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ORGANOFLUOROSILICATES IN ORGANIC SYNTHESIS

XV *. REACTION OF *exo*- AND *endo*-5-NORBORNEN-2-YLSILYL DERIVATIVES WITH *N*-BROMOSUCCINIMIDE. DIFFERENCE IN REACTIVITY BETWEEN HEXACOORDINATE AND TETRACOORDINATE SILICON COMPOUNDS **

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Summary

The reactions of potassium 5-norbornen-2-ylpentafluorosilicate (I) and 5-norbornen-2-yltrimethylsilane (II) with NBS were examined. The former reaction gave 3-nortricyclyl bromide (IV) as the only detectable product, arising from the carbon—silicon bond cleavage. The latter reaction, however, gave 3-bromo-1-nortricyclyltrimethylsilane (V) as the major product, resulting from cleavage of the carbon—hydrogen bond α to silicon, together with IV and an unidentified product. GLC-monitoring of the reactions showed the higher reactivity of the norbornenyl derivative having the leaving group in the *endo* position irrespective of whether the leaving group is SiF_5 or H. Since no inhibition was observed by the addition of hydroquinone in the dark, the reactions have been regarded as homoallylic electrophilic substitutions. A concerted mechanism seems to be consistent with the experimental data. Cleavage of 1-nortricyclyltrimethylsilane by iodine monochloride to give 1-iodonortricyclene has also been studied.

Introduction

The previous papers have demonstrated several synthetically useful reactions involving cleavage of the carbon—silicon bond in hexacoordinate organopentafluorosilicates [1]. In this paper attention is focused on the difference in

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* For Part XIV, see ref. 1.

** In honor of Professor Henry Gilman for his many years of outstanding research and teaching in the field of organometallic chemistry.

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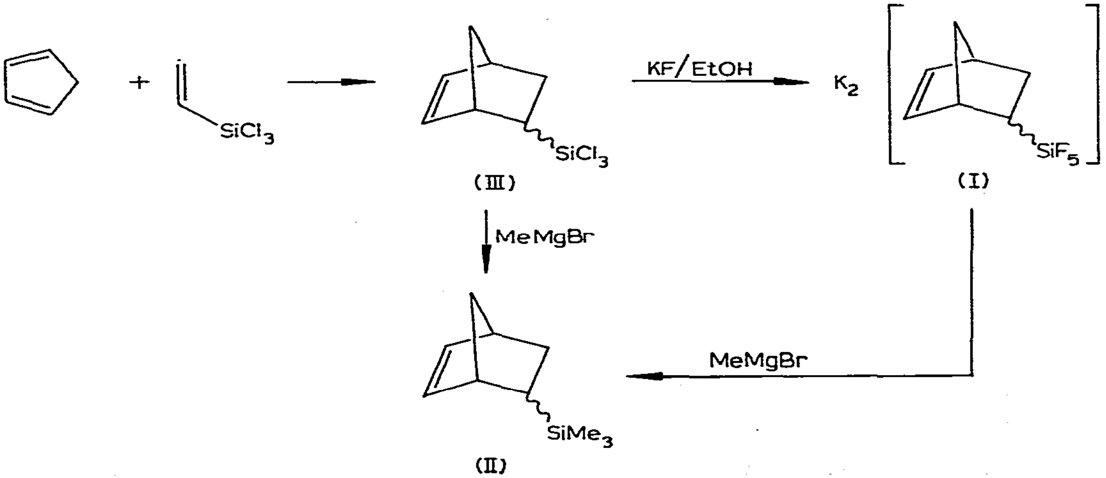
reactivity between the carbon—silicon bond in organopentafluorosilicates and that in ordinary tetracoordinate organosilanes. Since alkyl—silicon bonds in tetracoordinate organosilanes are generally inert to electrophiles under mild conditions [2], we chose the homoallylic 5-norbornen-2-ylsilyl system where a facile transannular electrophilic displacement was expected in both the tetracoordinate and hexacoordinate silicon compounds. A considerable interest in the present system may also stem from the stereochemical preference in the reaction which may be determined by relative reactivities of the *exo* and *endo* isomers. Thus we examined the reactions of 5-norbornen-2-ylpentafluorosilicate (I) and 5-norbornen-2-yltrimethylsilane (II) with NBS and obtained some informative results on the reactivity of the carbon—silicon bond and stereochemistry of the reaction.

