we carried out the reaction of *N*-chlorodiethylamine with norbornene in the presence of a harder Lewis acid, $AlBr_3$. In this case, no 2,3-addition products were found and both isolated dihalides were products of the Wagner—Meerwein rearrangement, *viz.*, 2-*exo*-7-*syn*- (**2**) and 2-*exo*-7-*anti*-dibromonorbornanes (**5**). Dibromide **2** was isolated and character-

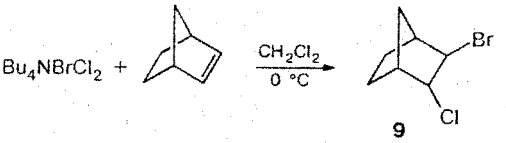


ized in an analytically pure state; dibromide **5** formed in a minor amount could be isolated only as a mixture with compound **2**. Thus, when the reagent formed is effectively a stronger electrophile (than the reagents formed upon activation with phosphorus bromides), bromination becomes the only reaction route.

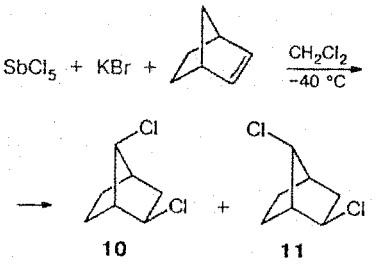
Previously, a two-step procedure for the introduction of chlorine and bromine into olefin molecules has been developed in our laboratory;[20] according to this procedure, the first step includes addition of *N*-chlorodiethylamine to the double bond in the presence of SO_3, and the second step is the reaction of chlorosulfamates **6** and **7** with hydrogen bromide. This procedure was used to transform norbornene into bromo chloride **8** and dibromide **5**.



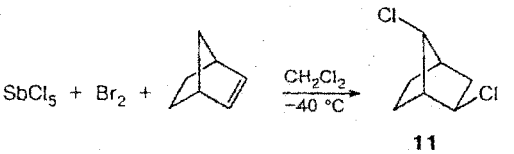
The next stage of our study was the attempt to synthesize bromochloronorbornanes, isomeric to compounds **1** and **8** but with the opposite arrangement of the halogens. In view of the fact that all the traditional one-step bromochlorination methods are based on the $[Br^+Cl^-]$ synthon, which corresponds to the normal polarization of the Br—Cl bond, we assumed that the configurations of the reaction products are determined by the following known factors: (1) an electrophile attacks the double bond in norbornene from the *exo*-side; (2) after the Wagner—Meerwein rearrangement, it occupies position 7; (3) the non-rearranged cation is attacked by a nucleophile from the *endo*-side.[21] In conformity with this, in the 2,3-adduct, a bromine atom should be *exo*-oriented, and in the 2,7-isomer, it should occupy position 7. The procedures that we used in the reactions of norbornene resulted in the formation of three different dihalogenation products, whose ratio makes it possible to judge the effective electrophilicity[21] of the reagents. An anionic electrophile, the $Bu_4N^+BrCl_2^-$ salt, was found to be the mildest among the reagents studied.[22] This salt reacts at 0 °C to give compound **9** as the only product, and thus, it is both effectively (thermodynamically) and kinetically the weakest electrophile in the studied series.



The $SbCl_5$—KBr system is a substantially stronger electrophile. It enters into the reaction at lower temperatures (−40 °C); however, this reaction gives only rearranged dichlorides **10** and **11** and no products of mixed halogenation.



The use of Br_2 in place of KBr [23] results in the formation of only one dichloride **11**. The fact that product **10** is not formed at all indicates that the lifetime of the cation is relatively long, so it has time to be converted into thermodynamically the most stable isomer. Of the reagents studied here, this one possesses the highest effective electrophilicity, although its "ordinary" (kinetic) electrophilicity is not higher than that of the *N*-chloramine complex with phosphorus bromide.



In the halogenation of norbornene, we used for the first time the *N*-bromosuccinimide—PCl_3 system, which is similar to the complex of *N*-chloramine with phosphorus bromide but ensures the addition of BrCl according to its traditional polarization. Note that in this case, too, mixed halogenation yields only the vicinal addition product (bromo chloride **9**).

