986 *Organometallics* **2002,** *21,* 986−988

1,2,3,4,5,6-Hexasila-7,8-distannabicyclo[2.2.2]octanes: A Novel Approach toward Bicyclo Derivatives of Group 14 Elements[†]

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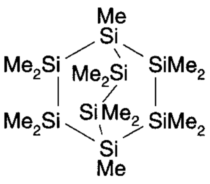
Received September 6, 2001

*Summary: Stannasilanes of the 1,2,3,4,5,6-hexasila-7,8-distannabicyclo[2.2.2]octane type ($Me_{10}R_4Si_6Sn_2$: R = Me, **5**; R = Ph, **6**) were synthesized by the reaction of 1,4-dihalogen-substituted decamethylcyclohexasilanes ($Si_6Me_{10}X_2$: X = F, **1**; X = Cl, **2**) with diorganodichlorostannanes (R_2SnCl_2: R = Me, **3**; R = Ph, **4**) in the presence of magnesium. Compounds **5** and **6** were characterized by NMR, MS, and elemental analysis. The solid-state structure of **6** was determined by X-ray crystallography.*

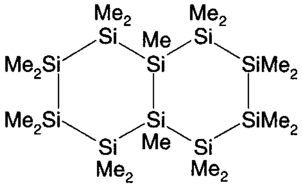
Introduction

The chemistry of monocyclic, oligomeric silanes of the type $(R_2Si)_n$ (n = 3−20) has been well-investigated over the past few decades.[1] In contrast, little is known about bicyclic silanes containing only group 14 atoms in the ring skeletons.[1−3]

Compound **A** is available as a byproduct from the reaction of Me_2SiCl_2 and $MeSiCl_3$ with sodium−potassium alloy[2] or as a rearrangement product in the thermolysis of octadecamethylbicyclo[4.4.0]decasilane (**B**).[3]



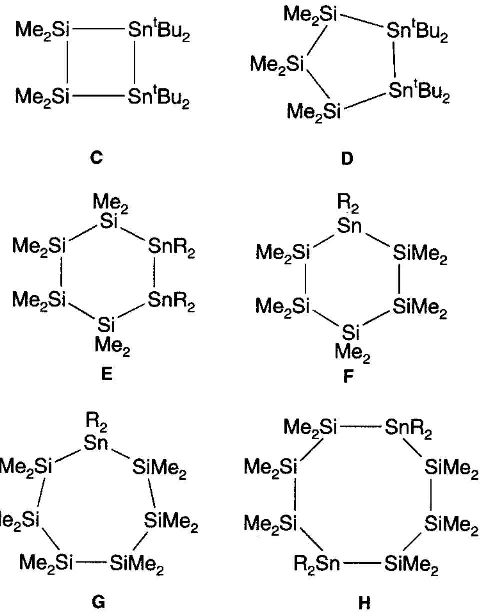
A



B

Recently, we reported the first attempts to synthesize group 14 bicyclo[2.2.2]octanes via multistep synthesis starting from $MeSi[SiMe_2Sn(H)\text{-}t\text{-}Bu_2]_3$.[4] However, in rather complex amine-catalyzed bond cleavage−coupling reactions, only monocyclic Si−Sn derivatives were accessible. During the last few years we also reported a number of novel monocyclic compounds exclusively containing tin and silicon atoms in the ring skeleton (Chart 1) in order to investigate the influence of organostannyl groups on the properties of cyclic oligosilanes.[5,6]

Chart 1: Examples for Monocyclic Six- and Seven-Membered Stannasilanes (R = Me, *t*-Bu, Ph)



The four-, five-, and six-membered rings **C**−**E** were obtained in a stepwise manner by starting from α,ω-bis(di-*tert*-butylhydridostannyl)silanes followed by halogenation and ring closure metathesis with magnesium.[5] One-pot reactions of halosilanes with chlorostannanes and magnesium yielded six-, seven-, and eight-membered Si−Sn rings of type **E**−**H** (Chart 1), indicating that this synthetic route should also be applicable to the synthesis of bicyclic stannasilanes.[6] This paper describes the synthesis and structure of novel compounds of the bicyclo[2.2.2]octane type containing only Sn and Si atoms in the ring skeletons.