Results and discussion

5-Norbornen-2-ylpentafluorosilicate (I) was prepared as follows. The Diels—Alder reaction between vinyltrichlorosilane and cyclopentadiene gave 5-norbornen-2-yltrichlorosilane (III) in the *exo/endo* ratio of 3/7 [3]. Careful fractional distillation of the adduct afforded several fractions involving one enriched in the *exo* isomer (*exo* 58%) and another enriched in the *endo* isomer (*endo* 95%). Both of them were converted into the corresponding silicates in the usual manner by treatment with KF in ethanol. Lack of appreciable stereochemical scrambling during the silicate formation was confirmed by comparison of the isomeric purity of 5-norbornen-2-yltrimethylsilane (II) obtained by methylation (MeMgBr in ether) of the silicate with that obtained from the trichlorosilyl precursor (III).



5-Norbornen-2-ylpentafluorosilicate (I) of the isomer ratio of *exo/endo* = 5/95 and 58/42 thus obtained was allowed to react with NBS. As shown in Table 1 the reaction proceeded smoothly at room temperature to give 3-nortricyclyl bromide (IV) [4] as the only detectable product. Because of the reaction proceeding very fast at room temperature, we carried out the reaction at 0°C and monitored it by GLC for comparison of reactivities of the *exo* and

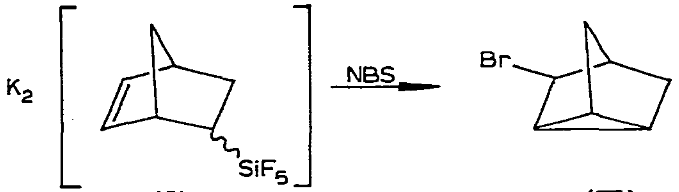
TABLE 1

REACTION OF 5-NORBORNEN-2-YLPENTAFLUOROSILICATE (I) WITH NBS [a]

exo/endo ratio	Solvent	Yield (%) of IV [b]
5/95	Et_2O	43
	MeOH	63
	Dioxane	54
58/42	Et_2O	56
	MeOH	63
	Dioxane	64

[a] The silicate I (1.0 mmol) was allowed to react with NBS (1.2 mmol) in 5.0 ml of a solvent at room temperature for 2 h. [b] Determined by GLC.

endo isomers. The results are presented in Fig. 1, which shows that the *endo* isomer reacted much faster than the *exo* isomer. It should be mentioned here that the present results make a sharp contrast to the preferential reactivity of the *exo* isomer in the electrophilic displacement of 5-norbornene-2-boronoic acid with mercuric chloride [5].



(I) (IV)

The trimethylsilyl analog (II) of the isomer ratio *exo/endo* = 4/96, 42/58, and 64/36 was prepared by direct methylation (MeMgBr in ether) of the corresponding trichlorosilyl precursor (III). The reaction of II with NBS in ether gave a mixture of 3-bromo-1-nortricyclyltrimethylsilane (V) as the major

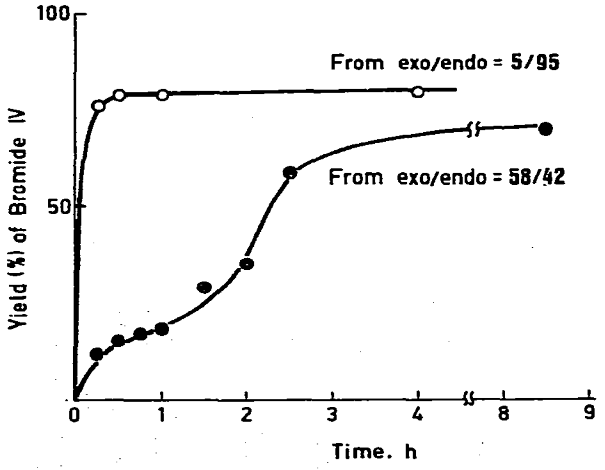


Fig. 1. Reactions of *exo*- and *endo*-5-norbornen-2-ylpentafluorosilicates (I) with NBS in ether at 0°C.