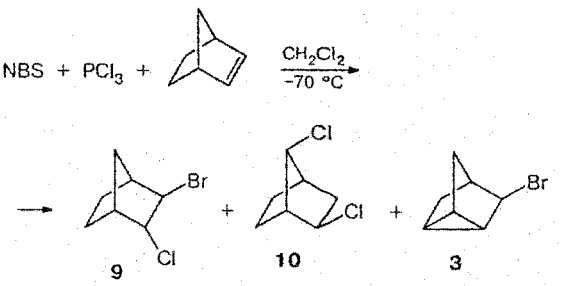


Table 2. ^1H Chemical shifts (ppm) and $^1H-^1H$ spin-spin coupling constants (J/Hz) in bromochloronorbornanes, dibromonorbornanes, and dichloronorbornanes ($CDCl_3$)

Compound	H(1)	H(2)	H(3)	H(4)	H(5)	H(6)	H(7)
1	2.500, $J_{1,2exo} = 4.4$	4.473, $J_{2,3} = 3.0$	3.901, $J_{3,7anti} = 2.7$	2.489	*endo*: 1.364; *exo*: 1.742	*endo*: 1.929; *exo*: 1.510	*anti*: 1.526; *syn*: 2.019, $J_{5endo,7} = 2.4$, $J_{7,7} = -10.5$
2	2.571, $J_{1,6exo} = 4.3$	3.956, $J_{2,3exo} = 3.6$, $J_{2,3endo} = 8.1$, $J_{2,7anti} = 1.4$	*endo*: 2.181, $J_{3,7} = 1.4$; *exo*: 2.487, $J_{3,4} = 4.2$, $J_{3,3} = -13.7$	2.427	*endo*: 1.28; *exo*: 1.68	*endo*: 1.27; *exo*: 1.66	3.972
8	2.542, $J_{1,6exo} = 4.7$	3.965, $J_{2,3exo} = 3.2$, $J_{2,3endo} = 8.4$	*endo*: 2.20; *exo*: 2.20, $J_{3,3} = -14.0$	2.344	*endo*: 1.28; *exo*: 2.011	*endo*: 1.25; *exo*: 2.075	4.452
9	2.517, $J_{1,6exo} = 4.8$ $J_{1,7} = 1.7$	3.739, $J_{2,3} = 2.9$, $J_{2,7anti} = 2.7$	4.439, $J_{3,4} = 4.4$	2.492, $J_{4,7} = 1.7$	*endo*: 1.958; *exo*: 1.475	*endo*: 1.401; *exo*: 1.765	*anti*: 1.545; *syn*: 2.027, $J_{7,7} = -10.6$
10	2.562, $J_{1,6exo} = 4.4$	3.959, $J_{2,3exo} = 4.5$, $J_{2,3endo} = 8.0$, $J_{2,7anti} = 1.5$	*endo*: 2.179, $J_{3,7} = 1.4$; *exo*: 2.488, $J_{3,4} = 4.1$, $J_{3,3} = -13.8$	2.424, $J_{4,5exo} = 4.3$	*endo*: 1.28; *exo*: 1.64	*endo*: 1.27; *exo*: 1.72	3.976
11	2.469, $J_{1,6exo} = 4.7$	3.895, $J_{2,3exo} = 3.6$, $J_{2,3endo} = 8.4$	*endo*: 2.070; *exo*: 1.926, $J_{3,4} = 4.2$, $J_{3,3} = -14.0$	2.341	*endo*: 1.237; *exo*: 1.92	*endo*: 1.191; *exo*: 2.08	4.365

It is obvious that the existing methods are markedly inferior to that proposed by us regarding both the mildness of the reaction conditions and, as a consequence, chemoselectivity and the yields of the bromochlorination products, except for the reaction with $Bu_4N^+BrCl_2^-$.

The six isomeric bromochloronorbornanes prepared in this study exhibit typical NMR spectra (Tables 2 and 3), which permit determination of the structures of these compounds using the well-developed criteria for the assignment of signals in the spectra of norbornene derivatives.[8]

It is of interest that, due to the fact that the effects of bromine and chlorine atoms on the shielding of the protons in the bicyclic cage differ only slightly, every two bromochloronorbornanes with the same character of substitution but opposite arrangement of the halogen atoms give similar ^1H NMR spectra. Since the signals of individual protons in all of the obtained dihalides substantially overlap even in a magnetic field of 9.4 T, the assignment was performed by virtue of the multifrequency resonance technique and 2D procedures using various solvents.

Table 3. ^{13}C Chemical shifts (ppm) in bromochloronorbornanes, dibromonorbornanes, and dichloronorbornanes ($CDCl_3$)

Compound	C(1)	C(2)	C(3)	C(4)	C(5)	C(6)	C(7)
1	47.78	61.90	62.45	45.56	28.75	23.98	36.13
2	50.26	47.94	41.96	44.42	28.393	25.16	53.56
8	52.11	49.12	42.21	43.08	25.22*	25.54*	63.63
9	47.52	59.86	70.48	44.89	21.39	28.22	35.96
10	50.25	59.02	41.23	43.69	25.20	26.86	63.76
11	51.80	59.07	41.83	42.48	25.44	24.42	63.42

* Assignment may be interchanged.