Results and Discussion

The reaction of equimolar amounts of the 1,4-dihalodecamethylcyclohexasilanes $Me(X)Si(Me_2SiSiMe_2)_2Si(X)Me$ (**1**, X = F; **2**, X = Cl) and diorganodihalogenostannanes R_2SnCl_2 (**3**, R = Me; **4**, R = Ph) with magnesium provided the 1,2,3,4,5,6-hexasila-7,8-distannabicyclo[2.2.2]octanes **5** and **6** in moderate yields (Scheme 1).

Compounds **5** and **6** are colorless solids which are well soluble in aprotic, polar organic solvents. Reactions in

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[†] Dedicated to Prof. H. Bürger on the occasion of his 65th birthday.

(1) Weidenbruch, M. *Chem. Rev.* **1995**, *95*, 1479. (b) Hengge, E.; Janoschek, R. *Chem. Rev.* **1995**, *95*, 1495. (c) *The Chemistry of Organic Silicon Compounds*; Rappoport, Z., Apeloig, Y., Eds.; Wiley: Chichester, U.K., 1998; Vol. 2, p 2177.

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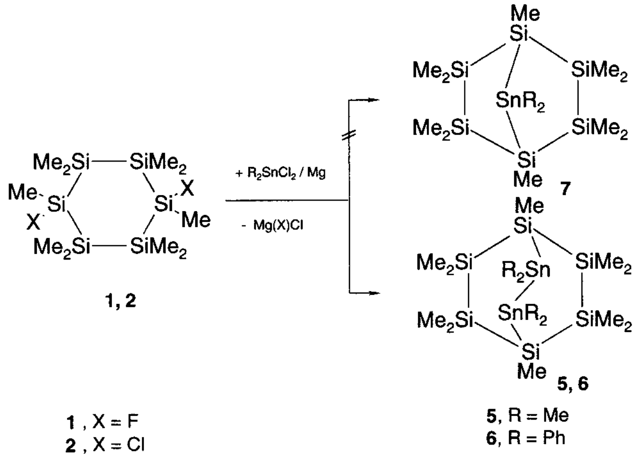
(4) Costisella, B.; Englich, U.; Prass, I.; Schürmann, M.; Ruhlandt-Senge, K.; Uhlig, F. *Organometallics* **2000**, *19*, 2546.

(5) Hermann, U.; Prass, I.; Uhlig, F. *Phosphorus, Sulfur, Silicon Relat. Elem.* **1997**, *124/125*, 425.

(6) (a) Kayser, C.; Klassen, R.; Schürmann, M.; Uhlig, F. *J. Organomet. Chem.* **1998**, *556*, 165. (b) Uhlig, F. Manuscript in preparation.

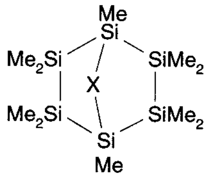
10.1021/om010801q CCC: $22.00
Publication on Web 02/02/2002

Scheme 1. Reactions of 1,4-Dihalocyclohexasilanes with R_2SiCl_2 in the Presence of Magnesium



a molar ratio of silane to stannane of 1.5:1 increased the yields of **5** and **6** to 35%. If the exact stoichiometric amounts of 2:1 were used, unidentified byproducts without Si−Sn moieties were observed, preventing the isolation of **5** and **6** from the reaction mixtures.

The starting materials **1** and **2** were used as a 1:1 mixture of the cis/trans isomers. We have no experimental evidence as to whether both or only one of the isomers react toward the cage-like compounds **5** and **6**. However, it is well-known from the literature that cis/trans mixtures of **2** can be converted nearly quantitatively into bicyclo[2.2.1]heptane derivatives.[7,8]



The tin−silicon moieties in compounds **5** and **6** were confirmed by NMR experiments, with coupling constants for $^1J(^{119}Sn-^{117}Sn)$ at 1505 Hz (**5**) and 1170 Hz (**6**). These values agree well with $^1J(^{119}Sn-^{117}Sn)$ for monocyclic rings of type **E**.[6] The $^1J(^{119}Sn-^{29}Si)$ (243 Hz (**5**), 238 Hz (**6**)) are around 100 Hz smaller than in the related compounds of types **E** and **F**. These differences might be explained by the different environments of the silicon atom. $^1J(^{29}Si-^{29}Si)$ and $^2J(^{29}Si-^{29}Si)$ have been determined at 50.5 and 10 Hz for **5** and 49.5 and 10 Hz for **6** and are therefore significantly smaller (8 and 3 Hz) than in monocyclic cyclohexasilane derivatives **1** and **2**. The lack of comparable data does not allow a complete discussion.