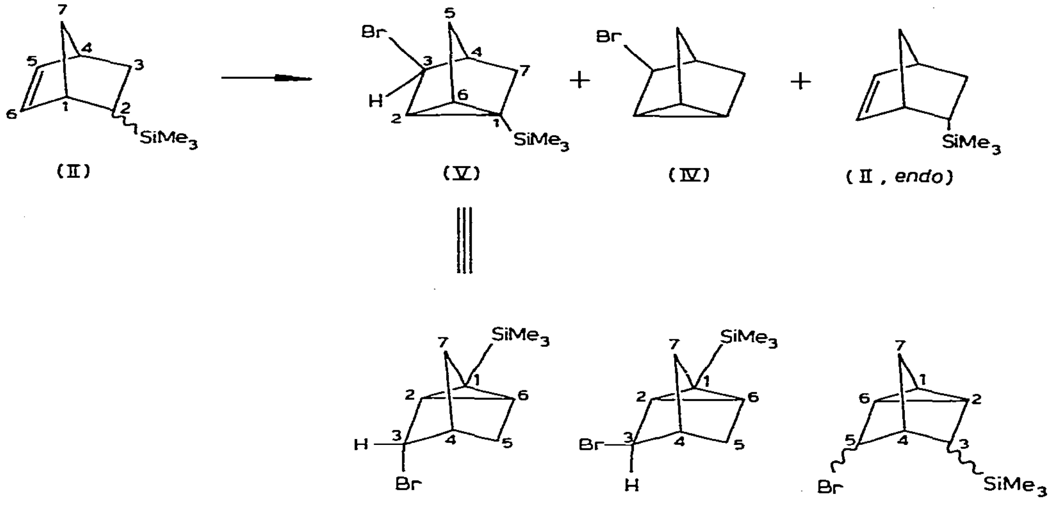
TABLE 2

REACTION OF 5-NORBORNEN-2-YLTRIMETHYLSILANE (II) WITH NBS [a]

exo/endo ratio	Product, yield (%) [b]		Recovered starting material (%) [b]
	IV	V	
6/94	12	21	33 [c]
42/58	9	37	21 [c]
64/36	6	61	3 [c]

[a] The trimethylsilyl derivative II (1.0 mmol) was allowed to react with NBS (1.2 mmol) in 5.0 ml of ether at room temperature for 24 h. [b] Determined by GLC. [c] ^{1}H NMR analysis of the recovered starting material indicated that only the *endo* isomer remained after the reaction.

product, 3-nortricyclyl bromide (IV), an unknown minor product, and the unchanged starting material consisting of only the *endo* isomer. A considerable amount (ca. 30%) of non-volatile viscous residue remained in every case. The results are summarized in Table 2.



(II) (V) (IV) (II, *endo*)

(V') (VI)

Product V was stereochemically pure as confirmed by ^{1}H and ^{13}C NMR, and reasonably assigned to be 3-*endo* bromide, based on the assumption of less hindered *exo*-attack on the norbornene systems by electrophiles. The *exo* isomer V' could not be detected *. The product expected from cleavage of the carbon—hydrogen bond at the 3 position, 5-bromo-3-nortricyclyltrimethylsilane (VI), was not formed.

The structure of V was further confirmed by reduction with i-PrMgBr/Cp$_2$TiCl$_2$ [7] or LiAlH$_4$/Cp$_2$TiCl$_2$ to give 1-nortricyclyltrimethylsilane (VII) [8].

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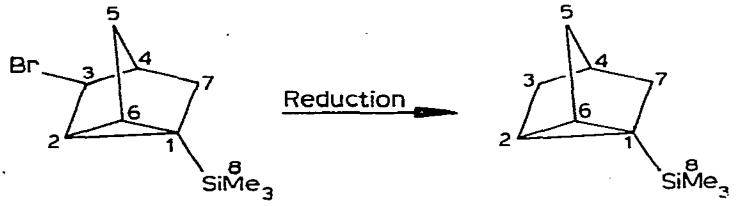
* Preparative GLC of V caused isomerization to give a mixture of these epimers. The epimerization is similar to that observed for 2-norbornyl bromide [6].



(V) (VII)

The results shown in Table 2 indicate that cleavage of the carbon—hydrogen bond located α to the silyl group occurred predominantly over cleavage of the carbon—silicon bond. It would be noteworthy that carbon—hydrogen bond cleavage leading to product V was more favored with an increase in the content of the *exo* isomer in the starting material. Thus, the observations indicate that the reaction proceeds more readily when the leaving group is in the *endo* position than in the *exo*. Higher reactivity of the *exo* isomer was clearly observed by GLC-monitoring of the reactions of 95% *endo*-II and 65% *exo*-II. The results are given in Fig. 2, where the plot for IV is omitted for clarity. It should be also noted that the stereochemistry of the recovered starting material was 100% *endo*, indicative of higher reactivity of the *exo* isomer.

Although the formation of the minor product IV arising from the trimethylsilyl group displacement seems to be more favored with increasing the content of the *endo* isomer, this tendency might be considered obscure, since it is not possible to rule out a possibility of preferential decomposition of either the *exo* or the *endo* isomer giving unknown viscous residue amounting about 30% of the starting material.