The Br and Cl atoms at C(2) and C(3) exert virtually identical effects on the shielding of the H(2) and H(3) protons and the bridge H(7) protons. In compounds **1** and **9**, as in norbornene,[24] *exo*-protons are less shielded than *endo*-protons (by 0.5—0.7 ppm in $CDCl_3$). The chemical shifts of the *anti*- and *syn*-bridge protons ($H(7)_{anti}$ and $H(7)_{syn}$) are also substantially different (by approximately 0.5 ppm). The $H(7)_{anti}$ proton experiences the paramagnetic influence of the closely located *exo*-halogen at the C(2) atom. For the same reason, about the same difference in shielding is observed for the bridgehead protons in the series of compounds **2**, **8**, **10**, and **11**. The influence of substituents on shielding of the bridgehead protons, H(1) and H(4), is small (~0.3 ppm). Due to substantial steric interactions, an *endo*-substituent strongly deshields the *endo*-proton separated by four bonds ($H(6)_{endo}$ in compound **1** and $H(5)_{endo}$ in compound **9**), so that its signal is substantially shifted downfield (by approximately 0.5 ppm) compared to the signal of the corresponding *exo*-proton. For the protons of the other methylene group, as in norbornane, the opposite arrangement of signals is observed.

The transoid arrangement of substituents in 2,3-dihalonorbornanes **1** and **9** is indicated by the relatively small spin-spin coupling constant, $^3J_{trans} \approx 3$ Hz, which differs appreciably from the corresponding *cis*-constant ($^3J_{cis} \geq 8$ Hz, see Table 2). The orientation of halogen atoms in these compounds follows from the vicinal constants $^3J_{1,2}$ and $^3J_{3,4}$, which are observed in practice only for *exo*-protons (4.4 Hz), as well as from the long-range *W*-type constants, $^4J_{2endo,7anti}$ and $^4J_{3endo,7anti}$ (2.7 Hz). The presence of these long-range interactions for *endo*-protons is confirmed by the corresponding cross-peaks in the COSY-45 spectra.[18] In addition, through-space contacts of the H(2) and H(3) *exo*-protons with the $H(7)_{syn}$ proton [or $H(5)_{exo}$ and $H(6)_{exo}$ with $H(7)_{anti}$], and the $H(2)_{endo}$ and $H(3)_{endo}$ protons with $H(6)_{endo}$ and $H(5)_{endo}$, respectively, are clearly distinguished in experiments with the Overhauser effect. The regioselectivity of the addition of each halogen atom can be proved by comparison of the ^1H and ^{13}C chemical shifts of the C(2)H(2)X and C(3)H(3)Y groups (X, Y = Br or Cl), determined using the $^1H-^{13}C$ COSY, selective double resonance, and the $^{13}C-\{^1H\}$ techniques.

The presence of a halogen atom in the bridge in compounds **2**, **8**, **10**, and **11** follows from the H(7) signal pattern determined by the absence of the geminal $J_{7,7}$ constant, equal to 10—11 Hz, which is typical of norbornane. The stereochemistry of the substituents at C(2) in these compounds was determined based on the same reasons as for compounds **1** and **9**. Thus the *endo*-orientation of H(2) is confirmed, upon its irradiation with a second radiofrequency field, by the presence of the positive Overhauser effect for the $H(6)_{endo}$ and $H(3)_{endo}$ signals and by the absence of this effect for $H(7)_{syn}$. The position of the halogen at the C(7) atom is characterized by the data on both dipole-dipole and spin-spin interactions. In fact, in the case of *syn*-orientation of the halogen atom (compounds **2** and **10**), the Overhauser effect points to a noticeable contact of the $H(5)_{exo}$ and $H(6)_{exo}$ protons with the $H(7)_{anti}$ proton; for the $H(7)_{anti}$ proton, the long-range spin-spin coupling with $H(2)_{endo}$ and $H(3)_{endo}$ is also manifested. For isomers with an *anti*-halogen atom (compounds **8** and **11**), the opposite pattern is observed, namely, the dipole-dipole interaction between $H(7)_{syn}$ and $H(3)_{exo}$ and the spin-spin coupling of $H(7)_{syn}$ with $H(5)_{endo}$ and $H(6)_{endo}$ (in the COSY-45 spectrum).