The bicyclooctane derivative **6**, depicted in Figure 1, crystallizes with two independent molecules in the unit cell, of which only one is shown. Crystallographic data and selected interatomic parameters are listed in Tables 1 and 2, respectively. The central tin−silicon backbone consists of Si_4Sn_2 and Si_6 rings each displaying a “twisted boat” conformation (Figure 1).

The two independent molecules differ only slightly in their bond lengths and angles. The tin and silicon atoms display a slightly distorted tetrahedral geometry, with bond distances of 2.7814(5) and 2.7866(5) Å for Sn−Sn and 2.354(2) and 2.336(2) Å for Si(1)−Si(4). The structural features of compound **6** compare favorably with those of other heteroatom-substituted silabicyclo[2.2.2]-octanes,[9] cyclic distannanes,[10] or the diphenyltin derivative of **F**.[6]

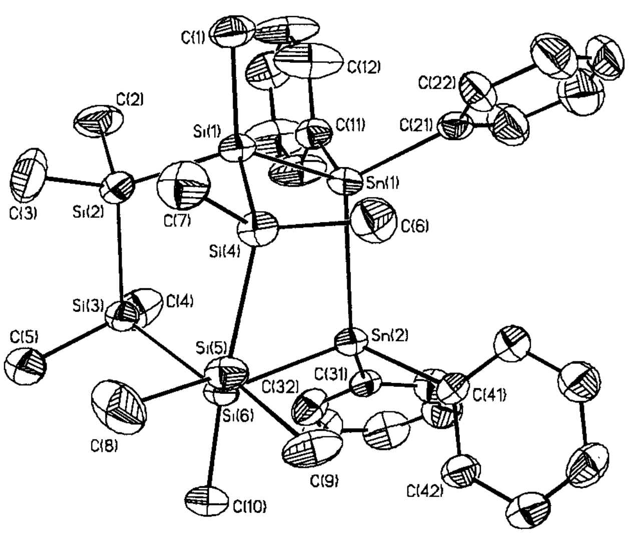


Figure 1. General view (SHELXTL-PLUS) of one of the two independent molecules of **6**, showing 30% probability displacement ellipsoids and the atom numbering.

Table 1. Crystal Data and Structure Refinement Details for 6

formula	$C_{34}H_{50}Si_6Sn_2$
fw	864.66
cryst syst	triclinic
cryst size, mm	0.40 × 0.12 × 0.10
space group	$P\bar{1}$
a, Å	10.639(1)
b, Å	19.879(1)
c, Å	20.708(1)
α, deg	94.402(1)
β, deg	102.718(1)
γ, deg	94.991(1)
V, Å^3	4256.7(5)
Z	4
ρ_{calcd}, Mg/m^3	1.349
μ, mm^{-1}	1.363
F(000)	1752
θ range, deg	2.95−25.70
index ranges	$-11 \le h \le 11$ $-24 \le k \le 24$ $-25 \le l \le 24$
no. of rflns collected	51 901
completeness to θ_{max}, %	91.7
no. of indep rflns/R_{int}	14 853/0.052
no. of rflns obsd with $I > 2\sigma(I)$	6933
no. of refined params	759
GOF(F^2)	0.828
R1(F) ($I > 2\sigma(I)$)	0.0389
wR2(F^2) (all data)	0.0678
$(\Delta/\sigma)_{max}$	0.001
largest diff peak/hole, e/Å^3	0.465/−0.428

The synthesis of the bicyclo[2.2.2]octane compounds **5** and **6** indicate not only the potentials but also the limitations of one-pot reactions between halogen silanes and chlorostannanes in the presence of magnesium.