The NBS-cleavage reactions of both the silicate and the trimethylsilyl derivative were neither retarded nor inhibited by the addition of hydroquinone in the

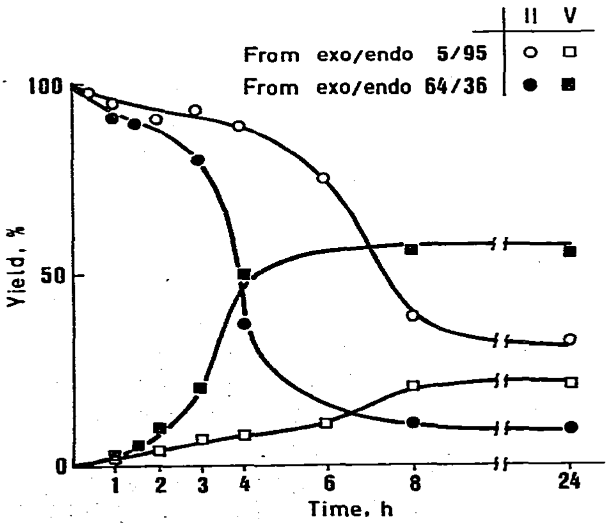
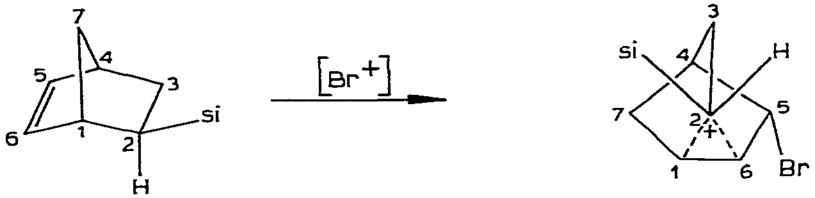


Fig. 2. Reaction of *exo*- and *endo*-5-norbornen-2-yltrimethylsilane (II) with NBS in ether at room temperature.

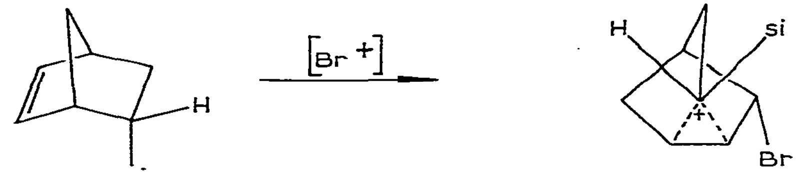
dark. The reactions, therefore, involve no radical chain processes, and should be regarded as electrophilic substitutions.

Prior to discussion of the mechanism the experimental results may be summarized as follows. (1) In the hexacoordinate silicate I exclusive cleavage of the carbon—silicon bond occurs, whereas in the tetracoordinate trimethylsilyl analog II cleavage of the carbon—hydrogen bond occurs predominantly over cleavage of the carbon—silicon bond. (2) The reaction proceeds more readily when the leaving group is in the *endo* position than in the *exo* position, irrespective of whether the leaving group is SiF_5 or H.

A cationic stepwise mechanism would lead to the formation of non-classical ions [9], VIII from the *exo* isomer and IX from the *endo* isomer. The bridging of the particular C(2) center would be in essentially the same circumstances in these cationic intermediates, provided that the influence by the 5-bromine substituent is small. Therefore, if this mechanism were valid, the reactivities of the *exo* and *endo* isomers would be equalized. The experimental results seem to be inconsistent with this mechanism.



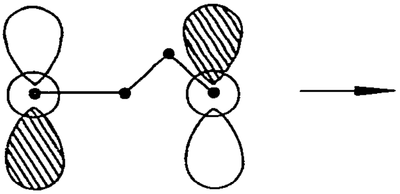
(VIII)



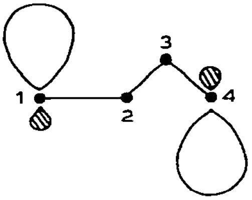
(IX)

The present experimental results may be most consistently explained in terms of concerted electrophilic homoallylic substitution. Firstly we consider the silicate case. We have recently reported briefly that the MO calculations on the phenylpentafluorosilicate show a remarkably low ionization potential around 8.3 eV assignable to the carbon—silicon σ bond, which is comparable with the phenyl π energy levels [6]. The calculation data imply that the σ—π mixing may be effectively attained in the case where the stereoelectronic conditions are satisfied. In the present 5-norbornen-2-yl silicate system, the olefin π electrons can interact much more effectively with the *endo* carbon—silicon σ bonding electrons than with the *exo* ones. This homoallylic σ—π conjugation may be the origin of the preferential cleavage of the *endo* silicate in the NBS cleavage reactions and provide suitable conditions for the concertedness of the reaction.