The ^{13}C chemical shifts for products **10** and **11** are in good agreement with the values reported previously.[25] The spatial interactions between the two halogen atoms have a substantial effect on the shielding of the carbon atoms in the bicyclic cage. For 2-*exo*,7-*anti*-dihalo derivatives, this is manifested to the least extent. The ^{13}C chemical shifts can be predicted with sufficient accuracy in terms of the additive scheme based on the spectral parameters of 2- and 7-monosubstituted norbornanes.[25,26] For the C(2) atom in compound **8**, the calculation error is ~2 ppm, while for the other carbon atoms it is 0.1—1.5 ppm. Conversely, in the case of 2,3-dihalo derivatives **1** and **9**, the influence of pair interactions on shielding is rather great, especially for the carbon atoms attached to Br and Cl, and for the C(7) atom. For the C(3) atom in compound **1**, the result obtained using the direct additive scheme deviates from the experimental value by more than 13 ppm. The steric diamagnetic γ-effect[27] occurs for both the *exo*-substituent (for the C(7) atom) and the *endo*-substituent. The latter factor accounts for the substantial difference between the shielding of the C(5) and C(6) atoms in compounds **1** and **9**.

The Br and Cl atoms occupying positions 2-*endo* and 7 exert α-effects on shielding of carbon atoms in accordance with their electronegativity. This permits unambiguous regiochemical assignment for compounds **1** and **9** and for compound **8**.

Experimental

NMR spectra were recorded on a Varian VXR-400 instrument operating at 400 MHz (^1H) and 100 MHz (^{13}C). The chemical shifts are given in the δ scale and referred to internal tetramethylsilane. Mass spectra were run on a VG-70/70 GC/MS spectrometer.

All the reactions with norbornene were carried out in a flow of dry argon. The course of the reactions was monitored by TLC on Silufol plates (using a 1 : 10 ethyl acetate—heptane mixture as the eluent). The reaction mixtures were washed with a 5% solution of Na_2CO_3 and water (2×20 mL), dried with Na_2SO_4, and passed through a filtering column (h = 5 cm) packed with Silpearl silica gel, and the solvent was evaporated *in vacuo*. The products were isolated by preparative TLC on Silufol plates using the same eluent.

N-Chlorodiethylamine was synthesized by a known procedure.[28]

Reaction of *N*-chlorodiethylamine with norbornene in the presence of phosphorus halides. A solution of *N*-chlorodiethylamine (540 mg, 5 mmol) in 10—15 mL of dichloromethane was added dropwise to a solution of phosphorus halide or oxohalide (5 mmol) in 20—30 mL of anhydrous dichloromethane stirred at −70 °C. The mixture was stirred for 5 min, norbornene (470 mg, 5 mmol) in 10 mL of dichloromethane was added at −70 °C, and the mixture was stirred for an additional 1 h. Then the temperature was gradually raised to 0 °C.

Reaction of *N*-chlorodiethylamine with norbornene in the presence of $AlBr_3$. At −40 °C, $AlBr_3$ (1.34 g, 5 mmol) was added to 30 mL of anhydrous dichloromethane, and the flask was cooled to −70 °C with stirring. A solution of *N*-chlorodiethylamine (540 mg, 5 mmol) in 10—15 mL of dichloromethane was added dropwise. The mixture was stirred for 5 min, and norbornene (470 mg, 5 mmol) in 10 mL of dichloromethane was added. A temperature of −70 °C was maintained for an additional 1 h, then it was gradually increased to 0 °C.

Reaction of *N*-chlorodiethylamine with norbornene in the presence of SO_3 and subsequent replacement of the sulfamate group by bromine on treatment with HBr. The transformation of norbornene (470 mg, 5 mmol) carried out by a known procedure[20] gave 387 mg of a crude oily product, whose chromatography gave 251 mg of compound **8**.

Reaction of norbornene with the $KBr \cdot SbCl_5$ system. The reaction was carried out by the general procedure[22] using KBr instead of LiBr. A mixture of norbornene (376 mg, 4 mmol), $SbCl_5$ (600 mg, 2 mmol), and KBr (206 mg, 2 mmol) in 40 mL of CCl_4 was refluxed for 5 min and allowed to cool.

Reaction of norbornene with the $SbCl_5$—Br_2 system. The reaction was carried out by the known procedure.[22] A mixture

of $SbCl_5$ (600 mg, 2 mmol) and Br_2 (320 mg, 2 mmol) in 40 mL of CCl_4 was stirred for 5 min, and cooled to −30 °C. Norbornene (188 mg, 2 mmol) was added, and the temperature was gradually raised to ~20 °C.