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Table 2. Selected Bond Lengths (Å) and Angles (deg) for the Two Independent Molecules of 6 (6′)

6		6′	
	Bond Lengths		
Sn(1)−Sn(2)	2.7814(5)	Sn(1′)−Sn(2′)	2.7866(5)
Sn(1)−Si(1)	2.573(1)	Sn(1′)−Si(1′)	2.589(1)
Sn(2)−Si(6)	2.576(1)	Sn(2′)−Si(6′)	2.571(1)
Si(1)−Si(2)	2.341(2)	Si(1′)−Si(2′)	2.353(2)
Si(2)−Si(3)	2.349(2)	Si(2′)−Si(3′)	2.362(2)
Si(3)−Si(6)	2.346(2)	Si(3′)−Si(6′)	2.337(2)
Si(4)−Si(5)	2.360(2)	Si(4′)−Si(5′)	2.350(2)
Si(5)−Si(6)	2.345(2)	Si(5′)−Si(6′)	2.345(2)
Si(1)−Si(4)	2.354(2)	Si(1′)−Si(4′)	2.336(2)
Sn(2)−C(31)	2.147(5)	Sn(2′)−C(31′)	2.152(5)
Sn(2)−C(41)	2.153(5)	Sn(2′)−C(41′)	2.146(5)
Sn(1)−C(11)	2.131(5)	Sn(1′)−C(11′)	2.141(5)
Sn(1)−C(21)	2.146(5)	Sn(1′)−C(21′)	2.132(5)
	Bond Angles		
C(11)−Sn(1)−C(21)	103.7(2)	C(11′)−Sn(1′)−C(21′)	102.9(2)
C(11)−Sn(1)−Si(1)	109.1(1)	C(11′)−Sn(1′)−Si(1′)	111.3(1)
C(21)−Sn(1)−Si(1)	112.0(2)	C(21′)−Sn(1′)−Si(1′)	110.6(2)
C(11)−Sn(1)−Sn(2)	113.6(2)	C(11′)−Sn(1′)−Sn(2′)	111.8(1)
C(21)−Sn(1)−Sn(2)	114.3(1)	C(21′)−Sn(1′)−Sn(2′)	115.3(2)
Si(1)−Sn(1)−Sn(2)	104.32(3)	Si(1′)−Sn(1′)−Sn(2′)	105.03(3)
C(1)−Si(1)−Si(2)	108.4(2)	C(1′)−Si(1′)−Si(2′)	108.0(2)
C(1)−Si(1)−Si(4)	112.6(2)	C(1′)−Si(1′)−Si(4′)	111.3(2)
Si(2)−Si(1)−Si(4)	108.37(7)	Si(2′)−Si(1′)−Si(4′)	109.86(8)
C(1)−Si(1)−Sn(1)	111.0(2)	C(1′)−Si(1′)−Sn(1′)	112.3(2)
Si(2)−Si(1)−Sn(1)	107.35(6)	Si(2′)−Si(1′)−Sn(1′)	108.83(7)
Si(4)−Si(1)−Sn(1)	108.94(6)	Si(4′)−Si(1′)−Sn(1′)	106.51(7)

There is no evidence for the formation of the thermodynamically less favored, more strained bicyclo[2.2.1]heptane **7** (Scheme 1), but the reactions are well suited for the formation of thermodynamically favored products such as six-, seven-, or eight-membered mono- and bicyclic Si−Sn rings.

Experimental Section

General Methods. All reactions were carried out under an atmosphere of inert gas (N_2 or Ar) using Schlenk techniques. All solvents were dried by standard methods and freshly distilled prior to use. The 1,4-dihalodecamethylcyclohexasilanes **1** and **2** were prepared according to published procedures.[11] All other chemicals were obtained commercially. ^{1}H and ^{13}C NMR spectra were recorded using a Bruker DPX 400 spectrometer (solvent $CDCl_3$ or C_6D_6, internal reference Me_4Si). ^{29}Si and ^{119}Sn NMR spectra were recorded using a Bruker DPX 400 spectrometer (solvent $CDCl_3$ or C_6D_6, internal reference Me_4Si or Me_4Sn, respectively) or a Bruker DRX 300 spectrometer (solvent hexane or THF with D_2O capillary, internal reference Me_4Si or Me_4Sn, respectively). The $^xJ(^{29}\mathrm{Si}-^{29}\mathrm{Si})$ coupling constants were determined as described previously.[12] MS analyses were recorded using a MAT 8200. Molecular mass determinations were performed with a Knauer osmometer at 56 °C. Elemental analyses were performed on a LECO-CHNS-932 analyzer.