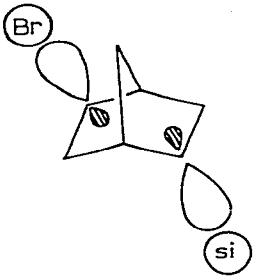
Anh's treatment [10] for the electrophilic allylic substitution may be applied to the transition state of the present homoallylic system. The transition state is formulated as a homoallylic anion interacting with two cations, an electrophile and a leaving group. The most important interaction is that between the highest-occupied molecular orbital (HOMO) of the homoallylic system and the vacant orbitals of the two cations. In the transition state the atomic orbitals of the carbon atoms C(1) and C(4) should be intermediate in structure between *p*-orbitals and sp^3 orbitals, and therefore the 2*s* atomic orbitals must be taken into account. Mixing of 2*s* and 2*p* orbitals results in the formation of B for the HOMO of the homoallyl anion. If two cations, the electrophile and the leaving group, are simultaneously "bonded" to the homoallyl system in the transition state, they must be *anti* to each other. This may be the case in our present system, since the σ—π mixing just mentioned above corresponds to the HOMO of the "homoallylic anion" of 5-norbornen-2-yl system. Thus, a one-step process involving the *exo* attack by a bromine cation and the *endo* leaving of the silicon moiety may be the most favorable process, which is consistent with the observations (cf. C).



(A)



(B)



(C)

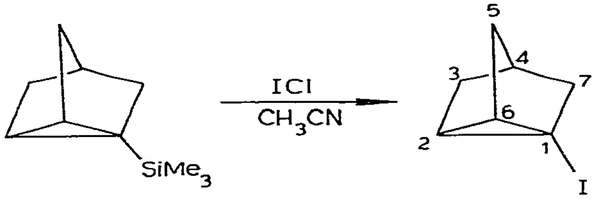
A similar treatment may be applicable to the reactions of the trimethylsilyl derivative II. The highly selective displacement of the proton α to the silicon, however, might argue against the above mechanism, since the σ—π conjugation may be favored with the carbon—silicon bond rather than the carbon—hydrogen bond. Alternatively, the preferred displacement of the hydrogen may arise from the stabilizing effect by the trimethylsilyl group on the "homoallylic anion" in the transition state of the concerted process.

Although no radical inhibition was observed, a radical mechanism could not be ruled out completely. It may be noted here that the reaction of allylsilanes with NBS is facilitated by a radical initiator to give a bromination product in which the hydrogen α to the silicon is abstracted with the silyl group being intact [11]. If a stepwise radical mechanism were still operative in the present system, the sterically less hindered *exo* hydrogen would be abstracted more readily, suggesting the higher reactivity of the *endo* isomer. On the contrary, the experimental data show that the *exo* isomer is more reactive than the *endo* isomer, and this makes a possibility of the radical mechanism unlikely.

It should be further noted that while the NBS cleavage reactions of the 2-norbornylsilicate, the saturated analog of I, proceed with inversion of configuration at the C(2) center [6], in the present unsaturated system retention of stereochemistry has been observed in the preferred process. This difference in the stereochemical preferences may also support the validity of the above mechanism.

Cleavage reaction of 1-nortricyclyltrimethylsilane (VII). Apart from the aforementioned mechanistic interest, electrophilic cleavage of VII seems to be also interesting, since it has novel structural features. Thus, the silyl group links to a tertiary, bridgehead carbon which is incorporated in a cyclopropane ring. It has recently been reported that a cyclopropyl group is selectively cleaved by electrophilic reagents from cyclopropyltrimethylsilane [12].

We have studied some cleavage reactions of VII and found that iodine monochloride in acetonitrile cleaved the 1-nortricyclyl—silicon bond to give 1-iodonortricyclene in 27—29% yield. To our best knowledge the product is the first member of 1-halonortricyclenes, while 3- and 4-halonortricyclenes have been reported [4,13].