Bromochlorination of norbornene with Bu_4NBrCl_2 was carried out by a procedure similar to that described previously.[22] An equimolar amount of a solution of Bu_4NBrCl_2 in dichloromethane (2.82 mmol mL^{-1}) was added with stirring at 0 °C to a solution of norbornene (470 mg, 5 mmol) in 40 mL of CH_2Cl_2, and the mixture was stirred for 1 h.

Reaction of *N*-bromosuccinimide with norbornene in the presence of PCl_3. *N*-Bromosuccinimide (535 mg, 3 mmol) in 5—10 mL of CH_2Cl_2 was added with stirring at −40 °C to a solution of PCl_3 (415 mg, 3 mmol) in 20 mL of CH_2Cl_2. The mixture was stirred for 5 min at −40 °C, and norbornene (285 mg, 3 mmol) in 10 mL of CH_2Cl_2 was added. The mixture was stirred for 1 h at −40 °C and gradually warmed up to ~20 °C.

2-*endo*-Bromo-3-*exo*-chlorobicyclo[2.2.1]heptane (1). R_f 0.64. Found (%): C, 39.67; H, 5.14. $C_7H_{10}BrCl$. Calculated (%): C, 40.13; H, 4.81. MS, *m/z* (*I* (%)): 93 $[C_7H_{11}]^+$ (100), 129 $[C_7H_{11}Cl]^+$ (48), 208 $[M]^+$ (1).

2-*exo*-7-*syn*-Dibromobicyclo[2.2.1]heptane (2). R_f 0.45. Found (%): C, 33.58; H, 4.05. $C_7H_{10}Br_2$. Calculated (%): C, 33.11; H, 3.97. MS, *m/z* (*I* (%)): 93 $[C_7H_{11}]^+$ (100), 173 $[C_7H_{11}Br]^+$ (48), 252 $[M]^+$ (1).

3-Bromotricyclo[2.2.1.$0^{2,6}$]heptane (3). R_f 0.57. ^1H NMR ($CDCl_3$), δ: 3.91 (m, 1 H, HC(3)); 2.10 (m, 1 H, HC(4)); 2.04 (m, 1 H, *syn*-HC(7)); 1.15—1.55 (m, 6 H, HC(1), HC(2), HC(5), HC(6), *anti*-HC(7)). The spectrum corresponded to the reported one.[29]

2-*exo*-7-*anti*-Dibromobicyclo[2.2.1]heptane (5). R_f 0.54. ^1H NMR ($CDCl_3$), δ: 4.50 (m, 1 H, HC(7)); 4.01 (dd, 1 H, HC(2), J_1 = 3.0 Hz, J_2 = 8.0 Hz); 2.58 (d, 1 H, HC(1), J = 3.0 Hz); 2.72 (d, 1 H, *exo*-HC(3), J = 14.1 Hz); 2.25 (d, 1 H, *endo*-HC(3), J_1 = 8.0 Hz, J_2 = 14.1 Hz); 2.39 (t, 1 H, HC(1), J = 3.0 Hz); 2.12—2.02 (m, 2 H, *exo*-HC(5), *exo*-HC(6)); 1.35—1.25 (m, 2 H, *endo*-HC(5), *endo*-HC(6)). Compound 5 could not be isolated in a pure state. The spectrum was recorded for the 5+2 mixture and corresponded to that reported in the literature.[29] Found (%): C, 32.53; H, 4.51. $C_7H_{10}Br_2$. Calculated (%): C, 33.11; H, 3.97.

2-*exo*-Bromo-7-*anti*-chlorobicyclo[2.2.1]heptane (8). R_f 0.66. Found (%): C, 40.95; H, 5.12. $C_7H_{10}BrCl$. Calculated (%): C, 40.13; H, 4.81.

2-*exo*-Bromo-3-*endo*-chlorobicyclo[2.2.1]heptane (9). R_f 0.64. Found (%): C, 39.67; H, 5.14. $C_7H_{10}BrCl$. Calculated (%): C, 40.13; H, 4.81.

7-*syn*-Bromo-2-*exo*-chlorobicyclo[2.2.1]heptane (10). R_f 0.54. The ^{13}C NMR spectrum corresponded to that reported in the literature.[25,30] Found (%): C, 32.53; H, 4.51. $C_7H_{10}Br_2$. Calculated (%): C, 33.11; H, 3.97.

2-*exo*-7-*anti*-Dichlorobicyclo[2.2.1]heptane (11). R_f 0.53. The ^{13}C NMR spectrum corresponded to that reported in the literature.[25,30]

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