General Procedure. In a 250 mL Schlenk tube 10 mmol of **1** or **2** and 10−20 mmol of **3** or **4** were dissolved in 100 mL of THF. A 2 g amount (83 mmol, excess) of magnesium (activated with iodine[13]) was added. The resulting reaction mixture was stirred at room temperature for 3 days (**1**) or 6 days (**2**). After evaporation of the THF the resulting residue was extracted twice with 50 mL portions of a *n*-hexane/Et_2O (1:1) mixture. The extracts were filtered through a frit (G3) to remove magnesium salts. After evaporation of the filtrate, the crude products were purified by recrystallization.

Tetradecamethyl-1,2,3,4,5,6-hexasila-7,8-distannabicyclo[2.2.2]octane, $Me_{14}Si_6Sn_4$ (5). (a) The starting materials used were 3.71 g (10 mmol) of **1** and 2.2 g (10 mmol) of **3**. Recrystallization from *n*-hexane/Et_2O (1:1) gave 1.23 g (20%) of **5** as colorless solid.

(b) The starting materials used were 3.71 g (10 mmol) **of 1** and 3.3 g (15 mmol) of **3**. Recrystallization from *n*-hexane/Et_2O (1:1) yielded 2.16 g (35%) of **5** as a colorless solid.

^{119}Sn NMR (111.92 MHz, $CDCl_3$): δ −227.9, $^1J(^{119}\mathrm{Sn}-^{117}\mathrm{Sn}) = 1505$ Hz. ^{29}Si NMR (59.63 MHz, $CDCl_3$): δ −80.9 ($^1J(^{119}\mathrm{Sn}-^{29}\mathrm{Si}) = 243$ Hz, $^2J(^{119}\mathrm{Sn}-^{29}\mathrm{Si}) = 94$ Hz, SiMe), −37.6 ($^2J(^{119}\mathrm{Sn}-^{29}\mathrm{Si}) = 58$ Hz, $^3J(^{119}\mathrm{Sn}-^{29}\mathrm{Si}) = 38$ Hz, $SiMe_2$), $^1J(^{29}\mathrm{Si}-^{29}\mathrm{Si}) = 50.5$ Hz, $^2J(^{29}\mathrm{Si}-^{29}\mathrm{Si}) = 10$ Hz. ^{13}C NMR (100.63 MHz, C_6D_6): δ −9.8 ($^2J(^{119}\mathrm{Sn}-^{13}\mathrm{C}) = 32$ Hz, SiMe), −2.8, −3.1 ($^3J(^{119}\mathrm{Sn}-^{13}\mathrm{C}) = 41$ Hz, $SiMe_2$), −5.6 ($^1J(^{119}\mathrm{Sn}-^{13}\mathrm{C}) = 195$ Hz, $SnMe_2$). ^{1}H NMR (400.13 MHz, $CDCl_3$): δ 0.41 ($^2J(^{119}\mathrm{Sn}-^1\mathrm{H}) = 36$ Hz, 12H 2 × $SnMe_2$), 0.37 ($^3J(^{119}\mathrm{Sn}-^1\mathrm{H}) = 24$ Hz, 6H, SiMe), 0.35 (12H, 2 × $SiMe_2$). Mp: 208−210 °C. Molecular mass determination ($CHCl_3$, 20 mg mL^{-1}): 612 g mol^{-1}. Anal. Calcd for $C_{14}H_{42}Si_6Sn_2$ (616.41): C, 27.28; H, 6.87. Found: C, 27.1; H, 6.6, MS: *m*/*z* 616 (M^+/80%), 601 (M^+ − Me/10%), 586 (M^+ − 2 Me/5%), 318 (Si_6Me_{10}/100%).

7,7,8,8-Tetraphenyldecamethyl-1,2,3,4,5,6-hexasila-7,8-distannabicyclo[2.2.2]octane, $Me_{10}Ph_4Si_6Sn_4$ (6). (a) The starting materials were 4.04 g (10 mmol) of **2** and 3.43 g (10 mmol) of **4**. Recrystallization from $CHCl_3$/Et_2O (1:1) yielded 1.29 g (15%) of **6** as a colorless solid.