Experimental

General

Infrared spectra were recorded on a Hitachi EPI-G3 Grating infrared spectrometer. ^{1}H NMR spectra were determined with a JEOL JNM-MH-100 (100 MHz) spectrometer in carbon tetrachloride. ^{13}C NMR spectra were determined with a Varian FT-80A spectrometer in $CDCl_3$. Chemical shifts (δ) are recorded in ppm downfield from Me_4Si. Mass spectra were measured on a JEOL JMS-D300 mass spectrometer connected with a JEOL LGC-20K gas chromatograph, equipped with a 1 m glass column packed with OV-17 (3%) on Chromosorb B, and a JMA-2000 data processing system. The ionization voltage was 24 eV for all compounds. GLC analyses and preparative purification were performed on a Shimadzu GC-4B gas chromatograph, equipped with a 3 m column packed with 30% Silicon DC550 on Chromsorb B or Celite 545. GC peak integrals were recorded using a Shimadzu Chromatopac C-E1B integrator.

Materials

Vinyltrichlorosilane was supplied by Shin-etsu Chemical Co., Ltd. All solvents were dried in the usual way and distilled before use. Other chemicals were used as obtained commercially.

Preparation of 5-norbornen-2-yltrichlorosilane (III)

The Diels—Alder reaction between vinyltrichlorosilane and cyclopentadiene was carried out according to the reported method [3]. Careful fractional distillation of the adduct (III) (*exo*/*endo* 3/7) through a column (ca. 30 cm) packed with glass helices afforded several fractions enriched in the *exo* isomer or the *endo* isomer. The *exo*/*endo* ratio of the fraction was determined by GLC analysis (Silicon DC550, 150°C, retention time ratio *exo*/*endo* = 1/1.13).

Preparation of 5-norbornen-2-ylpentafluorosilicate (I)

The trichlorosilyl derivative III enriched in the *endo* isomer (*endo* 95%)

was converted to the corresponding silicate I as follows. To a suspension of KF (32.0 g, 0.55 mol) in ethanol (64 ml) was added dropwise III (5.05 g, 22.0 mmol) at 0°C with vigorous stirring. After the addition the mixture was stirred at room temperature for 24 h. The mixture was poured into 80 ml of water at 0°C in order to dissolve the excess of KF and the resulting KCl. After stirring for 0.5 h the mixture was filtered (filter paper, Toyo Roshi Co., Ltd. No. 131), washed with water (30 ml), ethanol (50 ml), and then dried in vacuo; 6.25 g (96% yield): The *exo*-rich silicate was also prepared from the corresponding trichlorosilyl precursor (*exo* 58%) in 86% yield in essentially the same manner. IR: I (from *endo* 95%): 3050w, 2975m, 2960m, 2870m, 1570w, 1450w, 1340w, 1250m, 1207w, 1180w, 1155w, 1130w, 960w, 898m, 832w, 812w, 780w, 730(sh), 720s, 655vs, 620s, 550s, 487w, 460w, 450w. I (from *exo* 58%): 3050w, 2970m, 2860m, 1568w, 1445w, 1330w, 1245w, 1195w, 1178w, 1130w, 1100w, 960w, 895m, 832vw, 810m, 778w, 732s, 715s, 698s, 655vs, 620(sh), 550s, 490w, 481w, 470w, 450m cm^{-1}. Found: C, 27.80; H, 2.97; F, 32.34. $C_7H_9F_5K_2Si$ calcd.: C, 28.56; H, 3.08; F, 32.26%.

Silicate I obtained from the trichlorosilyl precursor (III) of the isomer ratio *exo*/*endo* = 58/42 was treated with a large excess of methylmagnesium bromide in ether. Usual work-up gave 5-norbornen-2-yltrimethylsilane (II) in 60% yield. GLC analysis of the product gave a single peak, but ^{1}H NMR analysis showed that the *exo*/*endo* ratio was 62/38 (*endo*-$SiMe_3$ δ 0.06, *exo*-$SiMe_3$ δ 0.16 ppm). Methylation of the *endo* rich silicate in a similar fashion afforded II in the isomer ratio *exo*/*endo* = 8/92. The results indicate that the silicate formation caused no appreciable stereochemical isomerization.

Reaction of 5-norbornen-2-ylpentafluorosilicate (I) with NBS

A mixture of I (1.0 equiv) and NBS (1.2 equiv) in a given solvent (5.0 ml per 1 mmol) was stirred at room temperature for 2 h. The mixture was filtered and the filtrate was washed three times with water, dried over Na_2SO_4, and distilled (bulb-to-bulb) to give 3-nortricyclyl bromide (IV): n_D^{20} 1.5292 (lit. [4] n_D^{25} 1.5296); ^{1}H NMR 0.95—1.45 (m, 6 H), 1.9 (br, s) and 2.01 (br, s) (total 2 H), 3.77 (br, s, 1 H). MS *m/e* (%) 174 (M^+ + 2, 4), 172 (M^+, 4), 93 (100), 91 (24), 77 (26).

Yields of IV obtained under various conditions were determined by GLC using an internal standard (n-dodecane or tridecane) and are summarized in Table 1.

For comparison of reactivities of the *exo* and *endo* isomers toward NBS the reactions of 95% *endo* I and 58% *exo* I were carried out at 0°C and the progress of the reaction was followed by GLC. The results are given in Fig. 1.

Preparation of 5-norbornen-2-yltrimethylsilane (II)

5-Norbornen-2-yltrimethylsilane (II) of the isomer ratio *exo*/*endo* = 5/95, 42/58, and 64/36 was prepared by methylation of the corresponding trichlorosilyl derivatives (III) with methylmagnesium bromide in ether. The isomer ratio was determined by ^{1}H NMR [3b,c] as described above.

Reaction of 5-norbornen-2-yltrimethylsilane (II) with NBS

A mixture of (*exo*/*endo* = 42/58, 166 mg, 1.0 mmol) and NBS (214 mg, 1.2

mmol) in ether (5.0 ml) was stirred at room temperature for 24 h. GLC analysis (130°C) of the reaction mixture showed four peaks due to the unchanged starting material (retention time, 3.0 min), 3-nortricyclyl bromide (IV) (4.5 min), an unknown minor product (12.3 min), and 3-bromo-1-nortricyclyltrimethylsilane (V) (14.0 min) in the area ratio of 26.0/8.6/8.9/56.5. Yields were determined by GLC using an internal standard (n-dodecane). The third unknown product could not be isolated, but the other three were isolated by preparative GLC and characterized. The reactions of II of the isomer ratio *exo/endo* = 5/95 and 64/36 with NBS were carried out in essentially the same manner. The results are given in Table 2. In all cases the unchanged starting material was found to be only the *endo* isomer, indicative of the higher reactivity of the *exo* isomer.

For comparison of reactivities of the *exo* and *endo* isomers toward NBS the progress of the reaction of the *exo* rich (*exo/endo* = 64/36) and the *endo* rich (*exo/endo* = 5/95) material was followed by GLC using an internal standard (n-dodecane). The results are presented in Fig. 2.

3-Bromo-1-nortricyclyltrimethylsilane (V) was prepared on a preparative scale as follows. A mixture of II *exo/endo* = 35/65 (21.5 g, 0.129 mol), NBS (34.8 g, 0.196 mol), and ether (100 ml) was heated to reflux for 15 h until the starting material completely disappeared. GLC analysis showed the production of a major product (V), together with a small amount of IV. The mixture was diluted with pentane (ca. 100 ml) to cause the precipitation of succinimide and filtered. The filtrate was washed twice with water and dried over Na_2SO_4. After evaporation of the solvents the residue was distilled under reduced pressure to give a fraction boiling over the range of 94—106°C/8 Torr (mainly 98°C/8 Torr). In the final stage of distillation some decomposition occurred. The distillate was about 94% pure, weighed 17.5 g (55% yield) and was characterized as 3-bromo-1-nortricyclyltrimethylsilane (V): n_D^{20} 1.5021; ^1H NMR 0.00 (s, 9 H), 1.1—1.4 (m, 5 H), 2.00 (br, s) and 2.11 (br, s) (total 2 H), 3.81 (br, s, 1 H); ^{13}C NMR 2.71 (q, C^8), 12.12 (s, C^1), 16.09 (d, C^2 or C^6), 22.55 (d, C^2 or C^6), 31.31 (t, C^5 or C^7), 32.64 (t, C^5 or C^7), 37.69 (d, C^4), 57.20 (d, C^3); MS *m/e* (%) 246 (M^+ +2, 10), 244 (M^+, 10), 231 (39), 229 (38), 165 (79), 139 (21), 137 (21), 99 (100), 91 (25), 73 (82). Found: C, 48.88; H, 7.21; Br, 32.78. $C_{10}H_{17}BrSi$ calcd.: C, 48.98; H, 7.00; Br, 32.58%.