(b) The starting materials were 4.24 g (11 mmol) of **1** and 5.5 g (16 mmol) of **4**. Recrystallization from $CHCl_3$/Et_2O (1:1) gave 2.59 g (27%) of **6** as a colorless solid.

^{119}Sn NMR (149.21 MHz, $CDCl_3$): δ −206.1, $^1J(^{119}\mathrm{Sn}-^{117}\mathrm{Sn}) = 1170$ Hz. ^{29}Si NMR (79.49 MHz, $CDCl_3$): δ −74.4 ($^1J(^{119}\mathrm{Sn}-^{29}\mathrm{Si}) = 238$ Hz, $^2J(^{119}\mathrm{Sn}-^{29}\mathrm{Si}) = 97$ Hz, SiMe), −37.1 ($^2J(^{119}\mathrm{Sn}-^{29}\mathrm{Si}) = 53$ Hz, $^3J(^{119}\mathrm{Sn}-^{29}\mathrm{Si}) = 40$ Hz, $SiMe_2$), $^1J(^{29}\mathrm{Si}-^{29}\mathrm{Si}) = 49.5$ Hz, $^2J(^{29}\mathrm{Si}-^{29}\mathrm{Si}) = 10$ Hz. ^{13}C NMR (100.63 MHz, C_6D_6): δ 139.8($^1J(^{119}\mathrm{Sn}-^{13}\mathrm{C}) = 298$ Hz, C_i), 138.4 ($^2J(^{119}\mathrm{Sn}-^{13}\mathrm{C}) = 41$ Hz, C_o), 128.0 ($^3J(^{119}\mathrm{Sn}-^{13}\mathrm{C}) = 42$ Hz, C_m), 127.7 (C_p), −10.7 ($^2J(^{119}\mathrm{Sn}-^{13}\mathrm{C}) = 34$ Hz, SiMe), −2.3, −2.5 ($^3J(^{119}\mathrm{Sn}-^{13}\mathrm{C}) = 39$ Hz, $SiMe_2$), ^{1}H NMR (400.13 MHz, C_6D_6): δ 7.75 ($^3J(^{119}\mathrm{Sn}-^1\mathrm{H}) = 45$ Hz, d, 8H, SnPh), 7.18 (m, 12H, SnPh), 0.64 ($^3J(^{119}\mathrm{Sn}-^1\mathrm{H}) = 23$ Hz, SiMe), 0.37, 0.30 ($SiMe_2$). Mp: 168−170 °C, Anal. Calcd for $C_{34}H_{50}Si_6Sn_2$ (864.69): C, 47.23; H, 5.82, Found: C, 46.8, H, 5.7, MS: *m*/*z* 863 (M^+/100%), 848 (M^+ − Me/3%), 786 (M^+ − Ph/10%), 333 (Si_6Me_{10}/90%), 272 ($SnPh_2$/60%).

Crystallography. The data of **6** were collected to a θ value of 25.70° with 360 frames via ω-rotation ($\Delta/\omega = 1°$) with a 60 s exposure time per frame on a Nonius KappaCCD diffractometer ($\lambda = 0.71073$ Å) and was corrected for LP but not for absorption effects. The structure was solved by direct methods SHELXS97.[14] Refinement used SHELXL97[15] full-matrix least-squares methods. The H atoms were placed on geometrically calculated positions using a riding model and refined with a common isotropic temperature factor for aliphatic and aromatic H atoms.

Acknowledgment. We thank the Deutsche Forschungsgemeinschaft (DFG), the Fonds der Chemischen Industrie (Germany), and the federal state Northrhine Westfalia for financial support. We are grateful to Prof. Dr. K. Jurkschat for his interest in this work.

Supporting Information Available: This material is available free of charge via the Internet at http://pubs.acs.org.

OM010801Q

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(13) A 10 g amount of magnesium was heated with 0.2 g iodine under inert conditions for 5 min up to 100 °C. After the mixture was cooled to room temperature, the magnesium was used without further purification.

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