Reduction of 3-bromo-1-nortricyclyltrimethylsilane (V)

(a) Reduction with i-PrMgBr/Cp_2TiCl_2: Corriu's method [7]. A solution of isopropylmagnesium bromide in ether was prepared from 7.7 g (62.5 mmol) of isopropyl bromide, 1.52 g (62.5 mg-atom) of magnesium, and 60 ml of dry ether. To the Grignard solution were added successively 157 mg (0.625 mmol) of titanocene dichloride (Cp_2TiCl_2) and 2.16 g (12.5 mmol) of V at room temperature with stirring. A slightly exothermic reaction occurred. After stirring at room temperature for 1 h the resulting dark brown mixture was hydrolyzed with aqueous ammonium chloride and dilute HCl. The aqueous layer was extracted twice with ether. The extracts and the organic layer were combined and washed with a sodium bicarbonate solution and water, and then dried over Na_2SO_4. After evaporation of the solvent the residue was distilled (bulb-to-bulb) to give 1-nortricyclyltrimethylsilane (VII) [8] in 52% yield: n_D^{20} 1.4588; ^1H NMR 0.00

(s, 9 H), 0.98 (s, 2 H), 1.10 (singlet with shoulder, 2 H), 1.20 (br, s, 4 H), 1.98 (br, s, 1 H); ^{13}C NMR 2.23 (q, C^9), 6.43 (s, C^1), 14.76 (2 d, C^2 and C^6), 30.12 (d, C^4), 33.50 (2t, C^3 and C^5), 34.81 (t, C^7). Found: C, 72.25; H, 10.92. $C_{10}H_{18}Si$ calcd.: C, 72.21; H, 10.90%.

(b) Reduction with $LiAlH_4/Cp_2TiCl_2$. To a mixture of $LiAlH_4$ (4.2 g, 110 mmol), Cp_2TiCl_2 (0.996 g, 2.97 mmol) and dry THF (40 ml) was added V (17.48 g, 71.4 mmol) at 0°C under nitrogen. After stirring at room temperature for 0.5 h the mixture was refluxed for 2.5 h. The dark brown mixture was decomposed by ethyl acetate and dilute HCl. The mixture was extracted three times with pentane. The pentane extracts were combined, washed with sodium bicarbonate solution and water, and dried over $CaCl_2$. After evaporation of the solvent, distillation gave 3.4 g (29% yield) of a colorless liquid boiling at 71—75°C/23 Torr. The purity of 1-nortricyclyltrimethylsilane was about 81%, The major impurity (ca. 15%) appeared to be norbornyltrimethylsilane based on the GCMS data.

Attempted inhibition of reactions of I and II with NBS

(a) A mixture of I (*exo*/*endo* = 58/42, 293 mg, 1.0 mmol), NBS (208 mg, 1.17 mmol), hydroquinone (14 mg), and ether (5 ml) was stirred at room temperature in the dark. The GLC monitoring showed no inhibition.

(b) A mixture of II (177 mg. 1.07 mmol), NBS (212 mg, 1.19 mmol), hydroquinone (10 mg), and ether (5 ml) was stirred at room temperature in the dark. The progress of the reaction followed by GLC was essentially the same as that observed without hydroquinone.

Reaction of 1-nortricyclyltrimethylsilane (VII) with iodine monochloride

To a mixture of VII (538 mg, 3.2 mmol) and dry acetonitrile (12 ml) was added dropwise at 0°C iodine monochloride (210 μl, 4.0 mmol). After the addition was completed, the mixture was stirred at room temperature for 3.5 h. GLC analysis showed that the starting material was no longer present and a new peak appeared (retention time ca. 13 min at 100°C). The mixture was treated with a dilute solution of $Na_2S_2O_3$ and extracted with ether (20 ml × 4). The ether layer was washed with saturated $NaHCO_3$ solution and water, and dried over Na_2SO_4. Evaporation of solvent gave a light brown viscous liquid which was not miscible with pentane. Therefore the viscous residue was extracted with pentane (2 ml × 5). The pentane layer was flash-distilled (around 105°C/27 Torr). The distillate was subjected to preparative GLC (the same conditions as above) to give the product, 1-iodonortricyclene: n_D^{20} 1.5622; IR (liquid film) 3070, 818, 780 cm^{-1} (characteristic bands of 1-substituted nortricyclene) [14]; ^{1}H NMR 1.05—1.85 (m); ^{13}C NMR ($CDCl_3$) 21.95 (d, C^2 and C^6), 32.16 (d, C^4), 33.52 (t, C^3 and C^5), 44.53 (t, C^7), a very weak signal around 52 ppm may be due to C^1; MS 220 (M^+, 100), 192 (5), 93 (M − I, 17), 91 (10), 77 (11). Found: C, 38.39; H, 4.22. C_7H_9I calcd.: C, 38.20; H, 4.13%.

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